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Richard M. Yager
USGS

Marcel P. Bergeron
USGS

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NITROGEN TRANSPORT IN A SHALLOW OUTWASH AQUIFER AT OLEAN, CATTARAUGUS COUNTY, NEW YORK

by Richard M. Yager and Marcel P. Bergeron

U.S. GEOLOGICAL SURVEY

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1988

UNITED STATES DEPARTMENT OF THE INTERIOR

DONALD PAUL HODEL, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

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CONVERSION FACTORS AND ABBREVIATIONS

For the convenience of readers who may prefer to use metric (International System) units rather than the inch-pound units used in this report, values may be converted by using the following factors:

Multiply inch-pound unit	By	To obtain metric unit
inch (in)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
square mile (mi^2)	2.59	square kilometer (km^2)
cubic foot per second (ft^3/s)	28.32	liter per second (L/s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
million gallons per day (Mgal/d)	43.81	liter per second (L/s)
foot squared per day (ft^2/d)	0.0929	meter squared per day (m^2/d)
foot per day (ft/d)	0.3048	meter per kilometer (m/km)
pound (lb)	453.5	gram (g)
pound per cubic foot (lb/ft^3)	0.01602	gram per cubic centimeter (g/cm^3)
ton, short	0.9072	metric tons

To convert degrees Fahrenheit to degrees Celsius

degree Fahrenheit	5/9 (°F-32)	degree Celsius

Other Abbreviations

milligram per liter (mg/L)
milligram per kilogram (mg/kg)
milliequivalent per kilogram (meq/kg)

National Geodetic Vertical Datum of 1929 (NGVD of 1929): A geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Mean Sea Level."

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Abstract

Ground water beneath an industrial park at Olean, N.Y., contains nitrogen compounds in concentrations that in 1983 ranged from 10 to 1,280 milligrams per liter as nitrogen, mainly in the form of ammonium. Continuous pumping from industrial production wells and a purge well at the site created a cone of depression that prevented the nitrogen compounds from migrating to nearby private and municipal supply wells nearly 7,000 feet away. The aquifer system consists of 20 to 100 feet of coarse sand and gravel outwash that underlies the valleys of the Allegheny River and its tributaries. Near the industrial park, a discontinuous layer of lacustrine clay or till separates the aquifer into an upper and a lower layer. Most of the nitrogen is contained within the upper, less permeable layer. A three-dimensional ground-water flow model used in a previous study of the area concluded that cessation of industrial pumping would allow water levels to recover and permit nitrogen-bearing ground water to migrate toward private and municipal supply wells.

In this study, a two-dimensional solute-transport model was used to simulate nitrogen migration through the lower aquifer, the likely conduit for transport to the municipal well field because it represents 90 percent of the transmissivity of the aquifer system near the industrial park. A nitrogen-source rate representing nitrogen flux from the upper to the lower aquifer was calibrated to nitrogen concentrations measured within the contaminated part of the lower aquifer during 1978-84. The source rate was decreased by an exponential decay term to account for the removal of nitrogen from the upper aquifer by pumping during the calibration period. Simulated concentrations that best matched the observed values were obtained with a decay constant of 0.30 per year. The nitrogen flux to the lower aquifer in 1984 was estimated to be 70,000 pounds per year. Nitrogen concentrations during an actual shutdown of the industrial well field in 1985 remained relatively unchanged over 6 months. This condition was reproduced by reducing the nitrogen-source rate by 80 percent, to 14,000 pounds per year. The lower rate offsets the decrease in vertical leakage from the upper aquifer that resulted from lower hydraulic gradients after the shutdown.

A proposed shutdown of the industrial well field was simulated with nitrogen moving as a conservative solute to obtain worst-case estimates of resulting nitrogen concentrations. Results obtained under this assumption suggest that (1) concentrations at the Olean municipal well field 15 years after a simulated shutdown would range from 2 to 5 milligrams per liter; (2) nitrogen-bearing ground water would reach the municipal well field within 5 years, and (3) concentrations at the boundary of the industrial park would

range from 20 to 25 milligrams per liter. The actual rate of nitrogen movement is likely to be slower, however, because the nitrogen in ground water is mainly in the form of ammonium, which is readily adsorbed onto aquifer material. Simulation of Langmuir adsorption of the dissolved ammonium indicated that the arrival time of the solute front at the municipal well field would be delayed by 10 years.

INTRODUCTION

High concentrations of nitrogen have been detected since 1969 in the glacial-outwash aquifer in the vicinity of an industrial park in North Olean, in southeast Cattaraugus County, N.Y. (fig. 1), where large amounts of nitrogen compounds, including ammonia and urea, were manufactured for fertilizer and animal feed from 1967 to 1983. The high concentrations are a result of spills and leaks of fertilizer, process compounds, and wastewater that have infiltrated into the soil and aquifer (Hydro Systems, Inc., 1979). The U.S. Geological Survey has conducted studies of the effects of industrial and municipal pumping on the aquifer since 1970. This aquifer ranges from 20 to 100 ft thick and is the most extensive and highest yielding ground-water source in the Olean area.

Pumping during the 1970's and early 1980's at an industrial well field in North Olean maintained a cone of depression 20 to 30 ft deep at the center of the field and several thousand feet in diameter. This cone of depression kept the nitrogen-bearing ground water within the boundaries of the industrial park.

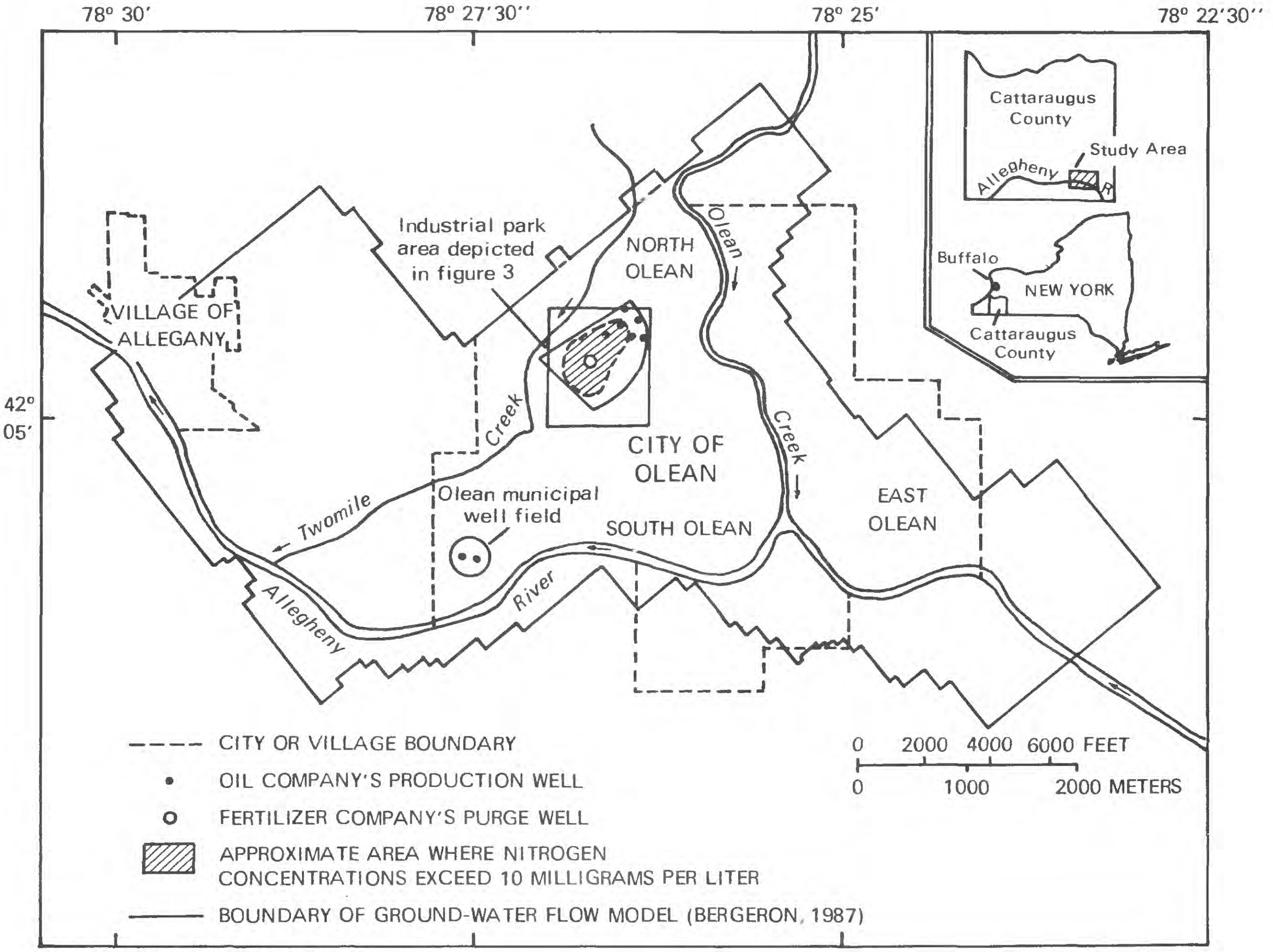
Decreasing industrial water needs and a shutdown of operations at the industrial park in 1985 resulted in a cessation of ground-water withdrawals in the area of contamination. A recent study by Bergeron (1987), which used a three-dimensional ground-water flow model of the aquifer, concluded that reductions in industrial pumping would cause water levels to recover and allow nitrogen-bearing ground water to migrate toward nearby private and municipal water supplies. It also concluded that, if all wells at the industrial park were shut down permanently, contaminated ground water would migrate south-southwestward for about 6 years before reaching the city of Olean's municipal well field about 1 mi away (Bergeron, 1987). The flow model used in that study could not predict the concentration of nitrogen in ground water arriving at the municipal well field.

Purpose and Scope

This report describes the results of a U.S. Geological Survey study, done during 1983-85 in cooperation with the New York State Department of Environmental Conservation, to examine the potential for nitrogen migration after a shutdown of the industrial well field. The study focused on the 2-mi^2 area between the industrial park and the Olean municipal well field 7,000 ft south-southwest of it (fig. 1), to which nitrogen-bearing ground water would migrate if pumping at the industrial well field were stopped permanently.

A two-dimensional solute-transport model was developed to predict nitrogen concentrations in ground water that would result from advection and hydrodynamic dispersion as it migrated from the source area. The nitrogen was represented as a conservative solute that was removed from the aquifer at a decreasing rate by pumping during 1978-84. The effects of adsorption on nitrogen concentrations were analyzed separately in a one-dimensional transport simulation. Biochemical transformations may play a role in nitrogen transport, but an assessment of these processes was beyond the scope of the study.

This report also summarizes the hydrogeologic setting of the study area, describes the historical trends in nitrogen concentrations in the area of contamination, and presents the hydrologic and chemical data used in the development and calibration of the solute-transport model. Several maps and graphs illustrate results of the simulations of dissolved nitrogen migration



Base from U.S. Geological Survey,
Olean, 1980, Knapp Creek, 1961, 1:24,000

Figure 1.--Location and major features of modeled area.

in terms of concentrations that would occur at specified intervals after a permanent shutdown of all wells within the industrial park. It also includes a brief discussion of nitrogen adsorption and biochemical reactions that may affect the transport rate.

Acknowledgments

The authors thank Daniel King and Robert Speed of the New York State Department of Environmental Conservation and Edward Anderson of C. F. Industries for collecting and sharing data during the investigation. The authors also thank Leonard F. Konikow of the U.S. Geological Survey for his assistance in the development of the solute-transport model.

HYDROGEOLOGIC SETTING

The Olean area lies within the glaciated Allegheny section of Appalachian Plateau physiographic province and is drained by the Allegheny River and several perennial and intermittent tributary streams. Streams closest to the industrial park and the Olean municipal well field include Olean Creek and Two Mile Creek--a small ephemeral stream west of the industrial park (fig. 1).

Geology

The Allegheny River and Olean Creek valley are deeply carved into bedrock, which consists of gray and black shale and interbedded siltsone and sandstone. These valleys contain unconsolidated sediments 150 to 300 ft thick that were deposited by glacial and postglacial processes. The deeper valley sediments are composed predominantly of clay and silt that formed in an extensive lake or lakes ponded in front of glacial ice. The upper sediments consist of till and stratified drift that were deposited by glacial ice in the Olean Creek valley. Evidence of end-moraine deposits is found along the valley wall south of the Allegheny River at Olean. Modern stream valleys are incised into the glacial deposits and contain as much 30 ft of postglacial alluvium that generally consists of sand and gravel overlain by silt.

Extent and Thickness of Outwash Aquifer

Ground water in the Olean area flows readily through glacial and postglacial sands and gravels, which reach 100 ft in thickness. These deposits form an extensive and high-yielding aquifer that provided 5.9 Mgal/d to industrial and municipal wells in 1984 (pl. 1A).

The thickness of the outwash aquifer in the 2-mi^2 area between the industrial park in North Olean and the Olean municipal well field along the Allegheny River is shown in a generalized geologic section A-A' in figure 2. Test wells and borings at the industrial park penetrate sand and gravel to a depth of about 80 ft. The upper 50 ft of the aquifer, which tends to be silty, is generally less permeable than the lower 30 ft. The lower part of

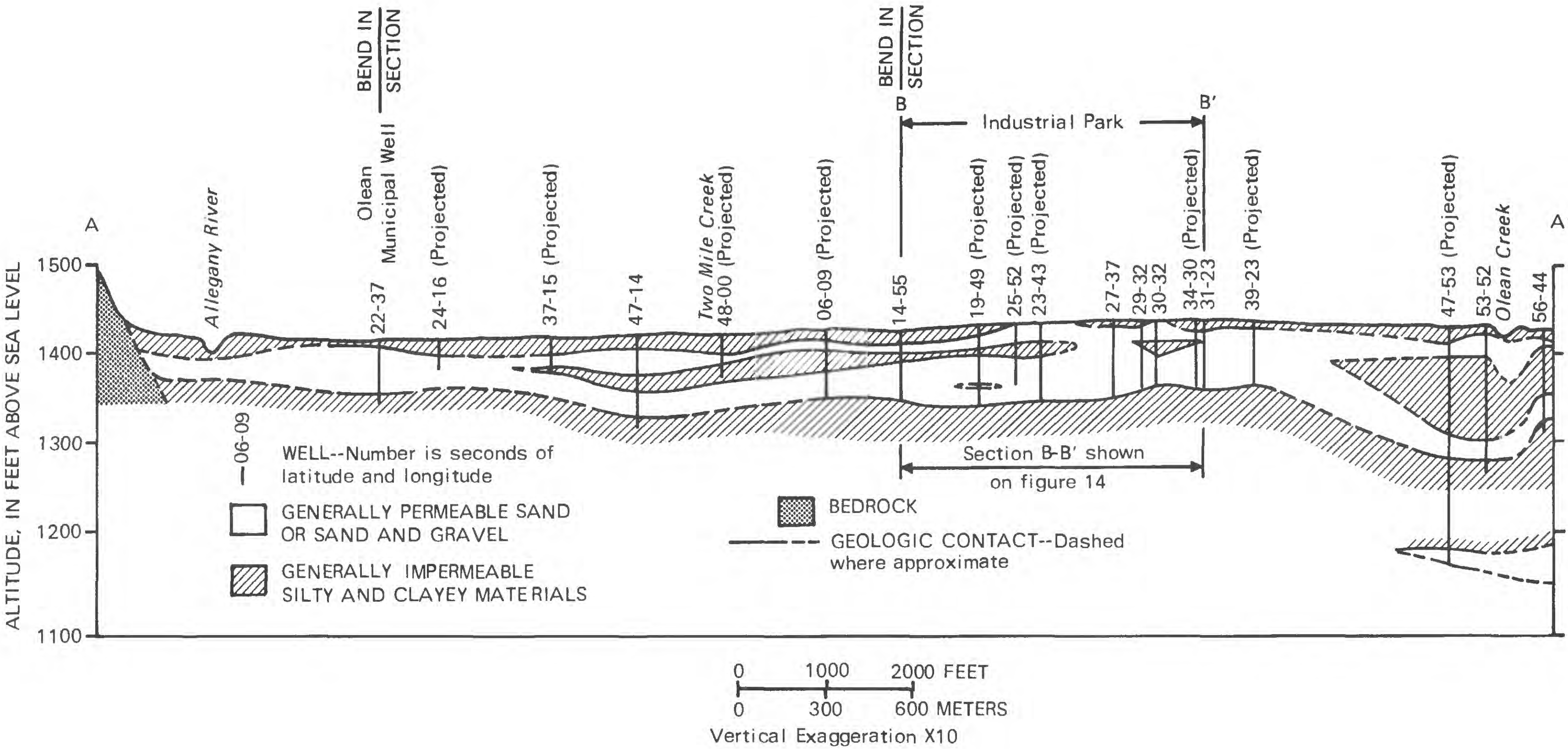


Figure 2.--Generalized geologic section A-A'; from the industrial park to the Olean municipal well field. (Location of section is shown on pl. 1B.)

the aquifer is highly productive and yields 500 to 1,000 gal/min to several production wells within the industrial park. Relatively thin lenses of silt and clay (5 to 25 ft thick) occur at depths between 30 and 50 ft in some areas in the park vicinity. These fine-grained materials act as a localized semiconfining bed that separates the aquifer into an upper and a lower layer.

The semiconfining bed extends beneath most of the industrial park and to the southwest but is absent at the Olean municipal well field near the Allegheny River (fig. 2). The aquifer in this area is about 40 ft thick, and two municipal-supply wells withdraw about 1.0 Mgal/d. Logs of several test holes in areas west of Olean along the Allegheny River suggest highly permeable sand and gravel to depths of 60 ft. The aquifer appears to thin eastward in South Olean, where it ranges from 40 ft thick near the western city limit to about 10 ft thick near South Union Street (pl. 1A).

Ground-Water Flow in Outwash Aquifer

The U.S. Geological Survey has measured ground-water levels in 50 to 95 observation wells in the Olean area periodically since the early 1970's to determine the direction of ground-water flow in the outwash aquifer. (Well locations are shown in pl. 1B.) A potentiometric-surface map of the aquifer, based on measurements made on March 20-21, 1984, is given in plate 2A. The contours are based mostly on hydraulic head in lower parts of the aquifer and thus may not reflect the position of the water table in localized areas where the aquifer is separated by the silt and clay into upper and lower layers.

The map indicates that ground water flows toward the Allegheny River and toward cones of depression created by localized pumping. Continuous pumping from production wells and the purge well in the industrial park in 1984 created a cone of depression a few hundred feet in diameter and about 7 ft deep at its center. This cone of depression is smaller than that produced in the 1970's, when pumpage was greater. If pumping were to cease permanently, ground water in this area would flow downvalley toward the Allegheny River.

The potentiometric-surface map of 1984 (pl. 2A) reflects recent conditions of pumping and is not indicative of the water-table altitude observed during the 1970's and early 1980's, when all production wells at the industrial park and several other well fields in the Olean area were in full operation. Since early 1984, pumpage at the industrial park has been derived from only four production wells and has amounted to about 3 Mgal/d. Before 1984, when ground water was withdrawn from as many as eight production wells, pumpage as high as 10 Mgal/d was reported, and water levels in the industrial park were as much as 20 ft lower than those of March 1984. Two other major well fields, one at 20th and State Street and another along the Allegheny River west of Olean (pl. 2A), pumped as much as 3.5 and 8 Mgal/d, respectively, and created localized cones of depression before 1984. These municipal and industrial well fields are not currently (1987) operating.

