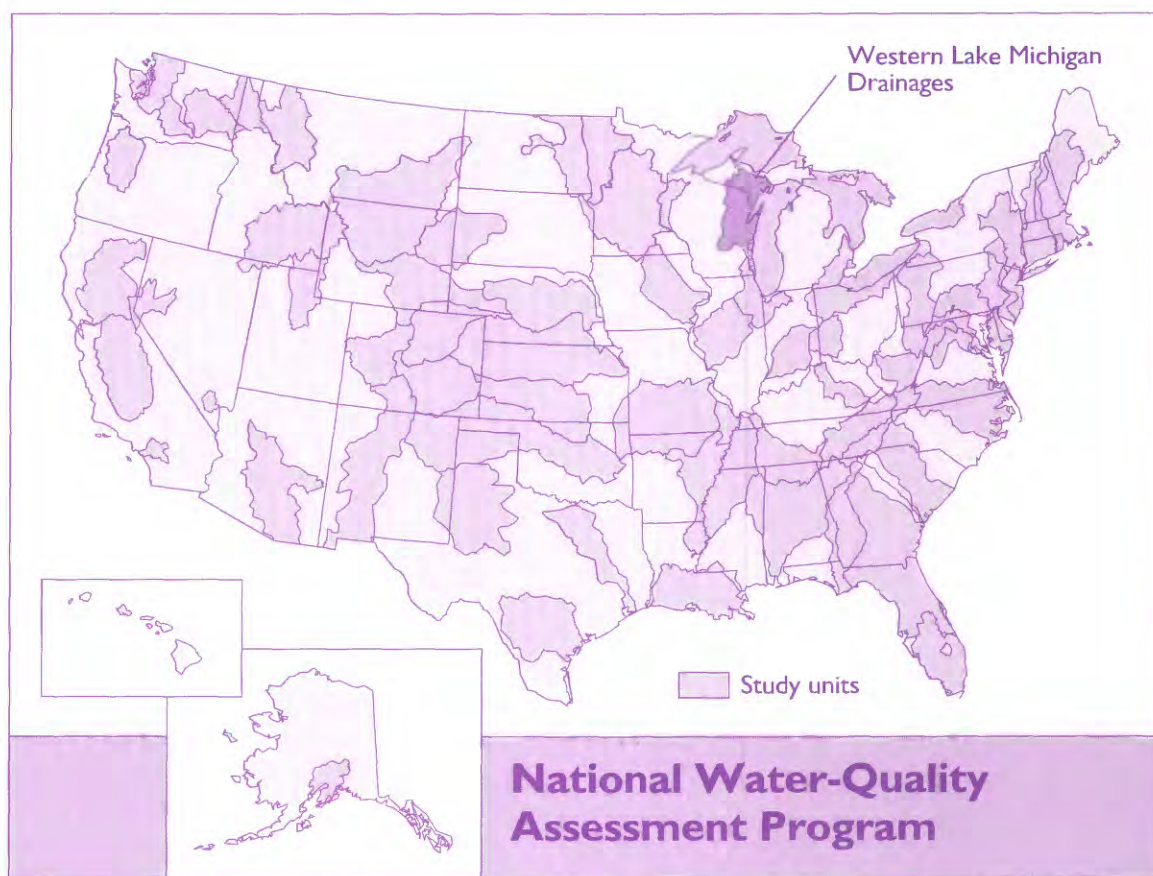# Flow and Geochemistry Along Shallow Ground-Water Flowpaths in an Agricultural Area in Southeastern Wisconsin

Western Lake Michigan Drainages

Study units

National Water-Quality Assessment Program

FLOW AND GEOCHEMISTRY ALONG SHALLOW GROUND-WATER FLOWPATHS IN AN AGRICULTURAL AREA IN SOUTHEASTERN WISCONSIN

By David A. Saad and Donald C. Thorstenson

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, Acting Director

FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
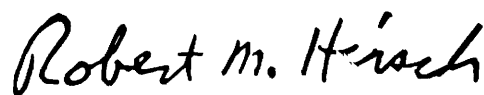- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as Study Units. These Study Units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 Study Units, and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the Study Units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground water and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch

Robert M. Hirsch
Chief Hydrologist

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FIGURES

FIGURES—Continued

CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To Obtain
foot (ft)	0.3048	meter
inch (in)	2.54	centimeter
mile (mi)	1.61	kilometer
square mile (mi^2)	2.59	square kilometer
pound (lb)	453,600	milligram
gallon (gal)	3.785	liter
tons per acre (ton/acre)	2,242	kilograms per hectare

Temperature, in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by use of the following equation:
$$°F = [1.8(°C)] + 32.$$

Sea level: In this report, "sea level" refers to the 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 Sea Level Datum of 1929.

Abbreviated water-quality units: Chemical concentrations and water temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) or micrograms per liter (μg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as mass (milligrams) of solute per unit volume (liter) of water. Conversion factors for dissolved constituents, between milligrams per liter, millimoles per liter, and milliequivalents per liter can be found in Hem (1985, p. 56).
One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million. Picograms per kilogram (pg/kg) is a unit expressing the concentration of chemical constituents in solution as mass (picograms) of solute per unit mass (kilogram) of water.

Radioactivity is expressed in picocuries per liter (pCi/L). A picocurie is the amount of radioactivity that yields 2.22 radioactive disintegrations per minute.

Isotopic data given in this report are in delta (δ) notation. The delta value, expressed as parts per thousand (per mil), represents the isotope ratio in the sample divided by the isotope ratio in the applicable geochemical standard, multiplied by 1,000.

MISCELLANEOUS ABBREVIATIONS

CFCs	Chlorofluorocarbons
DOC	Dissolved organic carbon
K_h	Horizontal hydraulic conductivity
NWQL	National Water Quality Laboratory
MDL	Laboratory Method Detection Limit
NAWQA	National Water-Quality Assessment
as $CaCO_3$	as quantified as measured calcium carbonate
as N	as quantified as measured nitrogen
as P	as quantified as measured phosphorus
as SO_4^{2-}	as quantified as measured sulfate
USGS	U.S. Geological Survey

ACKNOWLEDGMENTS

Flow and Geochemistry along Shallow Ground-Water Flowpaths in an Agricultural Area in Southeastern Wisconsin

By David A. Saad *and* Donald C. Thorstenson

Abstract

Water-quality and geohydrologic data were collected from 19 monitor wells and a stream in an agricultural area in southeastern Wisconsin. These sites were located along a 2,700-ft transect from a local ground-water high to the stream. The transect is approximately parallel to the horizontal direction of ground-water flow at the water table. Most of the wells were installed in unconsolidated deposits at five locations along the transect and include an upgradient well nest, a midgradient well nest, a downgradient well nest, wells in the lowland area near the stream, and wells installed in the stream bottom. The data collected from this study site were used to describe the water quality and geohydrology of the area and to explain and model the variations in water chemistry along selected ground-water flowpaths.

Water samples from most wells and the stream were analyzed for major ions, nutrients, pesticides, dissolved organic carbon, aluminum, tritium, CFCs, ^{15}N, ^{18}O, and dissolved gases. Measurements of temperature, pH, specific conductance, and dissolved oxygen were made in the field. Concentrations of all dissolved constituents were below Wisconsin ground-water quality enforcement standards. The concentrations of both nitrate and ammonium in precipitation concentrated by evapotranspiration are roughly equal to the concentrations of either in the shallow ground waters. The nitrogen and oxygen isotope data, however, indicate that soil ammonium, ammonium fertilizer, and animal waste are possible nitrate sources. Concentrated precipitation can also supply dissolved sulfate to the shallow ground waters and may be a principal source of pesticides to the ground water. However, some input of dissolved chloride to the ground water from mineral or anthropogenic sources is necessary.

X-ray diffraction analyses of samples from 2 cores show the most abundant mineral to be dolomite, with subordinate quartz, microcline, and plagioclase, and minor amounts of mica, hornblende, and chlorite. Hydraulic conductivities determined from slug tests at selected wells range from 0.006 to 55 feet per day, with most values between 0.4 and 12 feet per day.

A cross-sectional ground-water flow model, representing the water-table flow system, was developed for the site and was used to identify possible ground-water flowpaths for geochemical modeling. The model was calibrated against measured water levels and was most sensitive to variation in recharge and hydraulic conductivity. The calibrated model shows that downward flow from shallow to deeper wells within a nest may occur at the upgradient and midgradient well nests, but that flow from each well nest travels beneath downgradient nests to the stream. Pathline and travel-time analysis performed on the calibrated flow-model output yielded travel times to well screens that range from 5.8 to 59 years with a recharge of 4 inches per yr. Recharge dates based on tritium and CFC concentrations range from pre-1955 to 1986 and are consistent with flowpaths and travel times in the calibrated flow model.

Changes in water quality along ground-water flowpaths were evaluated using the geochemical model PHREEQC. Geochemical mole balance models of shallow ground-water formation show that the principal reaction, by an order of magnitude, is dissolution of dolomite with CO_2. Concentration factors in the mole-balance models range from 1 to 11, with most values between 5 and 10,

which provides independent support for the concentration factor of 8 based on recharge estimates used in the flow model.

Ground water recharging at mid- and down-gradient wells is oxic and contains dissolved nitrate, whereas the ground water discharging to the stream is anoxic and contains dissolved ammonium. Redox environments were defined at each well on the basis of relative concentrations of various dissolved redox-active species. Chemically permissible flowpaths inferred from the observed sequence of redox environments at well sites are consistent with flowpaths in the ground-water flow model. The transition from nitrate in recharging ground water to ammonium in ground water discharging to the stream suggests the possibility of nitrate reduction along the flowpath. None of the techniques employed in this study, however, were able to prove the occurrence of this reaction.

INTRODUCTION

This report describes data collected for a ground-water flowpath study which was done as part of the Western Lake Michigan Drainages study unit of the National Water-Quality Assessment (NAWQA) Program. The Western Lake Michigan Drainages encompass an area of about 19,900 mi^2 in eastern Wisconsin and central Upper Michigan (fig. 1). The NAWQA Program uses ground-water, surface-water, and biological data to assess the status and trends in the quality of the Nation's ground- and surface-water resources. Collection and analysis of ground-water data in the Western Lake Michigan Drainages began in 1993. The NAWQA design for examining ground-water quality includes study-unit surveys, land-use studies, and flowpath studies (Gilliom and others, 1995). Study-unit surveys are designed to provide an indication of water-quality conditions in the major aquifers or defined hydrogeologic settings within a study unit and typically cover an area ranging from several thousand to tens of thousands of square miles. Land-use studies are designed to examine natural and human factors that affect shallow ground-water quality in an area characterized by a specific land use, and typically cover an area ranging from several hundred to several thousand square miles. Flowpath studies are designed to examine trends in ground-water quality along inferred flowpaths and potential interactions of ground water and surface water and typically

are transects of hundreds of feet to several miles in length.

The flowpath study described in this report is in an agricultural area of the Western Lake Michigan Drainages. Agricultural land use has been shown to affect ground-water quality, mainly with regard to nutrients and pesticides, in the Western Lake Michigan Drainages (Saad, 1997). This study allowed for a close look at changes in ground-water chemistry along shallow ground-water flowpaths from a local ground-water high to a stream.

Purpose and Scope

The purpose of this report is to describe the geohydrology and water quality of the study site and the use of models to simulate and explain variations in ground-water quality along shallow ground-water flowpaths in an agricultural area in southeastern Wisconsin. Geologic, hydrologic, and water-chemistry information presented in this report is primarily based on data collected from September 1993 through November 1995 from 19 installed monitor wells and a stream at the study site. Hydraulic conductivity of glacial deposits was estimated from slug tests performed on nine of the monitor wells. Mineralogy of glacial deposits at the study site was determined from X-ray diffraction analysis of core samples collected near two monitor well nests. The direction and rate of ground-water flow was simulated using a one-layer, steady state, profile model. Water chemistry at the study site was determined from water samples collected from the monitor wells and stream and analyzed to determine the concentrations of major and minor ions, nutrients, dissolved organic carbon (DOC), aluminum, 85 pesticides or pesticide metabolites, and dissolved gases. Field measurements of temperature, pH, specific conductance, dissolved oxygen, and alkalinity also were made. The source and age of the sampled ground water was estimated by examining levels of deuterium (^{2}H) and oxygen-18 (^{18}O), chlorofluorocarbons (CFCs), and tritium (^{3}H). The source of dissolved nitrogen in selected ground-water samples was inferred from nitrogen (^{15}N) and oxygen (^{18}O) isotopes in dissolved nitrate or ammonium. Changes in water chemistry along selected flowpaths were simulated with geochemical models.

Information from this flowpath study is an aid to understanding the fate and transport of nutrients and pesticides as they move through a shallow ground-water
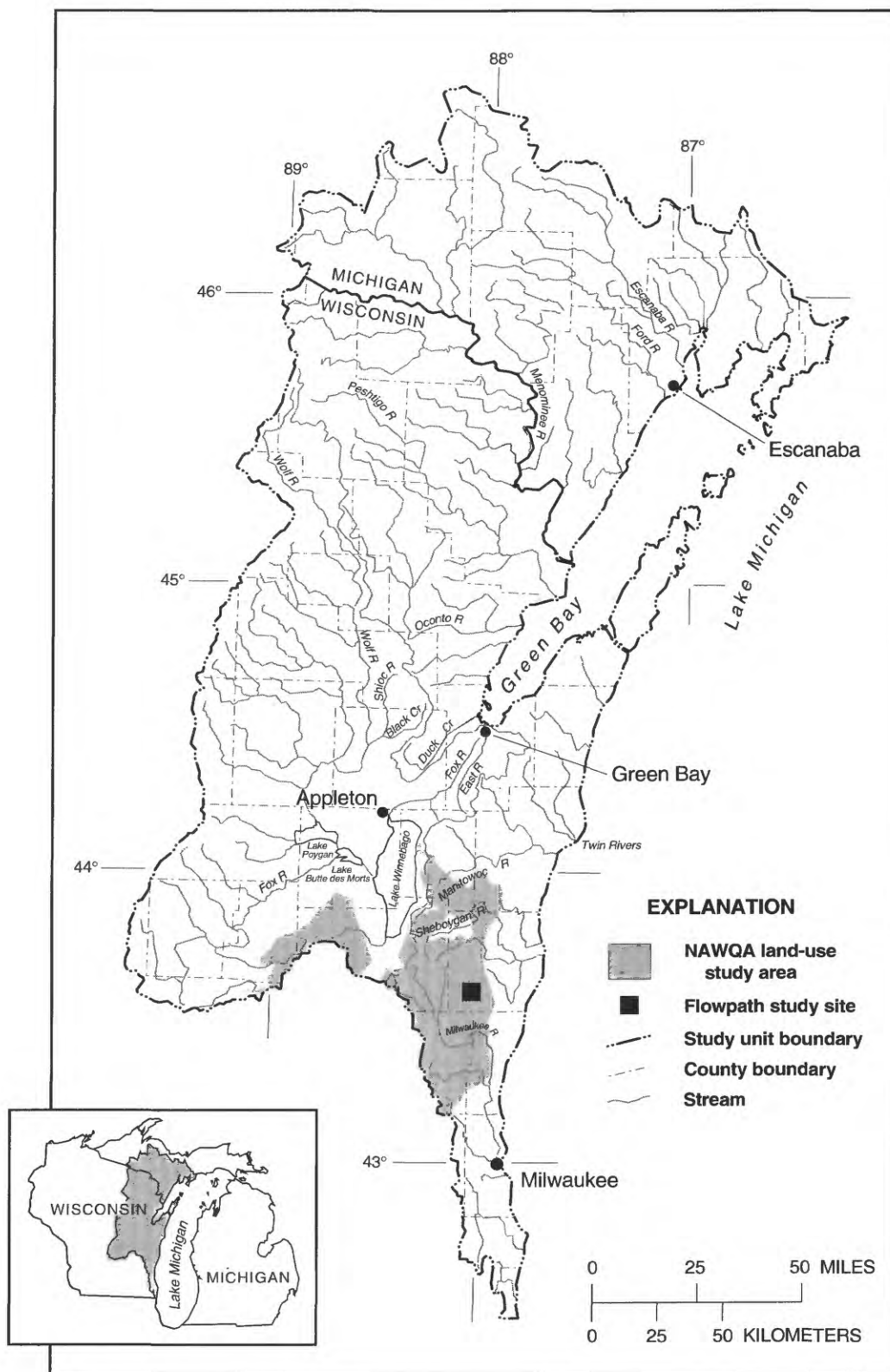
Figure 1. Location of the study site in the Western Lake Michigan Drainages study unit of the National Water-Quality Assessment Program.

flow system to a stream. The data described in this report provide a good starting point for continued study of this site and could also be useful for understanding movement of nutrients and pesticides through the hydrologic system at similar locations.

Acknowledgments

We thank the private landowners who allowed the USGS to install and sample monitor wells on their property.

DESCRIPTION OF STUDY AREA

The study site, located in Sheboygan County in southeastern Wisconsin (fig. 2), is a 2,700-foot transect from a local ground-water high to the North Branch Milwaukee River (fig. 3). Land-surface elevation along the transect ranges from about 980 to 825 ft above sea level. The water-table elevation ranges from about 970 to 825 ft above sea level (fig. 3). The transect is approximately parallel with the horizontal direction of ground-water flow at the water table as inferred from measured water levels.

Land Use

Land use and land cover, referred to hereafter as "land use", is primarily agriculture associated with dairy farming in the vicinity of the study site (fig. 4). Along the transect, land use changes from row crops (typically a 2- to 4-year rotation of corn, alfalfa, oats, and occasionally barley) near the local ground-water high (upgradient from UW) to alfalfa and occasional corn in the middle of the transect (downgradient from UW to DW) to grasses and small trees near the stream (DW to stream). Pesticides and nutrients have been regularly applied to the land surface upgradient from the upper sampling site, UW. Historical pesticide use was primarily atrazine until 1992, followed by glyphosate for several years. Detailed atrazine use information was not available for the study site. Regional information indicates that atrazine use steadily increased until the mid 1980's and then began to decrease (Wollenhaupt and others, 1990; WASS, 1978, 1986, 1991, and 1997). Nutrient applications were mainly liquid cow manure at 10 to 15 ton/acre. According to the landowner, pesticides have not been applied downgradient from UW in the last 30 years. Information about nutrient applica-

tions downgradient from UW was not available, however, and it is likely that some nutrients were applied downgradient from UW.

Geohydrology

The geology at the study site consists of glacial and fluvial deposits overlying dolomite bedrock (fig. 5). The dolomite is of Silurian age and is estimated to be about 450 ft thick in this area (Young and Batten, 1980; Conlon, 1995). The glacial deposits consist of till that, on the basis of drill cuttings and cores, varies in texture from clay to sand and gravel. The till is about 20 ft thick near the stream and, on the basis of depth to bedrock at several of the wells installed for this study, is estimated to be about 130 ft thick near the local ground-water high. The till is mostly dense, sandy clay with some gravel and cobbles near UW, mostly sand with some clay, gravel, and cobbles near MW, and mostly clayey sand and gravel near DW and LL. The lowland area between DW and the stream is also overlain by 2 to 3 ft of organic-rich soil. The fluvial deposits underlying the stream are mostly sand and gravel with some interbedded layers of organic matter. The geology of the surrounding area is described in more detail by Skinner and Borman (1973), Young and Batten (1980), and Olcott (1992).

Two ground-water flow systems have been identified in the vicinity of the study site: a shallow water-table system and a deeper, confined system (Young and Batten, 1980). The shallow water-table system consists of the sand and gravel aquifer and the Silurian dolomite aquifer. Where the glacial and fluvial deposits are sufficiently thick and permeable, as it is over much of the study site, they are considered part of the sand and gravel aquifer. In the water-table system, ground water moves along relatively short flowpaths from recharge areas to topographically lower areas (Young and Batten, 1980; Olcott, 1992). At the study site, ground water is expected to discharge predominantly to the stream. This study is mainly concerned with the shallow water-table system. The underlying, confined system is separated from the water-table system by the Maquoketa Shale, through which little leakage occurs. The confined system consists of the Cambrian-Ordovician sandstone aquifer in which ground-water flow is generally to the east towards Lake Michigan or towards pumping centers where ground water is withdrawn.
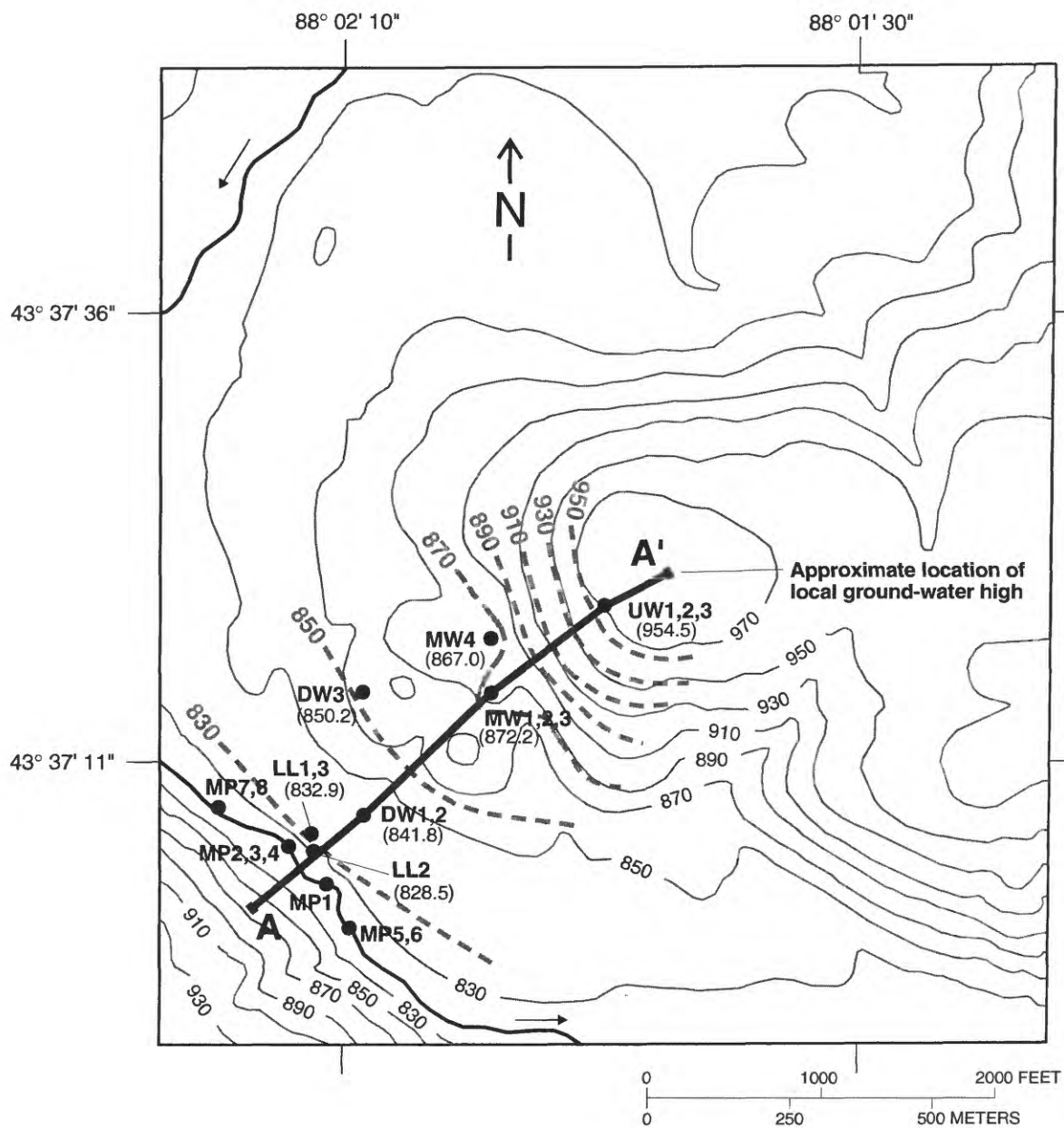
Figure 2. Location of study site near the North Branch Milwaukee River in Sheboygan County, Wisconsin.

Figure 3. Location of monitor wells, well name, land-surface elevation, and approximate water-table elevation in the vicinity of the study site, Sheboygan County, Wisconsin.
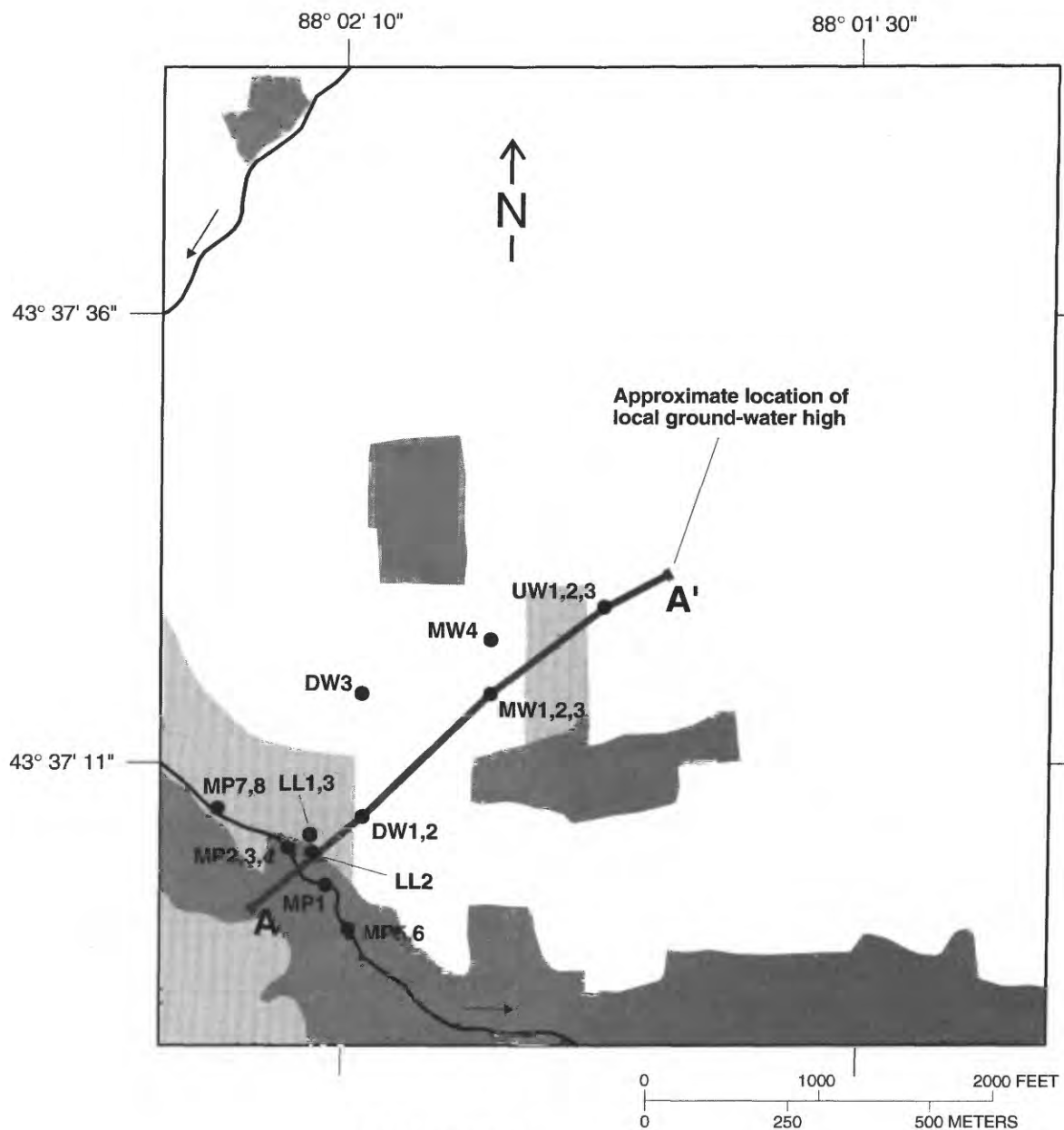
Figure 4. Land use/land cover in the vicinity of the study site, Sheboygan County, Wisconsin.
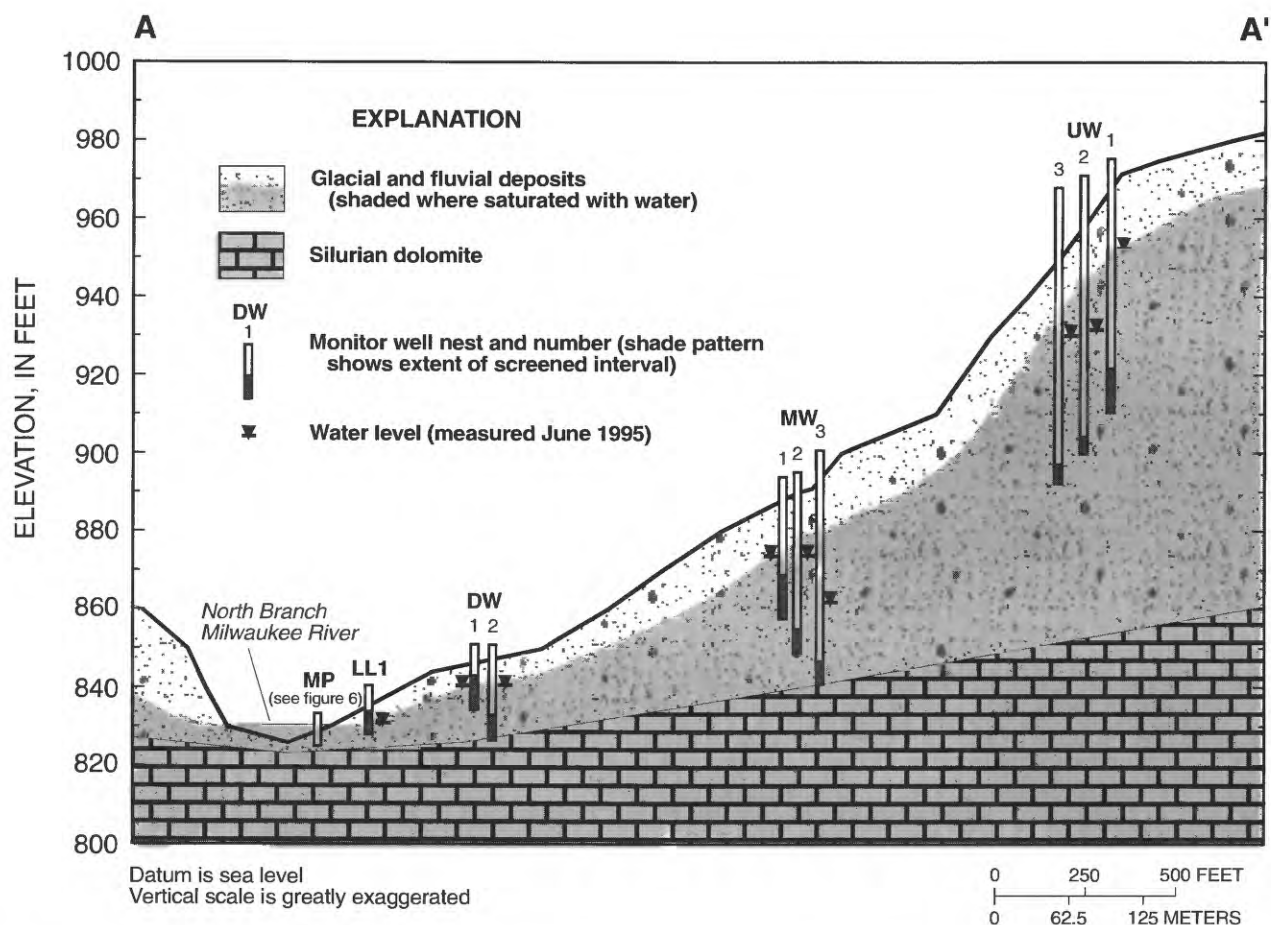
Figure 5. Geology, water levels, and monitor well locations along transect A - A' at the study site, Sheboygan County, Wisconsin (trace of section shown in figure 3).