Ground water is recharged by infiltration of precipitation and underflow from the Olean Creek and Allegheny River valleys north and east of Olean. Bergeron (1987) estimated an areal recharge rate of 19 in/yr. Recharge also occurs through induced infiltration in areas where pumping lowers water levels beneath streams to below stream stage. Bergeron (1987) identified areas of induced infiltration along parts of Two Mile Creek and Olean Creek from streamflow measurements made during 1977 and 1978, when total pumpage from the aquifer exceeded 15 Mgal/d. Results from Bergeron's flow model indicate that the Allegheny River supplied 0.3 to 0.4 Mgal/d to the Olean municipal well field in 1984.

Hydraulic Properties of Outwash Aquifer

Hydraulic properties of the outwash aquifer were estimated in previous studies from aquifer-test and specific-capacity data. Transmissivity values calculated from these data are highly variable locally and range from 1,700 to 200,000 ft^2/d; most values are between 10,000 and 60,000 ft^2/d (Bergeron, 1987). Hydraulic conductivity values, calculated by dividing the transmissivity by the average aquifer thickness at each well, were commonly between 300 and 1,500 ft/d.

These estimated hydraulic properties were modified during calibration of the ground-water flow model developed by Bergeron (1987). Values derived from the model analysis were in general agreement with those calculated from aquifer-test and specific-capacity data. Hydraulic conductivity values used in the flow model averaged 60 ft/d for the upper part of the aquifer in the industrial well-field area and 1,000 ft/d for the lower part. Model hydraulic conductivity values for the aquifer near the Olean municipal well field averaged 1,400 ft/d.

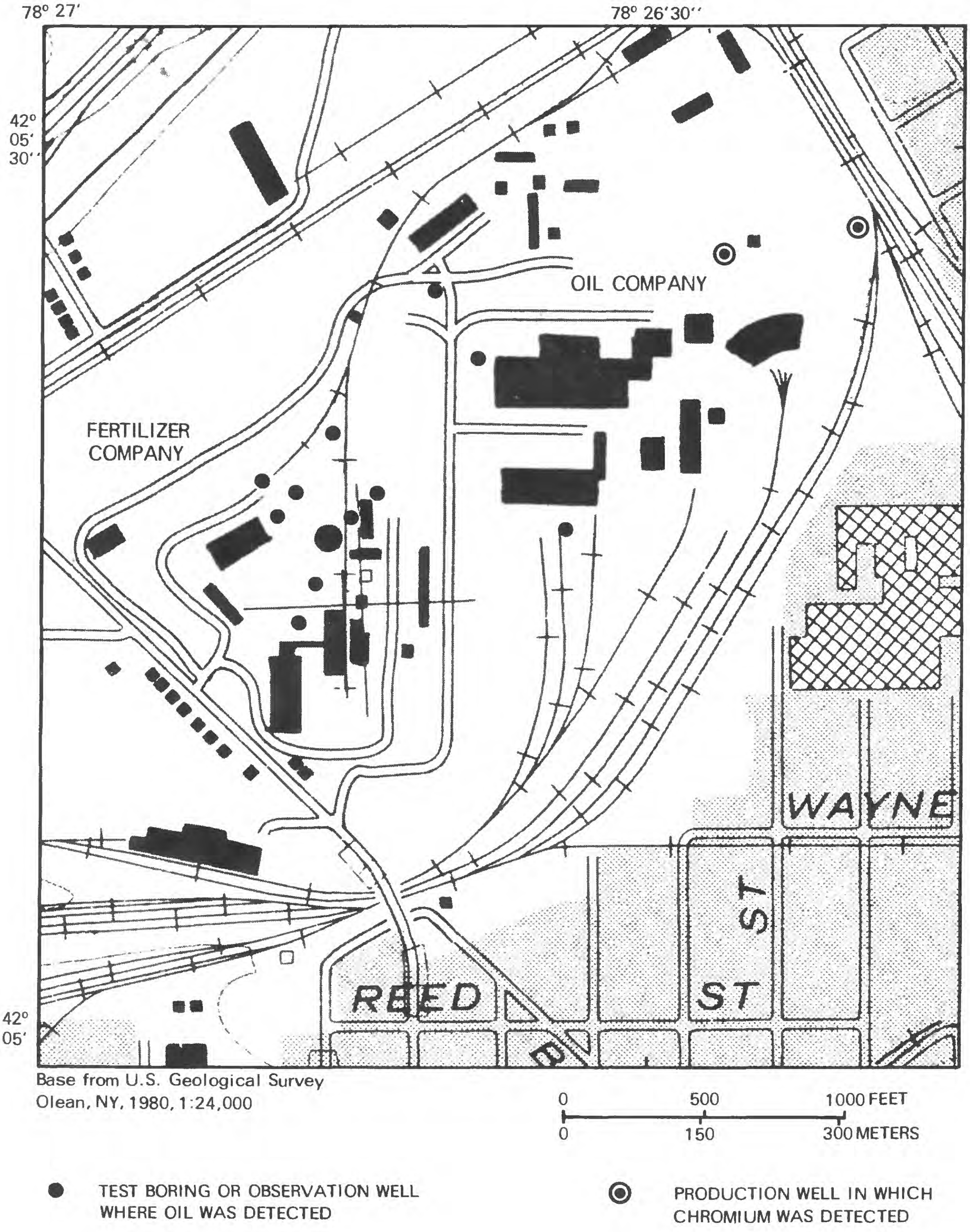
Ground-Water Quality

The quality of ground water in the area of the industrial park has been affected by industrial activities during the past 70 years. Both chromium and petroleum products have been detected in ground water in this area (Frimpter, 1974, p. 59-60). Nitrogen is the contaminant of primary concern, however, because a large amount is present and because it is mobile as well as potentially toxic.

Many ground-water samples have been collected in the area of the industrial park and analyzed for nitrogen compounds, but little information on other chemical constituents is available. Analytical results from samples collected during 1967-85 by several investigators are summarized in table 1.

In addition to nitrogen compounds, petroleum was detected as an oily film in nine test borings and observation wells (shown in fig. 3) in this area by the U.S. Geological Survey in 1978 (A. D. Randall, U.S. Geological Survey, written commun., 1985). Frimpter (1974, p. 59) quotes an account of petroleum contamination that occurred in 1922 near an oil refinery that occupied the present industrial park.

Metal-plating solutions containing hexavalent chromium have also infiltrated to ground water in North Olean (Frimpter, 1974, p. 60). Water from a production well contained 12 mg/L hexavalent chromium in 1967; the concentration had declined to 3.6 mg/L in 1980 (A. D. Randall, U.S. Geological Survey, written commun., 1985).



Base from U.S. Geological Survey
Olean, NY, 1980, 1:24,000

Figure 3.--Location of wells and test borings within the industrial park in which petroleum or chromium have been detected. (Location is shown in fig. 1.)

Table 1.--Concentration of chemical constituents of ground water beneath the industrial park, Olean, N.Y., 1967-85.

[Concentrations in milligrams per liter. First number is mean value; number in parentheses is standard deviation. A dash indicates no analysis was performed.]

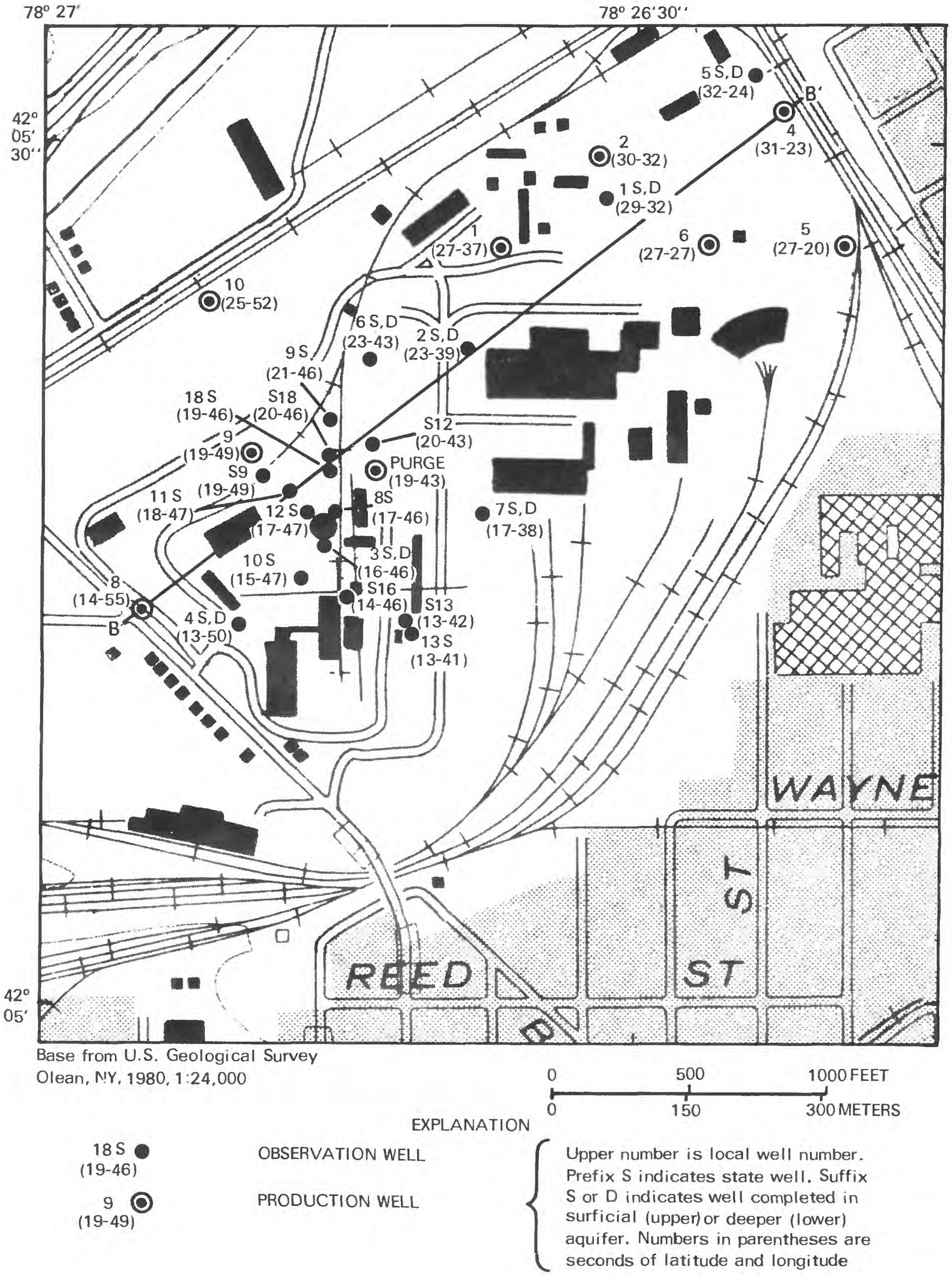
Constituent or characteristic	Date of sample collection and number of samples				
	[1]June 1967 (6)	[2]Oct. 1974 (8)	[2]Oct. 1975 (25)	[1]Nov. 1976 (6)	[3]June 1978 (10)
pH	7.7(0.1)	8.4(0.6)	8.0(0.5)	7.0(0.1)	7.6(0.3)
Specific conductance (microsiemens per cm at 25°C)	550(110)	--	--	--	2,500(1,200)
Hardness, as $CaCO_3$	310(62)	190(160)	--	--	--
Alkalinity, as $CaCO_3$	260(70)	--	--	--	--
Calcium	96(19)	110(84)	--	--	--
Magnesium	16(3.8)	74(99)	--	--	--
Sulfate	19(8.8)	--	--	34(12)	--
Chloride	16(5.3)	--	--	83(20)	--
Silica	9.3(1.5)	--	--	--	--
Phosphate	.27(0.19)	--	--	--	--
Iron	.27(0.19)	--	--	1.11(0.76)	--
Manganese	.30(0.19)	--	--	.71(0.79)	--

[1] Data from Felmont Oil Co.
[2] Data from Hydro Systems Inc.
[3] Data from U.S. Geological Survey

NITROGEN IN GROUND WATER

An oil company and a fertilizer company built two separate manufacturing plants within the industrial park in North Olean during the mid-1960's (fig. 3). The oil company's plant was designed to manufacture ammonia from natural gas, and the fertilizer plant used the ammonia in the manufacture of liquid and solid fertilizer and animal feed.

Both plants received noncontact cooling water from a well field containing ten large-capacity wells screened in the lower part of the aquifer (fig. 4). Each well was capable of producing about 1,000 gal/min. When in full operation, the wells together produced about 10 Mgal/d.



Base from U.S. Geological Survey
Olean, NY, 1980, 1:24,000

Upper number is local well number. Prefix S indicates state well. Suffix S or D indicates well completed in surficial (upper) or deeper (lower) aquifer. Numbers in parentheses are seconds of latitude and longitude

Figure 4.--Location of wells within the industrial park at North Olean.

Each of the firms obtained permits in 1966 from the State of New York to discharge the cooling water at a rate of 7 to 8 ft^3/s and 75° to 90° F, at two outfalls on nearby Two Mile Creek. In 1976, the oil company discontinued its discharge to the creek and discharged directly to the Allegheny River.

In 1969, elevated concentrations of nitrogen in the form of ammonia and nitrate were detected in the aquifer beneath the industrial park. Investigations of plant operation (Hydro Systems, Inc., 1975, 1976, 1977, 1978, 1979, 1980) identified several areas in the vicinity of the fertilizer plant where significant quantities of nitrogen compounds had been introduced into the soil and the aquifer system at or near land surface. The nitrogen was introduced primarily in the form of urea and ammonium through leakage and spills of liquid and solid fertilizer, process compounds, and wastewater. The highest concentrations of nitrogen were beneath areas where these materials were stored in lined and unlined holding ponds and sumps. Detailed descriptions of these areas are provided by Hydro Systems (1979, p. 12-13). The discharge of nitrogen compounds from the plant was eliminated by 1973 after a series of changes in operational practices.

Distribution Within the Aquifer

Water samples from production wells and several observation wells within the industrial park have been analyzed by the fertilizer company for ammonia and nitrate on a regular basis since 1969. More than 90 percent of the nitrogen in samples from the production wells has typically consisted of ammonia (Hydro Systems, 1979). The ammonia in the system is probably in the form of ammonium ion, NH_4^+, because the pH of ground water is below 9 (Hem, 1985, p. 124).

Concentrations of nitrogen have historically been highest in observation wells near the fertilizer company's plant, about 2,000 ft southwest of the center of the oil company's well field (fig. 4). Total nitrogen concentrations during the early 1970's regularly exceeded 2,000 mg/L in three wells (3S, S16, S18, fig. 4) and were as much as 7,200 mg/L in one well, S18 (Randall, 1976, and Hydro Systems, 1975).[1] The highest concentrations of nitrogen were produced at production wells 1 and 2 (fig. 4). Well 1 produced water containing as much as 95 mg/L of nitrogen during the early 1970's, and water from well 2 commonly contained 30 to 35 mg/L of nitrogen, except in late 1971, when concentrations exceeded 60 mg/L (Hydro Systems, 1975, figs. 8-11). Ground water east of the park has contained less than 0.3 mg/L ammonia and 4 to 10 mg/L nitrate, and ground water west of the park contained less than 1 mg/L ammonia and 1 to 4 mg/L nitrate (Randall, 1976).

Concentrations of nitrogen in wells completed in the upper part of the aquifer throughout the area of contamination have been consistently higher than in wells completed in the lower, more permeable part. This is evident through comparison of nitrogen concentrations in upper and lower parts of the aquifer in 1983 (figs. 5A, 5B). The data indicate that nitrogen concentrations

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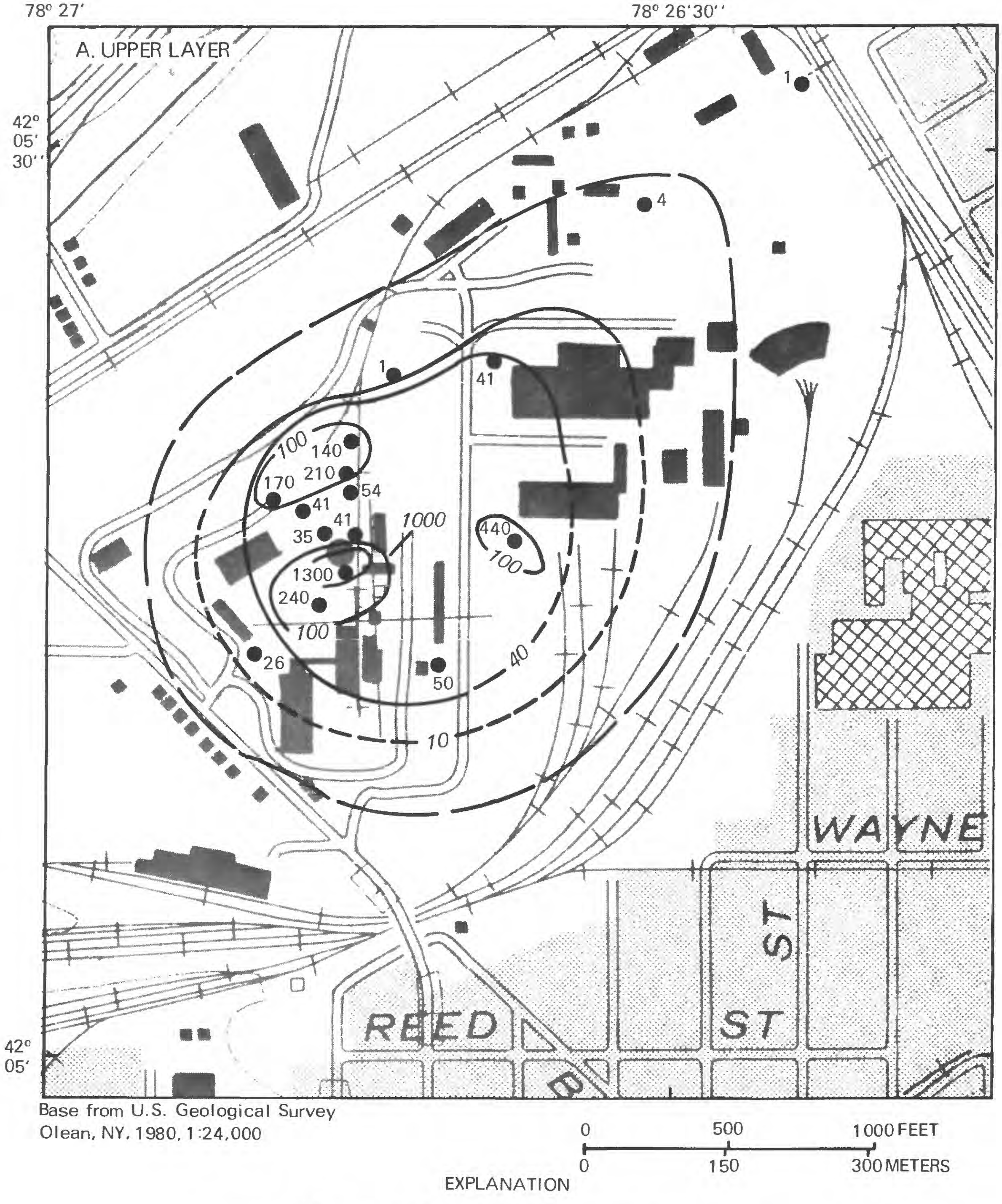
[1] Concentrations of nitrogen in this report are the sum of ammonia plus nitrate unless otherwise noted and are presented in mg/L as N. Concentrations of nitrogen species are also reported in mg/L as N.

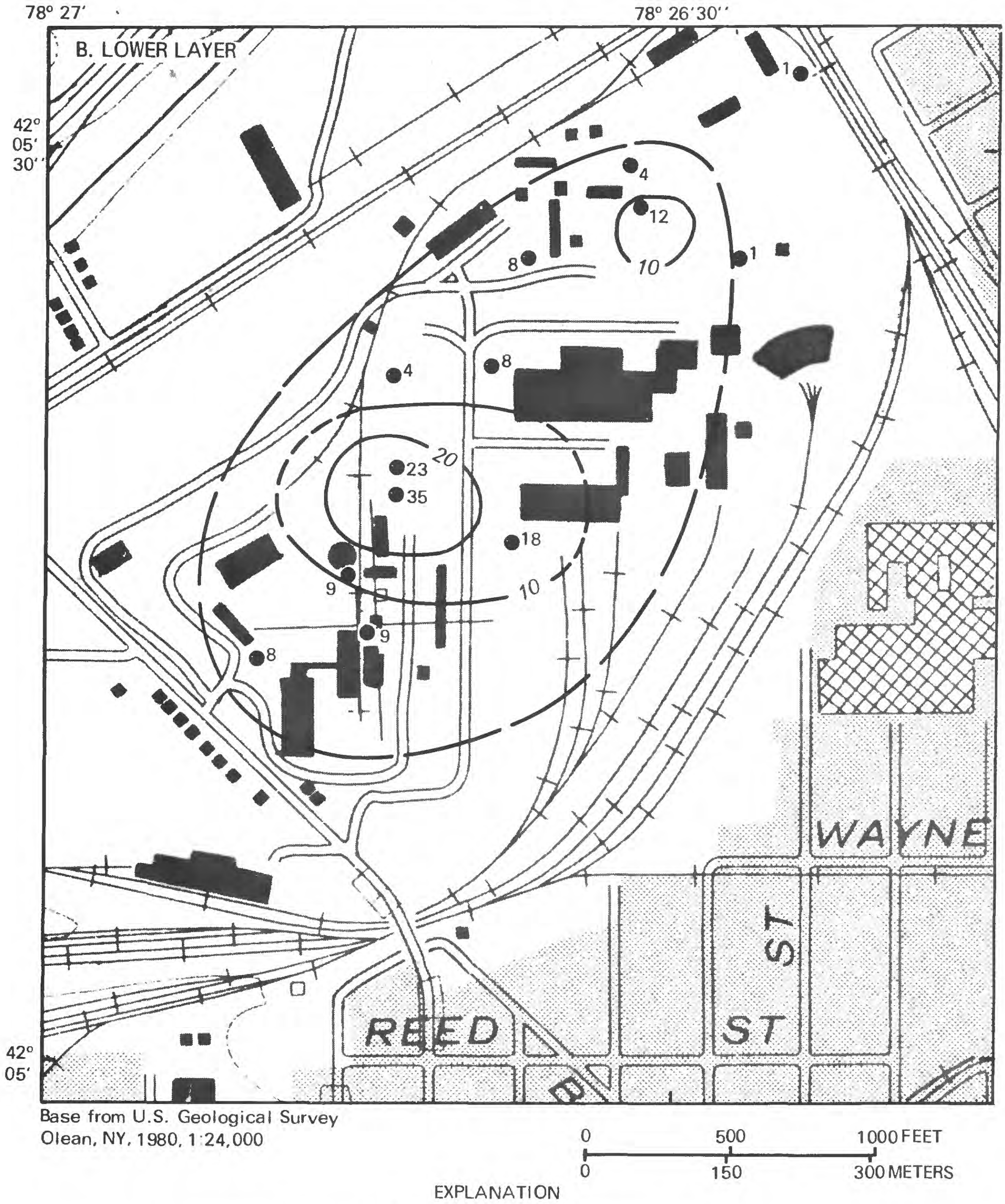


Base from U.S. Geological Survey
Olean, NY, 1980, 1:24,000

EXPLANATION

—— 100 — —	LINE OF EQUAL CONCENTRATION OF AMMONIA PLUS NITRATE, IN MILLIGRAMS PER LITER--Variable interval. Dashed where inferred
● 440	WELL LOCATION--Number is observed concentration of ammonia plus nitrate, in milligrams per liter
—— ——	ASSUMED EXTENT OF NITROGEN CONTAMINATION

Figure 5A.--Average nitrogen concentration of ground water in the upper 50 feet of the aquifer in the industrial park vicinity in 1983.



Base from U.S. Geological Survey
Olean, NY, 1980, 1:24,000

EXPLANATION

—— 20 — — LINE OF EQUAL CONCENTRATION OF AMMONIA PLUS NITRATE, IN MILLIGRAMS PER LITER--Variable interval. Dashed where inferred

●8 WELL LOCATION--Number is observed concentration of ammonia plus nitrate in milligrams per liter

—— —— ASSUMED EXTEXT OF NITROGEN CONTAMINATION

Figure 5B.--Average nitrogen concentration of ground water in the lower 30 feet of the aquifer in the industrial park vicinity in 1983.

in ground water ranged from background levels of 1 to 4 mg/L to as much as 1,300 mg/L at well 3S in the upper part of the aquifer. The smallest decline in concentration since sampling was begun in 1974 has been in the three areas where nitrogen concentrations exceeded 100 mg/L in 1983 (fig. 5A). Nitrogen concentrations in the lower part of the aquifer ranged from background levels to 35.0 mg/L.

The vertical distribution of nitrogen in ground water is consistent with the analyses of cores collected from series of borings by Hydro Systems (1975-80) and the U.S. Geological Survey (Randall, 1976). Core samples collected from the unsaturated zone and the upper part of the aquifer have consistently contained more ammonia and nitrate than samples from the lower part (Randall, 1976, p. 10; Hydro Systems, Inc., 1977). The highest concentrations of nitrogen detected were typically in core samples from just above the water table in the upper aquifer (Hydro Systems, Inc., 1978).

Effect of Industrial Pumping

Continuous pumping from production wells during the 1970's and early 1980's contained nitrogen-bearing ground water within the industrial park and removed nitrogen from the aquifer. In 1978, the fertilizer company installed a purge well screened in both the upper and lower aquifer near the area of highest nitrogen concentration to speed the removal of nitrogen (fig. 4). During the early 1980's, the purge well and three of the production wells that were closest to the area of highest nitrogen concentration (1, 2, and 6) produced almost 100 percent of the nitrogen being removed by pumping.

The total amount of nitrogen removed and the quantity of ground water withdrawn by the industrial well field and the purge well are shown in figures 6A and 6B. These data indicate that in the early 1970's, before installation of the purge well, 100 to 200 tons of nitrogen per year were being removed by the industrial well field. With reductions in pumpage beginning in 1978, nitrogen production from the well field dropped below 100 tons per year and declined steadily to a level of about 25 tons per year in 1983. The purge well produced about 75 tons of nitrogen annually during 1978-80, but by 1983 its production had also declined to about 25 tons per year. Total production of nitrogen decreased from 140 tons in 1979 to 50 tons in 1983, partly from a decrease in pumpage, but primarily because the concentrations of nitrogen in the pumped ground water had decreased significantly. The total amount of nitrogen removed by pumping during 1971-83 is estimated to be 1,900 tons.

Concentrations of nitrogen measured quarterly at the purge well and at production wells 1 and 2 are plotted in figure 7. These wells produced higher nitrogen concentrations than all other production wells in the industrial park during the 1970's and early 1980's. The concentrations show a decline similar to that of the annual production of nitrogen (fig. 6B). Before installation of the purge well, nitrogen concentrations in the production wells showed no clear pattern of decline. Since the purge well began operation in 1978, however, nitrogen concentrations declined steadily except for a slight rise in 1979. Declines have been most pronounced in the wells with the highest concentrations--the purge well and well 1.

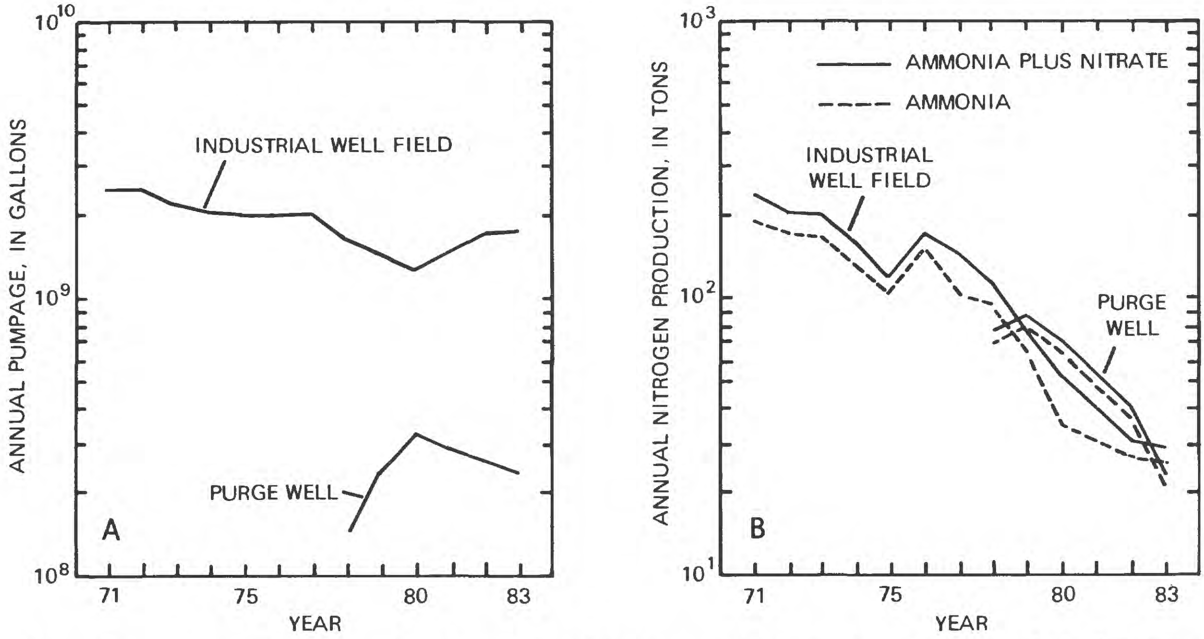


Figure 6.--Annual pumpage (left) and total nitrogen (right) produced from the industrial well field and the purge well, 1971-83.

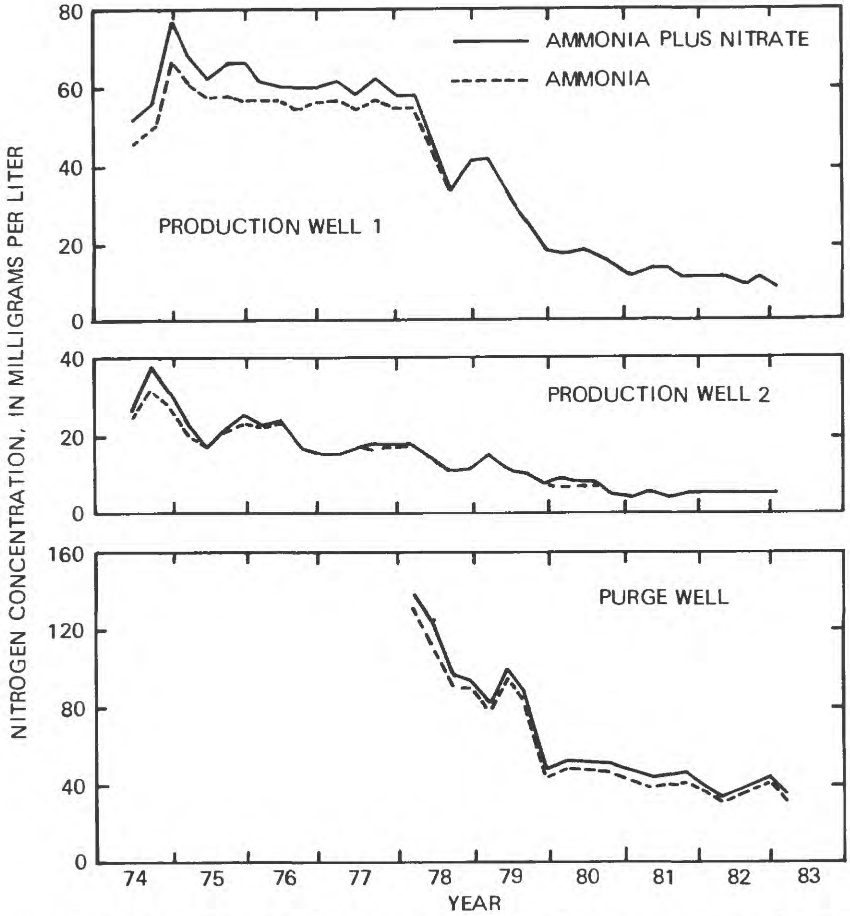


Figure 7.--Nitrogen concentrations at purge well and production wells 1 and 2, 1974-83.

Processes That Affect Nitrogen Transport

Nitrogen detected in ground water within the industrial park has generally been in the form of ammonium or nitrate. The relative concentrations of these two species is important in estimating the rate of nitrogen transport from the contaminated area because nitrate moves freely with ground water, whereas movement of ammonium is retarded by adsorption processes. Nitrogen also is involved in several microbial reactions that can transform it from one species to another. The effects of adsorption described below were incorporated into simulations with a one-dimensional model to estimate the rate of nitrogen migration and are discussed in a later section. The effects of microbial reactions, discussed later in this section, were not incorporated into the modeling.

Adsorption

Ammonium dissolved in ground water can be removed from solution by adsorption onto clay minerals in the aquifer. (Adsorbed ammonium can later desorb back into solution if the concentration of dissolved ammonium in ground water decreases.) As a result, ammonium is transported through the aquifer more slowly than ground water. The magnitude of this retardation depends on the adsorption characteristics of the sediment, the concentration of ammonium in solution, and the chemical composition of the ground water.

Adsorption properties of the aquifer material, including the cation-exchange capacity (CEC) and adsorption isotherm for ammonium, were measured in a laboratory study (In-situ Inc., 1984). The CEC, a measure of the maximum amount of cations that can be adsorbed onto sediments, was estimated to be 1.11 meq/kg of aquifer material. Measurements were made on the <325-mesh (44-μm) fraction of the aquifer material, and the results were extrapolated to the entire sample on the assumption that the >325-mesh fraction had a negligible exchange capacity.

The adsorption isotherm is a function relating the concentration of adsorbed ammonium to the concentration in solution. The laboratory study was performed on five samples of material from the lower aquifer in the industrial park. Concentrations of major cations in the test sample were the same as in ground water produced by production wells in the industrial park.

As the concentration of dissolved ammonium was increased in these experiments, the amount of ammonium adsorbed onto the aquifer material reached a maximum (fig. 8.). This property is characteristic of a Langmuir adsorption isotherm defined as:

$$\overline{C} = \frac{K_e C_{max} C}{1 + K_e C} \qquad (1)$$

where:

$\overline{C}$ is the concentration of the adsorbed species, M/M,
C is the concentration of the dissolved species, M/L^3,
C_{max} is the maximum concentration of the adsorbed species, M/M, and
K_e is a constant, L^3/M.

Values of C_{max} and K_e were obtained from a least-squares regression of the linearized form of equation 1, in which values of $\bar{C}$ and C were determined by the laboratory study. C_{max} was estimated as 18.5 mg/kg or 1.03 meq/kg, which compares favorably with the estimated CEC of the aquifer material. K_e was estimated to be 0.168 L/mg. The assumed Langmuir isotherm is included in figure 8.

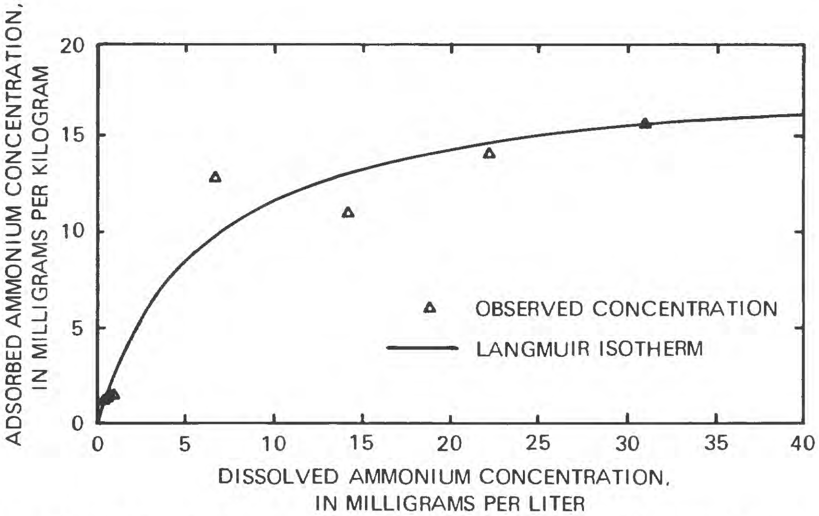


Figure 8.--Relation between amount of ammonium adsorbed onto aquifer material and amount dissolved in ground water.

Microbiological Transformations

Nitrogen is continually cycled within the environment through transformations that involve organic, inorganic, and volatile compounds. These transformations have been extensively studied in soil and surface-water systems and found to be controlled primarily by microorganisms. Nitrogen transformations in ground water have been studied less but are assumed to be similar.

The major nitrogen-transformation processes are immobilization and mineralization. Immobilization refers to the microbial conversions of volatile and inorganic forms of nitrogen to simple organic compounds, which in turn can be incorporated into more complex compounds by plants and animals. Mineralization refers to the conversion of organic nitrogen compounds to inorganic forms through microbial decay of organic material. Not all organic nitrogen is mineralized to inorganic forms, however; some is assimilated to form new microbial protoplasm (Alexander, 1977, p. 259). Organic nitrogen compounds persist for relatively long periods in nature; in soil systems, only a small percentage of the nitrogen reservoir is mineralized each growing season.

Mineralization involves two microbial processes--ammonification and nitrification. In ammonification, ammonium (NH_4^+) is formed from organic compounds under both aerobic and anaerobic conditions and over a wide range of pH. Ammonium is readily adsorbed to clay particles and is converted above pH 9.0 to ammonia (NH_3), which can be lost to the atmosphere in gaseous form. In nitrification, ammonium is oxidized to nitrite (NO_2^-) and nitrate (NO_3^-), a process that requires both aerobic and neutral to alkaline conditions. Nitrite generally converts rapidly to nitrate and is rare in nature.

Nitrate is the most mobile form of nitrogen in ground water and is readily susceptible to leaching in the unsaturated zone. It can be reduced under anaerobic conditions through a third microbial process, denitrification, to volatile forms of nitrogen (N_2) and nitrous oxide (N_2O), which can be lost to the atmosphere. Nitrate can also be reduced to ammonium through microbial respiration under anaerobic conditions. Nitrogen transformations that occur in nature are illustrated in figure 9.