Hydrologic Budget

The long-term average precipitation in the vicinity of the study area, based on data collected from 1931 through 1960, was about 30 in/yr (Skinner and Borman, 1973). Evapotranspiration and streamflow for the same period averaged about 23 and 7 in/yr, respectively. Underflow, water entering or leaving a basin through the ground-water system, was typically only a fraction of an inch per year.

Recharge to the water table in the vicinity of the study area is from precipitation and direct infiltration. Most of the water that reaches the ground-water system along the transect is assumed to discharge to the North Branch Milwaukee River, which is a gaining stream. Discharge measurements made during base flow condi-

tions on June 1 and August 23, 1995, show that streamflow increased by 9 to 10 percent along an 1,140 ft length of stream near the study site.

Base flow, the ground-water component of streamflow, can be used as an estimate of recharge to the water table where very little underflow occurs. Estimated daily streamflow values were available for the period from April 1993 through September 1995 (Holmstrom and others, 1996) from a streamflow-gaging station approximately 5 mi downstream from the study site (fig. 2). The drainage area for the gage is approximately 51.4 mi^2. The average discharge for the gage was about 31 cubic feet per second, which corresponds to about 8.2 in/yr of streamflow for that time period. This was slightly higher than the long-term average described by Skinner and Borman (1973). Base flow was estimated
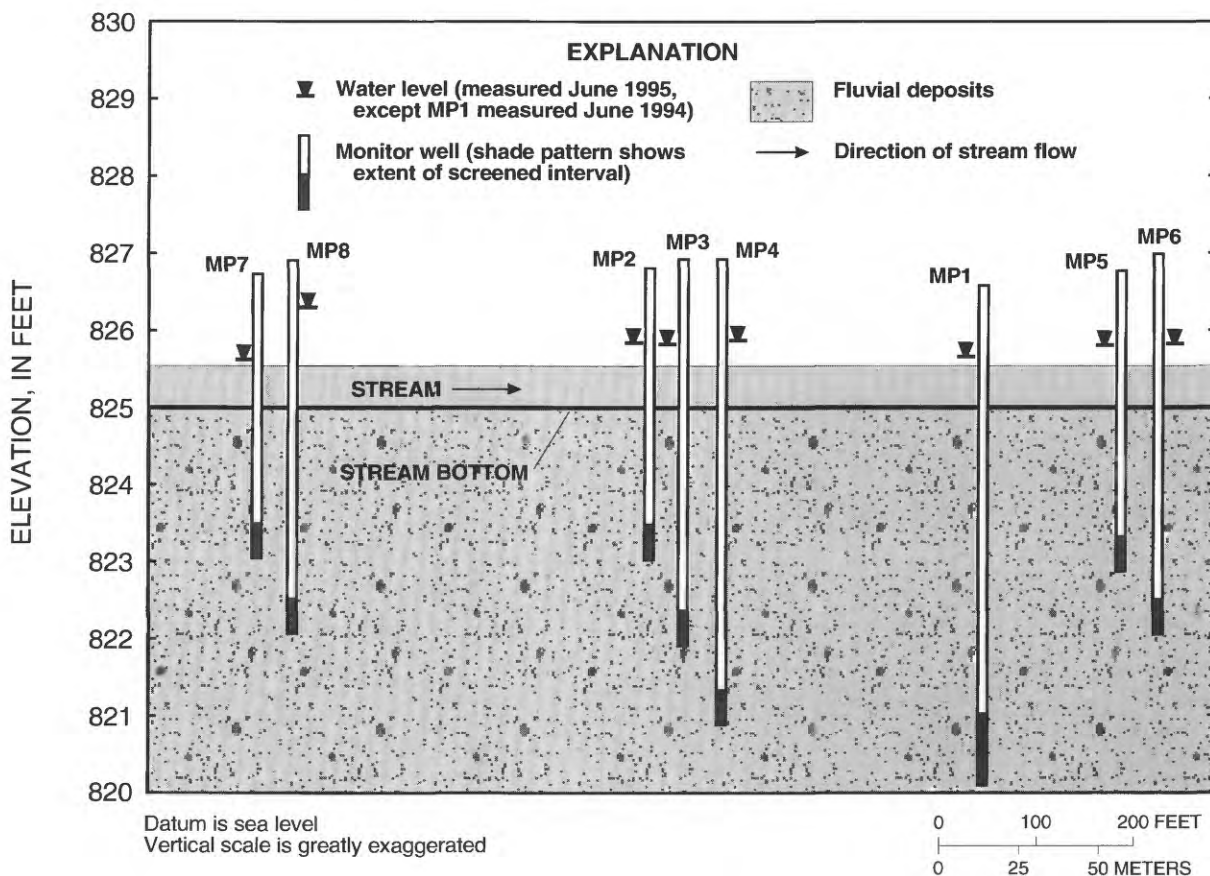
Figure 6. Geology, water levels, and location of MP wells at the study site, Sheboygan County, Wisconsin (location of MP wells shown in figure 3).

for the gaged site using the computer program HYSEP (Sloto and Crouse, 1996). The average base flow for the period of record was about 73 percent of streamflow, or about 6 in/yr. Previous estimates of recharge in the vicinity of the study area ranged from 1 to 10 in/yr (Young and Batten, 1980; Conlon, 1995).

STUDY DESIGN AND METHODS

This study was designed to describe the water quality and geohydrology along ground-water flowpaths in a shallow, water-table system, and to examine water-quality changes along those flowpaths. The study site was chosen in an agricultural area to focus on nutrients and pesticides. Water-quality and geohydrologic data were collected from monitor wells installed by the USGS and from a stream.

Site Selection and Monitor-Well Installation

The flowpath study site was selected to be nested within a NAWQA ground-water land-use study area (fig. 1) and also within the basin of one of the surface-water sampling locations (USGS station 040863075) of the Western Lake Michigan Drainages (fig. 2). Between September 1993 and August 1995, 19 monitor wells were installed along and near a transect from near the local ground-water high to the stream. The wells were installed in glacial deposits and nested at five locations along the transect corresponding to an upgradient well nest (UW), a midgradient well nest (MW), a downgradient well nest (DW), wells in the lowland area (LL) near the stream, and wells completed in sediments below the stream bottom (MP) (figs. 5 and 6). Well

Table 1. Location and characteristics of monitor wells installed at the study site, Sheboygan County, Wis.

[deg, degree; min, minutes; sec, second; mn, month; dd, day; yy, year; ---, no data; <, older than; >, younger than; CFC, chlorofluorocarbon]

Well name	Latitude and longitude (deg min sec)	Elevation, in feet above sea level	Well construction date mn/dd/yy	Well depth, in feet below land surface	Water level, in feet below land surface[1] minimum maximum	Date of water level measurement (mn/dd/yy)	Depth to top of screened interval (feet below land surface)	Length of screened interval (feet)	Hydraulic conductivity (K_h) (feet per day)[2]	Tritium-based ground-water recharge date	CFC-based ground-water recharge date
UW1	43 37 20 / 88 01 49	970	11/29/93	44	15.34 / 20.47	05/24/94 / 08/23/95	34	10	0.03	>1955	<1959.5
UW2	43 37 20 / 88 01 49	970	12/01/93	64	36.18 / 41.98	05/24/94 / 08/23/95	59	5	---	>1955	---
UW3	43 37 20 / 88 01 49	970	01/04/94	75	39.76 / 46.52	05/24/95 / 08/24/95	70	5	.006	>1955	1981.5
MW1	43 37 15 / 88 01 58	890	09/28/93	31	16.31 / 18.41	05/24/94 / 08/23/95	21	10	10	>1955	1979.5
MW2	43 37 15 / 88 01 58	890	09/28/93	43	16.39 / 18.08	06/15/94 / 08/23/95	38	5	.74	>1955	1967.0
MW3	43 37 15 / 88 01 58	890	09/28/93	53	27.06 / 30.79	05/24/94 / 08/23/95	48	5	11	>1955	1961.0
MW4	43 37 18 / 88 01 58	899	09/28/93	36	30.05 / 31.97	05/24/94 / 07/18/95	26	10	55	---	---
DW1	43 37 08 / 88 02 08	846	09/27/93	14.5	4.00 / 6.43	05/24/94 / 08/22/95	4.5	10	.41	>1955	1986.0
DW2	43 37 08 / 88 02 08	846	09/27/93	21	3.97 / 6.52	05/24/94 / 08/22/95	16	5	6.6	>1955	1982.5
DW3	43 37 15 / 88 02 08	871	09/27/93	32	19.35 / 20.81	05/24/94 / 07/18/95	22	10	.44	---	---
LL1	43 30 07 / 88 02 12	835	06/01/94	2.9	2.11 / 2.11	06/02/95 / 06/02/95	0.9	2	---	---	---
LL2	43 37 06 / 88 02 12	830	06/01/94	2.3	1.47 / 1.47	06/02/95 / 06/02/95	0.3	2	---	---	---
LL3	43 37 07 / 88 02 12	835	06/01/94	4.3	2.20 / 2.20	06/02/95 / 06/02/95	2.3	2	---	---	---

Table 1. Location and characteristics of monitor wells installed at the study site, Sheboygan County, Wis.—Continued

[deg, degree; min, minutes; sec, second; mn, month; dd, day; yy, year; ---, no data; >, younger than; <, older than; CFC, chlorofluorocarbon]

Well name	Latitude and longitude (deg min sec)	Elevation, in feet above sea level	Well construction date mn/dd/yy	Well depth, in feet below land surface	Water level, in feet below land surface[1] minimum	maximum	Date of water level measurement (mn/dd/yy)	Depth to top of screened interval (feet below land surface)	Length of screened interval (feet)	Hydraulic conductivity (K_h) (feet per day)[2]	Tritium-based ground-water recharge date	CFC-based ground-water recharge date
MP1	43 37 04 88 02 11	825	06/14/94	5.0	-0.20	-0.20	06/14/94 06/14/94	4.0	1	---	<1955	---
MP2	43 37 07 88 02 16	825	05/31/95	2.0	-0.41	-0.13	06/01/95 08/22/95	1.5	.5	---	>1955	1976.5
MP3	43 37 07 88 02 16	825	05/31/95	3.0	-0.38	-0.15	06/01/95 08/22/95	2.5	.5	---	>1955	1977.5
MP4	43 37 07 88 02 16	825	05/31/95	4.0	-0.40	-0.12	06/01/95 08/22/95	3.5	.5	---	>1955	1977.0
MP5	43 37 01 88 02 08	825	05/31/95	2.0	-0.33	-0.04	06/01/95 08/22/95	1.5	.5	---	---	---
MP6	43 37 01 88 02 08	825	05/31/95	3.0	-0.31	-0.01	06/01/95 08/22/95	2.5	.5	---	---	---
MP7	43 37 09 88 02 20	825	05/31/95	2.0	-0.05	-0.01	06/01/95 11/06/96	1.5	.5	---	---	---
MP8	43 37 09 88 02 20	825	05/31/95	3.0	-1.08	-0.01	06/01/95 11/06/96	2.5	.5	---	---	---

[1]Negative water levels for MP1 through MP8 indicate water levels above the stream surface at the time of measurement. Stream-surface elevation is approximately 825 feet.

[2]Based on slug tests analyzed by the Bouwer and Rice method (Bouwer, 1989).

UW1 (table 1) was also included in the network of wells that comprised one of the NAWQA ground-water land-use studies described by Saad (1997). All wells at UW, MW, and DW were installed by the USGS using protocols and procedures described by Lapham and others (1995). Holes were drilled using hollow-stem augers, and wells were constructed of 2-in PVC screens and casings. Screens were 5 or 10 ft in length (table 1) with 0.01-in slots. The annular space around the screen was filled with clean, coarse quartz sand to approximately 2 ft above the top of the screen. A bentonite seal was placed above the sandpack, and then the hole was back-filled with native material to land surface. A cement seal was added around the casing at land surface to help prevent overland flow from moving down the borehole. Wells installed in the lowland area (LL) near the stream were installed using a stainless steel hand auger and constructed of 2-in PVC screens and casings. Screens were 2 ft in length with 0.01 in slots. The annular space around the screen and casing was filled with native material to land surface.

MP wells, also called minipiezometers because of their small diameter, were installed in nests below the stream bottom at four locations along the stream near the edge closest to the transect (fig. 6). Three MP wells were near the end of the transect, two were approximately 400 ft downstream from the end of the transect, another one was about 200 ft downstream, and two were approximately 500 ft upstream from the end of the transect. MP wells were constructed of 0.5-in stainless steel pipe (outer casing) and 0.5-in Teflon tubing (inner casing) and were hand pounded into the stream bottom. The outer casing was then pulled up about 0.5 ft while the inner casing was held in place to expose the well screen. The screens are 0.5 or 1 ft long and were constructed by drilling 0.06-in diameter holes into the Teflon tubing. A bentonite seal was hand packed around the outer casing at the stream bottom to prevent mixing with surface water. Additional well characteristics and water level measurements are included in table 1.

Sample Collection

Water samples were collected from all monitor wells (except MW4 and DW3, whose purpose was only water table definition) and the stream. Wells were sampled according to USGS ground-water sampling protocols (Koterba and others, 1995) where recovery permitted. They were purged until at least three casing volumes had been removed and until the field measure-ments (temperature, pH, specific conductance, and dissolved oxygen) had stabilized for three successive measurements at least 5 minutes apart. Wells UW2, UW3, LL1, LL2, and LL3 recovered very slowly. These wells were purged dry, allowed to recover, and then sampled. Field measurements from these wells were recorded just prior to sample collection. Ground water was sampled from wells at UW, MW, and DW using stainless steel, positive-displacement pumps with Teflon discharge lines. Samples were collected from LL and MP wells using a peristaltic pump with Teflon and Viton discharge lines. Stream samples were collected using the equal-width-increment method with a Teflon bottle (Shelton, 1994). Stream samples were processed using a peristaltic pump with Teflon and Viton discharge lines.

Water from most wells at UW, MW, DW, MP, and from the stream was sampled for major ions, nutrients, pesticides, dissolved organic carbon (DOC), dissolved aluminum, and tritium. Water from wells at LL was sampled for major ions, nutrients, and DOC. Additionally, samples for chlorofluorocarbons (CFCs), ^{18}O, ^{15}N, and dissolved-gas analysis were collected from selected wells along the flowpath. CFC samples were collected using equipment and procedures developed by Busenberg and Plummer (1992). Samples for ^{18}O and ^{15}N analysis were collected using procedures developed by the USGS (Steven R. Silva, written commun., 1997). Dissolved-gas samples also were collected using procedures developed by the USGS (Eurybiades Busenberg, written commun., 1997).

Core samples of unconsolidated deposits were collected near MW and DW. The samples were collected at approximately 2-ft intervals using a Geoprobe. Core samples were stored in sealed plastic tubes.

Water-Quality Analysis

Water samples collected for this study were analyzed by the USGS for inorganic and organic constituents using methods described in table 2. Field measurements of temperature, pH, specific conductance, and dissolved oxygen were made in a flow-through cell with a Hydrolab H20, which was calibrated daily. A complete list of constituents for which water samples were analyzed, the number of constituents detected, and the laboratory method detection limit (MDL) for each constituent is in appendix 1. Water-chemistry data for constituents detected in at least one sample are in appendixes 2, 3, and 4.

Table 2. Laboratory analysis methods for inorganic and organic constituents

Constituent or category	Analysis method	Reference
Chlorofluorocarbons (CFCs)	Purge and trap gas chromatography with an electron capture detector	Busenberg and Plummer (1992)
Deuterium/hydrogen ratio from water	Hydrogen equilibrium technique and mass spectrometry	Coplen and others (1991)
Dissolved gases	Gas chromatography	Busenberg and others (1993)
Dissolved organic carbon (DOC)	Ultra-violet promoted persulfate oxidation and infrared spectrometry	Brenton and Arnett (1993)
Inorganics[1]	Various methods	Fishman and Friedman (1989)
$^{15}N/^{14}N$ ratio from nitrate	Nitrate concentrated in the field on anion exchange resin and then analysis by combustion with Cu, CuO, and CaO, and mass spectrometry	Kendall and Grim (1990)
$^{15}N/^{14}N$ ratio from nitrate and ammonia combined	Nitrate reduction to ammonium with NaOH and Dvarda's alloy follwed by NaOBr oxidation to nitrogen and mass spectrometry	Miyaki and Wada (1967)
$^{18}O/^{16}O$ ratio from nitrate	Nitrate concentrated in the field on anion exchange resin and then analysis by combustion with graphite and mass spectrometry	Steven R. Silva, U.S. Geological Survey, written commun., 1997
$^{18}O/^{16}O$ ratio from water	Carbon dioxide equilibrium technique	Epstein and Mayeda (1953)
Pesticides (USGS NWQL schedule 2001 and 2010)	Solid-phase extraction (SPE) technology on a C-18 cartridge and gas chromatography/mass spectrometry	Zaugg and others (1995)
Pesticides (USGS NWQL schedule 2050 and 2051)	SPE technology with a Carbopak-B cartridge and high performance liquid chromatography with UV detection	Werner and others (1996)
Tritium	Electrolytic enrichment with gas counting	Östlund and Dorsey (1975)

[1]Not including dissolved gases or stable and radioisotopes.

Quality control included submitting field blanks, sample replicates, and field-spiked samples for analysis with water samples. Quality-control samples included a total of (1) three field blanks for major ions, nutrients, DOC, and pesticides, (2) two sample replicates for major ions, nutrients, DOC, and pesticides, and one replicate each for oxygen and hydrogen isotopes and tritium, and (3) two field-spiked pesticide samples for schedule 2001/2010 and one field spiked pesticide sample for schedule 2050/2051.

Field blanks showed that sampling procedures did not contaminate water samples for most constituents. Several major ions (including dissolved calcium, chloride, fluoride, iron, magnesium, manganese, sodium, and sulfate), dissolved ammonium, and DOC were detected in at least one blank sample at concentrations

near the detection limit. Only dissolved iron, silica, and DOC were detected in at least two blank samples and at concentrations higher than 3 percent of measured water concentrations. Blank concentrations ranged from <3 to 7 µg/L for dissolved iron, 0.3 to 0.9 mg/L for dissolved silica, and 0.1 to 0.5 mg/L for DOC. Concentrations in water samples were not adjusted for the measured blank concentrations.

Analysis of replicate samples indicated that field and laboratory procedures had minimal effects on water-quality measurement variability. Measured concentrations from replicate samples averaged less than 10 percent difference (calculated as the difference between the two measurements divided by the average of the two measurements) for all constituents except for dissolved ammonium (47 percent average difference),

dissolved ammonium plus organic nitrogen (25 percent), dissolved bromide (20 percent), atrazine (20 percent), dissolved solids (16 percent), and deethyl atrazine (12 percent). In the cases of dissolved ammonium, ammonium plus organic nitrogen, and dissolved bromide, the measured concentrations were typically near the detection limit and the absolute range between measured values was typically small.

Field-spiked samples were used to determine the recovery of pesticide analytes in different water matrices. The average recovery for 46 pesticides from two schedule 2001/2010 field spikes was between 86 and 102 percent. For one schedule 2050/2051 field spike, the average recovery for 29 pesticides was about 50 percent. The average recoveries for the five pesticides detected in water samples were as follows: atrazine, 104 percent; cyanazine, 108 percent; deethyl atrazine, 35 percent; metolachlor, 112 percent; and simazine, 99 percent. Of the pesticides detected in water samples, only deethyl atrazine recoveries were outside of the acceptable range of 80 to 120 percent.

Determination of Hydraulic Conductivity, Mineralogy, and Ground-Water Age

Horizontal hydraulic conductivity (K_h) of the surficial deposits in the vicinity of the screened intervals for the wells at nests UW, MW, and DW was estimated from slug tests. Slugs were constructed of PVC and produced a 1- to 2- ft displacement when inserted into the water in the well. Slug-test data were analyzed using the Bouwer and Rice method (Bouwer, 1989). The thickness of the aquifer interval being tested was assumed to equal the thickness of the saturated zone penetrated by the well. This assumption can result in a slight overestimation of K_h when the top of the well screen is near the water table and a slight underestimation of K_h when the top of the screen is far below the water table (Brown and others, 1995). Estimates of K_h for the tested wells range from 0.006 to 55 ft/d (table 1).

The mineralogy of surficial deposits was determined from two cores collected near well nests MW and DW. X-ray diffraction analyses were performed individually on 25 samples taken from the cores. The analyses were done by the University of Wisconsin-Milwaukee Center for Great Lakes Studies, using an automated step-scan X-ray diffractometer with a copper tube and a graphite monochromator. A summary of minerals identified by X-ray diffraction is in table 3.

Table 3. Minerals identified by X-ray diffraction in core samples from the study site, Sheboygan County, Wis.

Mineral (mean weight percent/ range in weight percent)	Chemical composition[1]
Dolomite (55 / 0.0 to 82)	$CaMg(CO_3)_2$
Quartz (30 / 8.1 to 67)	SiO_2
Microcline (7.8 / 1.6 to 23)	$KAlSi_3O_8$
Plagioclase (Albite) (4.7 / 0.6 to 15)	$NaAlSi_3O_8$
Mica (1.3 / 0.0 to 6.8)	Chemistry varies but includes K, Al, Si, and sometimes Fe and Mg
Hornblende (0.5 / 0.0 to 4.2)	$(Ca, Na)_{2-3}(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH)_2$
Chlorite (0.4 / 0.0 to 4.2)	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$

[1]Chemical composition is from Klein and Hurlbut (1977)

Ground-water recharge dates were estimated at wells UW1 - 3; MW1 - 3; DW1 and 2; and MP1 - 4, using tritium or CFCs or both (table 1). Tritium-based ground-water recharge dates were estimated by matching the measured tritium concentrations in a ground-water sample (appendix 2c) to a decay-corrected tritium input curve for precipitation near Madison, Wis. (Bradbury, 1991). This method is based on the assumption that all of the sampled water comes from precipitation, and the dates refer to the time at which water first entered the subsurface. Using this input curve, ground-water samples from the study site were described as "modern" or "old." For this report, modern refers to water that entered the subsurface after about 1955 (identified as ">1955" in table 1) and old refers to water that entered the subsurface before about 1955 (identified as "<1955" in table 1). Using Bradbury's input curve, the cutoff point between modern and old water corresponds to about 16 pCi/L, or 5 tritium units (where 1 tritium unit = 3.193 pCi/L).

Tritium is not used for more specific age dating because the input curve shows an upward trend in tritium concentrations from the mid-1950's until the mid-1960's, followed by a downward trend thereafter. Tritium concentrations in ground water that recharged after about 1955 are generally greater than 5 tritium units. These higher concentrations typically match tritium input concentrations from both sides of the mid-1960's peak, giving a non-unique ground-water age.

CFC-based ground-water recharge dates were estimated by using measured ground-water concentrations of CFCs (CFC-11, CFC-12, and CFC-113) to calculate the CFC concentrations in the unsaturated-zone air when the water was recharged and subsequently matching the concentrations in the unsaturated-zone air to his-

torical concentrations of CFCs in the atmosphere. The temperature and atmospheric pressure in the unsaturated zone are used to determine the CFC concentrations in the unsaturated-zone air that was required to produce the measured concentrations in ground water (appendix 3). Atmospheric pressure at the time of recharge was not known, but it was estimated from the elevation at the sampled location (appendix 3). Recharge temperature was estimated from the mean annual air temperature ($7.5^{\circ}C$) near the site (Wisconsin Agricultural Statistics Service, 1987) and from dissolved nitrogen and argon gas concentrations (appendix 4) in ground-water samples collected along the flowpath (Michael Doughten, U.S. Geological Survey, written commun., 1997). Recharge temperatures based on nitrogen and argon concentrations ranged from 4 to $11^{\circ}C$, and averaged $7^{\circ}C$ for six samples containing minimal (less than about 5 cubic centimeters) excess air.

The CFC-based ground-water recharge dates refer to the time at which the water first became isolated from the atmosphere, which is assumed to occur at the water table. Also assumed is that dissolved CFCs in the saturated zone are stable. Additional assumptions are that the dissolved CFCs in water that is moving through the unsaturated zone are in equilibrium with CFCs in the unsaturated-zone air and that CFC concentrations in the unsaturated-zone air are similar to those in the atmosphere. These assumptions are reasonable if recharge occurs by relatively slow infiltration and if the unsaturated zone materials are somewhat permeable and relatively thin (less than 30 ft thick), conditions that are satisfied at the study site.

CFC-based recharge dates are based on three sequential samples collected on one occasion at each well (appendix 3). CFC-based recharge dates assigned to each sample reflect mainly CFC-12 results because CFC-12 is the most conservative of the CFCs that were measured (Cook and others, 1995). If there were a range of CFC-12 recharge dates for a sample, then the middle value was used unless a chronologically upward or downward trend in CFC concentrations was apparent for CFC-11, CFC-12, and CFC-113. An upward trend in concentration could indicate that younger water, which contains higher CFC concentrations, was drawn into the screened interval during the purging and sampling process. A downward trend could indicate that the well was not completely purged of the water that was in the well prior to sampling. None of the sample sets showed an upward trend; however, the samples at well UW1

showed a slight downward trend. The oldest recharge date, based on CFC-12, was assigned as the recharge date for that sample and was censored with a "<" in table 1 to show that the water may actually be older than indicated. The actual recharge date for UW1 is probably not much older than 1959.5 because the tritium sample from well UW1 indicates a recharge date younger than 1955.

SIMULATION OF GROUND-WATER FLOW

A cross-sectional ground-water flow model was developed for the study site using the computer program MODFLOW (McDonald and Harbaugh, 1988). The model represents the water-table flow system and was used to identify possible flowpaths that could be modeled geochemically and to verify ground-water ages estimated using CFCs. Pathline and traveltime analysis was performed on calibrated flow-model output using the computer program MODPATH (Pollock, 1994).

Description of Ground-Water Flow Model

A one-layer, steady-state profile model with 71 rows and 43 columns was used to represent a cross section through the study site from the local ground-water high to the stream (fig. 7). The study site was modeled as steady state because fluctuations in measured water levels were relatively small and ground-water pumpage near the site is minimal. The model layer is 1-ft thick and is modeled as confined. The model grid dimensions are 640 ft in the x-direction, which corresponds to vertical depth in the flow system, and 2,820 ft in the y-direction, which corresponds to horizontal length along the transect. Row width ranges from 10 to 50 ft in the y-direction, and column width ranges from 5 to 100 ft in the x-direction. The model is oriented parallel to the transect which is approximately parallel to the horizontal direction of ground-water flow at the water table. The actual direction of ground-water flow may deviate slightly from the inferred flowpath due to small, seasonal fluctuations in the water table.

The water table is simulated using a constant-flux boundary. No-flow cells represent the boundaries of the local water-table flow system, and a constant-head boundary represents the stream (fig. 7). Recharge is applied at a rate of 4 in/yr to the top of the constant-flux cells that approximate the location of the water table. Because this is a one-layer profile model, model input
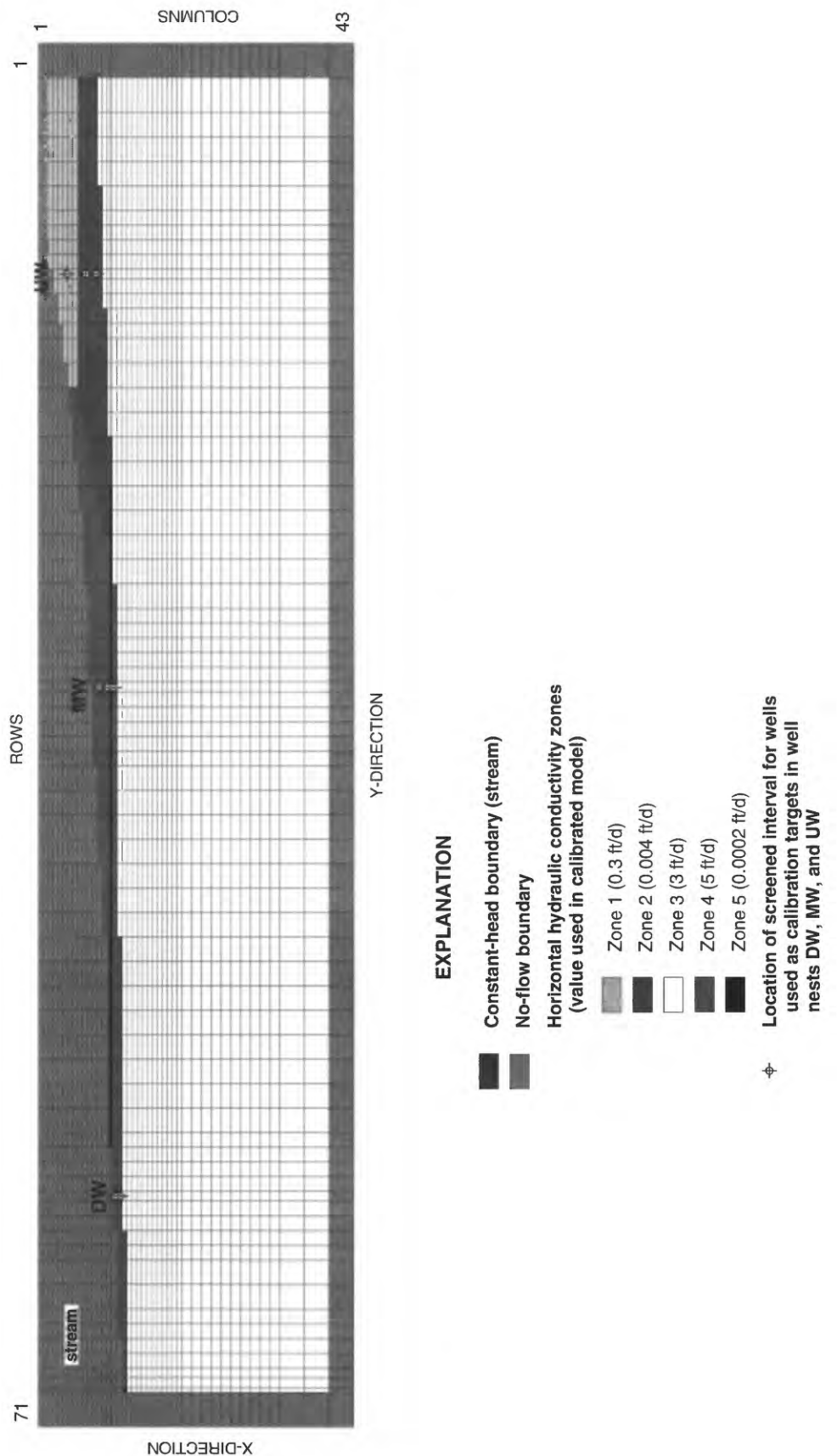
Figure 7. Grid, boundary conditions, and horizontal hydraulic conductivity zones used in the calibrated ground-water-flow model.

EXPLANATION

Constant-head boundary (stream)

No-flow boundary

Horizontal hydraulic conductivity zones
(value used in calibrated model)

Zone 1 (0.3 ft/d)

Zone 2 (0.004 ft/d)

Zone 3 (3 ft/d)

Zone 4 (5 ft/d)

Zone 5 (0.0002 ft/d)

Location of screened interval for wells
used as calibration targets in well
nests DW, MW, and UW

for recharge was adjusted using the method described by Anderson and Woessner (1992, p. 176). The no-flow cells representing the boundaries of the water-table flow system correspond to fully penetrating boundaries below the local ground-water high and the stream, and the bottom boundary is at the top of the Maquoketa Shale. The location of the bottom boundary was based on the estimated thickness of the Silurian dolomite near the site, which ranges from 430 to 470 ft. Vertically downward gradients measured near the local ground-water high and vertically upward gradients measured below the stream support the use of fully penetrating boundary conditions in the model. However, sufficient data were not available to completely verify this assumption. Simulation results were tested for sensitivity to changes in boundary conditions in addition to changes in hydraulic conductivity and recharge.

Measured water levels in installed wells were used as calibration targets. The model was calibrated by adjusting recharge, horizontal hydraulic conductivity (K_h), and anisotropy (horizontal hydraulic conductivity divided by vertical hydraulic conductivity, K_h/K_v) within specified ranges (table 4) until modeled heads matched closely to measured heads from wells in the unconsolidated deposits. The range of possible model recharge rates was estimated from the base-flow component of streamflow measurements at a nearby gaging station on the North Branch Milwaukee River and from previously published values (table 4). The active model area was divided into five K_h zones (fig. 7). Zones 1, 2, 4, and 5 represent the unconsolidated deposits and zone 3 represents the dolomite bedrock. Two zones near UW correspond to slug-test K_h values from UW1 (zone 1) and UW3 (zone 2). Two zones near MW and DW correspond to slug-test K_h values from MW and DW wells (zone 4) and a clay layer between the screened interval of wells MW2 and MW3, which was identified in one of the cores (zone 5). The K_h of the dolomite bedrock was based on previously published values (Young and Batten, 1980; Weaver and Bahr, 1991; Conlon, 1995) and is represented in the model as zone 3. Anisotropy values used in the model range from 1 to 10 (table 4) and were similar to previously published values for dolomite but were much lower for the unconsolidated deposits (Weaver and Bahr, 1991). The range of input parameters and the values for parameters used in the calibrated model are summarized in table 4. The parameters used in the calibrated model, with the exception of anisotropy of unconsolidated deposits, were generally within the specified input ranges or close to single values.

Table 4. Expected range of recharge, horizontal hydraulic conductivity, and anisotropy values at the study site and values used as input for the calibrated ground-water flow model

[K_h, horizontal hydraulic conductivity; K_h/K_v, anisotropy; ft/d, feet per day]

Parameter	Range of input values (source)	Values used in calibrated model
Recharge	1 to 10 inches per year (Young and Batten, 1980; Conlon, 1995)	4 inches per year
K_h zone 1	0.29 ft/d (slug test)	0.3 ft/d
K_h zone 2	0.006 ft/d (slug test)	0.004 ft/d
K_h zone 3	3 to 8 ft/d (Young and Batten, 1980; Weaver and Bahr, 1991; Conlon, 1995)	3 ft/d
K_h zone 4	0.4 to 55 ft/d (slug tests)	5 ft/d
K_h zone 5	2.8e-7 to 0.3 ft/d (Freeze and Cherry, 1979)	0.0002
K_h/K_v zone 1	250 (Weaver and Bahr, 1991)	10
K_h/K_v zone 2	250 (Weaver and Bahr, 1991)	10
K_h/K_v zone 3	10 (Weaver and Bahr, 1991)	5
K_h/K_v zone 4	250 (Weaver and Bahr, 1991)	5
K_h/K_v zone 5	250 (Weaver and Bahr, 1991)	1

The average difference between modeled and measured heads for the calibrated model was 0.8 ft, and the average absolute difference was about 4.5 ft (table 5). The largest head differences were for wells UW2 (-11.7 ft) and MW3 (12.5 ft). Modeled heads were independently tested for sensitivity to recharge, K_h of dolomite, K_h of unconsolidated deposits, location of the bottom boundary, and non-fully-penetrating boundary conditions below the stream and the local ground-water high.

Table 5. Measured and modeled heads for the calibrated ground-water flow model

Well name	Average measured head[1] (ft)	Modeled head (ft)	Difference[2] (ft)
DW1	840.0	839.9	0.1
DW2	840.0	839.8	.2
MW1	874.3	875.1	-.8
MW2	874.6	872.8	1.8
MW3	862.6	850.1	12.5
UW1	954.6	956.7	-2.1
UW2	930.9	942.6	-11.7
UW3	928.1	921.3	6.8

[1]Based on water levels measured at the study site from May 1994 through August 1995.
[2]Mean difference = 0.8 ft, absolute mean difference = 4.5 ft.

Recharge and K_h's were varied by a factor of 2 from the calibrated values. Varying recharge caused the modeled heads to range from an average of 62 ft above to 32 ft below the measured heads. Varying unconsolidated-deposit K_h's caused heads to average between 38 ft above to 21 ft below measured heads, whereas varying K_h of the dolomite caused heads to change by an average of only 9 ft above to 7 ft below measured heads.

The location of the bottom boundary was varied by reducing the dolomite thickness by 100 and 200 ft. The 100-ft reduction had minimal effects on the modeled heads. The average difference between modeled and measured heads was only about 1.2 ft, and the average absolute difference was only about 4.7 ft. Reducing the dolomite thickness by 200 ft resulted in an average difference of about 5.3 ft and an average absolute difference of about 6.7 ft.

Non-fully-penetrating boundary conditions were simulated by changing the active cells below the stream and the local ground-water high to constant-head cells. Initially, the constant-head cells were assigned head values equal to the head calculated for that cell from the calibrated model. This simulated fully penetrating boundary conditions (to approximately 450 ft below the stream) and produced the same distribution of modeled heads as the calibrated model. Depth of boundary penetration was then varied by assigning a uniform head value to all of the constant head cells that were 100 ft or greater below the stream and then 200 ft or greater below the stream. The uniform head values allowed for horizontal flow out of the model along these boundaries. The assigned uniform head values corresponded to the calibrated head values at 100 and 200 ft below the stream for cells at those locations along both boundaries. The average difference between modeled and measured heads for the 100-ft deep penetrating conditions was about 1.2 ft, and the average absolute difference was about 4.8 ft. For the 200-ft deep penetrating conditions, differences were about 0.9 and 4.6 ft, respectively.

In summary, modeled heads were most sensitive to recharge and K_h of the unconsolidated deposits and least sensitive to the location of the bottom boundary, non-fully-penetrating boundary conditions below the stream and the local ground-water high, and K_h of the dolomite. Additionally, modeled heads at nest UW were the most sensitive to all input parameters, whereas heads at DW were least sensitive.

Pathline and Traveltime Analysis

As mentioned previously, pathline and traveltime analysis was performed on the calibrated model head output to identify possible flowpaths for geochemical modeling and to verify ground-water ages estimated using CFCs. This analysis was done using the computer program MODPATH, which calculates the path and velocity of a particle of water placed anywhere in the model grid. Pathline and traveltime analysis requires porosity values, which are assumed to be 25 percent for unconsolidated deposits and 20 percent for the dolomite. These values are within the range of typical values reported by Freeze and Cherry (1979). A single particle was placed in each cell that corresponded to the location of the water table. These particles were tracked forward to the stream (fig. 8). The modeled pathlines show that flow to well nests UW, MW, and DW originates slightly upgradient from the nest and that there is no flow from one well nest to another. This means that water from a UW well does not flow to any of the MW wells, and water from MW wells does not flow to any of the DW wells.

These simulation results are generally consistent with the flowpath patterns that can be inferred from the CFC-based ground-water ages. For example, ground water at DW1 and DW2 is younger than any of the water at nest MW (fig. 9). Assuming no mixing, the younger ages indicate that ground water moving to wells DW1 and DW2 originated somewhere downgradient from nest MW. Water discharging to the stream originates from recharge all along the transect and is a combination of all flowpaths through the ground-water flow system. Water entering the MP's is a subset of the water entering the stream. Based on the particle tracking results, water to the MP's could be originating from any upgradient well nest or could possibly be a mixture of those waters. Within well nests, particle tracking indicates that water flowing to UW3 could have originated from near UW2 or UW1 and that water from MW3 could have originated from near MW2. Possible flowpath scenarios for geochemical modeling, based on pathline analysis are shown in fig. 10.

Pathline directions and possible flowpath scenarios for geochemical modeling were qualitatively checked for sensitivity to recharge, K_h of dolomite, K_h of unconsolidated deposits, and boundary conditions through comparisons with results from the calibrated model. Pathlines from the water table to well nests were rela-
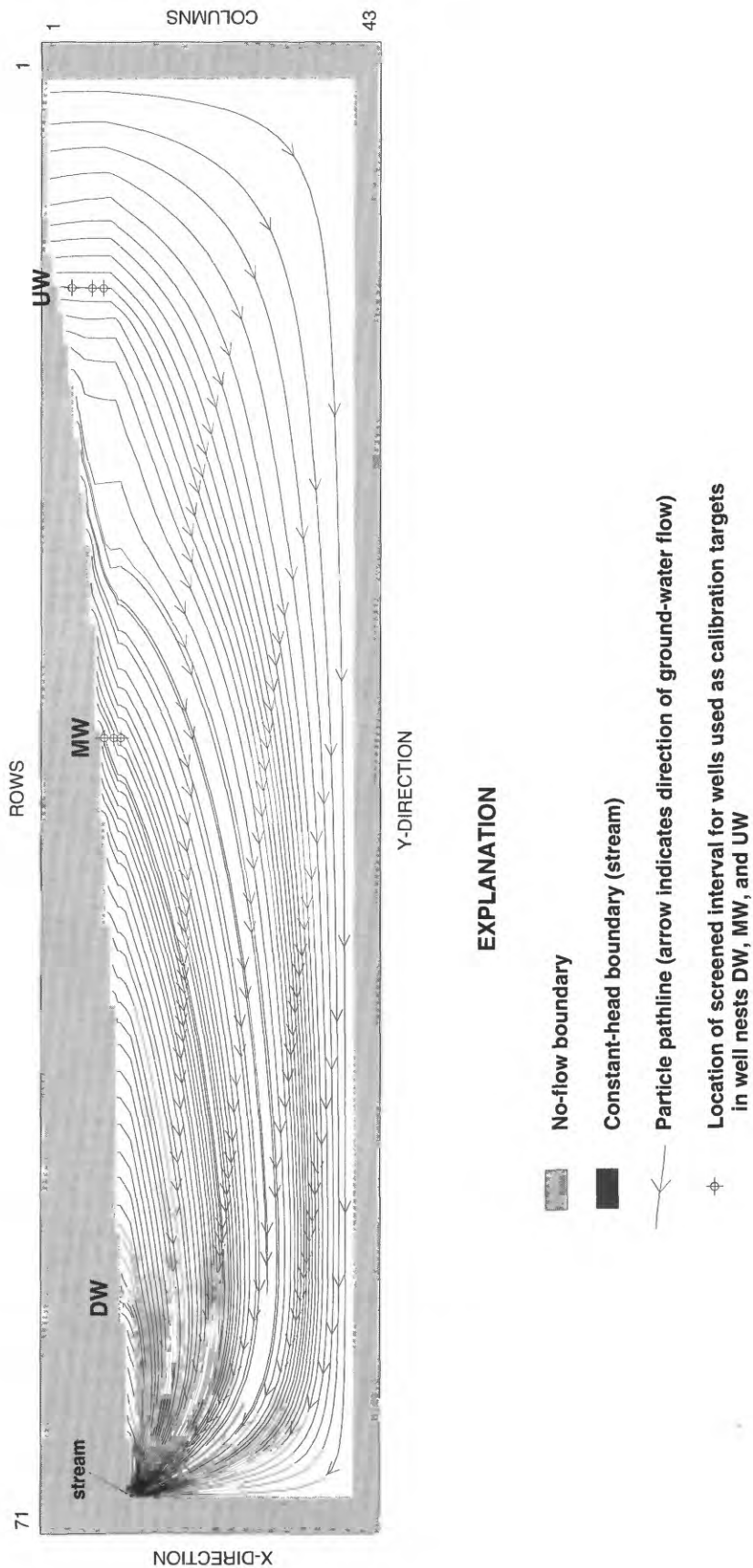
Figure 8. Particle pathlines tracked forward from the water table to the stream using the calibrated ground-water flow model.
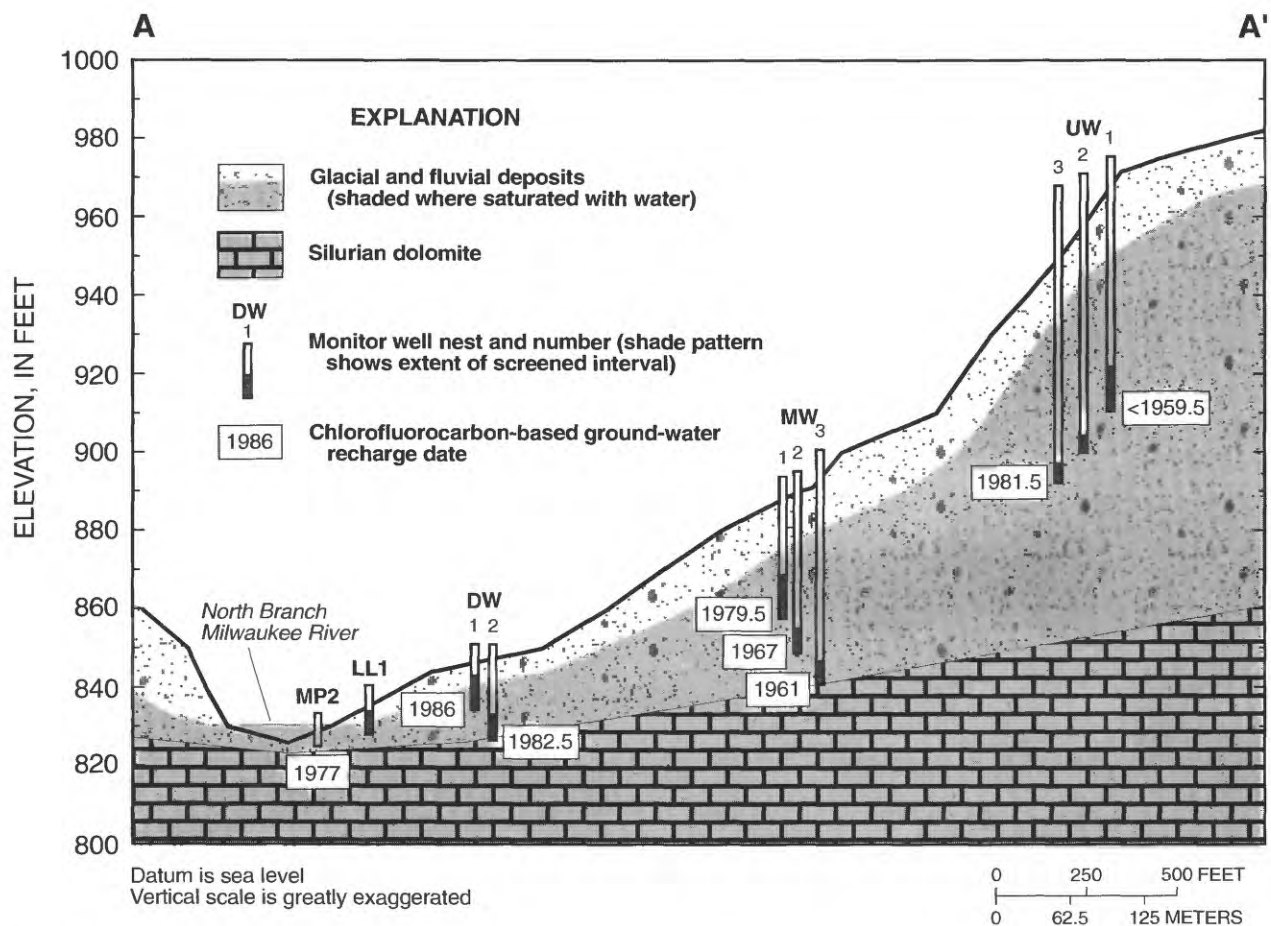
Figure 9. Chlorofluorocarbon-based ground-water recharge dates at the study site, Sheboygan County, Wisconsin (trace of section shown in figure 3).

tively insensitive to all changes. Pathline directions in other parts of the model were most notably changed along the boundary below the stream because of non-fully-penetration of boundary conditions. Non-fully-penetrating boundaries allowed particles to leave the model horizontally below the stream instead of vertically to the stream as in the calibrated model. The only change to possible flowpath scenarios for geochemical modeling was for the 100-ft deep non-fully-penetrating boundary condition. This condition allowed particles originating at the water table upgradient from MW to leave the model below the stream, a result that would eliminate the possible flowpath scenario UW to MP.

Modeled traveltimes for particles tracked from the water table to wells were, for the most part, similar to CFC-based traveltimes (table 6). CFC-based travel-

times were calculated as the difference of the CFC-based recharge date minus the sample date of June 1994. Modeled traveltimes are presented as minimum and maximum values. The minimum value was the time it took for a particle to travel from the water table to the top of the screened interval and the maximum was the time to the bottom of the screened interval. The minimum modeled traveltimes were typically within a few years of the CFC results, with the exception of UW3, where the difference was about 41 years. UW3 is unusual in that its CFC-based ground-water age is less (1981.5) than that determined for the shallower UW1 (<1959.5). CFC results indicate a faster pathway from land surface to UW3 than to UW1, a pathway that is not simulated by the flow model. Flow-model results indicate that ground water at UW3 is approximately 54 to
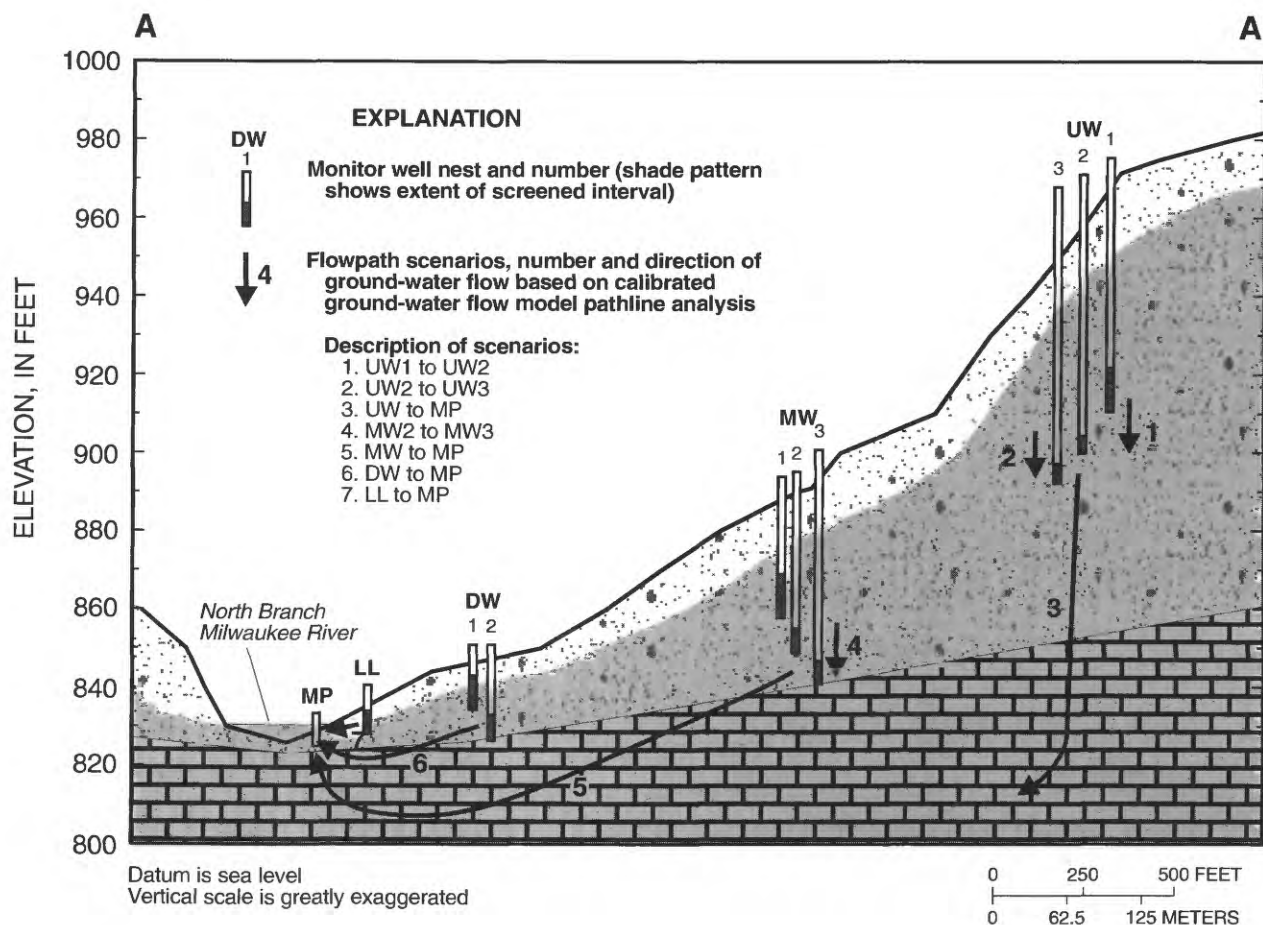
Figure 10. Possible flowpath scenarios for geochemical modeling and direction of ground-water flow, based on calibrated ground-water flow model pathline analysis (trace of section shown in figure 3).