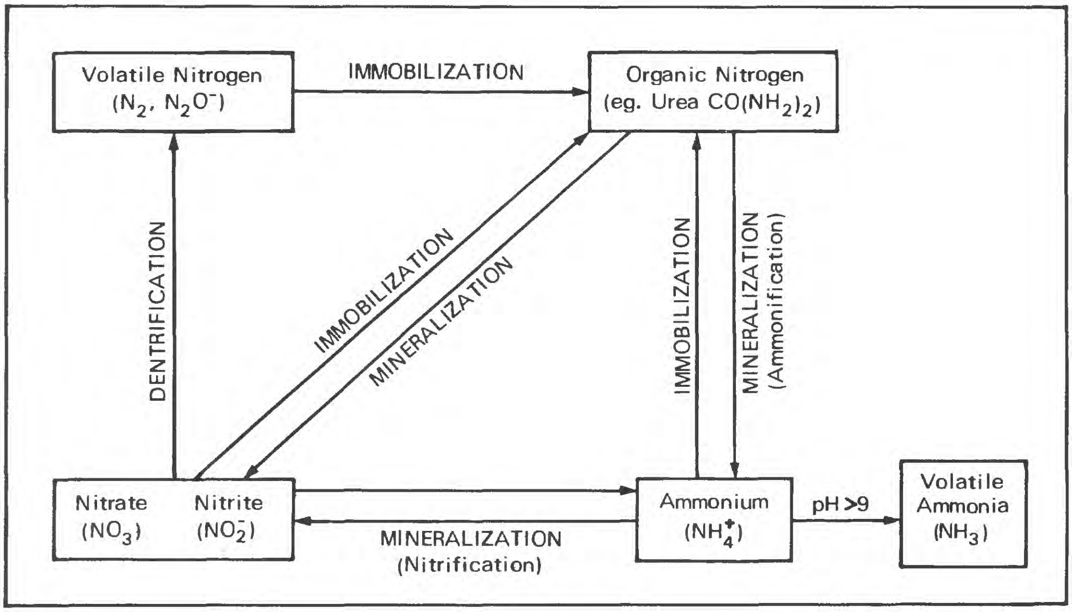


Figure 9.--Major microbiological transformations of nitrogen species.

Fate of Nitrogen at the Industrial Park

Urea and ammonium that leaked or spilled during operations at the fertilizer plant entered the soil in liquid form and infiltrated to the unsaturated zone. These compounds were probably converted through mineralization and immobilization to other forms of nitrogen as they leached to the underlying aquifer. The effects of these processes are described below.

Mineralization

The urea, $CO(NH_2)_2$, was probably mineralized to ammonium through urea hydrolysis, which is a rapid reaction (Alexander, 1977, p. 235). The ammonium would have been available for nitrification to nitrate under the aerobic conditions prevailing in the unsaturated zone. Both urea-hydrolyzing and nitrifying bacteria were identified in samples taken within 10 ft of land surface at the industrial park in 1976 (J. P. White, St. Bonaventure University, written commun., 1985). Both ammonium and nitrate leached from the unsaturated zone to the underlying aquifer by recharge from precipitation, but the movement of ammonium was retarded by adsorption. Both nitrogen species probably still remain in micropores, from which leaching still occurs at a slow rate.

Immobilization

Some of the nitrogen released during hydrolysis of urea to ammonium would have been immobilized as organic nitrogen through microbial action. Without information concerning the amount of available carbon present in soil and aquifer material, however, the amount of nitrogen immobilized cannot be estimated directly. Concentrations of organic nitrogen in aquifer material were calculated from total Kjeldahl nitrogen analysis of core samples from boreholes at the industrial park in 1978 (A. D. Randall, U.S. Geological Survey, written commun., 1985). Organic nitrogen concentrations in material from the unsaturated zone were as high as 9,800 mg/kg (dry weight) and were as much as 6,100 mg/kg in material from the upper aquifer (table 2). The mean concentration of organic nitrogen in both zones was about 1,000 mg/kg, slightly lower than the estimated mean concentration (1,300 mg/kg) in samples from three uncontaminated sites elsewhere in the Olean area. In contrast, organic nitrogen in most soils ranges from 500 to 2,500 mg/kg (Brady, 1974, p. 155).

Table 2.--Concentrations of nitrogen species and organic carbon measured in core samples from the industrial park in 1978.

[Concentrations in mg/kg (dry weight);
n = number of samples, $\overline{x}$ = mean,
s = standard deviation, r = range.]

Statistic or constituent	Soil	Unsaturated zone	Upper aquifer	Lower aquifer	Uncontaminated zone
Depth below land surface (ft)	0-6	7-36	37-59	59-80	5-73
Ammonium					
n	14	114	31	10	14
$\overline{x}$	110	8	93	19	8
s	230	70	160	33	14
r	3-850	2-300	3-660	3-110	2-55
Organic nitrogen[1]					
n	13	111	29	6	6
$\overline{x}$	5,200	1,100	1,000	340	1,300
s	5,400	1,000	1,300	60	990
r	410-19,000	320-9,800	240-6,100	280-460	520-1,500
Organic carbon					
n	3	17	7	2	4
$\overline{x}$	200	12,000	4,800	9,300	10,000
s	200	11,000	1,800	1,300	12,000
r	0-400	0-34,000	2,800-7,500	8,300-10,000	0-25,000
Ratio of organic carbon to organic nitrogen	.20	19	73	23	8

[1] Calculated from total Kjeldahl nitrogen minus ammonium

The organic nitrogen detected in the core samples at the industrial park could have been derived from three sources--microbial cells, petroleum residue, or organic material deposited with the aquifer material. Organic nitrogen in microbial cells would represent a potential source of inorganic nitrogen under anaerobic conditions; the other two forms of organic nitrogen are less available for mineralization and would not produce significant amounts of inorganic nitrogen.

The form of the organic nitrogen present cannot be determined from the measured concentrations of organic nitrogen and carbon, but microbial cells probably do not account for a large percentage of the total. If the weight of 10^{12} bacteria is assumed to be 1 g, and if nitrogen constitutes 5 percent of this weight, the mean concentration of 1,000 mg/kg of organic nitrogen would represent more than 10^{10} bacterial cells per gram of sediment (Atlas and Bartha, 1981, p. 400; Alexander, 1977, p. 242), which is considerably greater than the range of 10^6 to 10^9 bacteria per gram generally observed in soils (Atlas and Bartha, 1981, p. 212). By contrast, a sewage-contaminated aquifer on Cape Cod, Mass., is reported to contain 1.5 x 10^7 bacteria per gram (Harvey and others, 1984). Further investigation would be required to determine the significance of the organic nitrogen as a potential source of nitrogen contamination in ground water.

Potential for Migration

Three nitrogen species have been identified in the contaminated area of the industrial park--ammonium, nitrate, and organic nitrogen. Ammonium is the predominant form of nitrogen dissolved in ground water; nitrate occurs in low concentrations. Organic nitrogen accounts for most of the nitrogen within the aquifer material. A conceptual model of the relative rates of movement of these compounds is discussed below.

Ammonium.--A large amount of ammonium probably remains adsorbed to aquifer material but may occur in dissolved form in areas of low hydraulic conductivity in the upper aquifer. Adsorption may have little effect on ammonium migration near the center of the contaminated area, where the concentration of adsorbed ammonium exceeds the CEC of aquifer material, but may be significant at the periphery of the contaminated area, where concentrations are lower.

Nitrate.--Some ammonium is probably nitrified to nitrate, but the rate of this conversion in the aquifer may be limited by the lack of dissolved oxygen, as suggested by the considerably higher concentrations of ammonium than of nitrate in ground water beneath the industrial park. Movement of nitrate within the aquifer is determined primarily by ground-water velocity; thus, nitrate should have been quickly flushed from the aquifer by pumping of production wells. The continuing presence of nitrate indicates that some nitrification is occurring, however, perhaps supported by dissolved oxygen in uncontaminated ground water that is drawn into the contaminated area by production wells. Localized zones where nitrate concentrations exceed 100 mg/L may represent areas of low hydraulic conductivity through which little ground water flows. Some of the nitrate may be denitrified to volatile forms of nitrogen, but the rate of this conversion is unknown.

Organic nitrogen.--The organic nitrogen in the aquifer is assumed to be in a solid form and unlikely to migrate with ground water. Mineralization of the organic nitrogen may represent a potential source of ammonium or nitrate, but the potential rate of mineralization cannot be assessed without information concerning molecular forms.

NITROGEN TRANSPORT

Changes in nitrogen concentration in ground water as it migrates from contaminated areas within the industrial park toward the municipal well field were predicted by a solute-transport model developed by Konikow and Bredehoeft (1978), which simulates two-dimensional ground-water flow and solute transport. The assumptions used in the modeling approach, summarized below and in table 3, are approximations of the conceptual model discussed in the preceding section and limit the interpretation of the model results. The utility of the solute-transport model in predicting nitrogen concentrations is discussed in the concluding section of this report.

Approach

Nitrogen concentrations in ground water as it migrates from contaminated areas within the industrial park could be influenced by advection, adsorption, hydrodynamic dispersion, and microbiological transformations. To accurately represent the interaction of these processes would require a three-dimensional model that could simulate the transport of three nitrogen species and several reactions. Such a model was beyond the scope of this study, however, and the mechanisms and rates of potential reactions for this problem have not been accurately defined. Nitrogen transport was therefore simulated as two-dimensional movement of a single conservative species. To supplement the effort, the effects of adsorption along a flow path through the industrial park were simulated by a one-dimensional transport model; results are discussed in the concluding section.

The solute-transport model developed in this study did not simulate all processes that may affect nitrogen transport, and because it assumes all nitrogen in ground water to be in the mobile nitrate form, it could predict only the worst-case nitrogen concentrations that would result from a permanent shutdown of the industrial well field. As a result, model predictions would indicate earlier arrival times of nitrogen at the Olean municipal well field and possibly higher peak concentrations than would actually occur.

The solute-transport model was designed to simulate movement of nitrogen through the lower aquifer near the industrial park. The lower aquifer is the likely conduit for transport of nitrogen to the municipal well field 7,000 ft away because it represents 90 percent of the transmissivity of the aquifer system in this area. The model used nitrogen-bearing recharge to compute a "source rate" that simulated the nitrogen flux (lb/yr) from the upper to the lower aquifer. The source rate was calibrated by comparing observed nitrogen concentrations in production wells screened in the lower aquifer with those computed by the model.

Two calibration simulations were made. The first simulated nitrogen concentrations over the 7-year period 1978-84. Computed nitrogen concentrations at the end of this period were used as an initial condition to calibrate the model to nitrogen concentrations observed during an actual 6-month shutdown of the industrial well field in 1985. The model was then used to predict changes in nitrogen concentration that would result from a permanent shutdown of pumping wells at the industrial park.

Table 3.--Assumptions associated with conceptual and solute-transport models of nitrogen transport.

A. Nitrogen species and reactions affecting transport

Model	Species	Reaction
Conceptual	ammonium	adsorption, nitrification
	nitrate	denitrification
	organic nitrogen	adsorption, ammonification
Solute transport	nitrate	none

B. Nitrogen source and release mechanism

Model	Source	Release mechanism
Conceptual	unsaturated zone	leaching of ammonium and nitrate with recharge
	upper aquifer	advection of ammonium and nitrate from low-permeability areas
Solute transport	unsaturated zone	leaching of nitrate with recharge

Description of Solute-Transport Model

The solute-transport model uses an alternating-direction implicit numerical method to solve the finite-difference approximation of the ground-water flow equation:

$$\frac{\partial}{\partial x_i}\left(T_{ij}\frac{\partial h}{\partial x_j}\right) = S\frac{\partial h}{\partial t} + W(x_i,x_j,t) \qquad i,j = 1,2 \tag{2}$$

where:

$T_{i,j}$ is the transmissivity tensor, L^2/T;
h is the hydraulic head, L;
S is the storage coefficient, dimensionless;
t is the time, T;
$W(x,y,t)$ is the volume flux per unit area (positive sign for outflow and negative for inflow), L/T; and
x_i and x_j are the Cartesian coordinates, L.

The hydraulic head distribution computed from equation 2 was used to compute the velocity of ground-water flow at each point (x_i, x_j). Changes in concentration caused by advection and hydrodynamic dispersion were calculated by solving the following transport equation by the method of characteristics (Konikow and Bredehoeft, 1978, p. 3):

$$\frac{\partial(Cb)}{\partial t} = \frac{\partial}{\partial x_i}\left(bD_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(bCV_i) - \frac{C'W}{\varepsilon} \qquad i,j = 1,2 \tag{3}$$

where:

C is the concentration of the dissolved chemical species, M/L^3;
$D_{i,j}$ is the coefficient of hydrodynamic dispersion (a second-rank tensor), L^2/T;
ε is the effective porosity, dimensionless,
b is the saturated thickness of the aquifer, L;
C' is the concentration of the dissolved chemical in a source or sink fluid, M/L^3, and
V_i is the seepage velocity in the direction of x_i, L/T.

In the method of characteristics, a specific number of traceable particles or points are uniformly distributed in each cell of the finite-difference grid. A solute concentration equal to the average concentration of the water associated with the grid block is assigned to each particle. In one transport time step, every particle is moved a distance proportional to the length of the time increment and the velocity of the ground water at that particle's location. After all particles have been moved, the concentration in each grid cell is then temporarily assigned the average of the concentration of all particles within it. These are used to estimate concentration gradients so that particle concentrations can be adjusted for the effects of dispersion. This procedure is continued for the number of transport time steps required.

Hydrodynamic dispersion is a mixing process caused by mechanical dispersion and molecular diffusion. The model assumes that, in flowing ground-water systems, the contribution of molecular diffusion to hydrodynamic dispersion, which is significant at low velocities, is negligible. Thus the dispersion coefficient reflects only the contribution of mechanical dispersion. On a microscopic scale, mechanical dispersion is a result of differences in velocity and flow paths encountered by molecules moving through an aquifer. The dispersion coefficient in the model is related to the velocity of ground-water flow by a proportionality constant, the dispersivity. The dispersivity is expressed in terms of two components--longitudinal dispersity (also known as the characteristic length), which represents dispersion in the mean direction of flow, and transverse dispersivity, which represents dispersion perpendicular to the mean direction of flow.

Design

The solute-transport model uses a rectangular, block-centered, finite-difference grid that represents an area of about 10.3 mi^2 (pl. 3A). The grid was divided into 4,608 blocks (48 rows, 96 columns), each of which represents 250 ft on a side. Boundary conditions used in the model were selected to represent hydrologic boundaries or were designed such that they would have a minimal effect on the results of model experiments. No-flow boundaries were used to simulate the relatively impermeable shale bedrock at the edges of the outwash aquifer near the valley wall and the lacustrine clay and silt deposits at the base of the outwash aquifer. Constant-head boundaries simulated the lateral underflow of ground water to and from areas outside the model area within the Olean Creek and Allegheny River valleys. Head values assigned to the constant-head boundaries in the model were taken from the ground-water flow model developed by Bergeron (1987).

Leakage was simulated at nodes that approximated the location of Allegheny River, Olean Creek, and Two Mile Creek within the grid. Blocks at the Allegheny River and Olean Creek represented areas of induced infiltration or points of ground-water discharge. The direction of leakage and degree of hydraulic connection between the aquifer and the streams were determined from the difference between stream stage and aquifer head and average values of streambed leakance[1] obtained by Bergeron (1987). Two Mile Creek is an intermittent stream, and the ground-water flow model indicated that the stream would not receive ground-water discharge under any expected conditions. Leakage from the creek was simulated as additional recharge in simulations in which water pumped from the industrial well field was discharged to the creek. The amount of recharge applied was derived from the model analysis by Bergeron (1987).

Data Requirements

Hydraulic properties of the aquifer material (streambed leakance and transmissivity) and areal recharge values used in the two-dimensional solute-transport model were essentially those obtained from the three-dimensional model of Bergeron (1987), with some modifications. The recharge value of 19 in/yr used in the solute-transport model was identical to that used in the flow model. A single value of leakance for Allegheny River and Olean Creek in the solute-transport model duplicated the observed distribution of head. Streambed leakance terms used in both models are presented in table 4.

As noted previously, clay layers 5 to 25 ft thick separate the aquifer into upper and lower units at the industrial park. Bergeron (1987) represented the aquifer system as two separate layers to simulate this effect. Transmissivity values for the two aquifer layers in the flow model were added

Table 4.--Values of streambed leakance used in solute-transport model and ground-water flow model of Bergeron (1985).

[Values in days^{-1}]

Stream	Solute-transport model	Ground-water flow model
Allegheny River	0.9	0.1 - 1.0
Olean Creek	.9	.3 - 4.0
Two Mile Creek	Simulated by recharge	.001 - 5.4

---

[1] Leakance is K/m where K is the hydraulic conductivity (L/T) and m is the streambed thickness (L).

together to obtain the transmissivity of the single layer simulated by the two-dimensional solute-transport model. The resultant transmissivity distribution is presented in plate 3B.

Transport terms required for the solute-transport model include the effective porosity and the dispersivity of the aquifer material. The porosity of the aquifer in the Olean area has never been directly measured but was approximated from values of specific yield that have been reported in the literature for aquifers composed of similar material. A compilation of specific-yield values by Johnson (1967) indicates that specific yields of aquifers consisting mostly of coarse sand or gravel generally range between 20 and 30 percent. Konikow (1977) and Pinder (1973) used longitudinal dispersivity values ranging from 60 to 100 ft and transverse dispersivity values ranging from 10 to 100 ft in simulations of sand and gravel aquifers. The sensitivity of predicted nitrogen concentrations to dispersion was investigated in this study through a comparison of model results based on moderate dispersion (longitudinal dispersivity = 100 ft and transverse dispersivity = 30 ft) with results based on zero dispersion.

The sources of nitrogen contamination in the aquifer (leaching of nitrogen compounds from the unsaturated zone, and advection from areas of low hydraulic conductivity in the upper aquifer where high concentrations persist) were simulated in the transport model as recharge of nitrogen-bearing water at five blocks that best approximated areas of highest nitrogen concentration (fig. 10). The rate of recharge was 19 in/yr, estimated by Bergeron (1987). The nitrogen-source rate, W, was then computed from:

$$W = RAC \tag{4}$$

where: R is the recharge rate, L/T;
A is the area of the block, L^2, and;
C is the concentration of nitrogen-bearing recharge, M/L^3.

The flux of nitrogen to the lower aquifer was assumed to decrease during the calibration period because no nitrogen was discharged from the fertilizer plant and nitrogen was removed from the system by pumping. The decline in nitrogen flux was simulated by decreasing the source rate by an exponential decay term. This term was based on the assumption that the decline in the concentration of nitrogen-bearing recharge is proportional to its concentration:

$$\frac{dC}{dt} = -KC \tag{5}$$

where: t is the time, T; and
K is the decay constant, T^{-1}.

Solution of this equation yields

$$C = C_o e^{-Kt} \tag{6}$$

where: C_o is the concentration of nitrogen-bearing recharge at t = 0, M/L^3.