59 years old. Water-quality data, namely measured pesticide concentrations, support the faster pathway scenario; atrazine was detected at least once in UW3 but not in UW1 (appendix 2d). Atrazine has been used in Wisconsin only since the early 1960's, so at least some of the water entering UW3 recharged after that time. It is possible that most of the water from UW3 is 54 to 59 years old as indicated by the flow model and that a small amount of young water is entering UW3 through macropores from the land surface. Only a small amount of young water containing relatively high concentrations of atrazine and CFCs would be needed to produce the observed atrazine and CFC concentrations in water from UW3.

Table 6. Comparison of chlorofluorocarbon-based traveltimes and range of modeled traveltimes for the calibrated ground-water flow model
[CFC, chlorofluorocarbon]

Well name	CFC-based traveltime (years)	Modeled traveltimes[1] (years)	
		To top of screen	To bottom of screen
DW1	8.5	5.8	15
DW2	12	15	19
MW1	15	13	24
MW2	27.5	27	32
MW3	33.5	33	39
UW1	>35	25	40
UW3	13	54	59

[1]Assumed porosities are 25 percent for till and 20 percent for dolomite.

DESCRIPTION OF THE CHEMICAL COMPOSITION OF WATERS AT THE STUDY SITE

The chemical composition of ground-water, sur-face-water, and precipitation samples collected at or near the study site is described in the following sections. In addition to chemical composition, sources of dis-solved constituents and chemically defined ground-water flowpaths are described on the basis of available ground-water-quality data. Chemistry data for all water samples collected at the study site are included in appendixes 1, 2, 3, and 4, and in table 9. Concentrations used in the modeling sections of this report are in units of millimoles per liter or milliequivalents per liter. Con-version factors for calculating the corresponding units of milligrams per liter can be found in Hem (1985, p. 56).

Ground-Water Quality and Chemistry

A general description of ground-water quality at the site is given below. The sections that follow thereaf-ter describe the chemistry in more detail, including identification of sources of dissolved constituents and definition of the redox environments throughout the ground-water system. Also, a summary of chemically permissible ground-water flowpaths is presented for consideration in geochemical modeling.

The term "nitrogen" in the following text refers to the sum of nitrogen species reported in appendix 2c (ammonium + organic N + nitrite + nitrate). Dissolved nitrogen gas, N_2, which is present in all samples, will be referred to explicitly as "nitrogen gas" or "N_2." Nitro-gen was detected in nearly all samples; however, the form and concentrations differed along the transect. At UW, nitrogen was primarily in the form of ammonium, and concentrations ranged from about 0.5 to 2 mg/L, increasing with depth. At DW and MW, nitrogen was primarily in the form of nitrate, and concentrations ranged from 1.7 to 4.3 mg/L, generally decreasing with depth. Nitrogen from LL and MP wells was primarily in the form of ammonium, and the total dissolved nitrogen concentrations were relatively low compared to those at upgradient locations. Dissolved phosphorus and ortho-phosphate concentrations were generally near the detec-tion limit in ground-water samples with the exception of several MP wells, where concentrations as high as 0.09 mg/L dissolved orthophosphorus were measured.

Several pesticides and pesticide metabolites were detected in ground-water samples at the study site, including atrazine, deethyl atrazine (a metabolite of atrazine), and simazine. Most of the detected pesticides are herbicides typically used in agricultural areas where corn and soybeans are grown.

The most commonly detected pesticides at the study site were atrazine and one of its metabolites, deethyl atrazine. Atrazine was applied only near the local ground-water high at the study site; however, atra-zine or deethyl atrazine were detected at least once in samples from most of the wells in nests UW, MW, and DW (appendix 2d and figure 11). Deethyl atrazine was also detected in three MP wells (figure 12). Pesticides were not analyzed for in samples from LL wells.

None of the sampled water-quality constituents exceeded Wisconsin ground-water quality enforcement standards (Wisconsin Department of Natural Resources, 1994). Dissolved nitrate concentrations exceeded the Wisconsin ground-water quality preven-tive action limit of 2 mg/L in several samples from wells DW1, DW2, MW1, and MW2.

The dominant ions in most ground-water samples from the study site were calcium, magnesium, bicarbon-ate, and sulfate (appendix 2). Chloride, potassium, and sodium also were present in relatively high concentra-tions in samples from several monitor wells. Values of pH ranged from 6.6 to 8.0, and dissolved oxygen con-centrations measured in the field ranged from 0.1 to 10.3 mg/L. Dissolved oxygen concentrations based on dissolved gas analyses ranged from 0.01 to 7.5 mg/L (appendix 4). Most DOC concentrations from ground-water samples ranged from about 1 to 3 mg/L. At UW3, DOC concentrations ranged from 4 to 28 mg/L, and at wells MP5 and MP6, concentrations ranged from 4 to 7 mg/L.

The major-element concentrations in the flowpath ground waters are shown in figure 13 (pH, alkalinity, Ca^{2+}, Mg^{2+}) and figure 14 (SO_4^{2-}, Cl^-, Na^+, K^+). Field-titrated alkalinity values are available only for the MW and DW sites in the June 1994 sampling. The remainder of the alkalinity values from all sampling sites in figures 13 and 14 are from laboratory analyses. The data in fig-ures 13 and 14 are plotted as a function of flowpath well-nest site. The data are further classified according to the redox environment defined for each site and depth, but the data are not differentiated by sampling date. For example, the three diamonds at UW in figures 13 and 14 correspond to data collected from UW1 on June 16, 1994, and May 31 and August 24, 1995. The
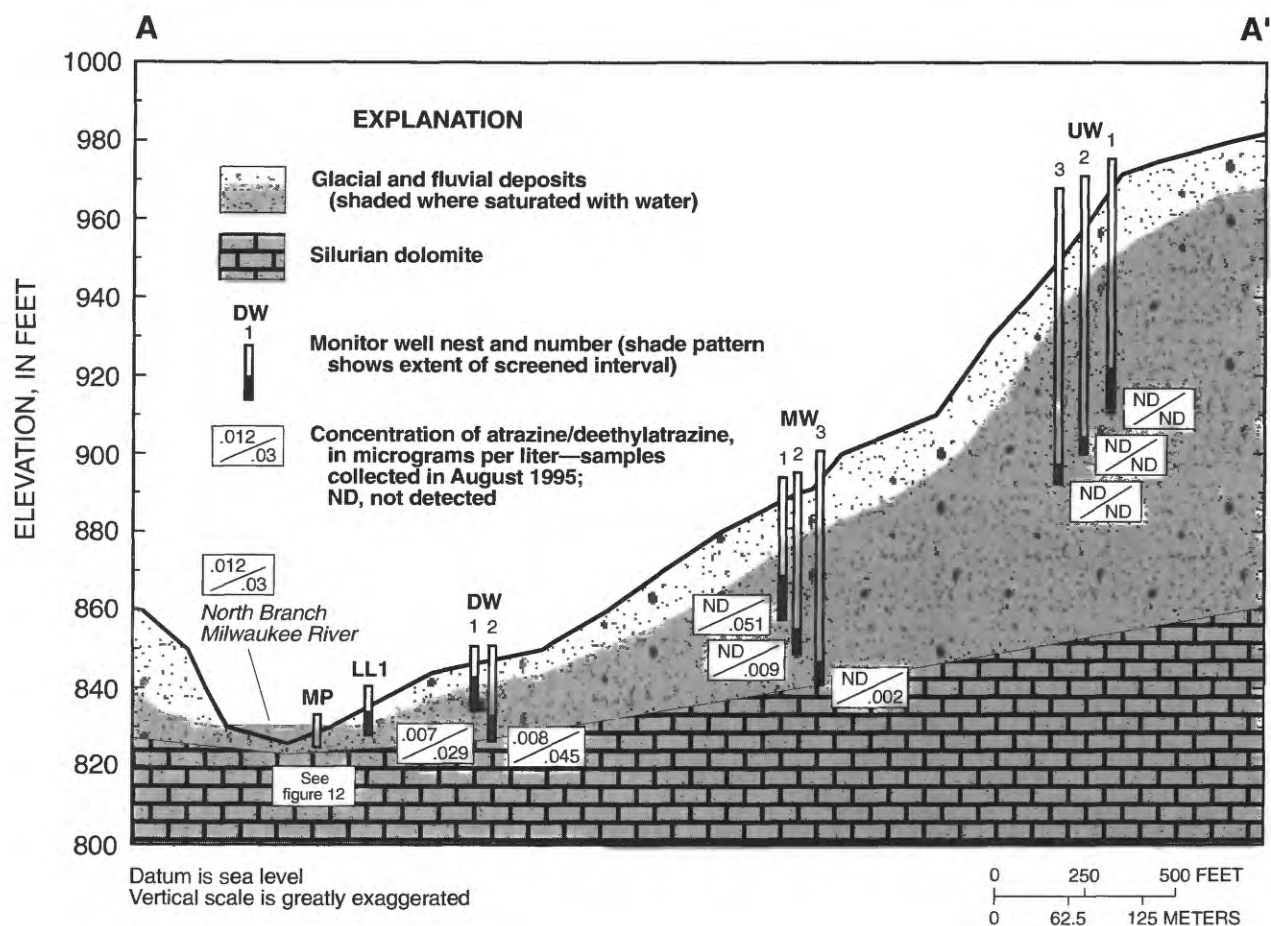
Figure 11. Concentration of atrazine and deethylatrazine in ground- and surface-water samples from the study site, Sheboygan County, Wisconsin (trace of section shown in figure 3).

diamond symbols indicate that the redox state of samples from UW1, as described in the "Redox environments" section, is post-oxic II. Data from MP2, MP3, and MP4 are plotted at MP.

As figures 13 and 14 show, the flowpath ground waters are predominantly Ca-Mg-HCO_3-SO_4 waters, with subordinate Cl, Na, and K. All other dissolved constituents are present in minor or trace concentrations. Exceptions are the samples from UW2 (sulfidic, "X" in figures 13 and 14) and UW3 (methanic, "*" in figures 13 and 14), which are a significantly different water type. Concentrations of calcium, magnesium, sulfate, and alkalinity in the UW2 and UW3 samples are lower than concentrations in other samples, but the sodium and chloride concentrations are substantially higher. The sulfate concentrations in UW3 are near zero. The

UW2 and UW3 waters do not appear to contribute significantly to the chemistry of the other flowpath waters.

Several trends in major element chemistry are evident with distance along the transect (figs. 13 and 14). From the upgradient UW1 samples to the minipiezometers in the river, MP, the pH decreases by about 1 unit, the alkalinity increases by about 1 meq/L, and calcium concentrations increase by about 0.2 mmol/L. Sulfate decreases by about 0.1 mmol/L, chloride decreases by roughly 0.15 mmol/L, and sodium and potassium concentrations are constant with downgradient location. These trends with distance along the transect should not be interpreted as reactions along flowpaths. The pathline analysis and redox chemistry of the ground waters (discussed below) show that well-to-well flow does not occur.
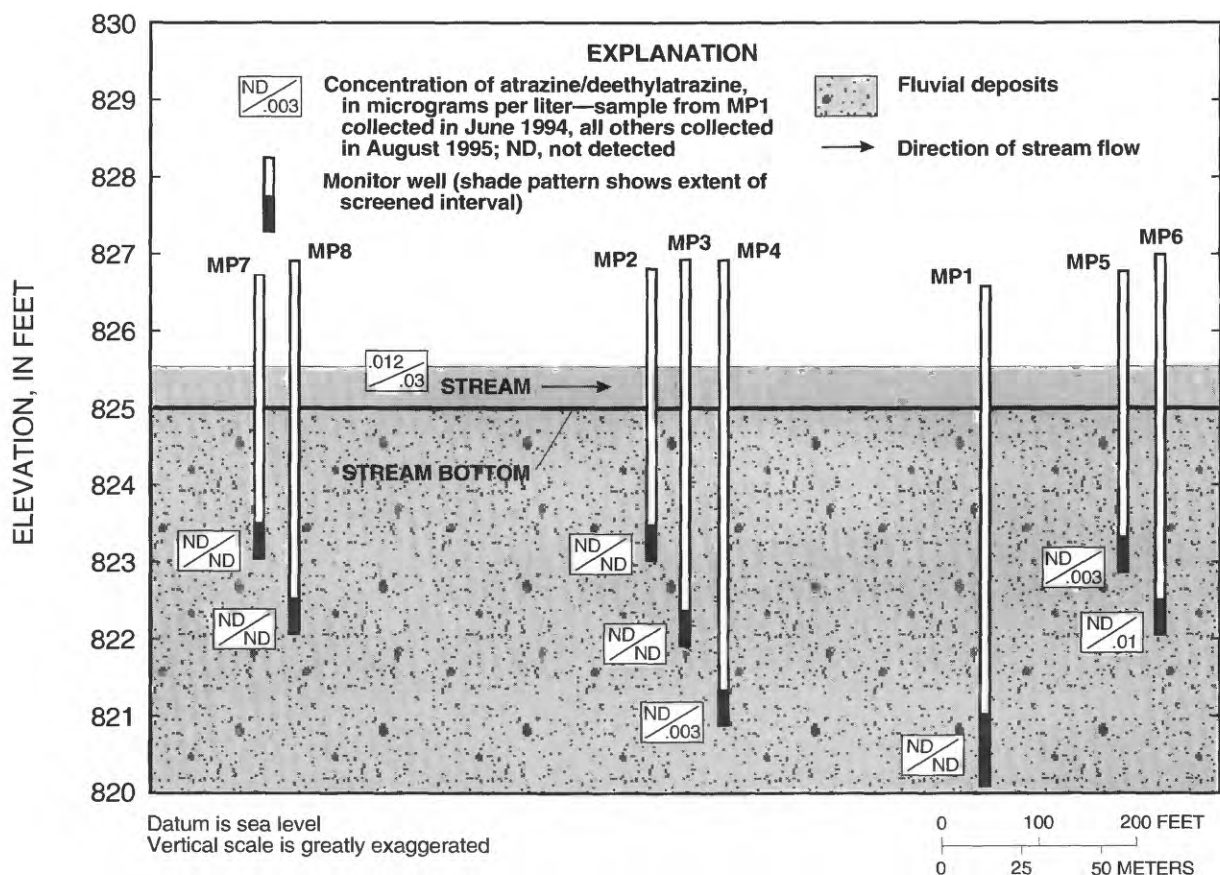
Figure 12. Concentration of atrazine and deethyl atrazine in water samples from MP wells and the stream at the study site, Sheboygan County, Wisconsin (location of MP wells shown in figure 3).

The excess of calcium over magnesium in flowpath waters is roughly 0.2 mmol/L, which is the approximate sulfate concentration in the flowpath waters. Figure 15 illustrates particularly well the fact that the UW2 and UW3 waters have a different origin than ground water in the rest of the flowpath samples.

Ground-Water Redox Environments

The biological and chemical fate of the dissolved nutrients and minerals in the flowpath system is interwoven with the general redox chemistry, and the descriptive features of both are described here. The redox chemistry of the elements C, N, S, and O is sometimes discussed in terms of "titrating" a water with

organic matter, generally assumed to have the composition CH_2O (Stumm and Morgan, 1996). As this reaction progresses, the aqueous environment in which it is reacting becomes increasingly more reducing. A classification of sedimentary redox environments based on this reaction concept has been published by Berner (1981), whose classification defines a series of environments (oxic, post-oxic, sulfidic, and methanic) on the basis of presence or absence of diagnostic dissolved redox-active aqueous species. Berner's classification does not include criteria based on nitrogen chemistry, which we include here in two subsets of the post-oxic redox environment.

The primary criterion for oxic environments is the presence of dissolved oxygen, but this seemingly simple criterion can be difficult to apply. The presence of
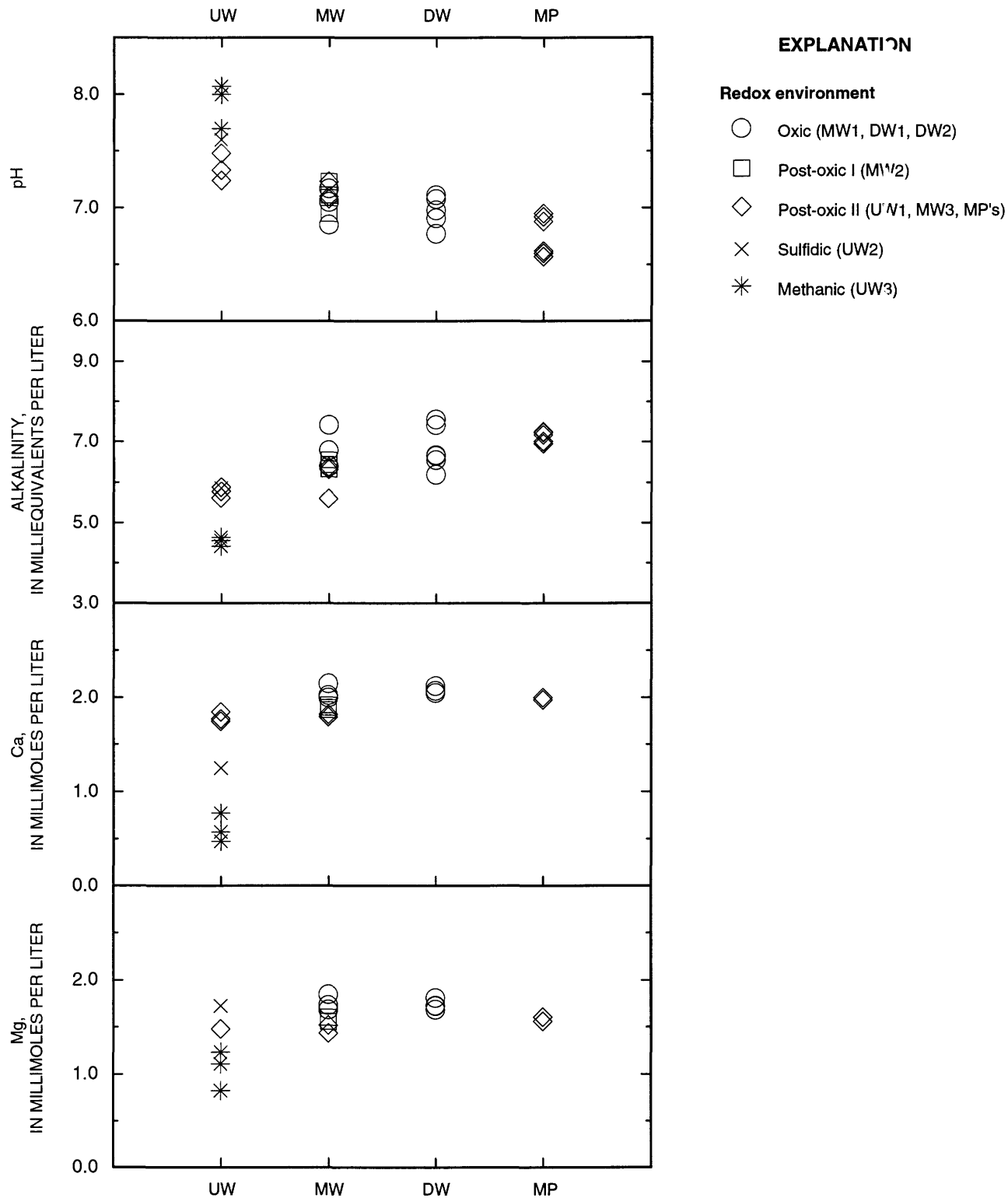
Figure 13. Redox environment, pH, alkalinity, and concentrations of calcium and magnesium in ground-water samples from the study site.
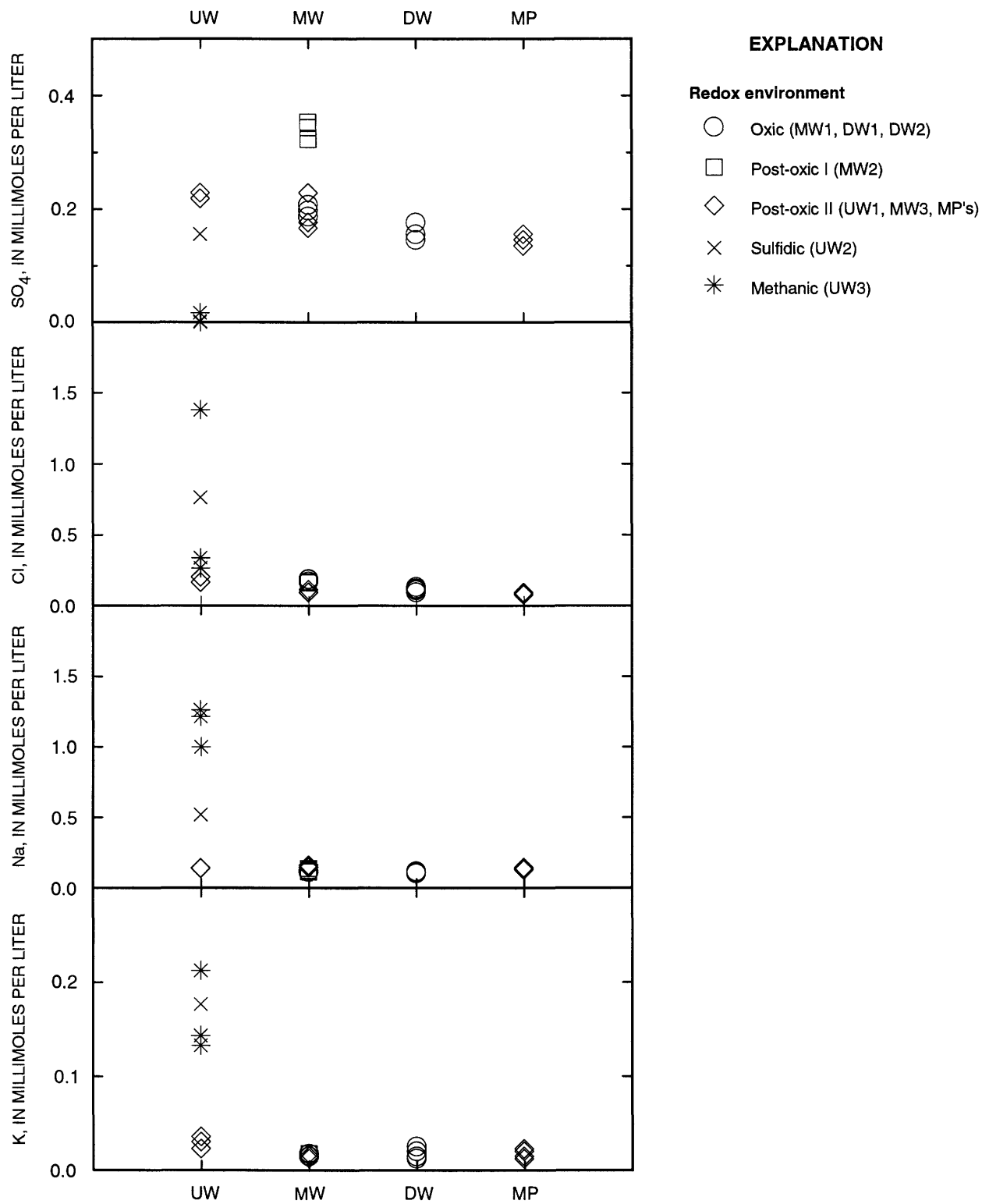
Figure 14. Redox environment and concentrations of potassium, sodium, chloride, and sulfate in ground-water samples from the study site.
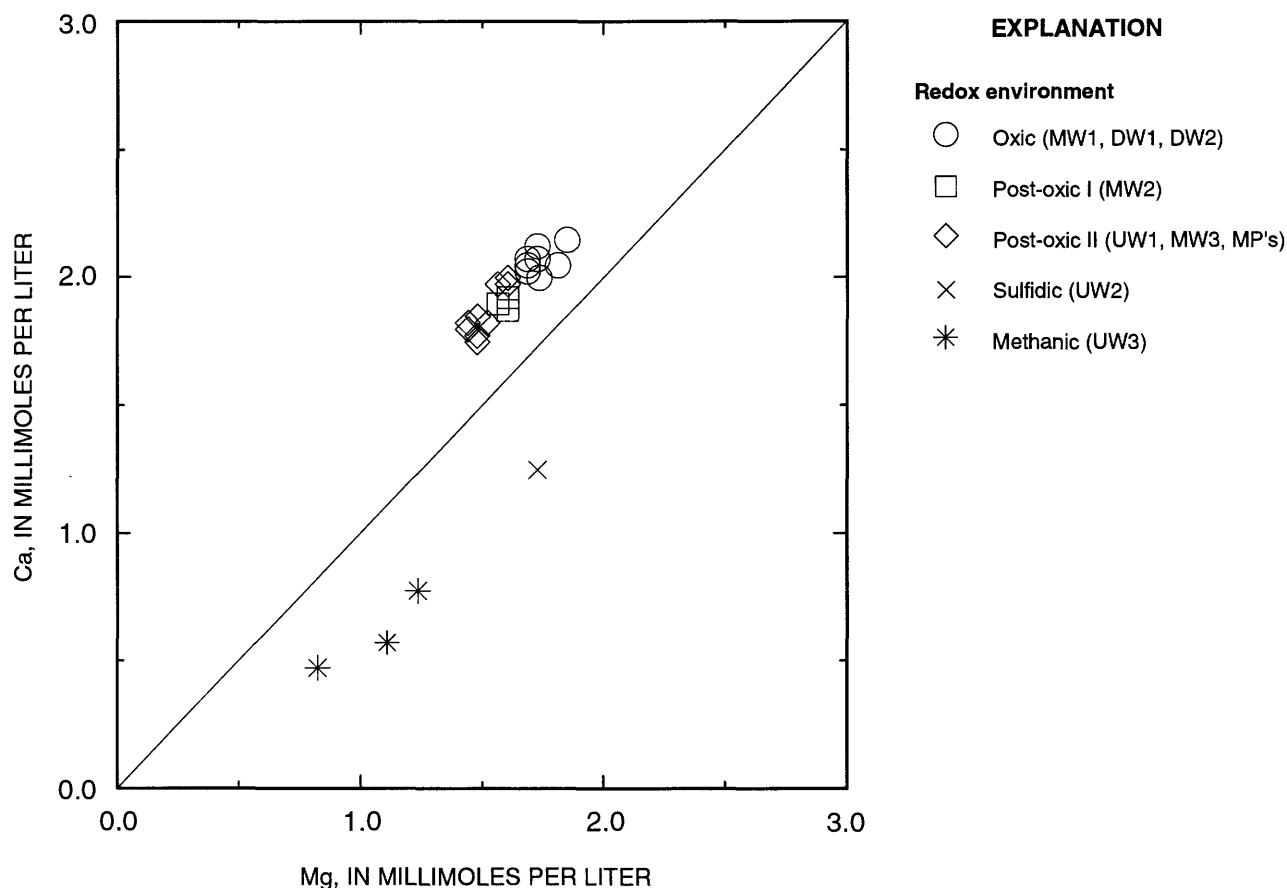
Figure 15. Redox environment and relation between calcium and magnesium concentrations in ground-water samples from the study site.

even trace quantities of dissolved oxygen thermodynamically implies a strongly oxidizing environment. Analytically detectable oxygen, if native to the environment, defines an oxic environment. The problem is that trace quantities of O_2 can easily be entrained in a sample during well flushing, pumping, and sampling. This entrainment can result in an apparently oxic environment (based on the dissolved oxygen concentration) when the in situ environment could be strongly reducing. In addition to the presence of dissolved oxygen, the oxic environment should be characterized by carbon as carbon dioxide (no methane), sulfur as sulfate (no sulfides), nitrogen principally as nitrate, and dissolved Fe and Mn at very low levels as a result of oxyhydroxide precipitation. If large quantities of dissolved oxygen are present and other redox criteria are also consistent, the environment is comfortably classified as oxic. If small or trace quantities of dissolved oxygen are present, but reducing species of other elements (carbon as methane, sulfur as sulfide, nitrogen as ammonium, ferrous iron) are present in abundance, the dissolved oxygen is presumed to be a sampling artifact and the ground water is classified as anoxic.

The post-oxic environment is one in which all dissolved oxygen has reacted, but without sufficient time or thermodynamic drive for reactions to progress to the point of significant sulfate reduction. The post-oxic environment is characterized by the absence of dissolved oxygen, carbon as carbon dioxide, sulfur as sulfate, and relatively high concentrations of dissolved iron and manganese that can accumulate in solution in the absence of dissolved oxygen. In the study-site flow-

path waters, there are two versions of the post-oxic environment: one with nitrate as the predominant nitrogen species, the other with ammonia. These two groups are defined here as "post-oxic I" (nitrogen predominantly as nitrate) and "post-oxic II" (nitrogen predominantly as ammonia). The post-oxic environment encompasses a wide range of redox potential, and the transformations from nitrate to ammonia, or from nitrate to nitrogen to ammonia occur within this range (Stumm and Morgan, 1996). The nitrate-N_2 transition occurs in the oxidizing part of the post-oxic redox environment. The nitrate-ammonia transition (in the absence of N_2) occurs is in the middle of the post-oxic environment. The N_2-ammonia transition occurs at the reducing limit of the post-oxic environment and nearly overlaps the onset of sulfate reduction.

Sulfidic environments are characterized by the presence of dissolved sulfides and/or sulfide minerals as indicators of active sulfate reduction, carbon as carbon dioxide (low concentrations of methane will be present), and low iron and manganese concentrations due to scavenging by sulfide produced by sulfate reduction.

Methanic environments occur when sulfate reduction is complete and methanogenesis becomes the predominant terminal electron accepting process. Methanogenic environments are characterized by carbon as methane (carbon dioxide is generally present also); sulfur should be either absent in systems containing sufficient iron to precipitate iron sulfides, or present as dissolved sulfides. Sulfate concentrations should be very low or zero, nitrogen should be present as ammonia, and dissolved iron and manganese may be high or low depending on the relative masses of iron(manganese) and sulfur in the system.

Concentrations of the redox-active elements in ground-water samples from along the flowpath are presented in appendixes 2 and 4. The redox environment assigned to each sampling site by Berner's classification is listed in table 7. Individual flowpath sites are discussed briefly below.

The UW3 waters are characterized by low iron and manganese concentrations, low concentrations of nitrate and abundant ammonium, the absence of sulfate, and abundant methane. All of these characteristics indicate strongly reducing methanic waters. However, oxygen is also abundant in these samples. These samples are interpreted as a methanic ground water that has been contaminated with oxygen during sampling.

No dissolved gas samples were collected at UW2. Nitrate was not detected, and ammonium concentrations are high. Iron and manganese concentrations are low, and sulfate concentrations are only half those of other flowpath waters. These criteria indicate reducing conditions and possible sulfate reduction. The presence of significant sulfate concentrations rules out the methanic classification for these samples. However, like UW3, oxygen is present (2.9 mg/L by electrode measurement). Samples from UW2 are interpreted as sulfidic ground water that has been contaminated with oxygen during sampling. The combination of low sulfate and high sodium chloride concentrations categorize UW2 and UW3 as non-flowpath ground water, because these waters cannot evolve by known reactions to any downgradient water compositions. UW2 and UW3 are not considered further for flowpath analysis.

Table 7. Redox environments[1] observed at flowpath sampling sites
[well name shown in paratheses]

Well nest			
UW	MW	DW	MP
Post-oxic II (UW1)	Oxic (MW1)	oxic (DW1)	Post-oxic II (MP2,3,4)
Sulfidic (UW2)	Post-oxic I (MW2)	oxic (DW2)	
Methanic (UW3)	Post-oxic II (MW3)		

[1]Modified from classification by Berner (1981).

Ground water at UW1 has measurable dissolved oxygen reported by electrode but only 2.5 μmol/L in the dissolved gas sample. Sulfur is present as sulfate and C as CO_2. Ammonia concentrations are high, with zero nitrate. The samples from UW1 contain low iron and manganese, and trace amounts (1.15 μmol/L) of methane. Because one measurement showed only trace concentrations of dissolved oxygen, the samples in which dissolved oxygen was present are assumed to be contaminated. UW1 waters are classified as post-oxic II.

The MW1, DW1, and DW2 ground waters contain abundant dissolved oxygen (by both electrode and dissolved-gas methods); iron and manganese concentrations are virtually zero, nitrate is abundant and ammonium very low, and methane concentrations are virtually zero. These waters are classified as oxic.

Samples from MW2 and MW3 show only trace concentrations of dissolved oxygen (0.3 and 6 μmol/L, respectively); sulfur is present as sulfate, and methane

concentrations are 0.19 and 24.6 μmol/L, respectively. Iron and manganese concentrations are high in MW2 and very high in MW3. In MW2 nitrate >> ammonium, and in MW3 the reverse is true. Both sites are post-oxic; on the basis of nitrate/ammonia ratios, MW2 is classified as post-oxic I and MW3 is classified as post-oxic II. The higher methane concentration at MW3 may imply incipient methanogenesis, but with sulfate concentrations of about 0.17 mmol/L the MW3 redox environment is still post-oxic II, not methanic.

All MP ground water is post-oxic II. Sulfur is present as sulfate, and dissolved oxygen concentrations are at trace levels. Methane concentrations are low (between 1.5 and 2.0 μmol/L), iron and manganese concentrations are high, and nitrate and ammonium concentrations are both low, with ammonium >> nitrate. Not enough data were gathered from LL wells to define redox conditions. Therefore, LL wells will not be considered further for geochemical modeling.

The redox reaction sequence to be expected as a result of degradation of organic material is oxic --> post-oxic I --> post-oxic II --> sulfidic --> methanic. The chemically permissible flowpaths based on this redox sequence are (1) vertically downward at the UW and MW sites (2) UW1, MW1, and MW2 to the MP's (3) DW1 and DW2 to the MP's and (4) flow without reaction from UW1 --> MW3 --> MP's or between MW1, DW1, and DW2. All other flowpaths require the redox environments to become more oxidizing along the path.

Most of the chemically permissible flowpaths just described compare favorably with those identified from the ground-water flow model. All flowpaths based on the redox reaction sequence can be represented by flow-model results except for MW1 --> MW2. Chemically permissible flowpaths between nests UW, MW, and DW, (for example UW1--> MW3), which involve no change in redox environments, are not represented by flow-model results. These flowpaths may still be possible by preferred pathways along the water table or bedrock surface; however, these conditions were not simulated in the flow model.

Surface-Water Quality and Chemistry

Surface water at the study site is derived from a combination of local and upstream sources. Samples were collected during base-flow conditions for compar-

ison to ground water collected from below the stream bottom and from upgradient locations at the study site.

The dominant ions in most surface-water samples from the study site were calcium, magnesium, and bicarbonate (appendix 2). Chloride, potassium, sodium, and sulfate were also present in relatively high concentrations in surface-water samples. Values of pH ranged from 7.8 to 8.2, and dissolved oxygen concentrations ranged from 8.4 to 12.7 mg/L for surface-water samples. Concentrations of DOC ranged from about 5 to 8 mg/L.

In the stream, nitrogen was primarily in the form of nitrate, and concentrations ranged from 1.8 to 2.7 mg/L. Concentrations of dissolved phosphorus and orthophosphorus in the stream both ranged from about 0.09 to 0.12 mg/L. Several pesticides were detected in surface-water samples at the study site, including atrazine, deethyl atrazine, cyanazine, metolachlor, and simazine.

Chemical Models

On the basis of analysis of chemical data and results from the ground-water flow model, selected flowpath scenarios were chemically modeled using the computer program PHREEQC (Parkhurst, 1995). The purpose of modeling the chemistry of the site was to test hypotheses and answer questions about mixing and reactions taking place along selected flowpaths; for example, How important is precipitation to the chemistry of the site? Is denitrification occurring at the site? Can dissolution of minerals identified by X-ray diffraction explain most of the predominant ions in solution? Does atmospheric CO_2 and organic matter have an effect on water chemistry at the site? These types of questions were addressed with inverse and forward modeling and will be discussed in detail in following sections. The program PHREEQC was used to simulate the chemical reactions that occur as precipitation moves to the shallow ground-water system, and as the water moves along possible flowpaths, specifically those reactions involving nitrogen species.

Reactions Generating Shallow Ground Water from Precipitation

The reactions required to generate shallow ground water from precipitation were simulated by inverse modeling, also referred to as mole-balance modeling or mass-balance modeling. Inverse modeling concepts are

discussed in Plummer and Back (1980), Plummer (1984), and Plummer and others (1983, 1991, 1994). Detailed examples are available in the NETPATH manuals (Plummer and others, 1991, 1994). The general theory of inverse modeling with uncertainty is provided by Parkhurst (1997), with a detailed example in the PHREEQC manual (Parkhurst, 1995). The following discussion is taken from Parkhurst (1995), Parkhurst and others (1996), and Parkhurst (1997).

A mole-balance model is a set of mixing fractions of initial aqueous solutions and mole transfers (quantities of minerals and gases dissolved and precipitated, or degassed) that quantitatively account for the chemical composition of the final solution. Implicit in this approach is the assumption that the final solution did indeed evolve from the initial aqueous solutions by reaction with the proposed minerals and gases. Plausible mole-balance models account for the chemical differences between initial solutions and the final water; in addition, they must be consistent with petrographic and isotopic data and saturation indices.

Mole-balance modeling with uncertain data includes an additional set of unknowns that are uncertainty terms for each chemical and isotopic datum. These uncertainty terms allow each datum to increase or decrease, but the magnitude of the increase or decrease is constrained to vary only within a specified limit. Each limit is specified on the basis of the sources of uncertainty in the datum, which include analytical uncertainty and sampling uncertainty, and may also include uncertainty due to spatial variability. The uncertainty formulation uses the same chemical and analytical data as previous approaches to mole-balance modeling but requires the additional specification of the uncertainly limits for all chemical and isotopic data.

Mole-balance modeling requires the definition of all of the potential reactants and products in the ground-water system. Saturation indices and petrographic data (if available) must be evaluated to determine the minerals that appear to be dissolving and precipitating within the aquifer. The mole-balance models need to be consistent with these determinations. For example, a mole-balance model is not plausible if a phase precipitates in the model when the saturation index indicates undersaturation and dissolution textures are observed for this phase. Conclusions about dissolution and precipitation of phases were formulated into constraints on mole-balance models. These dissolution and precipitation constraints were also needed to limit the number of models. The number of plausible phases in most natural systems

is significantly larger than the number of mole-balance equations that are available, allowing very large numbers of models to be generated in the absence of such constraints.

Sources of Dissolved Constituents in Ground Water

The sources of major and minor dissolved constituents, including nitrogen and pesticides, are discussed in this section. Reactions involving pesticides were not chemically modeled. The available solid phase information consists of the X-ray mineral identification presented in table 3. Petrographic analyses are not available at this time. The selection of phases to be used in the mole-balance models, particularly those present in minor or trace amounts in the aquifer matrix, is thus somewhat arbitrary. The mineral dissolution and precipitation constraints are chosen on the basis of saturation indices calculated for flowpath ground waters and general knowledge of the geochemical behavior of aquifer minerals.

Precipitation

At the flowpath study site, the only source of ground water is recharge from precipitation. The dissolved constituents in the ground water can be derived either from the precipitation itself (possibly enhanced by evapotranspiration), from mineral dissolution in the aquifer, or from chemicals applied at the land surface such as fertilizer, manure, and pesticides.

Precipitation-weighted concentrations of cations and anions in precipitation reported by the NADP (National Atmospheric Deposition Program) station WI99, Lake Geneva, Wis., are listed in table 8. The precipitation data are averaged over the collection period 1984–95. An estimate of the possible concentration effects due to evapotranspiration can be computed from the quantity (precipitation - runoff)/(recharge). At the Lake Geneva NADP site, the average annual precipitation for the period of record is 32 in. The recharge estimate from the ground-water model is 4 in. The maximum concentration effect (with zero runoff) would be calculated as a concentration factor of 8.0. This factor is consistent with precipitation and evapotranspiration estimates in this part of Wisconsin (Skinner and Borman, 1973). The composition of precipitation and the calculated solution chemistry that results from its eightfold evaporation are listed in table 8, "precip. x 8." The remaining entries in table 8 show the concentra-

Table 8. Comparison of the composition of precipitation near the study site and the composition of shallow ground waters at the study site

[concentrations are in millimoles per liter; precip., precipitation; na=not applicable; CF, concentration factor]

Site or well name	Constituent concentration							
	Ca	Mg	Na	K	NH₄	NO₃	Cl	SO₄
Lake Geneva precip. (precip. x 8)	0.00625 (.05)	0.00211 (.0169)	0.00272 (.0218)	0.00111 (.00888)	0.0242 (.194)	0.026 (.208)	0.00359 (.0287)	0.0228 (.182)
UW1 8/24/95 (Post-ET CF)[1]	1.75 (35)	1.48 (88)	.139 (6.4)	.023 (2.6)	.036 (.19)	0 (na)	.167 (5.8)	.219 (1.2)
MW1 6/15/94 (Post-ET CF)	2 (40)	1.74 (103)	.118 (5.4)	.015 (1.7)	.0007 (.004)	.293 (1.4)	.186 (6.5)	.208 (1.1)
DW1 6/13/94 (Post-ET CF)	2.12 (42)	1.73 (102)	.113 (5.2)	.02 (2.3)	.0064 (.033)	.136 (.65)	.11 (3.8)	.146 (.8)

[1] (Post-ET CF) = additional concentration factor after evapotranspiration = (concentration in ground water)/(precip. x 8 concentration). For a complete description of the data in table 8 see the preceding text.

tions of constituents at the three shallowest groundwater sites along the flowpath and the concentration factor required to produce each from the "evaporated" recharge water. The post-evapotranspiration concentration factor (Post-ET CF) equals (concentration in ground water)/(concentration in "precip x 8").

The data in table 8 show that precipitation-derived recharge can be only a trace contributor to aquifer Ca and Mg (Post-ET concentration factors of 35-42 and 88-102 respectively). For sodium, chloride, and potassium, concentration factors are about 5, 2, and 5, respectively, so recharge is still a minor input. For sulfate, ammonium, and nitrate, however, recharge can be a significant contributor, perhaps even a major contributor. The average pH of rain over the period of record is 4.5, so

alkalinity in the rain is assumed to be zero and has not been considered in table 8.

Information regarding evapotranspiration might also be obtained from the abundances of deuterium and oxygen-18 in the ground water. The relation between $\delta\ ^2H$ and $\delta\ ^{18}O$ for the flowpath waters is shown in figure 16. The data cover a relatively narrow range of isotopic values, plot roughly parallel to the Meteoric Water Line (Craig, 1961), and show no sign of major evapotranspiration effects.

Not shown in table 8 but potentially important at the study site are pesticide concentrations in precipitation. Data collected during 1990 and 1991 at the WI99 NADP station show that the pesticides alachlor, atrazine, cyanazine, and metolachlor were detected at relatively high concentrations in precipitation (Goolsby and
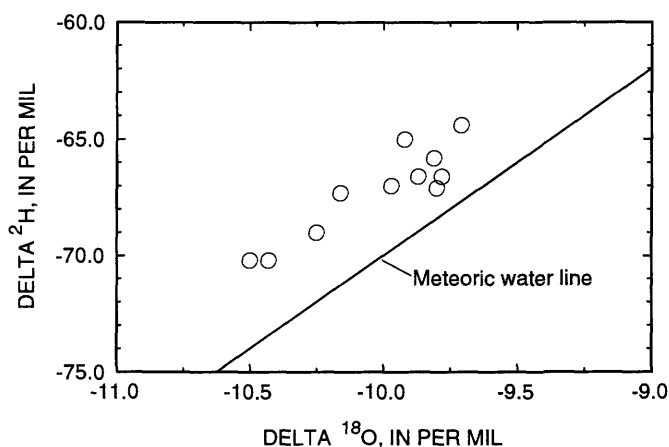
Figure 16. Relation between ^2H and ^{18}O in flowpath waters.

others, 1995). Atrazine, which was the most commonly detected pesticide in ground water at the study site, was detected in 38 percent (25 of 65) of precipitation samples at concentrations as high as 2.6 μg/L (two orders of magnitude greater than the highest ground-water concentration). Detections of atrazine in the precipitation samples mainly occurred in the spring and early summer after application. Spring is one of the main periods of ground-water recharge in Wisconsin. On the basis of this information, pesticides in precipitation could be an important source for pesticides in ground water at the study site.

Terrigenous Sources

Carbon, Ca, and Mg.   From the preceding discussion, it is clear that carbon, calcium, and magnesium must be provided by dissolution of aquifer materials. Carbon in solution in the ground waters exists principally as dissolved CO_2 species, mostly HCO_3^-. Plausible sources of carbon are dissolution of $CO_{2(g)}$ from the subsoil unsaturated zone and dissolution of the minerals dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) from the aquifer matrix. Dolomite was identified in core samples from the site by X-ray diffraction (table 3). The recharge waters are undersaturated with respect to calcite and dolomite, and the shallow ground waters approach saturation with respect to both minerals. In addition, as discussed earlier, the Ca/Mg ratio is close to 1:1 (figure 15), an indication of dolomite dissolution. Calcite can also precipitate readily at low temperatures, but reactions kinetics are slow for dolomite precipitation and it is considered only to dissolve in the mass balance models. Carbon also is present in solution as DOC and as solid organic material (OM) in the aquifer matrix. These are conventionally approximated by CH_2O for modeling. Organic matter can react with oxygen to produce CO_2 and thus must be considered as a possible carbon source in mass balance models. Other reactions of CH_2O are usually redox reactions in which the CH_2O is a reducing agent. Organic matter is allowed only to dissolve (react) in mass-balance models because of the absence of underground photosynthesis or chemosynthesis. The reaction constraints are CO_2 [+] (dissolve), calcite [+ or -] (dissolve or precipitate), dolomite [+] (dissolve), and CH_2O [+] (dissolve).

Sulfate.   Data in table 8 show that sulfate might be derived totally from precipitation. If not, there are two plausible sources of dissolved sulfate, dissolution of gypsum and pyrite. Both are common minerals in carbonate aquifers, but neither mineral is abundant at the study site because neither was detected by X-ray diffraction analysis. The flowpath waters are everywhere undersaturated with respect to gypsum. Thus, if gypsum is the sulfate source, the dissolution mass transfer must be controlled by its distribution within the aquifer. Another possible sulfate source is oxidation of pyrite by oxygen present in the unsaturated zone. If this reaction occurs, carbonate dissolution by the produced sulfuric acid also is likely. The reaction constraints are: gypsum [+] and pyrite [+].

Na and Cl.   Dissolved chloride and associated equimolar sodium (in excess of precipitation) are assumed to arise from the dissolution of halite, which is assumed to be present in trace amounts in aquifer materials, or from dissolution of fluid inclusions in aquifer minerals. All flowpath waters are undersaturated with respect to halite, and halite is thus considered only to dissolve in the mass-balance models. Fertilizer and manure were not considered as a source of sodium and chloride in these models. The reaction constraint is halite [+].

Silica.   Sources of silica are abundant in the flowpath. The mass-balance models assume a phase, SiO_2, and permit that phase to both dissolve and precipitate. Dissolved silica can also be produced or consumed through dissolution or precipitation of many silicate and aluminosilicate minerals. The silica reaction constraint is [+ or -].

K and Na (in excess of Cl).   Potassium and sodium can potentially be derived from dissolution of various aluminosilicate minerals. The most likely sources are the microcline, plagioclase, and mica identified by X-ray diffraction. In the mass-balance models the two feldspars, $KAlSi_3O_8$ and $NaAlSi_3O_8$, are used as proxies for any aluminosilicate sources and sinks of these elements. This substitution is acceptable because these are minor or trace elements in solution; if concentrations were higher, this would be unsatisfactory. If aluminosilicates are involved in reactions, then a mineral source/sink is needed for aluminum, because aluminum is not detected in the waters. Kaolinite ($Al_2Si_2O_5(OH)_4$) serves this function in the mass-balance equations. An additional source of Na that must be considered is exchange of Ca and Mg for Na. The reactions constraints are: albite [+], k-feldspar [+], kaolinite [-], CaX_2 [-], MgX_2 [-], and NaX [+].

Fe and Mn.   Iron is present in several minerals identified by X-ray diffraction. In general however, dissolved iron and manganese are presumed to result from
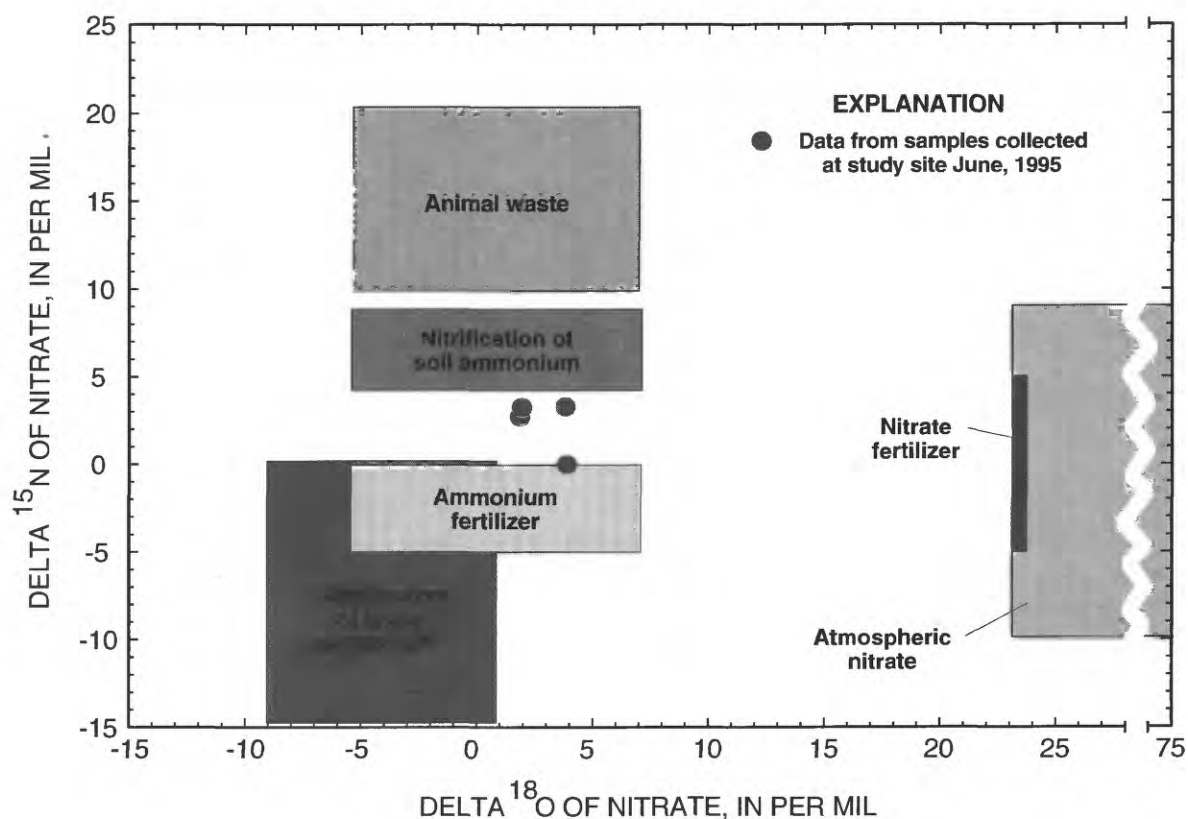
Figure 17. Oxygen and nitrogen isotopic composition of nitrate in ground-water samples collected from the study site in relation to typical ranges for several potential sources (Kendall and others, 1995).

the dissolution of Fe and Mn oxyhydroxides by means of reduction with organic matter. MnO_2 is presumed only to dissolve, whereas $FeOOH$ is allowed to either precipitate or dissolve. Reaction constraints are pyrolusite [+] and goethite [+ or -].

Oxygen. Oxygen can be considered as a phase in these models, distinct from dissolved oxygen that might be present in the precipitation or ground waters. With oxygen included as a phase, the models will determine whether atmospheric or unsaturated-zone oxygen is required to produce mole balance. Oxygen is only used in the models as a dissolving phase. Reactions that produce oxygen in the absence of photosynthesis are not known. The O_2 reaction constraint is [+].

Nitrogen. Nitrogen at the study site can come from various sources and can undergo various transformations. Nitrogen in ground water can occur naturally as a result of nitrogen-containing substances in aquifer materials. Other sources of nitrogen include manure and fertilizer applied at the land surface, atmospheric deposition, and fixation. The source of nitrogen in groundwater at the study site was investigated using isotopic

data for $\delta^{18}O$ and $\delta^{15}N$ of nitrate in water samples from wells DW1, DW2, MW1, and MW2, and $\delta^{15}N$ of nitrate and ammonium combined in water samples from wells MW3, UW1, and UW3 (table 9 and figure 17). Nitrogen isotope values are reported in per mil relative to atmospheric air, and oxygen isotope values are reported in per mil relative to standard mean ocean water (SMOW).

Table 9. Oxygen and nitrogen isotopic composition of nitrate or ammonium in ground-water samples collected at the study site, Sheboygan County, Wis., June 1995
[---, no data]

| Well name | Isotope ratios, in per mil | | |
	$d^{18}O$	$d^{15}N$	Form of N
DW1	3.95	3.14	Nitrate
DW2	3.67	-.03	Nitrate
MW1	2.04	2.69	Nitrate
MW2	2.04	3.07	Nitrate
MW3	---	4.50	Ammonium
UW1	---	2.80	Ammonium
UW3	---	5.90	Ammonium

Oxygen and nitrogen isotopic composition of nitrate in water samples collected from nests DW and MW were within the typical range of several potential sources based on previously collected data (figure 17). Samples from DW1, DW2, MW1, and MW2 plot between ammonium fertilizer and nitrification of soil ammonium, an indication that the isotopic composition of these samples could have resulted from a combination of those sources. Denitrification can affect isotopic composition (resulting in higher ^{15}N concentrations); however, dissolved oxygen concentrations in these wells were relatively high, making denitrification unlikely. Samples from MW3, UW1, and UW3 were analyzed for only ^{15}N, owing to low concentrations of nitrate, but the ^{15}N values of these wells were similar to ^{15}N values from wells DW1, DW2, MW1, and MW2. Wells MW3, UW1, and UW3 are generally deeper wells, yet they probably have the same source of N as the shallow wells.

Mixtures of ammonium fertilizer and animal waste can produce the observed isotopic composition without denitrification. Soil ammonium that has leached to ground water is also a possible source because atmospheric fixation from the alfalfa grown at the site may produce elevated concentrations of soil ammonium. Atmospheric fixation of N_2 by buffalo grass, causing elevated concentrations of soil ammonium, and subsequent leaching were suspected as the source of high nitrate concentrations in an isotopic study of ground water in Texas (Chapelle, 1993, p. 252). Animal waste is known to have been applied upgradient from UW and likely between DW and UW intermittently in the past and must also be included as a potential source. On the basis of the isotopic data and the record of historical manure applications, several sources of nitrogen to ground water are likely at the study site. An atmospheric source of nitrate or ammonia is not consistent with the isotopic data (figure 17), although there can be an excess of both NO_3^- and NH_4^+ in evaporated precipitation (table 8) relative to shallow ground water. In the mole-balance models the only nitrogen-containing phase that is considered is N_2, which can be a source and (or) a sink for both species in the mole balance models. The N_2 reaction constraint is [+ or -].

Pesticides. The only plausible terrigenous source of pesticides in ground water at the study site is land application immediately upgradient from nest UW. As previously mentioned, pesticides have not been applied downgradient from UW in the last 30 years and historically the primary pesticide used upgradient has

been atrazine. Based on CFC and tritium recharge dates, concentrations of atrazine plus deethyl atrazine in ground water appear to mimic historic use patterns in east central Wisconsin (fig. 18). Older water had lower concentrations while concentrations in younger water were higher. It is possible that this observed pattern is because the land owner followed historic trends in atrazine use. Another possibility is that regional historic use patterns influenced concentrations in the atmosphere and precipitation at the study site.