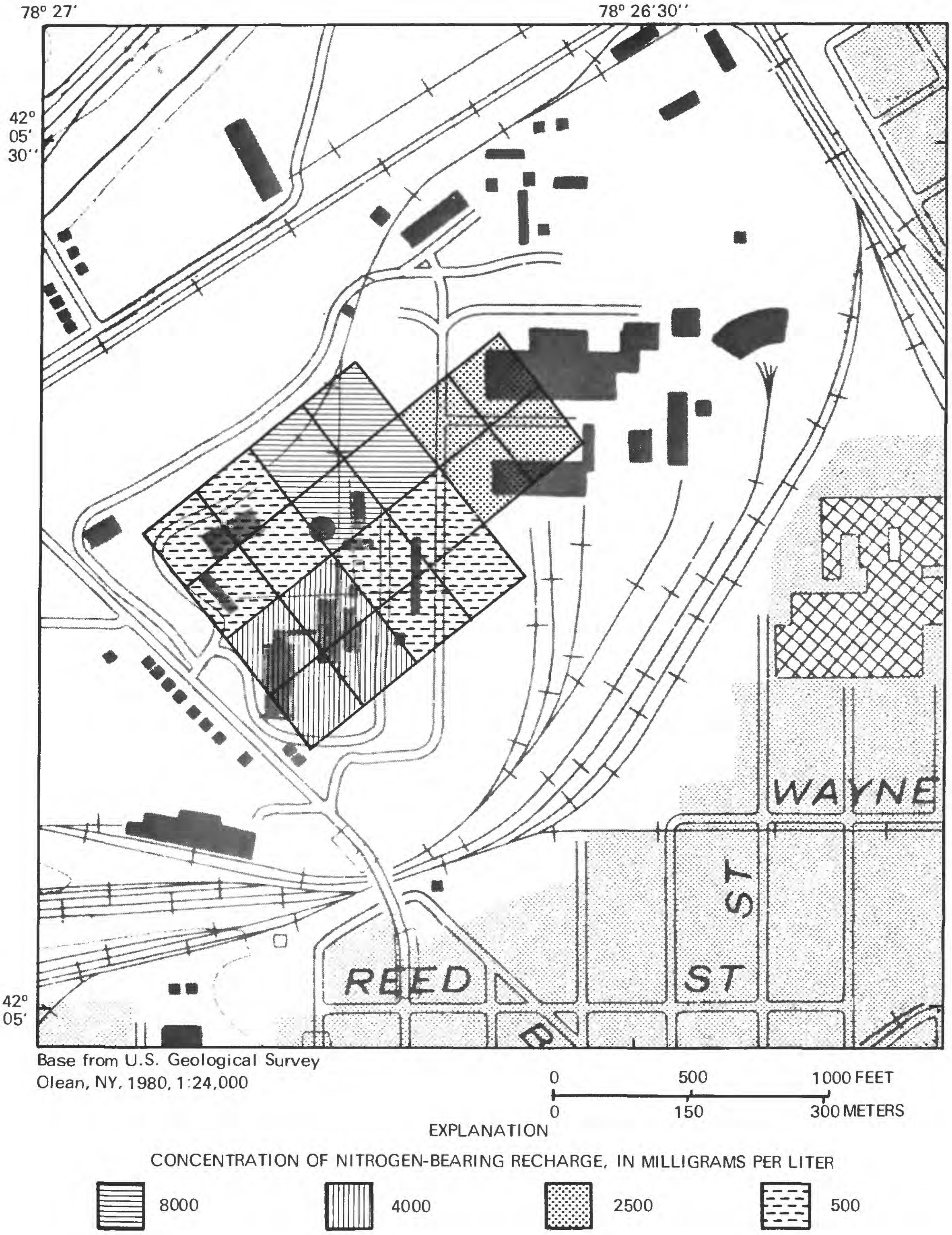


Figure--10. Location of blocks used to simulate nitrogen source and nitrogen concentration of ground-water recharge at beginning of calibration period.

Calibration

Calibration of the solute-transport model consisted of adjusting (1) the initial concentration of nitrogen-bearing recharge in 1978, C_o, and (2) the decay constant, K, which represented the yearly decrease in nitrogen concentrations at the source during 1978-84. Hydraulic properties of the aquifer materials were left unchanged during model calibration because hydraulic head distributions computed by the transport model closely matched ground-water levels recorded in observation wells.

The initial concentrations at the nitrogen source and the decay constant were adjusted during model calibrations to match the observed decline in nitrogen concentrations in water pumped from production wells screened in lower aquifer during 1978-84. Nitrogen concentrations computed by the model were also compared with concentrations measured in 1983 in observation wells screened in the lower aquifer. The highest initial concentration at the source, 8,000 mg/L (fig. 10), represents a 0.8-percent increase in the density of water. The effect of ground-water density on nitrogen movement was neglected in this study because nitrogen concentrations were generally below this level.

Ground-Water Flow

The solute-transport model computed the steady-state hydraulic-head distribution for the 7-year calibration period (1978-84) using average pumpage rates reported from those years. The root-mean-square difference between calculated values and those measured in observation wells in November 1981 was 2.0 ft, 9 percent of the observed 21.9-ft range in water levels. The largest differences were generally near production wells, where simulated pumping rates differed from actual rates on the date of measurement. The ground-water flow paths generated by the model (pl. 2B) are similar to those indicated by water levels observed at the end of the calibration period in March 1984 (pl. 2A). Water levels were higher in March 1984 than those in November 1981 because pumpage from industrial wells had been reduced.

Ground-water inflows as precipitation and leakage, and discharges through pumpage and leakage that were computed by the solute-transport model were also similar to those computed by the ground-water flow model of Bergeron (1987); (see table 5). Total inflows computed by the transport model are lower because it simulates a smaller area. Discharges from the aquifer to streambeds are also lower because the solute-transport model does not simulate discharge to Two Mile Creek.

Nitrogen Concentrations

The solute-transport model calculated nitrogen concentrations in ground water underlying the industrial park in a simulation representing the same period (1978-84). Hydraulic head distribution was assumed to be constant through time, and the concentration at the nitrogen source was assumed to decrease at a specified exponential rate (see eq. 6). Nitrogen concentrations that best matched observed concentrations in well 1 and the purge well were obtained with a decay constant of 0.3/yr. A decay constant of 0.2/yr overestimated nitrogen concentrations throughout the 7-year period, and a decay

Table 5.--Comparison of water budgets for steady-state simulations of 1978-84 hydrologic conditions with solute-transport model and ground-water flow model of Bergeron (1987).

[ft^3/s is rate of flow.]

Source	Solute-transport model		Ground-water-flow model	
	Rate (ft^3/s)	Percentage of total	Rate (ft^3/s)	Percentage of total
Inflow to aquifer				
Recharge from precipitation	9.04	42.3	11.61	41.9
Leakage to aquifer through constant-head boundaries and streambeds	12.33	57.7	16.12	58.3
Total	21.37	100.0	27.73	100.0
Discharge from aquifer				
Pumpage	20.36	95.5	24.46	88.0
Leakage from aquifer through constant-head boundaries and streambeds	.96	4.5	3.32	12.0
Total	21.32	100.0	27.78	100.0
Percent discrepancy	0.23		0.18	

constant of 0.4/yr gave the closest match to observed values during the middle of the period but gave lower values at the end. Results over the 7-year period are plotted in figure 11.

The simulated discharge of nitrogen from wells during the calibration period is plotted against the calculated mass produced annually in figure 12; the simulated values closely match the observed production rate throughout this period. The simulated rate of nitrogen entering the aquifer at the end of the period in 1984 was estimated to be 70,000 lb/yr.

The distribution of nitrogen in the aquifer as simulated with a decay constant of 0.3/yr and moderate dispersion are shown in figure 13 with observed concentrations in 1983 at wells screened in the lower part of the aquifer. Simulated concentrations agree fairly well with those measured in observation wells. The distribution of nitrogen simulated with zero dispersion (not shown) was characterized by a steep concentration gradient surrounding the boundary of the contaminated area. Because this pattern is not evident in the field data, dispersion is probably affecting the transport of nitrogen.

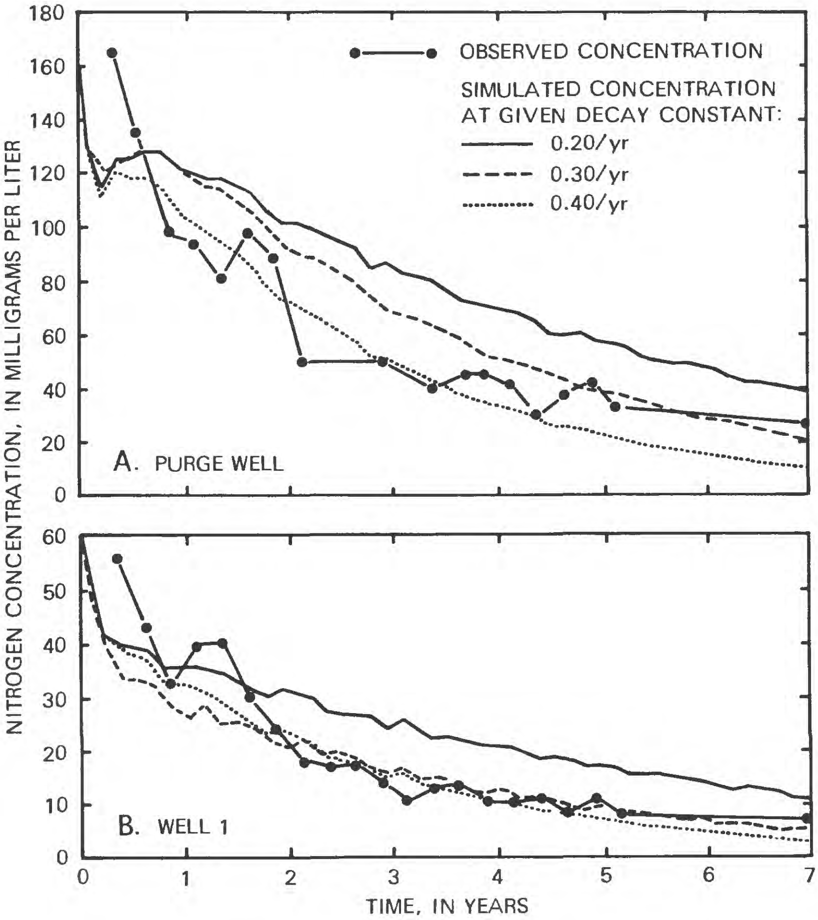


Figure 11.--Simulated and observed nitrogen concentrations resulting from selected decay constants, 1978-84. A. At purge well. B. At well 1.

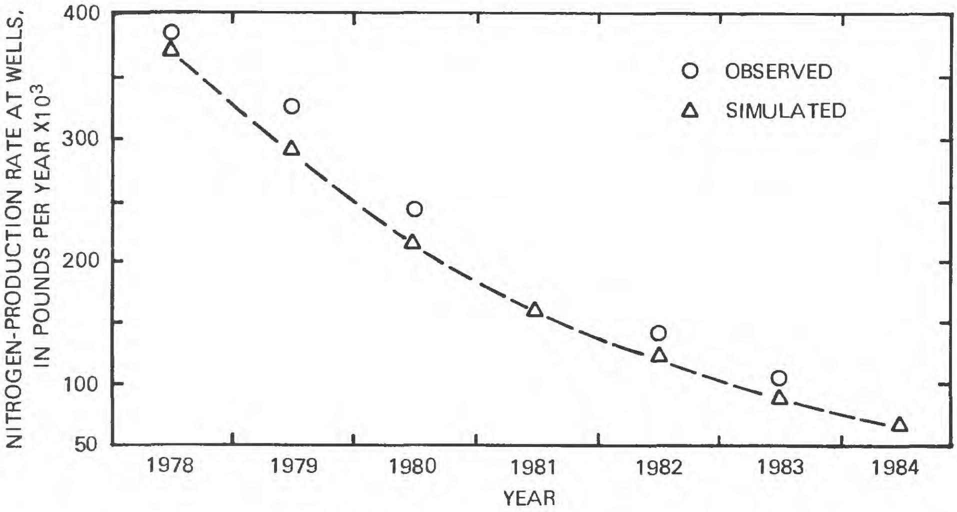
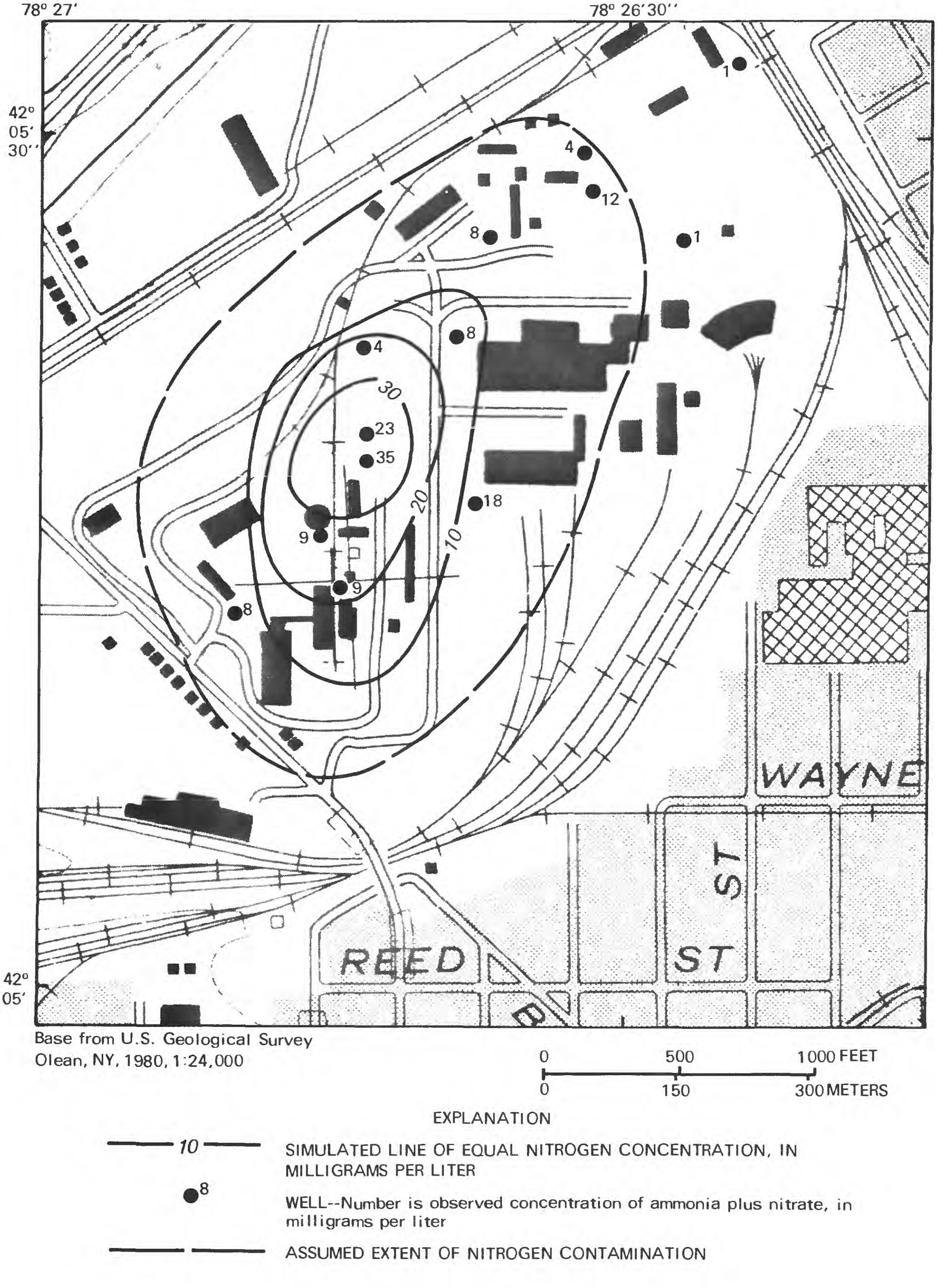


Figure 12.--Simulated and observed rate of nitrogen produced annually by industrial well field.



Base from U.S. Geological Survey
Olean, NY, 1980, 1:24,000

Figure 13.--Simulated and measured nitrogen concentrations in industrial park area in 1983.

SIMULATION OF PROPOSED INDUSTRIAL WELL-FIELD SHUTDOWN

The calibrated solute-transport model was used to predict the nitrogen concentrations that would result at the Olean municipal well field and other areas downgradient of the industrial park after a permanent shutdown of the industrial well field in North Olean.

Possible Effects on the Aquifer

The effect of a shutdown on the rate of nitrogen movement to the lower aquifer (herein called the source rate) is uncertain. The ground-water flow model of Bergeron (1987) and the solute-transport model were used in steady- and transient-state simulations to investigate possible effects of a shutdown.

Simulation of the aquifer system by the ground-water-flow model indicates that 25 percent of the ground water produced by industrial wells is derived from flow through the upper part of the aquifer; the remaining 75 percent is derived from the more permeable lower part. Rates of ground-water flow toward the industrial wells along section B-B' through the industrial park under steady-state pumping conditions are shown in figure 14A. The hydraulic gradient between the upper and lower parts of the aquifer in the ground-water-flow model was reduced from 0.0030 ft/ft under pumping conditions to 0.0006 ft/ft without pumping (fig. 14B). The reduction in hydraulic gradient decreased the simulated vertical leakage from the upper part of the aquifer downward through the semiconfining layer by 50 percent. The reduced volume of water passing through contaminated material in the upper part would decrease the nitrogen flux to the lower part.

The solute-transport model was used to predict steady-state water levels that would result from a permanent shutdown of the industrial well field; results are shown in fig. 15. First the cone of depression beneath the industrial park would fill as water levels recovered, and ground water would then move southwestward toward the Olean municipal well field. Rising water levels would resaturate the previously unsaturated part of the aquifer within the cone of depression and release nitrogen from micropores, which could increase the nitrogen concentration of ground water.

Effects of 1985 Shutdown

An actual 6-month shutdown was begun at the industrial well field on March 15, 1985, to gather information on the effects of a shutdown on nitrogen movement. Water levels were measured periodically before and during the shutdown to determine the amount of time required for complete recovery. Water samples were collected from selected observation wells as water levels recovered and were analyzed for ammonia and nitrate to record changes in nitrogen concentrations.

Ground-water levels near the center of the cone of depression rose 7 ft within 35 days of the shutdown (fig. 16). No snowmelt occurred during this period, and precipitation totaled 2.8 inches. The solute-transport model was used in transient-state simulations of the shutdown with varying specific yield values to predict water levels. A specific-yield value of 0.25 gave the closest match to the observed recovery.