Uncertainties in the Data

The major element chemistry of the flowpath ground water is spatially uniform (figures 13 and 14) and the analyses for all elements are reproducible from one sampling period to another (appendix 2). An uncertainty of 0.05 (five percent of the amount present) was assigned to all chemical data in the groundwater samples, except for iron, manganese, sodium, and chloride. Absolute uncertainties of 0.06 and 0.02 micromoles per liter were assigned to iron and manganese, respectively, on the basis of the analytical limits of detection for these elements. An uncertainly of 0.2 for sodium and chloride in ground water samples from MW1 was used because the Na/Cl ratio was only 0.63 (discussed below).

The mean ion concentrations in precipitation are listed in table 8. Charge balance among these mean concentrations was achieved by numerically adjusting the pH in PHREEQC. The calculated molality of H^+ is 30.38 μmol/L for precipitation, at a calculated pH of 4.522. The mean field-measured H^+ molality in precipitation is 33.16 μmol/L - very close agreement. Thus the errors introduced by using this charge balance option are small. However, the precipitation chemistry varies substantially with time. An uncertainty of 0.2 was assigned to the species concentrations in precipitation on the basis of examination of the NAPD data for the period of record. Thus the concentrations of ions in precipitation may be increased or decreased by a factor of 0.2 as needed to calculate models. Iron and manganese were again individually assigned absolute uncertainties of 0.06 and 0.02 micromoles per liter, respectively, as in the ground waters.

Mole Balance Models for Shallow Ground Waters

The conceptual model for the origin of the dissolved constituents in shallow ground water is straightforward. Precipitation that falls on land surface is
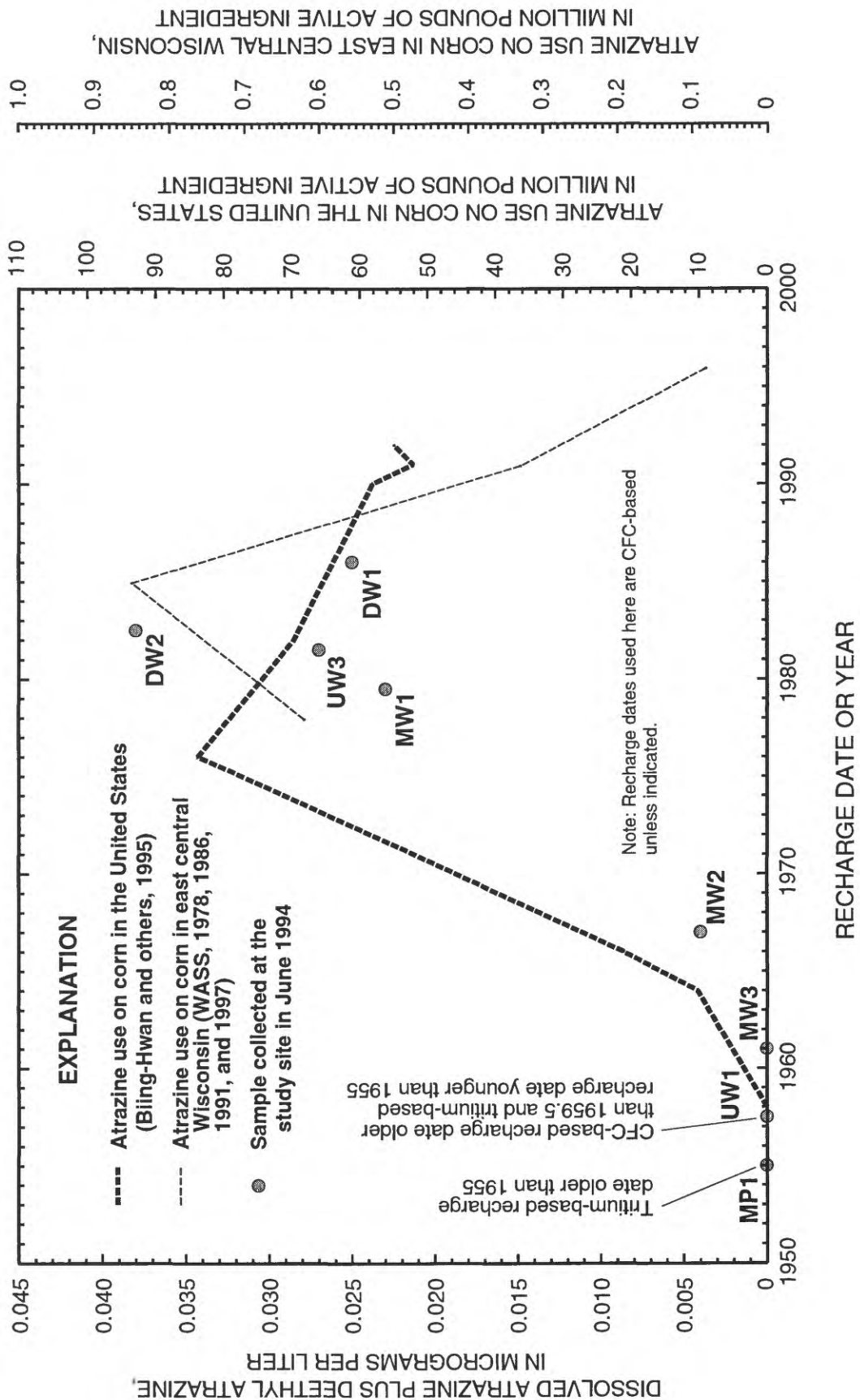
Figure 18. Relation between dissolved atrazine plus deethyl atrazine concentrations and recharge date for ground-water samples from the study site, and historical use of atrazine on corn in the United States and in east central Wisconsin.

subject to evapotranspiration before infiltrating through the soil and shallow unsaturated zone, where reactions occur. Carbon dioxide, oxygen, and nitrogen gas are presumed to be present as unsaturated-zone gases, available for dissolution and reaction in the infiltrating waters. Nitrogen gas, if produced by reactions, can degas from the aqueous phase to the unsaturated-zone pore spaces. The remaining dissolved constituents in the shallow ground waters, if not provided by precipitation, must be obtained by dissolution of aquifer minerals.

The mole-balance models for shallow ground waters UW1, MW1, and DW1 are listed in tables 10a, 10b, and 10c, respectively. The first three lines in each table list the concentration factors and the amounts of evaporated water, in moles and kilograms, for the models that include evapotranspiration. These are the concentration factors from the original precipitation, not from the "precip x 8" used to calculate the post-evapo-

transpiration concentration factors in table 8. The remaining table entries are the mole transfers - the amounts in mmol of each mineral or gas that are required to enter [+] or leave [-] the aqueous phase in order to produce the observed ground-water composition.

The following phases, and their reaction constraints, were included as possible phases in all model calculations. Water [- (evaporation)], $CO_{2(g)}$ [+], dolomite [+], calcite [+ or -], gypsum [+], halite [+], $N_{2(g)}$ [+ or -], $O_{2(g)}$ [+], organic matter, CH_2O [+], goethite [+ or -], pyrite [+], pyrolusite [+], K-feldspar [+], chalcedony [+ or -], kaolinite [+ or -], albite [+], CaX2 [-], MgX2 [-], and NaX [+]. Although the last four phases are not listed in tables 10a,b,c they were considered in all model calculations. Their absence in the models means that none of the models required a source of dissolved sodium from either dissolution of albite or from exchange of dissolved calcium for sodium.

Table 10a. Mole-balance models for formation of shallow ground water from precipitation at flowpath site UW1[1]

[Units are in millimoles/L unless otherwise stated; ---, mineral or phase not included in model]

Mineral, phase, or concentration factor	Model				
	a	b	c	d	e
Concentration factor, unitless	9.67	9.361	6.869	6.795	6.494
H_2O evaporation, in moles	-481.2	-464.1	-325.8	-321.7	-305
H_2O evaporation, in kg	-8.67	-8.361	-5.869	-5.795	-5.494
$CO_{2(g)}$	3.106	3.121	3.273	3.249	3.291
Dolomite	1.45	1.451	1.541	1.456	1.542
Calcite	.15	.151	---	.161	---
Gypsum	---	---	.076	---	.0776
Halite	.12	.121	.129	.129	.13
$N_{2(g)}$	-.225	-.217	-.155	-.153	-.145
$O_{2(g)}$	---	---	---	---	---
CH_2O	.167	.149	.126	---	.108
Goethite	.0036	---	.0036	-.0298	---
Pyrite	---	.0036	---	.0334	.0036
Pyrolusite	.0006	.0006	.0006	.0006	.0006
K-spar	.0123	.0126	.0154	.0155	.0158
Silica	.259	.258	.252	.252	.251
Kaolinite	-.0061	-.0063	-.0077	-.0077	-.0079

[1]UW1 data are from 8/24/95. Uncertainties are assigned as follows: precipitation = 0.2; UW1 = 0.05; iron and manganese are assigned an absolute uncertainty of 0.06 and 0.02 micromoles per liter, respectively in both precipitation and ground water.

Table 10b. Mole-balance models for formation of shallow ground water from precipitation at flowpath site MW1[1]

[Units are in millimoles/L unless otherwise stated; ---, mineral or phase not included in model]

Mineral, phase, or concentration factor	Model			
	a	b	c	d
Concentration factor, unitless	10.95	10.95	7.511	5.834
H_2O evaporation, in moles	-552.3	-552.3	-361.4	-268.3
H_2O evaporation, in kg	9.095	9.095	6.511	4.834
$CO_{2(g)}$	5.314	5.271	5.309	5.356
Dolomite	1.174	1.803	1.721	1.811
Calcite	.242	---	.232	---
Gypsum	---	.019	---	.0763
Halite	.11	.11	.121	.125
$N_{2(g)}$	-.153	-.13	---	---
$O_{2(g)}$	.366	.333	.537	.517
CH_2O	---	---	---	---
Goethite	---	---	---	---
Pyrite	---	---	---	---
Pyrolusite	---	---	---	---
K-spar	---	---	.007	.0089
Silica	.266	.266	.252	.249
Kaolinite	---	---	-.0035	-.0044

[1]MW1 data are from 6/15/94. Uncertainties are assigned as follows: precipitation = 0.2; MW1 = 0.05; sodium and chloride in MW1 = 0.2; iron and manganese are assigned an absolute uncertainty of 0.06 and 0.02 micromoles per liter, respectively in both precipitation and ground water.

Table 10c. Mole-balance models for formation of shallow ground water from precipitation at flowpath site DW1[1]

[Units are in millimoles/L unless otherwise stated; ---, mineral or phase not included in model]

Mineral, phase, or concentration factor	Model					
	a	b	c	d	e	f
Concentration factor, unitless	1	1	1	8.151	2.832	2.832
H_2O evaporation, in moles	---	---	---	-369.9	-101.7	-101.7
H_2O evaporation, in kg	---	---	---	-7.151	1.832	1.832
$CO_{2(g)}$	6.305	6.305	6.182	6.214	6.276	6.195
Dolomite	1.726	1.726	1.726	1.711	1.723	1.723
Calcite	.372	.373	.495	.466	.407	.488
Gypsum	.123	.123	---	---	.0811	---
Halite	.107	.107	.107	.0853	.0999	.0999
$N_{2(g)}$	.046	.046	.046	-.143	---	---
$O_{2(g)}$	.259	.260	.489	.085	.232	.385
CH_2O	---	---	---	---	---	---
Goethite	.0003	---	-.0612	---	---	-.0404
Pyrite	---	.0003	.0615	---	---	.0406
Pyrolusite	.0004	.0004	.0004	---	.0004	.0004
K-spar	.0194	.0194	.0194	.0114	.0173	.0173
Silica	.211	.211	.211	.227	.215	.215
Kaolinite	-.0097	-.0097	-.0097	-.0057	-.0087	-.0087

[1]DW1 data are from 6/13/94. Uncertainties are assigned as follows: precipitation = 0.2; DW1 = 0.05; iron and manganese are assigned an absolute uncertainty of 0.06 and 0.02 micromoles per liter, respectively in both precipitation and ground water

Modeling Results

The models in tables 10a,b,c show that the predominant reactions, by an order of magnitude, are the dissolution of CO_2 (3.106 to 6.305 mmol) and dolomite (1.45 to 1.811 mmol). The combined mole transfers of $CO_{2(g)}$ and dolomite comprise about 90 percent of the total mole transfers in any given model, independent of the amount of evaporation calculated for the model. The CO_2 exists initially as a component of unsaturated-zone gas. The principal reaction of the CO_2 is the dissolution of dolomite. However, a significant portion of the CO_2 simply dissolves without reaction, contributing dissolved CO_2 (or H_2CO_3) to the ground waters, particularly to the relatively low-pH waters of the MW and DW samples. The reactions are:

$$CaMg(CO3)_{2(dolomite)} + 2\ CO_{2(g)} + 2\ H_2O = Ca^{2+} + Mg^{2+} + 4\ HCO_3^-, \tag{1}$$

$$\text{and } CO_{2(g)} + H_2O = H_2CO_3. \tag{2}$$
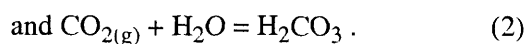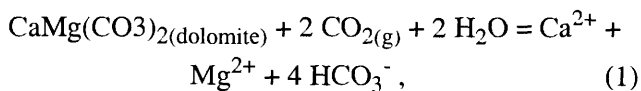
These are highly plausible reactions for shallow ground water in glacial till overlying dolomite bedrock and are consistent with the occurrence of dolomite as the most abundant mineral in the aquifer matrix (table 3).

Two minor reactions occur with similar mole transfers in all models. Halite, the only mineral source of chloride, dissolves in each model (0.0853 to 0.130 mmol). The reaction is

$$NaCl_{(halite)} = Na^+ + Cl^-. \tag{3}$$
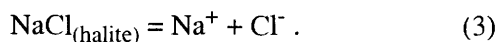
A source of silica is required for each model (0.211 to 0.266 mmol). The reaction is:

$$SiO_{2(chalcedony)} + 2\ H_2O = H_4SiO_4. \tag{4}$$
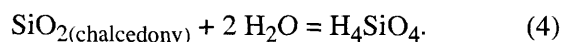
The mole transfers K-feldspar and pyrolusite are small and variable. The K-feldspar dissolution is always accompanied by kaolinite precipitation to remove aluminum from solution. In some models precipitation is the sole source of potassium and/or manganese. The reactions are

$$2\ KAlSi_3O_{8(K\text{-}feldspar)} + 2\ CO_2 + 11\ H_2O = Al_2Si_2O_5(OH)_4 + 2\ K^+ + 2\ HCO_3^- + 4\ H_4SiO_4, \tag{5}$$

$$\text{and } 2\ MnO_{2(pyrolusite)} + CH_2O + 3\ CO_2 + H_2O = 2\ Mn^{2+} + 4\ HCO_3^-. \tag{6}$$
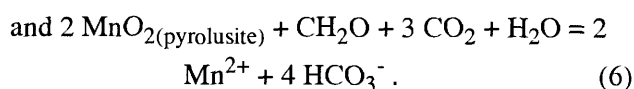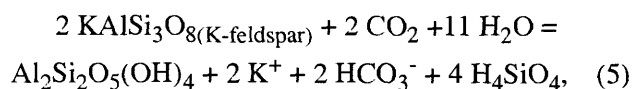
The relative mole transfers of calcite, gypsum, goethite, and pyrite (all minor minerals) provide the mineralogical distinction between models. In models UW1a and UW1b sulfate is provided by precipitation. In model UW1a neither gypsum nor pyrite dissolve, and iron is provided by goethite dissolution. In model UW1b iron, and a small amount of sulfate, are provided by pyrite dissolution. Calcium, in excess of that from dolomite dissolution, is obtained from calcite. Reactions are

$$4\ FeOOH_{(goethite)} + CH_2O + 7\ CO_2 + H_2O = 4\ Fe^{2+} + 8HCO_3^-, \tag{7}$$

$$4\ FeS_{2(pyrite)} + 14\ O_2 + 4\ H_2O = 4\ Fe^{2+} + 8\ SO_4^{2-} + 8\ H^+, \tag{8}$$

$$\text{and } CaCO_{3(calcite)} + CO_{2(g)} + H_2O = Ca^{2+} + 2\ HCO_3^-. \tag{9}$$
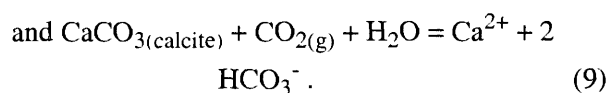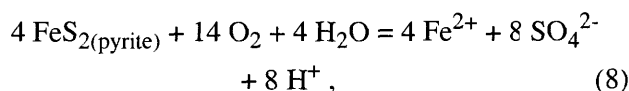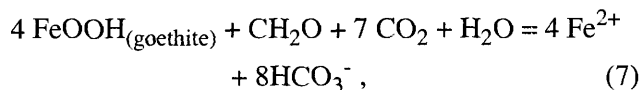
Models UW1 c-e invoke less evapotranspiration. Sulfate in the ground waters is still provided principally by precipitation, with small mineral contributions from gypsum (models UW1c and UW1e) and pyrite (UW1d). UW1c and UW1e are distinguished only by the source of dissolved iron - goethite in UW1c and pyrite in UW1e. In model UW1d the mineral-derived sulfate comes only from pyrite. In this case, dissolved iron would be present in excess and must precipitate. The reactions are

$$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2\ H_2O. \tag{10}$$

$$\text{and } 4\ FeS_2 + 15\ O_2 + 10\ H_2O = 4\ FeOOH + 8\ SO_4^{2-} + 16\ H^+. \tag{11}$$
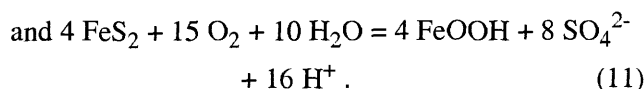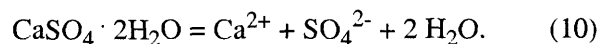
The shallow ground water at flowpath site MW1 has a Na/Cl ratio = 0.63. This is lower than any ratio permitted by the twenty percent uncertainty assumed for precipitation, and well below the 1:1 ratio that is obtained from dissolving halite. No mineral sink is available for sodium, so no models are found with the uncertainties used to this point. To model MW1 the uncertainty was increased to 0.2 for sodium and chloride only in the ground water. This is well beyond the anticipated variability in the ground waters, and is equivalent to allowing an independent source of chloride, as discussed earlier. Four models were found with the increased uncertainty. All involve significant evaporation as the principal sulfate source, evidenced by the lack of pyrite dissolution and small or zero mole transfers of gypsum. In models MW1a and MW1b potassium is also provided by precipitation, and N_2 is required to

degas. Calcite is a calcium source in MW1a but not in MW1b. The remaining two models, with smaller amounts of evaporation, do not require degassing of N_2. Models are again distinguished by calcite as a calcium source in MW1c and its absence in MW1d.

At site DW1 the Na/Cl ratio in the ground water is 1.03. At this site all of the dissolved chloride can be derived from halite dissolution without posing a sodium-disposal problem. This is reflected in the models of table 10c. The first three involve no evapotranspiration. The mineral characteristics of the models are similar to earlier models. Models DW1a and DW1b derive sulfate from gypsum dissolution; DW1a obtains iron from goethite, DW1b obtains iron from pyrite. Model DW1c obtains all dissolved sulfate, and the small amount of dissolved iron, from pyrite oxidation with attendant goethite precipitation. Sodium and chloride are derived from halite. These three models are the only models that require a small input of N_2. Evapotranspiration models are also plausible at DW1. Model DW1d derives sulfate totally from precipitation, Models DW1e and DW1f the evaporation is just sufficient to provide the nitrogen species necessary for the nitrate in the groundwater; the mole transfer of $N_{2(gas)}$ is zero. DW1e obtains sulfate from precipitation and gypsum, whereas DW1f derives sulfate from precipitation and pyrite oxidation.

Several general conclusions can be drawn from these models.

(1) The flowpath ground waters can be derived from the dissolution of CO_2 and dolomite, with only minor contribution from gypsum, pyrite and other minerals. All of the shallow ground waters are Ca-Mg-HCO_3-SO_4 waters with these 4 ions constituting > 95% (on a milliequivalent basis) of ions in solution in all flowpath samples. This conclusion is essentially independent of the extent of evapotranspiration in the models.

(2) The models make a strong case for evapotranspiration as an important influence on ground water chemistry. All of the models but three (DW1 a,b, and c) call upon significant concentration of rain by evaporation as a source of dissolved constituents in the ground water. Most of these evaporative models have concentration factors that are reasonably close to the concentration factor of 8 derived from the ground water models. This concentration factor is sufficient to derive most or all of the dissolved sulfate, nitrate, and ammonium from precipitation. Precipitation-derived sulfate is

consistent with the lack of detection of gypsum or pyrite in the X-ray mineralogical analyses (table 3).

The extent of evaporation that is possible is determined by the dissolution vs. precipitation constraints postulated for the plausible phases. The elements C, N, O, Ca, Si, Al, and Fe are mathematically free to enter or leave the aqueous phase; the elements Mg, Na, K, Cl, and S are not. The minerals that contain the latter elements are constrained in the models only to dissolve. If, for example, chloride in the ground waters were derived only by evaporative concentration of rain whose composition is listed in table 8, the resulting concentrations of sulfate and potassium, also sodium in MW1, would be higher than in the ground waters. In the absence of mineral sinks for sulfate, potassium, and sodium, a mole-balance model that requires this extent of evaporation would be possible only if unrealistically high levels of uncertainty were assigned to the element concentrations in question.

An additional complexity is provided by the fact that halite is the only chloride-containing phase in the models, whose dissolution provides Na and Cl to the solution only in a 1:1 ratio. The Na/Cl ratios in the ground waters are 0.84 (UW1), 0.63 (MW1), and 1.03 (DW1). Thus dissolution of NaCl alone cannot provide the waters at UW1 and MW1 without high uncertainty limits. The amount of evaporation in a mole-balance model will represent a balance between the relative concentrations of SO_4^{2-}, Cl^-, K^+, and Na^+ in precipitation and ground waters, and the 1:1 ratio of Na to Cl from dissolving halite, subject to the uncertainty limits assigned to each element.

(3) Some input of chloride from mineral or anthropogenic sources is necessary. No models were found that derived chloride only from precipitation, which would have required precipitation of sulfate - unlikely in these dilute non-sulfidic waters. If an independent source of chloride were available, not linked stoichiometrically to cations, then reaction-only models would have been found for generation of all three shallow ground waters, instead of only for those at DW1, whose NaCl ratio is 1.03. Such a chloride source would seem readily available from NH_4Cl in either fertilizer or liquid manure. However, in the absence of information on the timing and location of nutrient applications, this source was not modeled, and reader is simply reminded that such models would exist with an independent chloride source. Inspection of the six models for the DW1 water (table 10c) shows that the major mineral mole transfers in evaporative and non-evaporative models are

similar, indicating that little error is introduced by this omission. The flowpath site is topographically above and hydrologically upgradient of any highways; road salt seems impossible as a chloride source.

(4) The concentrations of both nitrate and ammonium in "precip x 8" (table 8) are roughly equal to the concentrations of either in the shallow ground waters. For example, The small amounts of N_2 degassing (all UW1 models, MW1a,b, and DW1 d) indicate that the evaporative models concentrate the dissolved nitrogen species in rain to a slight excess of the concentrations in the ground waters. Nitrogen sources from fertilizer and animal waste are not required for mole balance, even though the isotopic data suggest these sources.

(5) The inclusion of a strong oxidizing agent, O_2, a strong reducing agent, CH_2O, and of N_2 as plausible phases in the model calculations ensures that all redox transformations necessary to achieve mole balance can occur within the models. Because these reactions can occur in amounts necessary for mole balance using only ammonium and nitrate in precipitation, the models cannot differentiate with respect to ammonium and nitrate available in fertilizer or waste. Thus for the modest ammonium and nitrate concentrations in the flowpath ground waters, mole balance modeling alone is not a useful tool for identifying nutrient sources.

Reactions Along Ground-Water Flowpaths

The reaction of most interest in this study is the possibility of reducing nitrate to nitrogen, thus providing a mechanism for removing nitrate from the ground waters. The reaction representing this process is:

$$5\,CH_2O + 4\,NO_3^- = 2\,N_2 + 4\,HCO_3^- + CO_2 + 3\,H_2O. \quad (12)$$
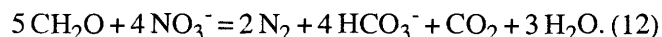
The reaction essentially replaces each nitrate ion with a bicarbonate ion, leading to an increase in titration alkalinity at near-constant pH. In concept the reaction could be identified by looking at the changes in stoichiometry along a flowpath and comparing the observed changes with those predicted by chemical modeling. This will be pursued here from two perspectives, forward and inverse modeling.

Of the possible flowpaths provided by the ground-water model, the most plausible in terms of the sequence of redox reactions, and the CFC data, is from DW to the MP's. The chemical analyses with the smallest charge imbalances will be used as the basis for the modeling. These are DW1 (6/13/94) and MP2 (8/22/95).

Forward Reaction Modeling

This section will look at the changes that would be expected as the ground water at DW1 is subject to increasingly reducing conditions caused by reactions with organic material, CH_2O, in the aquifer. The modeling is done with PHREEQC, and is subject to the following assumptions: (1) In the model, CH_2O is added incrementally to the aqueous phase, and the system reacts to equilibrium after each addition. (2) The reactions occur in a closed system; no equilibria are assumed with minerals or gases. (3) Dissolved nitrogen, N_2, accumulates in the aqueous phase because the system is closed.

Results of the forward calculation are shown in figure 19. The initial reaction is the consumption of oxygen (and production of CO_2, not plotted in the figure). This reaction produces decreasing pH while alkalinity remains constant. The redox conditions are oxic during this part of the reaction, and nitrate concentrations remain constant. When oxygen consumption is complete, after reaction of 0.17 mmol of CH_2O, additional reaction drives the redox environment to post-oxic I and reduces nitrate to N_2 (denitrification). In this model, N_2 is simply allowed to accumulate in solution. Partial pressures remain below those required for bubble formation in the aquifer because only 0.068 mmol of N_2 are formed. This part of the reaction occurs at virtually constant pH. Alkalinity, on the other hand, increases systematically. These reactions continue until 0.34 mmol of CH_2O have reacted, and the initially present nitrate has all been consumed.

The last portion of the graph shows the beginnings of the reduction of N_2 to NH_4^+, nitrogen fixation, as more organic matter reacts. In the absence of kinetic restraints, these are the reactions that should occur. But, the transformation of N_2 directly to ammonia is not one that occurs in the absence of nitrogen-fixing organisms, and these reactions are not expected in the flowpath waters.

Although these reactions are conceptually well defined, the nitrate concentrations in the flowpath waters are so low that the expected changes in pH and alkalinity are very small. In the oxygen-consumption portion of the reaction, the calculated pH decrease is only 0.025 pH units; in the nitrate-reduction portion of the reaction, the calculated alkalinity increase is only 0.15 meq/L. These changes are so small (for example, about 2 percent for alkalinity) that detecting them reliably in flowpath waters is not feasible.
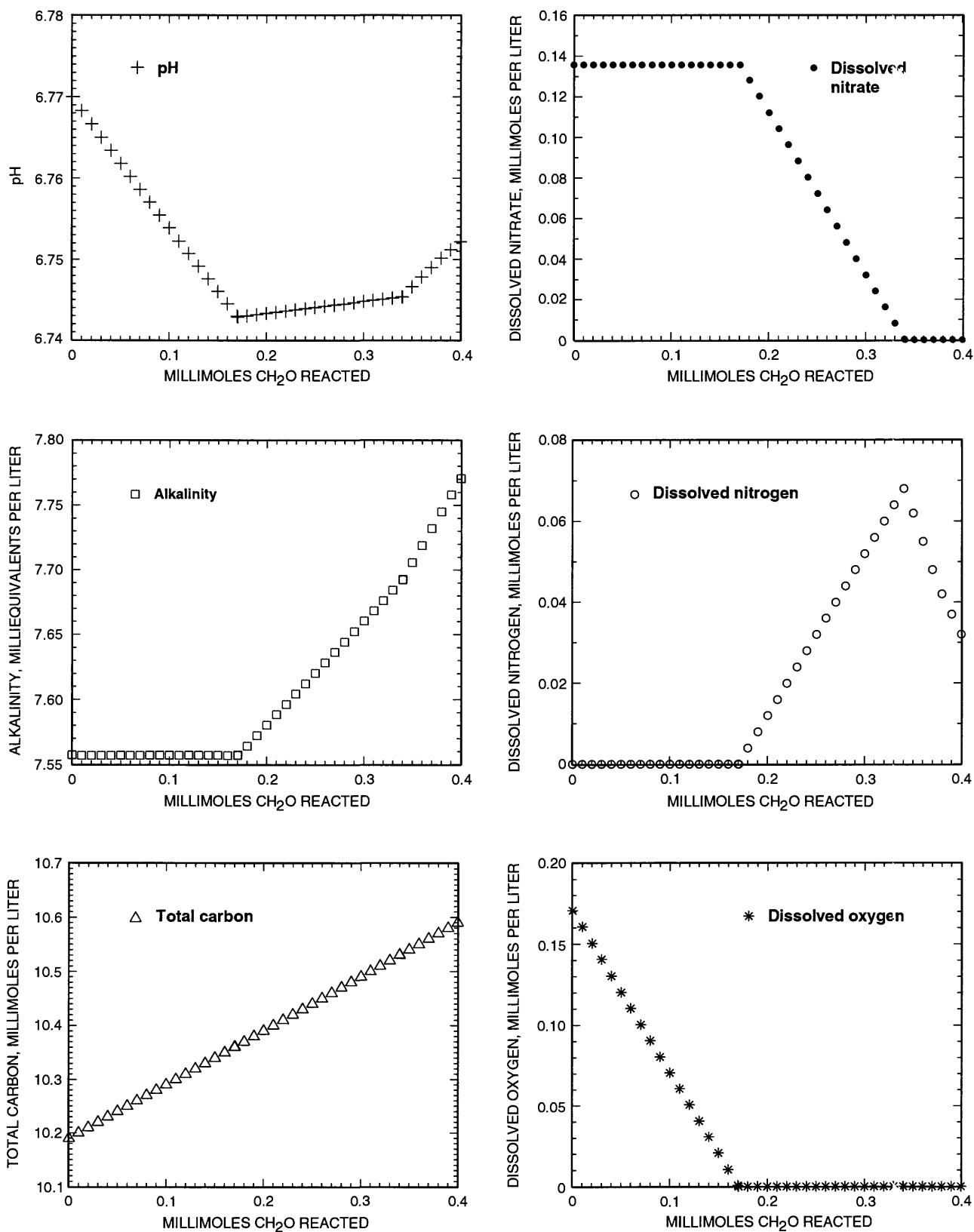
Figure 19. pH, alkalinity, and concentrations of total carbon, dissolved nitrate, nitrogen, and oxygen as a function of the amount of organic matter (CH_2O) reacted in reaction simulations calculated with PHREEQC.
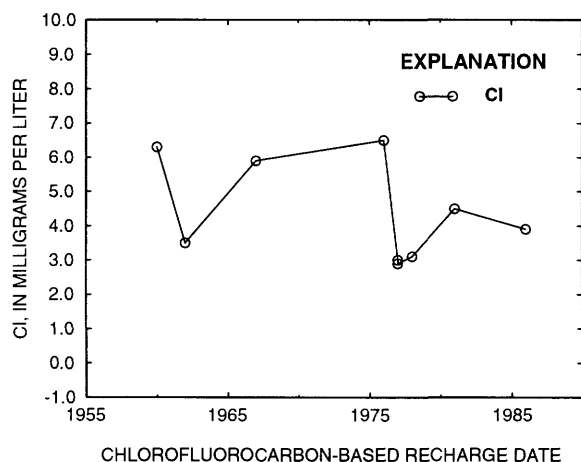
Figure 20. Relation between chloride and chlorofluoro-carbon-based recharge dates for flowpath ground waters.

Figure 21. Precipitation and chloride concentrations in precipitation as a function of time near the study site.

Inverse Reaction Modeling of Flowpath Waters

Inverse modeling provides another approach to modeling of flowpath waters, one that introduces problems not present in the inverse modeling of the recharge waters. Examination of the dissolved chloride data shows a systematic decrease in chloride downgradient (appendix 2b). The data are sufficiently reproducible to rule out analytical problems. It is difficult to explain the loss of chloride by chemical processes in the aquifer system. Chloride is a conservative constituent of ground waters, and at these concentrations, the waters are undersaturated with all chloride-containing minerals. If the waters to be modeled are truly sequential along a flowpath, then the variations in chloride must be caused by some unknown chemical mechanism or by variations in the concentration of chloride in recharge water and(or) the relative amount of evapotranspiration. Either chemical reaction or recharge processes could lead to changes in chloride concentration without affecting the concentrations of other constituents in solution, which are governed principally by mineral dissolution and equilibria.

The concentrations of dissolved chloride in ground water and precipitation show substantial temporal variation. In figure 20, chloride concentrations in ground water are plotted as a function of CFC-based recharge dates from 1960 to 1990. The pattern in the chloride concentrations is cyclic, and the concentrations vary by a factor of 2 in the time period represented by the figure. Chloride concentrations and precipitation (centimeters per year) at the Lake Geneva NADP station from 1984 to 1995 are shown in figure 21. Relative to the highest concentration, the 1984 chloride in rain is low by a factor of 2. Thus the chloride concentrations both in pre-

cipitation and in the flowpath ground waters vary by a factor of 2 over the period of record. The cyclicity in the chloride concentrations in precipitation and ground water cannot be compared because there is only one CFC recharge date, at DW1, that overlaps the NADP data. The chloride concentration in DW1 is 110 µmol/L, and the NADP chloride concentration in 1984 is 3.2 µmol/l.
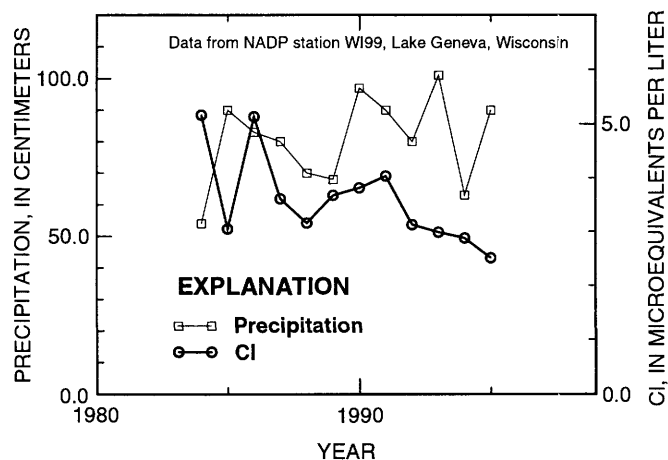
The chloride data suggest two modeling possibilities. The first is simply to assign a sufficiently large uncertainty to Cl in the inverse models that no reactions are necessary to balance it and to evaluate the other reactions necessary to derive ground water at MP2 from that at DW1. This approach assumes that Cl can vary independently and that all other dissolved constituents are controlled by mineral equilibria and reactions. These are the first two inverse models, 11a and 11b, presented in table 11. Both models use uncertainty = 0.05, with uncertainty = 0.5 for chloride. The principal reaction in both models is the reaction of organic matter with the initial dissolved oxygen to produce dissolved CO_2, and with initial dissolved nitrate produce N_2 gas. Model 11a requires the precipitation of 0.204 mmol of calcite. Model 11b requires the dissolution of 1.109 mmol of CO_2 gas. The difference between the two models results is due primarily to adjustment of the CO_2 concentrations in DW1 and MP2 within the stated uncertainty limits. Little mass transfer of other mineral phases is needed to produce water MP2 from water DW1.

The second set of models allows dilution to account for the observed decrease in Cl, which is accomplished by allowing pure water to be a plausible phase. These models assume that Cl concentrations are

set by the interplay between Cl concentrations in precipitation and relative amounts of evapotranspiration, whereas the concentrations of other constituents are governed principally by mineral processes in the shallow unsaturated zone. Thus, water recharged at DW1 in 1977, now at the MP's, is assumed to have the same composition as water now at DW1, recharged in 1986, except that it may be diluted relative to the present water. The mole transfers in table 11 represent a combination of dilution of present DW1 water and reaction with aquifer materials to produce MP2 water. The models represent the net reactions; the composition of diluted DW1 water never appears in the models, although it could be calculated. The principal mole transfers in models 11c and 11d are dissolution of approximately 2 mmol of CO_2 and 0.2 to 0.3 mmol of dolomite. Organic matter reacts to consume dissolved oxygen and reduce nitrate to N_2, as in models 11a and 11b. Other mole transfers are again small.

The reactions in table 11 are generally similar in type to those necessary to create the shallow ground waters from precipitation, but with substantially different mole transfers. Models 11b,c, and d require the dissolution of 1 to 2 mmol/L of CO_2 gas each. A mechanism for this process is hard to visualize for ground water moving along flowpaths well below the water table. Model 11a thus appears to be the model of choice for these reactions. The mole transfers of N_2 are small in all models, supporting the conclusion reached

from forward modeling that the extent of reaction is too small to be reliably detected from general changes in ground water chemistry.

Reduction of the 1.9 mg/L dissolved nitrate at DW1 to nitrogen gas can produce 0.0678 mmol of N_2. The average increase in dissolved nitrogen from DW1 to MP2 is $0.782 - 0.721 = 0.061$ mmol/L (table 12, data are from appendix 4). The agreement between available nitrate and increased dissolved N_2 would be consistent with nitrate reduction in the aquifer. However, nitrogen gas can be introduced to ground waters by physical as well as chemical processes. These processes are equilibration with atmospheric- or unsaturated-zone air and the possible trapping of air bubbles during the recharge process (Heaton and Vogel, 1981). Air bubbles entrained during recharge will add both N_2 and Ar to the ground water, and the concentrations of the two allow calculation of the amount of trapped "excess" N_2 and the recharge temperature. These calculated parameters (Michael Doughten, personal communication, 1997) are also listed in table 12. The calculated amounts of trapped excess N_2 are small and the recharge temperatures are reasonable for this location and ground-water system. Thus the increase in dissolved N_2 from DW1 to MP2 could be due to recharge of the MP2 water at a slightly lower temperature with attendant higher gas solubilities. Nitrate reduction cannot be inferred unequivocally from the dissolved gas data.

Table 11. Mole-balance models for reactions along a flowpath from DW1 to minipiezometer MP2[1]

[Units are in millimoles unless otherwise stated; ---, mineral or phase not included in model]

Mineral, phase, or fraction	Model			
	a	b	c	d
Fraction of DW1 water added	1.000	1.000	0.744	0.783
Fraction of H_2O added	0	0	.256	.217
Moles of H_2O added	0	0	14.24	12.06
$CO_{2(g)}$	---	1.109	2.186	1.954
Dolomite	---	---	.307	.247
Calcite	-.204	---	---	---
Gypsum	---	---	.027	---
$N_{2(g)}$	-.0682	-.0682	-.05	-.0528
CH_2O	.339	.339	.253	.235
Goethite	.0082	.0082	.0082	---
Pyrite	---	--	---	.0082
Pyrolusite	.00016	.00016	.00025	.00024
K-spar	---	---	.0052	.0044
Albite	.0218	.0218	.0508	.0463
Silica	-.0602	-.0602	-.0647	-.0640
Kaolinite	-.0109	-.0109	-.028	-.00254

[1]DW1 data are from 6/13/94, MP2 data are from 8/22/95. For all models, an uncertainty of 0.05 was assigned for DW1 and MP2; iron and manganese were assigned an absolute uncertainty of 0.06 and 0.02 micromoles per liter, respectively in both waters. For models a and b, Cl was assigned an uncertainty of 0.5 millimoles per liter for both waters.

Table 12. Concentrations of dissolved nitrogen and argon gas in DW and MP wells, and calculated values of excess N_2 and recharge temperature

[mmol/L=millimoles per liter; mmol=millimole]

Well name	Constituent			
	Total dissolved N_2 mmol/L	Total dissolved Ar mmol/L	Calculated excess N_2 mmol/L	Recharge temp °C
DW1	.718	.0180	.086	9.0
DW2	.724	.0182	.084	8.4
MP2	.814	.0205	.105	3.8
MP3	.748	.0193	.060	5.4
MP4	.784	.0200	.079	4.3

SUMMARY AND CONCLUSIONS

Water-quality and geohydrologic data were collected from September 1993 through November 1996 from 19 monitor wells and a stream in an agricultural area in southeastern Wisconsin. These sites were located along a 2,700-ft transect from a local ground-water high to the stream. The transect is approximately parallel to the horizontal direction of ground-water flow at the water table. Most of the wells were installed in unconsolidated deposits at five locations along the transect corresponding to an upgradient well nest (UW), a midgradient well nest (MW), a downgradient well nest (DW), wells in the lowland area (LL) near the stream, and wells installed in the stream bottom (MP).

Water levels and discharge were measured intermittently at all wells and the stream. Slug tests were done at selected wells to estimate hydraulic conductivity of the surficial deposits and values range from 0.006 to 55 feet per day, with most values between 0.4 and 12 feet per day. X-ray diffraction analyses of samples from 2 cores show the most abundant mineral to be dolomite, with subordinate quartz, microcline, and plagioclase, and minor mica, hornblende, and chlorite. Water samples from most wells and the stream were analyzed for major ions, nutrients, pesticides, dissolved organic carbon, aluminum, tritium, CFCs, ^{15}N, ^{18}O, and dissolved gases. Measurements of temperature, pH, specific conductance, and dissolved oxygen were made in the field. Concentrations of all dissolved constituents were below Wisconsin ground-water quality enforcement standards. Precipitation data was obtained from a nearby National Atmospheric Deposition Program station.

A cross-sectional ground-water flow model, representing the water-table flow system, was developed for the site and was used to identify possible ground-water flowpaths for geochemical modeling. The model was calibrated against measured water levels and was most sensitive to variation in recharge and hydraulic conductivity. The modeled value of recharge was consistent with literature values and with estimates from baseflow measurements in the stream. Hydraulic conductivity values used in the model were also consistent with literature values as well as values determined from slug tests at the site. The calibrated model shows that downward flow from shallow to deeper wells within a nest may occur at the upgradient and midgradient well nests, but that flow from each well nest travels beneath downgradient nests to the stream. Pathline and travel time analysis performed on the calibrated flow-model output yielded travel times to well screens that range from 5.8 to 59 years, with a recharge of 4 inches per yr. Recharge dates based on tritium and CFC concentrations range from pre-1955 to 1986 and are consistent with flowpaths and travel times in the calibrated flow model.

Changes in water quality along ground-water flowpaths were evaluated using the geochemical model PHREEQC. Geochemical mole balance models of shallow ground-water formation show that the principal reaction, by an order of magnitude, is dissolution of dolomite with CO_2. Concentration factors in the mole-balance models range from 1 to 11 with most values between 5 and 10, providing independent support for the concentration factor of 8 based on recharge estimates used in the flow model.

Redox environments were defined for most wells at the study site based on the relative concentrations of dissolved O_2, CO_2, CH_4, SO_4, $S^=$, NO_3^-, N_2, NH_4^+, Fe^{2+}, and Mn^{2+}. Flowpaths inferred from thermodynamically permissible sequences of redox reactions were consistent with flowpaths inferred from the ground-water flow model. Shallow ground water recharging at sites MW and DW is oxic, evolving along flowpaths to anoxic (redox environment post-oxic II) in ground water discharging upward to the stream at the MP sites. The oxic waters at the study site are relatively young and shallow. They contain abundant dissolved oxygen and little or no Fe, Mn, and methane. Post-oxic waters at the study site are somewhat older than the oxic waters and contain only trace amounts of oxygen, sulfide, or methane, and relatively high concentrations of Fe and Mn.

Ground water at all depths at UW is much more reducing than at other flowpath sites, perhaps due to the

nearby application of nutrients and fertilizers. Sulfidic and methanic waters are found in the deepest wells at UW and likely represent some of the oldest water sampled at the study site. However, water from well UW3 has a relatively young CFC age and detectable concentrations of atrazine; this could be caused by small amounts of young water entering the screened interval through macropores. Most of the water sampled from UW3 probably is relatively old as indicated by the flow model. These old waters contain little or no sulfate, Fe, or Mn but contain high concentrations of Na and Cl. They are distinct from other waters at the site.

The major ions in ground water at the study site, Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-}, predominate throughout the flow system. Precipitation concentrated by evaporation can provide all of the sulfate, nitrate, and pesticides (the latter two are discussed below) and 10 to 50 percent of the Cl, Na, and K dissolved in the ground water. Precipitation provides no significant contribution to dissolved calcium, magnesium, and bicarbonate. Plausible mineral sources and sinks exist for Ca, Mg, Na, K, Al, SiO_2, HCO_3, and Cl in excess of precipitation input. Geochemical mole balance models developed for the origin of the shallow flowpath ground waters show that the principal reaction, by an order of magnitude, is dissolution of dolomite by CO_2. There are systematic lateral variations in pH, alkalinity, and the concentrations of calcium, magnesium, sulfate and chloride from UW to MW to DW. These variations should not be attributed to sequential reactions, because the only flowpaths are from well nests UW, MW, and DW individually to the MP sites; there is no flow between well nests.

Chloride concentrations diminish downgradient between sites and along flowpaths, but not because of reactions in the aquifer. The decreases can be accounted for by possible variation in the Cl input concentrations in precipitation, by the higher proportion of fertilizer or manure used in the upgradient parts of the transect, or by occasional application of fertilizer or manure in the lower parts of the transect.

The nitrogen chemistry at the study site is complex. Isotopic data indicate that the sources of nitrate and ammonium include ammonium fertilizer, soil ammonium, and manure. Precipitation concentrated by evapotranspiration, however, is also capable of providing the observed nitrogen in nitrate and ammonium. Nitrate or ammonium concentrations were typically 2 to 4 mg/L at most wells in nests DW, MW, and UW, and less than 1 mg/L at most MP and LL wells. The form of non-N_2 nitrogen differs throughout the study site. It is primarily

in the form of nitrate where oxic conditions are present, and primarily in the form of ammonium or organic nitrogen where more reducing conditions predominate. The sum of nitrate and ammonium concentrations at the site tend to decrease and concentrations of dissolved N_2 tends to increase going from oxic to more reducing environments, indicating possible denitrification. The differences in dissolved N_2, however, can also be due to different recharge temperatures.

At UW, non-N_2 nitrogen is primarily in the form of ammonium. Ground water moves vertically downward near UW, so nitrogen in ground water near the water table can move vertically between wells in the nest. Water from UW does not interact with other water collected at the flowpath until possibly at MP and the stream. Some overland flow in the vicinity of UW is possible because the surficial deposits are relatively impermeable. Overland flow containing nitrogen could move downgradient from UW and then recharge ground water upgradient from MW, where surficial deposits are more permeable. This scenario was not simulated with the flow model or chemical models, but is a possible pathway (supported by the presence of atrazine, discussed below).

Non-N_2 nitrogen at MW is primarily in the form of nitrate, and concentrations decrease with depth. Ammonium concentrations increase with depth. Reducing conditions increase with depth and (nitrate + ammonium) concentrations decrease with depth, indicating that denitrification may occur with depth here; however, this process could not be verified with geochemical models. Nitrogen entering the system near MW could come from a combination of sources near MW or from the postulated overland flow originating near UW. Ground-water flow between UW and MW is unlikely, given the results from flow and chemical models. Ground water does move vertically from MW2 to MW3, according to flow-model results; however, flow between MW and DW does not occur. Permeable surficial deposits between MW and DW probably limit the amount of overland flow between the two sites. Ground-water flow between MW wells and MP wells is a possibility, in light of model results, and the sum of nitrate and ammonium concentrations decrease between the two nests. The change in concentrations may be due to denitrification, mixing of waters, or different recharge temperatures.

Non-N_2 nitrogen at DW is primarily in the form of nitrate. Nitrogen entering the system near DW likely originates upgradient from DW and downgradient from

MW; it appears to have a similar combination of sources as at upgradient locations. Ground-water flow between DW wells and LL and MP wells is likely, according to model results, and the sum of nitrate and ammonium concentrations decreases between the nests. As with the MW to MP flowpath, the change in concentrations downgradient from DW may be due to denitrification, mixing of waters, or different recharge temperatures.

Inverse mole balance models for reactions along the flowpath from DW1 to MP2, and forward reaction models of DW1 ground water reacting with organic matter were constructed. Both modeling approaches failed to provide useful criteria for documenting nitrate reduction in the flowpath waters because the relatively small amount of nitrate initially available for reaction is not sufficient to produce significant changes in the stoichiometry of the ground water. The organic material in the LL area and below the stream bottom may cause nitrate reduction there, but more information is needed to clearly show that denitrification is occurring between DW and LL or MP. Isotopic analysis of dissolved N_2 might provide information that would confirm this hypothesis.

Atrazine and one of its metabolites, deethyl atrazine, were the most commonly detected pesticides in ground water at the study site. The plausible sources of atrazine at the study site include land applications upgradient from UW and precipitation. Differentiating between these two potential sources of atrazine is difficult.

At nest UW, atrazine or deethyl atrazine were not detected in the shallowest well, but were detected at least once in the two deeper wells and concentrations increased with depth. The higher concentrations with depth may indicate the presence of macropores in the surficial deposits upgradient from UW. The likely source is land applications but precipitation is also a possibility.

At nest MW, concentrations of atrazine plus deethyl atrazine decreased with depth. Ground water at MW does not originate as ground water from UW, according to flow-model and chemical results. Therefore, atrazine in ground water at MW originates either as overland flow from near UW or from precipitation.

Concentrations of atrazine plus deethyl atrazine at DW are similar to concentrations measured in samples from well MW1. Again, on the basis of model results, ground water to DW originates upgradient from DW and downgradient from MW. Therefore, atrazine at DW

originates either as overland flow from upgradient areas or from precipitation. Overland flow is unlikely between MW and DW because of the permeable surficial deposits, so precipitation seems to be the more likely source of atrazine to DW wells. Pesticides were not analyzed for in samples from LL wells.

Deethyl atrazine was detected in several MP wells, a finding that indicates movement of the pesticide from the local ground water into the stream. The fact that pesticides were not detected in all MP wells indicates that not all ground water entering the stream near the study site contains pesticides. Pesticides in the stream that were not detected in ground-water samples likely originated from an upstream source.

On the basis of CFC and tritium recharge dates, concentrations of atrazine plus deethyl atrazine in ground water appear to mimic historical use patterns of atrazine in east central Wisconsin. It is unclear whether this is because the land owner followed historical trends or because historical use patterns influenced concentrations in the atmosphere and precipitation. In either case, most of the ground-water recharge dates correspond to the period of increasing use and, if the pattern holds true, concentrations at those wells should continue to increase in time for the near future. In fact, a comparison of atrazine plus deethyl atrazine concentrations for samples collected in 1994 and 1995 for the wells included in figure 18 shows an increase in concentration with time for all wells except UW3. It is unclear why UW3 decreased with time. On the basis of the pattern described above it should be expected that the water from wells DW1 and DW2, the youngest ground water at the study site, would be the first to show signs of decreasing concentrations of atrazine plus deethyl atrazine.

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APPENDIXES 1–4

Appendix 1. Water-quality determinations for water samples from the study site, Sheboygan County, Wis.

[na, not applicable; °C, degrees Celsius; μS/cm, microsiemens per centimeter; mg/L, milligrams per liter; μg/L, micrograms per liter; pCi/L, picocuries per liter]

Constituent	Laboratory parameter code	Number of samples / number of detections	Laboratory method detection limit (MDL)
FIELD MEASUREMENTS			
Alkalinity, as $CaCO_3$, field	00410	5 / 5	na
Water temperature (°C)	00010	44 / 44	na
Specific conductance (μS/cm at 25°C)	00095	43 / 43	na
Dissolved oxygen, mg/L	00300	43 / 43	na
pH (standard units)	00400	43 / 43	na
INORGANICS			
Dissolved solids (residue at 180°C)	70300	42 / 42	1
Major ions (sample passed through 0.45 micrometer filter; MDL in mg/L unless otherwise noted)			
Alkalinity, as $CaCO_3$, lab	90410	42 / 42	1
Aluminum	01106	11 / 6	0.01
Bromide	71870	41 / 37	.01
Calcium	00915	42 / 42	.02
Chloride	00940	42 / 42	.1
Fluoride	00950	42 / 30	.1
Iron	01046	42 / 32	3.0 μg/L
Magnesium	00925	42 / 42	.01
Manganese	01056	42 / 36	1.0 μg/L
Potassium	00935	42 / 41	.1
Silica	00955	42 / 42	.01
Sodium	00930	42 / 42	.2
Sulfate, as SO_4^{2-}	00945	42 / 41	.1
Nutrients (sample passed through 0.45-micrometer filter; MDL in mg/L)			
Ammonia, as N (described as ammonium in text and appendix 2)	00608	44 / 40	.01
Ammonia plus organic nitrogen, as N (described as ammonium plus organic in text and appendix 2)	00623	44 / 32	.2
Nitrite, as N	00613	44 / 5	.01
Nitrite plus nitrate, as N	00631	44 / 18	.05
Orthophosphate, as P	00671	44 / 14	.01
Phosphorus, as P	00666	44 / 16	.01
Radionuclides (whole-water sample)			
Tritium	07000	13 / 13	.3 pCi/L
Isotopes (whole-water sample)			
Deuterium / hydrogen ratio from water, reported in per mil relative to Standard Mean Ocean Water (SMOW)	82082	12 / 12	2 per mil precision
^{18}O / ^{16}O ratio from water, reported in per mil relative to SMOW	82085	12 / 12	.2 per mil precision
^{15}N / ^{14}N ratio from nitrate and ammonia combined, reported in per mil relative to atmospheric air	None	3 / 3	.2 per mil precision

Appendix 1. Water-quality determinations for water samples from the study site, Sheboygan County, Wis.—Continued

[na, not applicable; °C, degrees Celsius; μS/cm, microsiemens per centimeter; mg/L, milligrams per liter; μg/L, micrograms per liter; pCi/L, picocuries per liter]

Constituent	Laboratory parameter code	Number of samples / number of detections	Laboratory method detection limit (MDL)
Isotopes (whole-water sample)—Continued			
^{18}O / ^{16}O ratio from nitrate, reported in per mil relative to SMOW	None	4 / 4	0.05 per mil precision
^{15}N / ^{14}N ratio from nitrate, reported in per mil relative to atmospheric air	None	4 / 4	.05 per mil precision
Dissolved gases (whole-water sample)			
Argon	None	10 / 10	None available
Carbon dioxide	None	10 / 10	None available
Methane	None	10 / 8	None available
Nitrogen	None	10 / 10	None available
Oxygen	None	10 / 10	None available
ORGANICS			
Dissolved organic carbon (sample passed through 0.45- micrometer silver filter)	00681	43 / 43	.1 mg/L
Chlorofluorocarbons (whole-water sample)	None	30 / 29	None available
Pesticides or metabolites (Schedules 2001 and 2010[1]; sample passed through 0.7-micrometer filter; MDL in μg/L)			
Acetochlor	49260	24 / 0	.002
Alachlor	46342	24 / 0	.002
Atrazine	39632	24 / 6	.001
Atrazine, deethyl-[2]	04040	24 / 15	.002
Azinphos, methyl-[2]	82686	24 / 0	.001
Benfluralin	82673	24 / 0	.002
Butylate	04028	24 / 0	.002
Carbaryl[2]	82680	24 / 0	.003
Carbofuran[2]	82674	24 / 0	.003
Chlorpyrifos	38933	24 / 0	.004
Cyanazine	04041	24 / 1	.004
DCPA	82682	24 / 0	.002
DDE, p,p'-	34653	24 / 0	.006
Diazinon	39572	24 / 0	.002
Dieldrin	39381	24 / 0	.001
Diethylaniline, 2'6-	82660	24 / 0	.003
Disulfoton	82677	24 / 0	.017
EPTC	82668	24 / 0	.002
Ethalfluralin	82663	24 / 0	.004
Ethoprop	82672	24 / 0	.003
Fonofos	04095	24 / 0	.003
HCH, alpha	34253	24 / 0	.002
Lindane	39341	24 / 0	.004