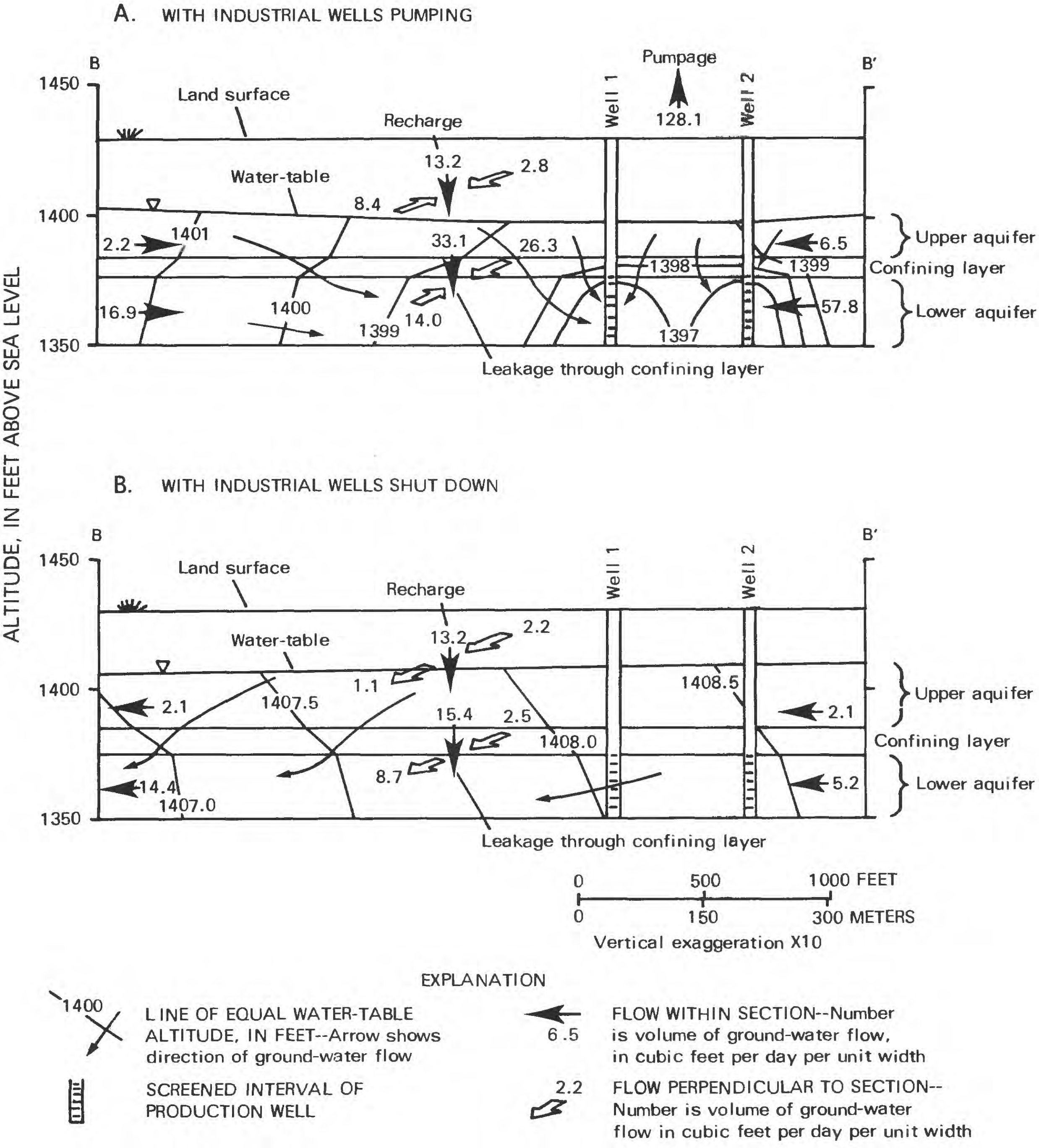
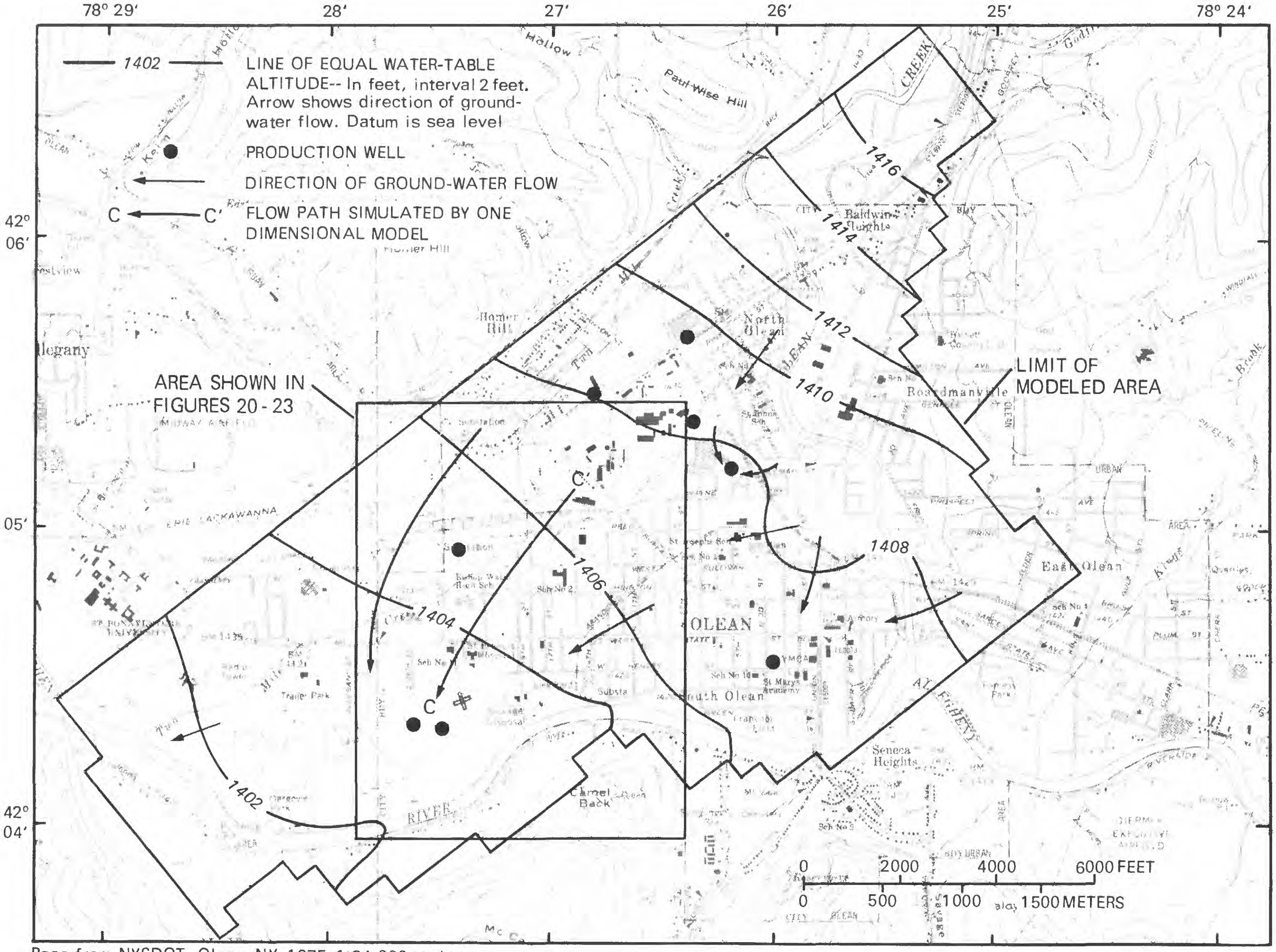


Figure 14.--Schematic diagrams showing simulated ground-water flow along section B-B' in model of Bergeron (1987): A. With industrial wells pumping. B. With industrial wells shut down. (Location of section is shown in fig. 4.)



Base from NYSDOT, Olean, NY, 1975, 1:24,000 scale

Figure 15.--Predicted water-table altitude after simulated industrial well-field shutdown and observed water-table altitude on December 4, 1984.

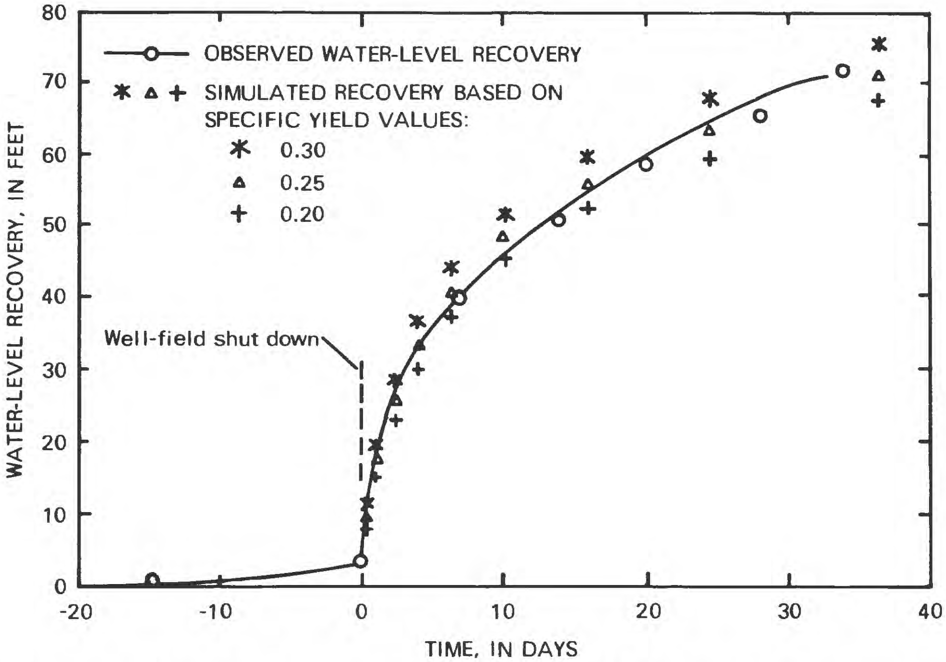


Figure 16.--Water-level recovery observed in well 3D during 6-month well shutdown and water levels predicted by solute-transport model in transient-state simulations. (Well location is shown in fig. 4.)

Nitrogen concentrations at some wells decreased slightly after the shutdown and increased slightly in others. Nitrogen concentrations at wells 4S and 7D are shown in figure 17; well 4S is screened in the upper part of the aquifer, and 7D is screened in the lower part. Little change in nitrogen concentrations occurred in the sampled wells after the shutdown except in well 4S, which is on the downgradient boundary of the industrial park (fig. 4). The concentration in this well increased significantly, probably because of nitrogen migration to the southwest during water-level recovery.

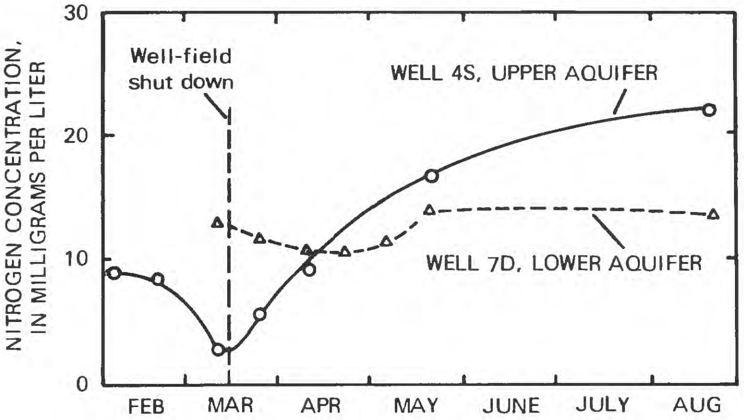


Figure 17.

Nitrogen concentrations observed in wells 4S and 7D before and during 1985 shutdown. (Well locations are shown in fig. 4.)

The nitrogen flux to the lower aquifer decreased after the shutdown as water levels recovered and vertical leakage from the upper aquifer decreased. Release of nitrogen from newly saturated aquifer material did not appear to significantly increase nitrogen concentrations in the upper aquifer. Nitrogen in the upper aquifer probably would migrate horizontally southwestward to the municipal well field, but some would continue to move downward to the lower aquifer during periods of recharge.

The decrease in nitrogen flux to the lower aquifer after the shutdown was calibrated through a comparison of nitrogen concentrations computed by the solute-transport model with those observed during the shutdown (fig. 18). The best match with observed concentrations resulted from a source rate of 14,000 lb/yr--20 percent of the 70,000-lb/yr rate calculated for the end of the calibration period (fig. 12). Higher source rates yielded higher nitrogen concentrations than those observed during the shutdown.

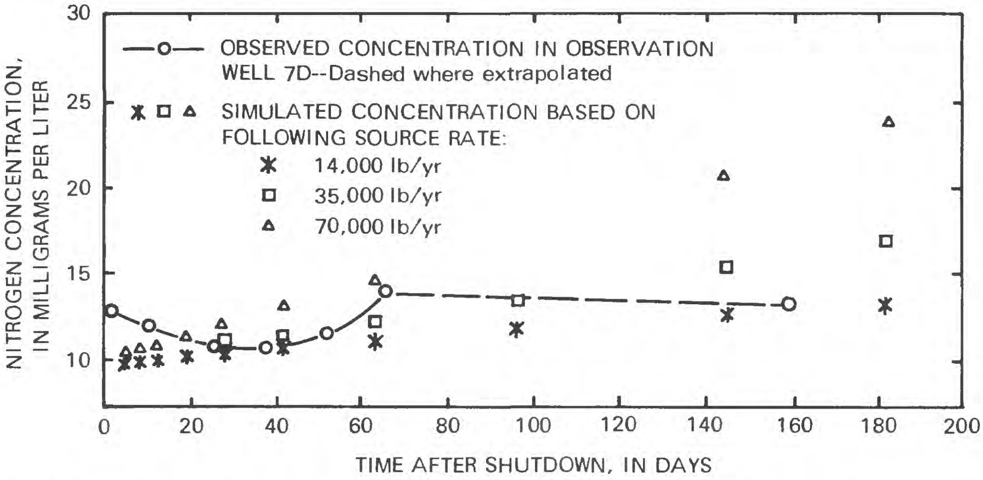


Figure 18.--Observed and predicted nitrogen concentrations in well 7D after well shutdown, based on three nitrogen-source rates.

Migration of Nitrogen From the Industrial Park

The solute-transport model was used to simulate the 30-year period after a permanent shutdown of the industrial well field and to predict nitrogen concentrations of ground water downgradient of the industrial park, including the southwestern boundary of the park near well 4S (fig. 4) and the Olean municipal well field (pl. 1A). The 30-year simulation used hydraulic-head distributions obtained in the previously mentioned simulation of the 6-month shutdown in 1985 (fig. 15). The distribution of nitrogen in the aquifer at the end of the 1978-84 calibration period provided the initial concentrations of nitrogen in the aquifer.

Four transport simulations were run to investigate the sensitivity of model predictions to the source rate, the decay constant, and dispersion. Three simulations used the initial source rate of 14,000 lb/yr that had been successful in simulations of the 6-month shutdown (fig. 18); the fourth used the initial rate of 70,000 lb/yr. Other transport terms used are summarized in table 6 (p. 41). Run A simulated transport with moderate dispersion and with the source rate decreased exponentially by the decay constant of 0.3/yr obtained in previous calibration runs (fig. 11). Run B simulated transport without dispersion and with a decay constant of 0.3/yr. Run C simulated transport with moderate dispersion and zero decay. Run D simulated transport with moderate dispersion and the original source rate of 70,000 lb/yr decreased exponentially by the decay constant of 0.3/yr.

Run A predicted that nitrogen migrating from the industrial park would reach the Olean municipal well field within 5 years. The peak concentration of nitrogen at the municipal well field would be less than 3 mg/L and would occur 10 years after the shutdown (fig. 19A). Predicted nitrogen concentrations at the southwestern boundary of the industrial park would increase to 19 mg/L 3 years after the shutdown and would decrease to less than 1 mg/L within 14 years (fig. 19B). The extent of the nitrogen plume in the aquifer after 5, 10, and 15 years is shown in figures 20A, 20B, and 20C (p. 38). These maps indicate that the area affected by nitrogen contamination becomes much larger but has lower concentrations after 5 years, then decreases to a small area with low concentrations after 15 years.

The nitrogen's arrival time at the municipal well field is directly related to effective porosity because ground-water velocity is inversely proportional to this term. Decreasing the effective porosity from 0.3 to 0.2 would reduce the arrival time from 5 to 3.3 years but would have no effect on predicted peak concentrations of nitrogen.

Run B predicted that the peak concentration would be 8 mg/L after 10 years at the municipal well field and 23 mg/L after 3 years at the southwest boundary of the industrial park (fig. 19). The concentrations after 10 years are higher than those predicted by run A because dispersion was omitted, making the contaminated area smaller (fig. 21). These predictions are probably exaggerated because simulations of the calibration period (1978-84) indicated that dispersion does influence nitrogen migration. Run B confirms, however, that lesser dispersion would significantly increase the peak concentration at the well field but not at the southwest boundary of the industrial park.

Run C predicted that the peak concentration would increase to 4 mg/L at the municipal well field after 14 years and to 24 mg/L at the southwestern boundary of the industrial park after 3 years (fig. 19). In this run, the distribution of nitrogen at both locations reached approximate steady state after 15 years. The predicted steady-state distribution of nitrogen after 30 years (fig. 22) indicates that a constant source rate would cause higher concentrations of nitrogen than a decaying rate and that maximum concentrations would be 20 mg/L.

Run D predicted that the peak concentration would increase to 5 mg/L at the municipal well field after 10 years and to 54 mg/L at the southwestern boundary of the industrial park after 3 years (fig. 19). In this run, a larger area of the aquifer was affected by nitrogen contamination than with the lower source rate 14,000 lb/yr (fig. 23, p. 40). The larger concentration gradient resulting from higher nitrogen concentrations in the aquifer (over 40 mg/L) caused the plume to spread laterally across the major flow path, widening the area of contamination. Some of the nitrogen transported in this run bypassed the municipal well field and was discharged to the Allegheny River.

Nitrogen concentrations that would result from a permanent well-field shutdown are probably best represented by run A (fig. 20). Concentrations predicted by runs B and D are probably higher than those that would occur, but the simulations indicate that the model predictions are quite sensitive to estimates of dispersivity and the nitrogen-source rate. Run C indicates that the value of the decay constant would affect the time required to flush nitrogen from the aquifer but is less important in predicting peak concentrations.

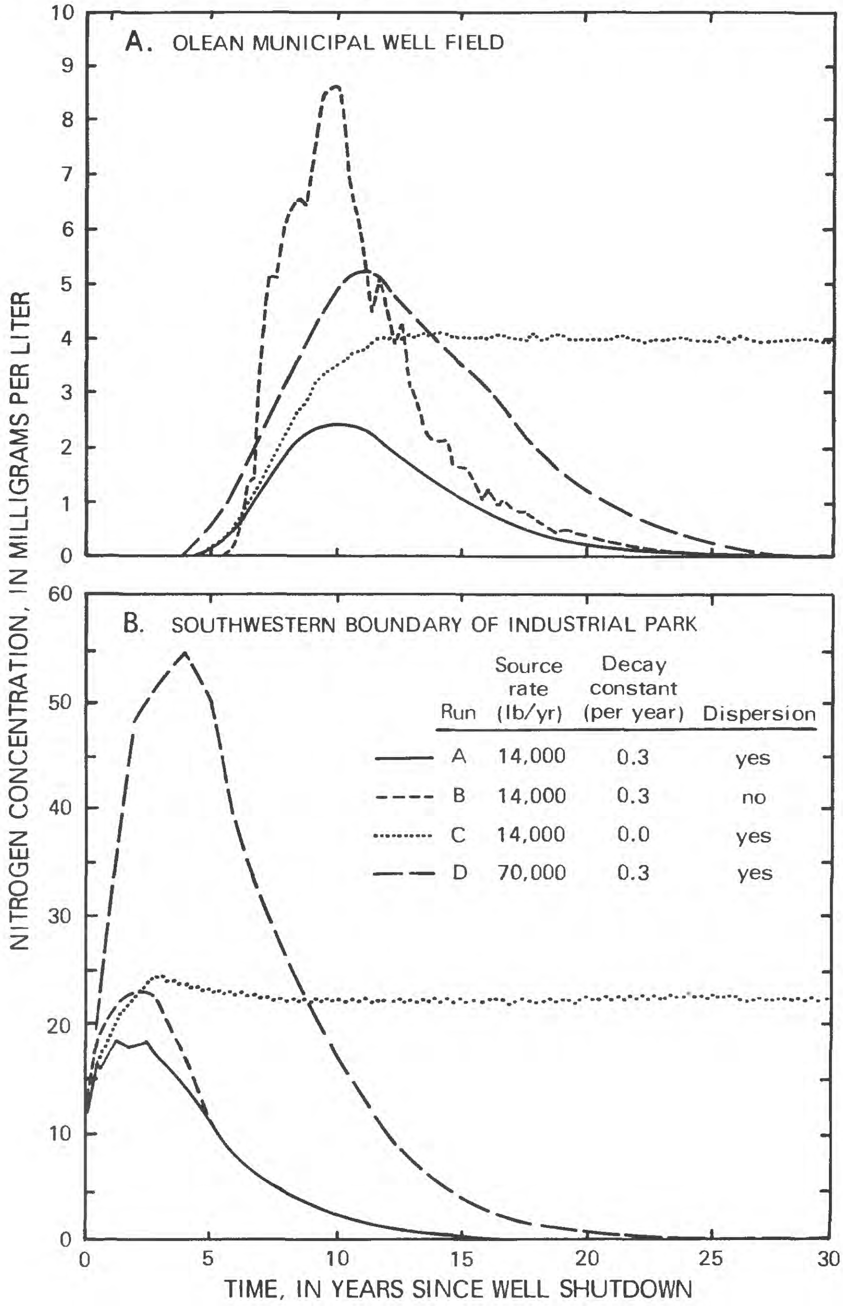


Figure 19.--Nitrogen concentrations predicted by simulations of a 30-year shutdown of the industrial well field with nitrogen-source rate, decay constant, and dispersion varied. A. At Olean municipal well field. B. At southwestern boundary of industrial park.