[na, not applicable; °C, degrees Celsius; μS/cm, microsiemens per centimeter; mg/L, milligrams per liter; μg/L, micrograms per liter; pCi/L, picocuries per liter]

Constituent	Laboratory parameter code	Number of samples / number of detections	Laboratory method detection limit (MDL)
Pesticides or metabolites (Schedules 2001 and 2010)—Continued			
Linuron	82666	24 / 0	0.002
Malathion	39532	24 / 0	.005
Metolachlor	39415	24 / 1	.002
Metribuzin	82630	24 / 0	.004
Molinate	82671	24 / 0	.004
Napropamide	82684	24 / 0	.003
Parathion, ethyl-	39542	24 / 0	.004
Parathion, methyl-	82667	24 / 0	.006
Pebulate	82669	24 / 0	.004
Pendimethalin	82683	24 / 0	.004
Permethrin, cis-	82687	24 / 0	.005
Phorate	82664	24 / 0	.002
Prometon	04037	24 / 0	.018
Pronamide	82676	24 / 0	.003
Propachlor	04024	24 / 0	.007
Propanil	82679	24 / 0	.004
Propargite	82685	24 / 0	.013
Simazine	04035	24 / 2	.005
Thiobencarb	82670	24 / 0	.002
Tebuthiuron	82665	24 / 0	.010
Terbacil[2]	82675	24 / 0	.007
Terbufos	82681	24 / 0	.013
Triallate	82678	24 / 0	.001
Trifluralin	82661	24 / 0	.002
Pesticides or metabolites (Schedules 2050 and 2051; sample passed through 0.7-micrometer filter, MDL in μg/L)			
2,4,5-T	39742	9 / 0	.035
2,4-D	39732	9 / 0	.035
2,4-DB	38746	9 / 0	.035
Acifluorfen	49315	9 / 0	.035
Aldicarb	49312	9 / 0	.016
Aldicarb sulfone	49313	9 / 0	.016
Aldicarb sulfoxide	49314	9 / 0	.021
Bentazon	38711	9 / 0	.014
Bromacil	04029	9 / 0	.035
Bromoxynil	49311	9 / 0	.035
Carbaryl	49310	9 / 0	.008
Carbofuran	49309	9 / 0	.028

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Appendix 1. Water-quality determinations for water samples from the study site, Sheboygan County, Wis.—Continued

[na, not applicable; °C, degrees Celsius; μS/cm, microsiemens per centimeter; mg/L, milligrams per liter; μg/L, micrograms per liter; pCi/L, picocuries per liter]

Constituent	Laboratory parameter code	Number of samples / number of detections	Laboratory method detection limit (MDL)
Pesticides or metabolites (Schedules 2050 and 2051)—Continued			
Carbofuran, 3-hydroxy-	49308	9 / 0	0.014
Chloramben	49307	9 / 0	.011
Chlorothalonil[2]	49306	9 / 0	.035
Clopyralid	49305	9 / 0	.05
Dacthal, mono-acid-	49304	9 / 0	.017
Dicamba	38442	9 / 0	.035
Dichlobenil[2]	49303	9 / 0	.02
Dichlorprop	49302	9 / 0	.032
Dinoseb	49301	9 / 0	.035
Diuron	49300	9 / 0	.02
DNOC[2]	49299	9 / 0	.035
Esfenvalerate[2]	49298	9 / 0	.019
Fenuron	49297	9 / 0	.013
Fluometuron	38811	9 / 0	.035
Linuron	38478	9 / 0	.018
MCPA	38482	9 / 0	.05
MCPB	38487	9 / 0	.035
Methiocarb	38501	9 / 0	.026
Methomyl	49296	9 / 0	.017
1-Naphthol[2]	49295	9 / 0	.007
Neburon	49294	9 / 0	.015
Norflurazon	49293	9 / 0	.024
Oryzalin	49292	9 / 0	.019
Oxamyl	38866	9 / 0	.018
Picloram	49291	9 / 0	.05
Propham	49236	9 / 0	.035
Propoxur	38538	9 / 0	.035
Silvex	39762	9 / 0	.021
Triclopyr	49235	9 / 0	.05

[1]The pesticide dimethoate was originally included on schedules 2001 and 2010 but it was later deleted because of poor recoveries, th s dimethoate data are not included in this report.

[2]Recoveries for these pesticides were variable and are reported as estimated values in appendix 2 if measured concentrations were above the MDL.

Appendix 2a. Selected water-quality data for water samples from the study site, Sheboygan County, Wis.

[All concentrations in milligrams per liter, unless otherwise indicated: mn, month; dd, day; yy,year; °C, degrees Celsius; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; <, less than; ---, no data]

Site name (USGS site identification number)	Sample date (mn/dd/yy)	Sample time	Water temperature (°C)	Specific conductance, field (µS/cm at 25 °C)	Dissolved oxygen, field	pH, field (standard units)	Alkalinity, field (as CaCO3)	Alkalinity, lab (as CaCO3)	Aluminum, in µg/L	Bromide
Well UW1 (433720088014901)	06/16/94	1200	9.8	605	2.9	7.2	---	281	---	0.02
	05/31/95	1630	14.6	613	.8	7.3	---	289	---	.04
	08/24/95	1100	12.9	597	1.0	7.5	---	294	<10	.02
Well UW2 (433720088014902)	06/16/94	1000	10.6	637	2.8	7.6	---	293	---	.11
	06/01/95	1015	15.6	511	2.8	7.8	---	---	---	---
Well UW3 (433720088014903)	06/16/94	0845	21.8	525	.7	7.7	---	221	---	.19
	06/01/95	0900	13.2	438	.8	8.1	---	228	---	.05
	08/24/95	1130	12.8	430	1.7	8.0	---	232	<10	.03
Well MW1 (433715088015801)	06/15/94	0930	15.3	689	7.7	6.9	340	292	---	.02
	05/30/95	1545	12.3	692	7.0	7.1	---	320	---	.03
	08/23/95	1100	17.5	699	5.1	7.2	---	314	20	.03
Well MW2 (433715088015802)	06/15/94	1200	22.8	637	.5	7.0	320	284	---	.03
	05/31/95	0900	12.8	---	1.4	7.1	---	322	---	.03
	08/23/95	1300	15.1	622	.3	7.2	---	317	<10	.03
Well MW3 (433715088015803)	06/15/94	1330	13.0	600	.1	7.1	312	310	---	.02
	05/30/95	1730	11.3	286	.2	7.2	---	319	---	.03
	08/23/95	0900	13.0	615	.3	7.1	---	280	<10	.10
Well DW1 (433708088020801)	06/13/94	1330	21.4	691	5.5	6.8	378	337	---	.02
	05/31/95	1230	11.3	679	5.9	7.0	---	333	---	.03
	08/22/95	1200	19.1	681	9.3	7.0	---	310	<10	.03
Well DW2 (433708088020802)	06/13/94	1540	11.1	680	6.9	6.9	329	316	---	.02
	05/31/95	1330	11.8	681	6.5	7.1	---	334	---	.03
	08/22/95	1300	14.2	679	10.3	7.1	---	324	20	.02
Well LL1 (433707088021201)	06/02/95	1100	16.8	415	---	7.2	---	---	---	---
Well LL2 (433707088021203)	06/02/95	1130	11.8	657	0.7	6.8	---	373	---	0.04

Appendix 2a. Selected water-quality data for water samples from the study site, Sheboygan County, Wis.—Continued

[All concentrations in milligrams per liter, unless otherwise indicated; mn, month; dd, day; yy,year; °C, degrees Celsius; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; <, less than; ---, no data]

Site name (USGS site identification number)	Sample date (mn/dd/yy)	Sample time	Water temperature (°C)	Specific conductance, field (µS/cm at 25 °C)	Dissolved oxygen, field	pH, field (standard units)	Alkalinity, field (as CaCO₃)	Alkalinity, lab (as CaCO₃)	Aluminum, in µg/L	Bromide
Well LL3 (43370708021204)	06/02/95	1200	12.0	657	1.6	6.9	---	365	---	.04
Well MP1 (43370408021101)	06/14/94	1000	14.3	550	4.6	7.3	---	316	---	.01
Well MP2 (43370308021301)	06/01/95	1200	12.7	654	.4	6.9	---	362	---	.02
	08/22/95	1200	19.1	640	.4	6.6	---	351	20	.02
	08/23/95	1300	---	---	---	---	---	---	---	---
Well MP3 (43370308021302)	06/01/95	1230	12.2	651	.3	6.9	---	363	---	.04
	08/22/95	1230	18.9	641	.4	6.6	---	348	20	.02
	08/23/95	1310	---	---	---	---	---	---	---	---
Well MP4 (43370308021303)	06/01/95	1300	11.7	647	.5	7.0	---	359	---	.03
	08/22/95	1300	18.5	639	.4	6.6	---	351	20	.03
	08/23/95	1320	---	---	---	---	---	---	---	---
Well MP5 (433701088020901)	06/01/95	1330	17.0	744	.7	6.9	---	426	---	.03
	08/22/95	1530	18.7	714	.5	6.6	---	401	---	.02
Well MP6 (433701088020902)	06/01/95	1400	12.7	743	.3	6.9	---	425	---	.02
	08/22/95	1600	18.7	680	.3	6.6	---	376	---	.02
Well MP7 (433706088021507)	06/01/95	1430	17.0	597	.5	7.3	---	336	---	.03
	08/22/95	1630	20.6	651	.4	7.0	---	321	---	<.01
Well MP8 (433706088020902)	06/01/95	1500	15.5	605	.3	7.3	---	337	---	.03
	08/22/95	1700	20.0	643	.3	7.0	---	326	---	<.01
N. Br. Milwaukee River (04035297)	06/06/94	1430	22.5	698	12.7	7.8	---	308	---	---
	06/01/95	1315	22.7	672	10.7	8.2	---	310	---	<.01
	08/23/95	1200	21.1	708	10.0	8.0	---	316	10	<.01

Appendix 2b. Selected water-quality data for water samples from the study site, Sheboygan County, Wis.

[All concentrations in milligrams per liter, unless otherwise indicated; µg/L, micrograms per liter; <, less than; ---, no data]

Site name	Calcium	Chloride	Fluoride	Iron, in µg/L	Magnesium	Manganese, in µg/L	Potassium	Silica	Sodium	Sulfate (as SO_4^{2-})	Dissolved solids
Well UW1	71	5.9	0.1	<3	36	78	1.4	18	3.2	21	306
	74	7.2	.1	32	36	48	1.2	17	3.3	22	349
	70	5.9	.1	200	36	33	.9	17	3.2	21	335
Well UW2	50	27	.4	<3	42	45	6.9	15	12	15	326
	--	--	--	--	--	--	--	--	--	--	--
Well UW3	31	49	.6	<3	30	16	8.3	4.9	28	1.6	300
	19	12	.5	9	20	9	5.2	4.2	23	.2	202
	23	9.0	.5	17	27	8	5.6	5.5	29	<.1	233
Well MW1	80	6.6	<.1	27	42	1	.6	16	2.7	20	284
	81	6.2	<.1	14	41	<1	.7	16	2.7	19	393
	86	6.8	<.1	<3	45	<1	.6	16	2.8	18	392
Well MW2	77	5.9	.1	110	39	810	.7	14	3.2	34	325
	76	6.1	.1	110	38	570	.7	14	2.7	31	369
	75	5.8	.1	130	39	590	.7	14	2.9	33	363
Well MW3	72	3.4	.2	2100	35	290	.7	17	3.8	16	335
	73	3.5	.1	2000	35	220	.6	17	3.5	17	341
	73	4.1	.1	1800	37	210	.5	16	3.4	22	348
Well DW1	85	3.9	<.1	15	42	19	.8	15	2.6	14	258
	83	3.5	<.1	<3	41	<1	.5	14	2.5	14	374
	82	4.2	.1	<3	44	1	1.0	16	2.8	15	392
Well DW2	83	4.7	<.1	<3	42	<1	.6	15	2.8	17	387
	83	4.4	<.1	<3	41	<1	.6	15	2.6	15	381
	82	4.3	.1	<3	44	<1	.8	16	2.8	15	385
Well LL1	--	--	--	--	--	--	--	--	--	--	--
Well LL2	88	2.1	<0.1	5	37	4	<0.1	10	2.3	9.5	372
Well LL3	85	2.6	<.1	35	38	270	.4	11	2.5	11	365
Well MP1	61	1.2	.2	380	37	27	1.0	21	5.7	.7	269

Appendix 2b. Selected water-quality data for water samples from the study site, Sheboygan County, Wis.—Continued

[All concentrations in milligrams per liter, unless otherwise indicated; µg/L, micrograms per liter; <, less than; ---, no data]

Site name	Calcium	Chloride	Fluoride	Iron, in µg/L	Magnesium	Manganese, in µg/L	Potassium	Silica	Sodium	Sulfate (as SO_4^{2-})	Dissolved solids
Well MP2	80	3.1	.1	510	39	28	.5	13	3.0	14	359
	80	2.9	.1	470	39	28	.8	14	3.1	13	363
	--	--	--	--	--	--	--	--	--	--	--
Well MP3	80	3.3	.1	540	39	28	.6	13	3.1	15	369
	79	2.9	.2	540	38	27	.8	14	3.2	14	362
	--	--	--	--	--	--	--	--	--	--	--
Well MP4	79	3.0	.1	580	39	29	.6	13	3.4	15	368
	79	2.8	.2	600	39	30	.9	15	3.3	14	363
	--	--	--	--	--	--	--	--	--	--	--
Well MP5	97	3.7	.1	950	42	170	.5	20	3.8	6.9	437
	94	3.4	.2	330	43	180	.7	22	4.0	8.1	421
Well MP6	96	3.4	.2	1100	42	210	.5	19	3.6	7.0	434
	90	3.7	.2	160	42	190	.7	21	3.9	11	398
Well MP7	67	1.3	.3	12	36	37	1.3	19	8.3	9.4	333
	70	19	.4	<3	38	39	1.7	22	15.0	11	364
Well MP8	69	1.3	.3	54	37	37	1.2	19	8.2	10	335
	68	17	.4	6	37	36	1.7	21	14	11	363
N. Br. Milwauke River	68	36	<.1	14	40	44	2.9	12	24	30	434
	69	30	<.1	54	39	36	2.1	10	18	22	407
	71	36	<.1	25	43	14	2.6	13	21	29	424

Appendix 2c. Selected water-quality data for water samples from the study site, Sheboygan County, Wis.

[All concentrations in milligrams per liter, unless otherwise indicated; pCi/L, picocuries per liter; <, less than; ---, no data]

Site name	Ammonium, as N	Ammonium plus organic nitrogen, as N	Nitrite, as N	Nitrite plus nitrate, as N	Phosphorus, as P	Ortho phosphate, as P	Tritium, in pCi/L	Deuterium/hydrogen ratio from water, in per mil	$^{18}O/^{16}O$ ratio from water, in per mil	Dissolved organic carbon (DOC)
Well UW1	0.51	0.7	<0.01	<0.05	<0.01	<0.01	68	-70.2	-10.4	1.6
	.45	.6	<.01	<.05	<.01	<.01	---	---	---	1.6
	.50	2.6	<.01	<.05	.02	.01	---	---	---	1.4
Well UW2	.71	1.1	<.01	<.05	.01	<.01	92	-69.0	-10.3	4.8
	.38	.7	<.01	.10	<.01	<.01	---	---	---	2.6
Well UW3	2.0	2.7	<.01	<.05	<.01	<.01	60	-70.7	-10.5	28
	.98	1.2	<.01	<.05	<.01	<.01	---	---	---	6.2
	1.2	1.4	<.01	<.05	.02	<.01	---	---	---	3.5
Well MW1	.01	<.2	<.01	4.1	<.01	<.01	63	-19.2	-3.64	1.2
	.02	.4	<.01	4.3	.03	<.01	---	---	---	1.0
	<.01	<.2	<.01	4.1	<.01	<.01	---	---	---	1.2
Well MW2	.18	.2	.01	1.1	.01	<.01	75	-64.4	-9.71	1.0
	.12	<.2	.01	2.0	<.01	<.01	---	---	---	1.0
	.12	.2	<.01	.65	<.01	<.01	---	---	---	1.4
Well MW3	.36	.3	<.01	<.05	<.01	<.01	38	-67.3	-10.2	1.6
	.28	.3	<.01	<.05	<.01	<.01	---	---	---	1.3
	.23	.3	<.01	<.05	<.01	<.01	---	---	---	1.2
Well DW1	.09	<.2	<.01	1.9	<.01	<.01	59	-65.0	-9.92	1.1
	.02	<.2	<.01	1.7	<.01	<.01	---	---	---	1.2
	<.01	<.2	<.01	2.1	<.01	<.01	---	---	---	1.2
Well DW2	.05	<.2	<.01	2.1	<.01	.01	66	-67.0	-9.97	1.0
	.02	<.2	<.01	2.1	<.01	<.01	---	---	---	.9
	<.01	<.2	<.01	2.0	<.01	<.01	---	---	---	.9
Well LL1	.16	.2	<.01	<.05	<.01	<.01	---	---	---	2.3
Well LL2	0.02	<0.2	<0.01	<0.05	<0.01	<0.01	---	---	---	2.0
Well LL3	.04	<.2	<.01	.09	<.01	.02	---	---	---	1.4
Well MP1	.54	.7	<.01	<.05	.03	.04	7.8	-66.6	-9.87	1.2

Appendix 2c. Selected water-quality data for water samples from the study site, Sheboygan County, Wis.—Continued

[All concentrations in milligrams per liter, unless otherwise indicated; pCi/L, picocuries per liter; <, less than; ---, no data]

Site name	Ammonium, as N	Ammonium plus organic nitrogen, as N	Nitrite, as N	Nitrite plus nitrate, as N	Phosphorus, as P	Ortho phosphate, as P	Tritium, in pCi/L	Deuterium/ hydrogen ratio from water, in per mil	$^{18}O/^{16}O$ ratio from water, in per mil	Dissolved organic carbon (DOC)
Well MP2	.10	.2	<.01	<.05	<.01	<.01	---	---	---	2.8
	.08	.2	<.01	.12	<.01	<.01	---	---	---	2.7
	---	---	---	---	---	---	41	-65.8	-9.81	---
Well MP3	.10	.2	<.01	<.05	<.01	<.01	---	---	---	2.7
	.07	.2	<.01	<.05	<.01	<.01	---	---	---	2.6
	---	---	---	---	---	---	43	-67.1	-9.80	---
Well MP4	.11	<.2	<.01	<.05	<.01	<.01	---	---	---	2.3
	.11	.2	<.01	<.05	<.01	<.01	---	---	---	2.8
	---	---	---	---	---	---	38	-66.6	-9.78	---
Well MP5	.28	.5	<.01	<.05	.07	.09	---	---	---	6.6
	.28	.6	<.01	<.05	.06	.06	---	---	---	5.6
Well MP6	.25	.5	<.01	<.05	.07	.09	---	---	---	6.3
	.24	.6	<.01	<.05	.04	.05	---	---	---	4.3
Well MP7	.28	.2	<.01	<.05	.01	.03	---	---	---	1.5
	.40	.6	<.01	<.05	.04	.04	---	---	---	2.4
Well MP8	.27	.2	<.01	<.05	<.01	.03	---	---	---	1.6
	.40	.6	<.01	<.05	.03	.04	---	---	---	2.3
N. Br. Mil- waukee River	.12	.5	.08	2.4	.09	.10	---	---	---	---
	.09	.6	.05	1.8	.11	.13	---	---	---	7.6
	<.01	.4	.02	2.1	.11	.12	57	---	---	4.4

Appendix 2d. Selected water-quality data for water samples from the study site, Sheboygan County, Wis.

[All concentrations in micrograms per liter; <, less than; E, estimated; ---, no data]

Site Name	Atrazine	Deethyl atrazine	Cyanazine	Metolachlor	Simazine
Well UW1	<0.001	<0.002	<0.004	<0.002	<0.005
	---	---	---	---	---
	<.001	<.002	<.004	<.002	<.005
Well UW2	<.001	E .003	<.004	<.002	<.005
	---	---	---	---	---
Well UW3	.013	E .014	<.004	<.002	<.005
	---	---	---	---	---
	<.001	<.002	<.004	<.002	<.005
Well MW1	<.001	E .023	<.004	<.002	<.005
	---	---	---	---	---
	<.001	E .051	<.004	<.002	<.005
Well MW2	<.001	E .004	<.004	<.002	<.005
	---	---	---	---	---
	<.001	E .009	<.004	<.002	<.005
Well MW3	<.001	<.002	<.004	<.002	<.005
	---	---	---	---	---
	<.001	E .002	<.004	<.002	<.005
Well DW1	.006	E .019	<.004	<.002	<.005
	---	---	---	---	---
	.007	E .029	<.004	<.002	<.005
Well DW2	.007	E .031	<.004	<.002	<.005
	---	---	---	---	---
	.008	E .045	<.004	<.002	<.005
Well LL1	---	---	---	---	---
Well LL2	---	---	---	---	---
Well LL3	---	---	---	---	---
Well MP1	<.001	<.002	<.004	<.002	<.005
Well MP2	---	---	---	---	---
	<.001	<.002	<.004	<.002	<.005
	---	---	---	---	---
Well MP3	---	---	---	---	---
	<.001	<.002	<.004	<.002	<.005
	---	---	---	---	---
Well MP4	---	---	---	---	---
	<.001	E .003	<.004	---	<.005
	---	---	---	<.002	---
Well MP5	---	---	---	---	---
	<.001	E .003	<.004	<.002	<.005
Well MP6	---	---	---	---	---
	<.001	E .01	<.004	<.002	<.005
Well MP7	---	---	---	---	---
	<.001	<.002	<.004	<.002	<.005
Well MP8	---	---	---	---	---
	<.001	<.002	<.004	<.002	.006
N. Br. Milwaukee River	---	---	---	---	---
	---	---	---	---	---
	.012	E .03	.005	E .002	.045

Appendix 3. Concentrations of dissolved CFC-11, CFC-12, and CFC-113 and recharge dates for ground-water samples collected at the study site, Sheboygan County, Wis.

[°C, degrees Celsius; BP, barometric pressure; mm, millimeters of mercury; mn, month; dd, day; yy, year; CFC, chlorofluorocarbon; pg/kg, picogram per kilogram; pptv, parts per trillion by volume; contam, contaminated]

Well name	Recharge[1] Temp (°C)	Recharge[1] BP (mm)	Sample Date (mn/dd/yy)	Sample Time	Concentration in solution, in pg/kg CFC-11	CFC-12	CFC-113	Calculated atmospheric partial pressure, in pptv CFC-11	CFC-12	CFC-113	CFC recharge dates[2] CFC-11	CFC-12	CFC-113
UW1	7.5	733.4	06/16/94	1535	63.9	61.8	634.5	19.8	85.2	466.0	1963.0	1966.5	contam
				1540	33.6	30.0	24.5	10.4	41.4	18.0	1960.0	1961.0	1976.5
				1600	18.1	23.0	10.1	5.6	31.7	7.4	1956.5	(**1959.5**)	1970.0
UW3	7.5	733.4	06/21/94	1245	122.6	283.8	258.9	38.0	391.1	190.1	1967.0	1985.0	contam
				1255	135.7	232.3	248.4	42.1	320.2	182.4	1967.5	1981.0	contam
				1300	114.1	242.0	234.9	35.4	333.6	172.5	1966.5	**1981.5**	contam
MW1	7.5	735.6	06/15/94	1535	399.8	218.8	34.5	123.7	300.7	25.2	1975.5	1979.5	1980.0
				1550	408.1	216.1	33.9	126.2	296.9	24.9	1975.5	**1979.5**	1980.0
				1555	414.3	222.6	4.1	128.1	306.0	3.0	1975.5	1979.5	1967.5
MW2	7.5	735.6	06/15/94	1630	69.0	65.2	38.1	21.3	89.6	27.9	1963.5	**1967.0**	1981.0
				1645	62.8	63.3	19.0	19.4	87.0	13.9	1963.0	1966.5	1974.0
				1650	64.6	66.1	19.1	20.0	90.8	14.0	1963.5	1967.0	1974.0
MW3	7.5	735.6	06/15/94	1725	55.1	28.6	25.2	17.0	39.3	18.5	1962.5	**1961.0**	1976.5
				1735	53.4	23.4	29.0	16.5	32.1	21.2	1962.5	1959.5	1978.0
				1740	38.6	37.5	23.1	12.0	51.6	16.9	1960.5	1963.0	1975.5
DW1	7.5	736.8	06/15/94	1915	525.3	323.2	65.3	162.2	443.5	47.7	1979.0	1987.5	1985.5
				1925	502.0	296.1	66.8	155.0	406.3	48.8	1978.0	1985.5	1985.5
				1930	505.1	297.3	55.7	156.0	408.0	40.7	1978.0	**1986.0**	1984.0
DW2	7.5	736.8	06/13/94	1620	455.8	246.2	41.5	140.8	337.8	30.4	1976.5	1981.5	1981.5
				1635	463.8	252.9	37.4	143.2	347.0	27.3	1977.0	**1982.5**	1981.0
				1645	460.3	253.3	38.1	142.2	347.5	27.8	1976.5	1982.5	1981.0
MP2	7.7	737.3	09/06/95	1130	4.8	186.8	2.3	1.5	258.8	1.7	1952.0	1976.5	1966.0
				1135	3.6	181.6	1.1	1.1	251.5	.8	1951.5	**1976.5**	1965.5
				1140	2.9	195.9	0	.9	271.3	.0	1951.0	1977.5	1965.0
MP3	7.7	737.3	09/06/95	0945	2.2	200.9	3.9	.7	278.3	2.9	1950.0	1978.0	1966.5
				0950	1.5	196.3	1.4	.5	271.9	1.1	1949.5	**1977.5**	1965.5
				1000	1.0	194.8	1.5	.3	269.9	1.1	1948.4	1977.5	1965.5
MP4	7.7	737.3	09/06/95	1035	14.6	191.6	3.6	4.6	265.4	2.6	1955.5	1977.0	1966.5
				1040	2.0	187.7	2.3	.6	259.9	1.7	1950.0	**1977.0**	1966.0
				1100	1.9	197.0	1.1	.6	272.8	.8	1950.0	1977.5	1965.5

[1] The recharge temperature and barometric pressure used influence the calculated CFC recharge dates. Higher temperatures and pressures yield younger CFC ages. Temperature was estimated from mean annual air temperature, and barometric pressure was determined based on elevations from table 1.

[2] Recharge dates in **bold** were assigned as the recharge date for that site and are also listed in table 1. Recharge dates in parentheses indicate that concentrations were decreasing, and they are censored with a "<" in table 1 to indicate that the actual recharge date may be older than the assigned recharge date. A sample identified as contaminated (contam) indicates that it could not be dated because the calculated CFC partial pressures were greater than the CFC concentrations in the atmosphere in 1994 or 1995.

Appendix 4. Concentrations of dissolved gases, excess nitrogen, and calculated recharge temperatures for ground-water samples collected at the study site, Sheboygan County, Wis., during the period from November 5–6, 1996

[All concentrations in milligrams per liter, unless otherwise indicated; ND, not detected; cc, cubic centimeters; temp., temperature; °C, degrees celsius]

Well name	Argon	Carbon dioxide	Methane	Nitrogen	Oxygen	Excess nitrogen, cc	Calculated recharge temp. (°C)
UW1	0.75	17.7	0.018	29.3	0.08	16.32	26.3
UW3	.89	2.60	1.13	37.2	6.58	23.97	25.3
MW1	.74	35.3	ND	22.4	7.50	5.17	11.2
MW2	.77	30.2	.003	27.1	.01	12.04	17.8
MW3	.77	24.6	.39	26.4	.19	10.54	15.2
DW1	.72	47.2	.001	20.1	3.46	2.05	9.0
DW2	.73	38.4	ND	20.3	4.51	2.00	8.4
MP2	.82	51.5	.031	22.8	.09	2.47	3.8
MP3	.77	48.4	.025	21.0	.23	1.41	5.4
MP4	.80	51.1	.031	21.9	.06	1.86	4.3