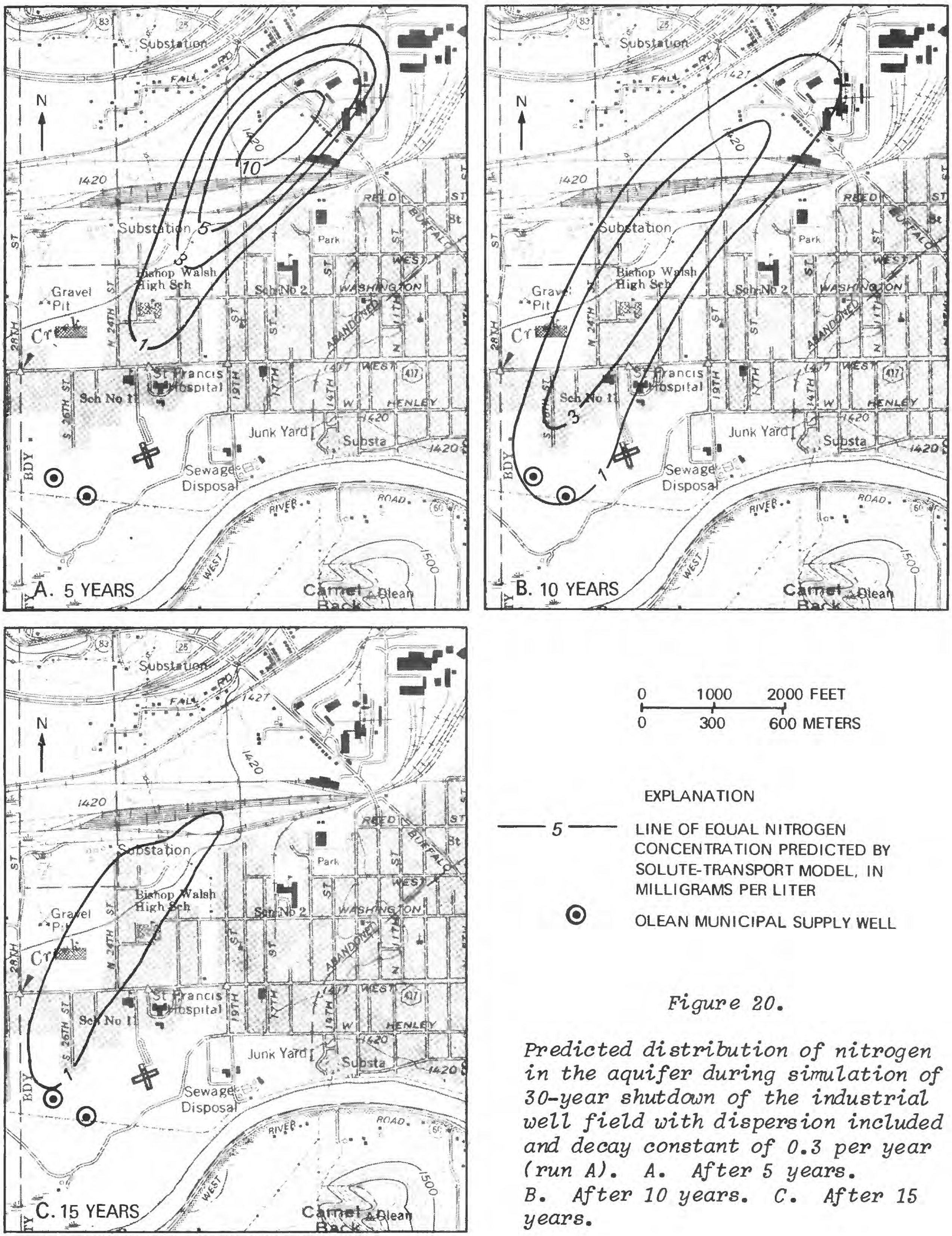


Figure 20.

Predicted distribution of nitrogen in the aquifer during simulation of 30-year shutdown of the industrial well field with dispersion included and decay constant of 0.3 per year (run A). A. After 5 years. B. After 10 years. C. After 15 years.

Base from NYSDOT, Olean, NY, 1975, 1:24,000

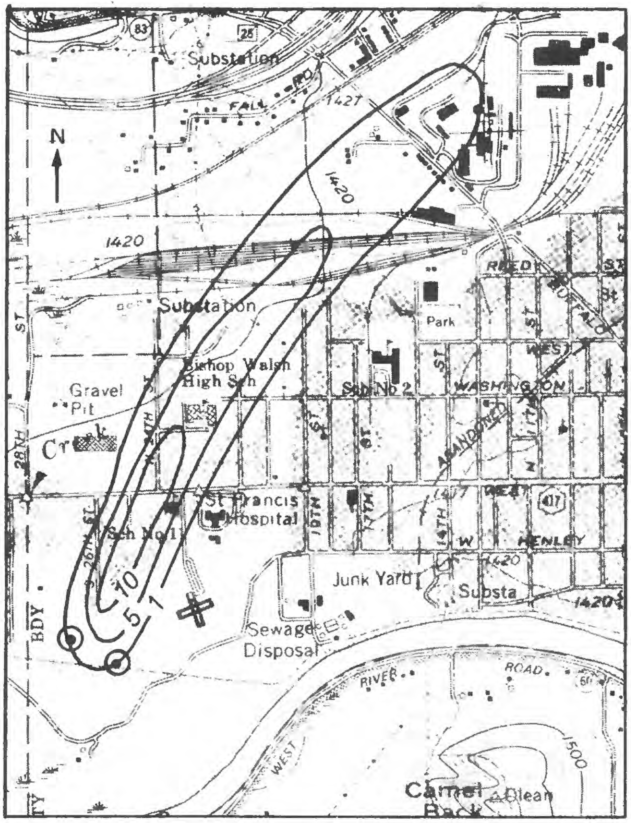


Figure 21.

Predicted distribution of nitrogen in the aquifer 10 years after shutdown of industrial well field with zero dispersion and decay constant of 0.3 per year (run B).

0 1000 2000 FEET
0 300 600 METERS

EXPLANATION

—— 5 —— LINE OF EQUAL NITROGEN CONCENTRATION PREDICTED BY SOLUTE-TRANSPORT MODEL, IN MILLIGRAMS PER LITER

⊙ OLEAN MUNICIPAL SUPPLY WELL

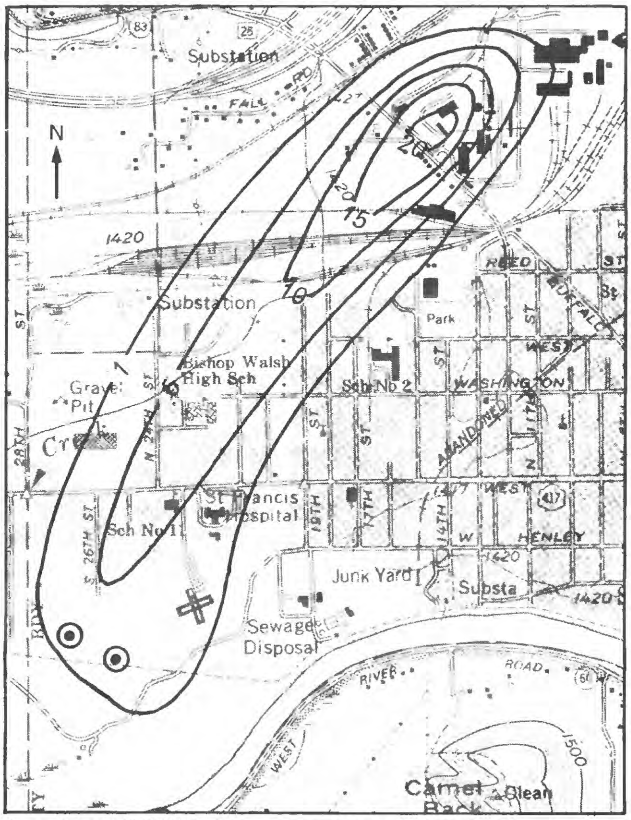
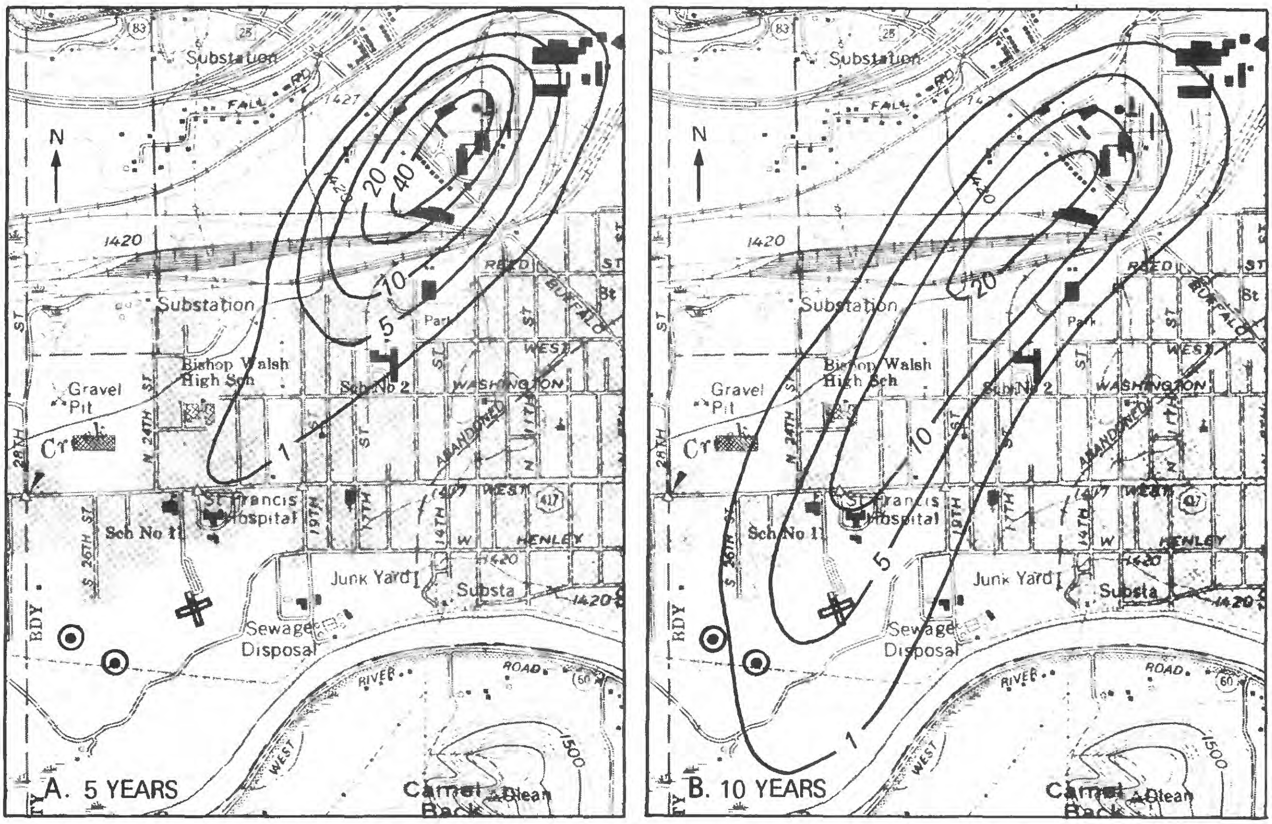
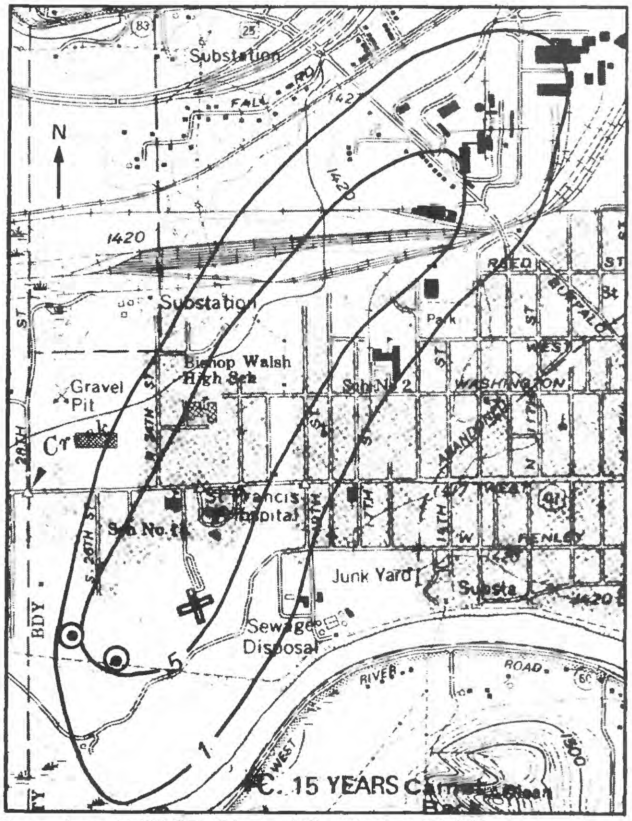


Figure 22.

Predicted steady-state distribution of nitrogen in the aquifer resulting from shutdown of industrial well field at constant nitrogen-source rate of 14,000 pounds per year (run C).

Base from NYSDOT, Olean, NY, 1975, 1:24,000





Base from NYSDOT, Olean, NY, 1975, 1:24,000

EXPLANATION

—— 5 —— LINE OF EQUAL NITROGEN CONCENTRATION PREDICTED BY SOLUTE-TRANSPORT MODEL, IN MILLIGRAMS PER LITER

⊙ OLEAN MUNICIPAL SUPPLY WELL

Figure 23.

Predicted distribution of nitrogen in the aquifer during simulation of 30-year shutdown of the industrial well field with dispersion included, decay constant of 0.3 per year, and nitrogen-source rate of 70,000 pounds per year (run D). A. After 5 years. B. After 10 years. C. After 15 years.

Table 6.--Values used to simulate migration of nitrogen after permanent shutdown of industrial well field.

[All runs are described on p. 35-36.]

Term	Model run[1] A	B	C	D
Effective porosity	0.3	0.3	0.3	0.3
Dispersivity:				
Longitudinal (ft)	100	0	100	100
Transverse (ft)	30	0	30	30
Initial source rate of nitrogen to aquifer (lb/yr)	14,000	14,000	14,000	70,000
Decay constant (per year)	0.3	0.3	0.0	0.3

[1] Extent of migration is shown in figures 20 - 23. Run A = figure 20; run B = figure 21; run C = figure 22; run D = figure 23.

Effect of Adsorption on Predicted Nitrogen Concentrations

Simulations with the solute-transport model predicted that nitrogen concentrations at the municipal well field after cessation of pumping at the industrial well field would eventually range from 2 to 5 mg/L after 10 years. These predictions are based on the simplifying assumption that nitrogen migrates as a conservative solute. Nitrogen migration in the aquifer will probably be retarded by adsorption, however, because the predominant nitrogen species is ammonium. The effect of adsorption on nitrogen concentrations was simulated with a one-dimensional (1-D) transport model based on the following equation for equilibrium-controlled adsorption described by a Langmuir isotherm:

$$\frac{\partial C}{\partial t} = \frac{D}{\bar{\varepsilon}} \frac{\partial^2 C}{\partial x^2} - \frac{Q}{\bar{\varepsilon}} \frac{\partial C}{\partial x} \qquad (7)$$

where: C is the concentration of the dissolved species, M/L^3;
D is the coefficient of hydrodynamic dispersion, L^2/T;
Q is the specific discharge, L/T;
t is the time, T;
x is the distance, L; and

$$\bar{\varepsilon} = \varepsilon + \frac{\rho_b K_e C_{max}}{(1 + K_e C)^2} \qquad (8)$$

where: ε is the effective porosity, dimensionless;
ρ_b is the bulk density of aquifer material, M/L^3;
C_{max} is the maximum adsorbed concentration, M/M; and
K_e is the Langmuir constant, L^3/M.

Derivation of equation 7 is discussed in Lai and Jurinak (1972) and Greenkorn (1983, p. 236). The prediction-corrector linearization method was used to solve a finite-difference approximation of this equation.

The 1-D transport model was applied along the flow path C-C' (fig. 15) to simulate nitrogen migration in the lower aquifer from the center of the industrial park toward the Olean municipal well field. The assumption of one-dimensional transport best approximates conditions in the aquifer near the industrial park, where the ground-water flow field after a shutdown would be fairly uniform in direction and magnitude. The 1-D equation does not account for radial flow components near the municipal well field where flow converges, however, nor does it account for transverse dispersion perpendicular to the direction of ground-water flow. For these reasons the 1-D analysis can give only a qualitative indication of the effects of adsorption on predicted nitrogen concentrations at the municipal well field.

Constant-concentration boundary conditions were used in the 1-D transport analysis; thus, results of these simulations can be compared with results of the solute-transport model's 30-year simulation in which the nitrogen-source rate was held constant (run C). Concentrations of nitrogen in the aquifer were assumed to be 26 mg/L at the upgradient boundary and 0 mg/L elsewhere.

The values used in the 1-D model are listed in table 7. The specific discharge, Q, along the flow path was estimated from the solute-transport model. The dispersion coefficient was calculated by multiplying the mean velocity by a longitudinal dispersivity of 100 ft. The coefficients describing the Langmuir isotherm were those obtained from the laboratory study previously discussed.

Nitrogen concentrations predicted by one-dimensional transport of a conservative solute, obtained by setting the Langmuir coefficients to zero, are compared with concentrations predicted by the solute-transport model in run C after 5 years of shutdown (fig. 24). The solute front predicted by the

Table 7.--Values used in one-dimensional simulation of nitrogen concentrations along flow path C-C' (fig. 15) after shutdown of industrial well field.

Variable	Symbol	Value
Specific discharge	Q	0.26 ft/d
Coefficient of hydrologic dispersion	D	90 ft^2/d
Effective porosity	ε	0.3
Bulk density	ρ_b	1.6 g/cm^3
Maximum adsorbed nitrogen concentration	C_{max}	18.5 mg/kg
Langmuir constant	K_e	0.17 L/mg

solute-transport model travels more slowly than the front predicted by the 1-D model because nitrogen concentrations in the solute-transport model are decreased by transverse dispersion along the flow path. In addition, the two fronts differ in shape because ground-water velocity increases along the flow path in the solute-transport model but is constant in the 1-D model.

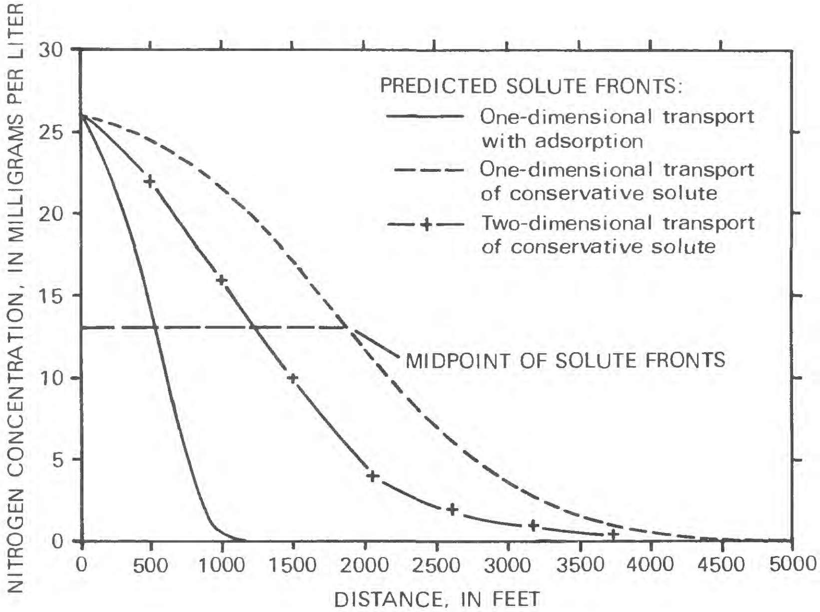
The 1-D model indicates that adsorption would significantly retard movement of the solute front (fig. 24) and suggests that, with adsorption, the midpoint of the front would move about one-third the distance of a conservative solute in 5 years. If adsorption is assumed to have a similar effect in the solute-transport model, the midpoint of the predicted solute front would move about 400 ft in 5 years.

The effects of adsorption and desorption were further investigated with the 1-D model in a simulation of 30 years of transport with a constant nitrogen source-rate followed by 30 years of transport with zero source rate. This run simulated the adsorption of ammonium onto aquifer material within the nitrogen plume and the subsequent desorption of ammonium as the plume is flushed from the aquifer by uncontaminated ground water. Concentrations predicted for distances 500 and 1,000 ft downgradient of the industrial park are plotted in figures 25A and 25B. The curves indicate that arrival of the midpoint of the solute front would be retarded 3 to 7 years at distances between 500 and 1,000 ft along the flow path, and that concentrations of 5 mg/L or less may persist in ground water for many years because nitrogen desorbs from the aquifer at a relatively slow rate.

Adsorption retards the movement of nitrogen more strongly at low concentrations because the adsorption capacity of the aquifer material is limited. Figure 26 depicts the concentration 1,000 ft along the flow path as simulated with the nitrogen-source rate reduced by one-half. The curve indicates that the midpoint of the nitrogen front would be retarded 14 years. This suggests that decreasing nitrogen concentrations in the contaminated area before a shutdown by prolonging the present containment efforts would slow the migration of nitrogen through the aquifer.

Figure 24.

Positions of nitrogen front after 5 years of transport at a constant nitrogen-source rate, as predicted by one-dimensional simulations.



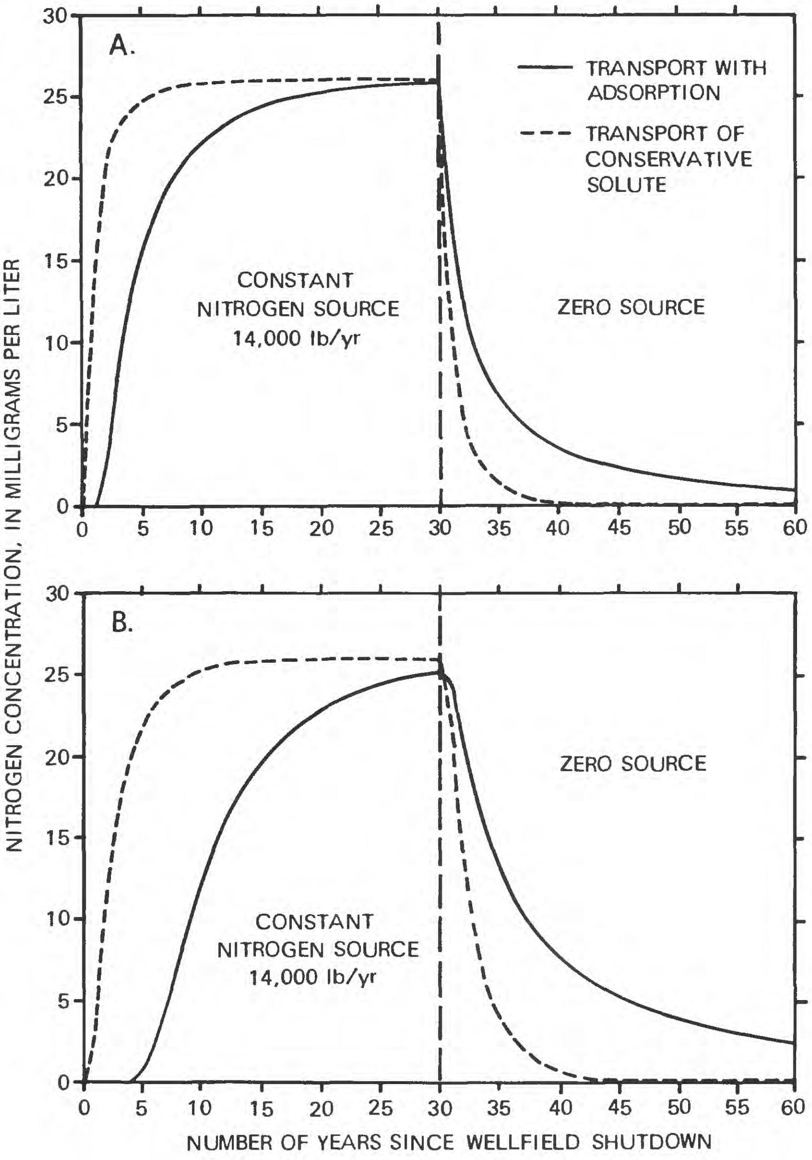


Figure 25.

Nitrogen concentrations during 30 years of transport with a constant nitrogen-source rate followed by 30 years of transport with zero source rate, as predicted by one-dimensional simulations.

- *A. 500 feet along flow path.*
- *B. 1,000 feet along flow path.*

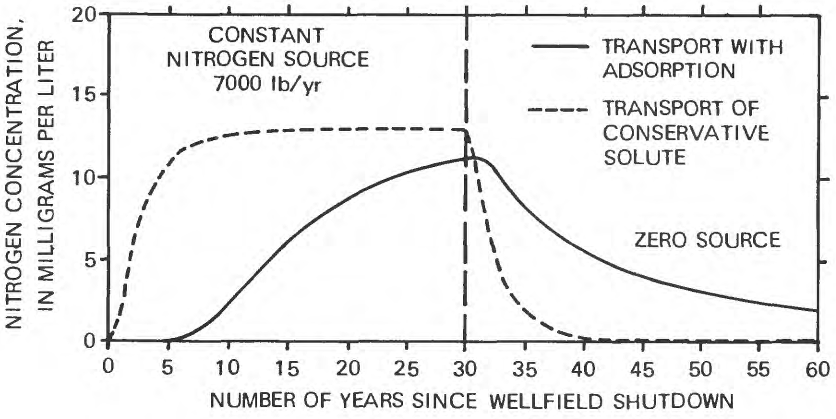


Figure 26.

Nitrogen concentrations at a point 1,000 feet along flow path as predicted by one-dimensional simulation with constant nitrogen-source rate decreased by half throughout 60 year period.

Solute-Transport Model as a Management Tool

The solute-transport model was developed to aid in making decisions on future containment pumping and remedial efforts within the contaminated part of the aquifer at the industrial park. These decisions may include maintaining certain pumping rates at selected production wells and installing downgradient observation wells to monitor the migration of nitrogen. The model provides a useful means for assessing several options because it adequately simulates the shape and direction of the plume in response to major hydraulic stresses in the area. The utility of the model is limited by assumptions inherent in the modeling approach, however. These limitations are summarized as follows:

1. The model is a simplification of a complex process and as such cannot predict with certainty the nitrogen concentrations that would result from cessation of industrial pumping. Model predictions generally underestimate the arrival time at the municipal well field because nitrogen is simulated as a conservative solute, which is only partly correct.

2. The model is two dimensional and does not incorporate the vertical movement of nitrogen in the aquifer. The model was designed to simulate movement of nitrogen in the lower, more permeable aquifer and thus cannot predict nitrogen concentrations in the upper aquifer. Nitrogen will move at a slower rate through the upper aquifer because the hydraulic conductivity is less than 10 percent of that in the lower aquifer.

3. Modeling results suggest that the nitrogen flux to the lower aquifer is affected by the magnitude of vertical leakage from the upper aquifer. Source rates obtained from the model during calibration and the simulated decrease in source rate over time may not be valid for all pumping conditions. This limits the utility of the model in evaluating alternative pumping schedules to contain the plume. The model can, however, give conservative predictions based on a constant source rate equivalent to that estimated for the period of maximum pumping, which was in 1984, the end of the calibration period.

4. The solute-transport model does not include adsorption of ammonium. Simulations with the one-dimensional transport model indicate that adsorption will retard movement of ammonium from the industrial park by a factor of 3; the magnitude of retardation within 1,000 ft of the industrial park may range between 3 and 7 years. Results of the one-dimensional analysis suggest that, if observation wells were placed 400 ft downgradient of the industrial park, they could be used to detect ammonium migration that might occur in less than 5 years.

5. The effect of neglecting biochemical reactions on model predictions is difficult to assess. Either nitrification or denitrification could occur at the edges of the plume, depending on the concentration of dissolved oxygen in ground water. Nitrification would convert nitrogen to the more mobile species and speed the movement of the plume. Denitrification would have the opposite effect, dissipating nitrogen in ground water and slowing the plume. Neither of these effects can be quantified without knowledge

of the reaction rates and the factors that control them. In addition, mineralization of organic nitrogen in the contaminated area could cause the source to persist. This condition was approximated in transport simulations by holding the source rate constant.

A monitoring network designed to accompany a permanent shutdown of the industrial well field could be used to track the movement of the nitrogen plume through both the upper and lower aquifers. Data collected from the monitoring network could be used to evaluate model predictions and further assess the uncertainties of model results. Additional studies may be warranted if actual concentrations fail to conform to model predictions.

Some limitations of the present two-dimensional model could be rectified in future studies. The vertical movement of nitrogen near the area of contamination could be simulated in detail by a two-dimensional cross-sectional model to represent the two-layer aquifer system along the main ground-water flow path. This model could be used with nitrogen concentrations observed in downgradient wells screened in the upper and lower aquifers to recalibrate the nitrogen source rate to the lower aquifer after a well shutdown. Such a model could not predict nitrogen concentrations that would result at the municipal well field because it would not represent radial flow components near the wells. However, the source rate obtained by the cross-sectional model could be used in the solute-transport model described in this report to predict nitrogen concentrations at the municipal well field.

Laboratory experiments to investigate biochemical reactions between nitrogen and ground water in core samples taken from the aquifer could provide data on reaction rates and factors that control the reactions, such as the availability of oxygen and carbon. In addition, ground-water samples could be analyzed for major dissolved inorganic species as well as pH and dissolved oxygen to fully characterize the chemical composition of ground water. Results of these studies could be used to determine which nitrogen species should be included in transport simulations and possibly the reaction rates that affect their concentrations. A multicomponent model with several reaction terms could be developed if the reaction rates could be estimated.

SUMMARY AND CONCLUSIONS

A glacial-outwash aquifer system in southeastern Cattaraugus County contains large amounts of nitrogen compounds beneath an industrial park in North Olean. The nitrogen compounds were introduced into the aquifer over a 6-year period by operations of a fertilizer plant. Pumping from production wells at the site until 1985 maintained a cone of depression that contained the nitrogen compounds and thus prevented them from migrating to nearby public, private, and industrial supply wells. Ground water within the cone of depression contained nitrogen concentrations ranging from 10 to 1,280 mg/L in 1983.

The aquifer system consists of extensive unconsolidated outwash deposits that consist primarily of coarse sand and gravel. These deposits are less than 100 ft thick and are the only potential source of large amounts of ground water near Olean. The aquifer thickness is about 80 ft at and near the industrial park, but the lower 30 ft is generally more permeable than the upper 50 ft, which contains gravel with a higher silt content. Thin lenses of silty clay occur locally between depths of 30 and 50 ft in this area and separate the aquifer into an upper and lower layer.

Under nonpumping conditions, ground water would flow downvalley to the southwest and toward the Allegheny River and Olean Creek. Ground-water withdrawals at several pumping centers in the 1970's and early 1980's, principally at the industrial park, altered this pattern locally, however. Simulations with a ground-water flow model have predicted that a shutdown of the well field at the industrial park would allow water levels to recover, whereupon ground water would flow southwestward toward the municipal well field.

High concentrations of nitrogen in the form of ammonia and nitrate were detected in ground water beneath the industrial park in 1969; petroleum products and hexavalent chromium have also been detected. The most prevalent nitrogen species is ammonium, which represents 90 percent of the nitrogen produced by industrial pumping from the contaminated area. Nitrogen concentrations are highest near the previous site of the fertilizer plant and exceeded 2,000 mg/L as nitrogen in the 1970's. Nitrogen concentrations at wells completed in the upper aquifer have been consistently higher than those at wells completed in the more transmissive lower aquifer. Continuous pumping of industrial wells during 1970-84 removed much nitrogen from the aquifer. As a result, concentrations of nitrogen at the production wells and most observation wells have declined.

Rates of nitrogen transport in the aquifer (as ammonium, nitrate, and organic nitrogen) may be affected by physical and biochemical reactions. Adsorption would slow the movement of ammonium but would not affect movement of nitrate. An isotherm for ammonium adsorption was developed in a laboratory study from samples of aquifer material from the industrial park (In-Situ Inc., 1984). The adsorption data were approximated by a Langmuir isotherm with a maximum adsorbed concentration of 18.5 mg/kg. Some ammonium may be nitrified to nitrate, but the rate of this conversion seems to be inhibited because nitrate concentrations are much lower than ammonium concentrations.

Nitrate is assumed to migrate in the aquifer as a conservative solute and therefore would be removed from the aquifer by industrial pumping. The continuing presence of nitrate indicates that some nitrification is occurring or that areas of low hydraulic conductivity are restricting its migration. Some nitrate may be denitrified to volatile forms of nitrogen, but the rate of this conversion is unknown.

Organic nitrogen within the aquifer may have been partly derived from immobilized nitrogen that formed during mineralization of urea and ammonium that were spilled at the fertilizer plant. If so, the organic nitrogen represents an available source of ammonium or nitrate. The organic nitrogen may also have been derived from petroleum products or organic sediments within the aquifer material; however, the potential rate of mineralization of the organic nitrogen cannot be assessed without information on its molecular form.

The two-dimensional solute-transport model of Konikow and Bredehoeft (1978) was used to simulate movement of nitrogen through the lower aquifer near the industrial park. The model simulates advection and dispersion of a conservative solute; thus the model predictions can be interpreted as worst-case estimates. Nitrogen flux to the lower aquifer was represented in the model by a specified source rate. Source concentrations were calibrated to observed trends in nitrogen concentrations during 1978-84 within the contaminated part of the aquifer. The model was then used to predict changes in nitrogen concentration that would occur between the industrial park and the municipal well field after a permanent shutdown of pumping wells at the industrial park.

Hydraulic properties of the aquifer material in the area of the industrial park were obtained from the ground-water-flow model by Bergeron (1987); transmissivity of the upper and lower aquifers was 1,000 ft^2/d and 18,000 ft^2/d, respectively, and transmissivity at the Olean municipal well field was 55,000 ft^2/d. The hydraulic head distribution computed by a steady-state simulation with the solute-transport model based on these values closely matched water levels measured in observation wells in November 1981. A ground-water budget computed by the solute-transport model was similar to that computed by the ground-water flow model.

The solute-transport model closely simulated observed nitrogen concentrations in ground water beneath the industrial park when the source rate to the lower aquifer was decreased by an exponential decay term to account for the removal of nitrogen from the aquifer by pumping during the calibration period. A decay constant of 0.3/yr provided the best match to nitrogen concentrations observed during 1978-84. The nitrogen flux in 1984 was estimated to be 70,000 lb/yr. During an actual well shutdown that began in March 1985, nitrogen concentrations remained generally unchanged for 6 months. The solute-transport model simulated this condition when the nitrogen-source rate was decreased by 80 percent to 14,000 lb/yr to offset the decrease in vertical leakage from the upper aquifer that resulted from the lower hydraulic gradients that formed after the shutdown.

Thirty-year transport simulations were used to predict nitrogen concentrations that would develop within the aquifer after a permanent well shutdown. Results indicate that nitrogen-bearing ground water would reach the Olean municipal well field within 5 years, predicted nitrogen concentrations there would range from 2 to 5 mg/L, and those at the southwest boundary of the industrial park would range from 20 to 25 mg/L. Model predictions were sensitive to changes in the nitrogen source rate and dispersivity. The value of the decay constant would affect the time required to flush nitrogen from the aquifer but did not significantly alter predicted peak concentrations.

The effect that nitrogen adsorption to the aquifer material would have on nitrogen concentrations was simulated by a one-dimensional transport model with equilibrium-controlled adsorption described by a Langmuir isotherm. That model gave a qualitative indication of the effect of adsorption on nitrogen-transport rates near the industrial park. Results indicated that the midpoint of the solute front would be retarded by a factor of 3 at distances 500 to 1,000 ft downgradient of the industrial park.

The solute-transport model provides a means of assessing various management options regarding future containment of contaminated ground water and remedial efforts within the industrial park. The model adequately simulates the shape and direction of the plume and its general response to local changes in major hydraulic stresses in the area. Interpretation of the results must be qualified, however, because the model makes several simplifying assumptions, which are summarized as follows:

1. Nitrogen is simulated as a conservative solute, unaffected by physical or biochemical reaction. Thus, model predictions underestimate the arrival time at the municipal well field.

2. The model is two dimensional and ignores vertical differences in hydraulic conductivity and nitrogen concentration. The model was designed to predict nitrogen concentrations in the lower, more permeable aquifer; nitrogen in the upper aquifer will move at a slower rate, and concentrations will be higher than in the lower aquifer.

3. The nitrogen source rate calculated by the model and its decrease through time may not be valid for pumping conditions other than those studied.

4. Adsorption will retard the rate of ammonium migration from the industrial park by a factor of three.

5. Effects of biochemical reactions on nitrogen concentrations cannot be assessed because the reaction rates and the factors that control them have not been defined for these field conditions.

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