

In cooperation with the Geauga County Planning Commission and Board of County Commissioners

Ground-Water Quality in Geauga County, Ohio– Review of Previous Studies, Status in 1999, and Comparison of 1986 and 1999 Data

Water-Resources Investigations Report 01-4160



U.S. Department of the Interior U.S. Geological Survey

Ground-Water Quality in Geauga County, Ohio—Review of Previous Studies, Status in 1999, and Comparison of 1986 and 1999 Data

By Martha L. Jagucki and Robert A. Darner

Water-Resources Investigations Report 01-4160

U.S. Department of the Interior Gale A. Norton, Secretary

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For additional information write to:

District Chief U.S. Geological Survey 6480 Doubletree Avenue Columbus, OH 43229-1111

Copies of this report can be purchased from:

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	Ву	To obtain	
	Length		
inch (in.)	25.4	millimeter	
foot (ft)	0.3048	meter	
mile (mi)	1.609	kilometer	
acre	0.4047	square hectometer	
square mile (mi ²)	2.590	square kilometer	
gallon (gal)	3.785	liter	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second	
cubic foot per day (ft^3/d)	0.02832	cubic meter per day	
gallon per minute (gal/min)	0.06309	liter per second	
million gallons per day	0.04381	cubic meter per second	

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation: $^{\circ}F = 1.8(^{\circ}C) + 32$

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 used in this report: Water volumes and chemical concentrations referred to in water-quality discussions are given in metric units. Volume is given in milliliters (mL). Chemical concentration is given in milligrams per liter (mg/L), micrograms per liter (μ g/L), or milliequivalents per liter (μ g/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is approximately the same as for concentrations in parts per million. Milliequivalents per liter is the concentration in milligrams per liter divided by the equivalent weight of the ion of interest.

Specific conductance of water is expressed in microsiemens per centimeter at 25 degrees Celsius (μ S/cm). This unit is equivalent to micromhos per centimeter at 25 degrees Celsius (μ mho/cm), formerly used by the U.S. Geological Survey.

Tritium concentration is expressed in tritium units (TU). One tritium unit is equal to one tritium atom per 10¹⁸ hydrogen atoms; in terms of radioactivity, it is equivalent to 3.24 picocuries per liter.

Concentrations of bacteria are given as number of colonies per 100 milliliters of sample (col/100 mL).

Pore size of filters is given in micrometers (µm).

Other abbreviations used in this report:

MCL	Maximum Contaminant Level
NWQL	National Water Quality Laboratory
OEPA	Ohio Environmental Protection Agency
SMCL	Secondary Maximum Contaminant Level
SVOC	Semivolatile organic compound

USEPA U.S. Environmental Protection Agency
USGS U.S. Geological Survey

VOC Volatile organic compound

Ground-Water Quality in Geauga County, Ohio—Review of Previous Studies, Status in 1999, and Comparison of 1986 and 1999 Data

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ABSTRACT

Most residents in Geauga County, Ohio, rely on ground water as their primary source of drinking water. With population growing at a steady rate, the possibility that human activity will affect ground-water quality becomes considerable. This report presents the results of a study by the U.S. Geological Survey (USGS), in cooperation with the Geauga County Planning Commission and Board of County Commissioners, to provide a brief synopsis of work previously done within the county, to assess the present (1999) ground-water quality, and to determine any changes in ground-water quality between 1986 and 1999.

Previous studies of ground-water quality in the county have consistently reported that manganese and iron concentrations in ground water in Geauga County often exceed the U.S. Environmental Protection Agency (USEPA) Secondary Maximum Contaminant Level (SMCL). Road salt and, less commonly, oil-field brines and volatile organic compounds (VOCs) have been found in ground water at isolated locations. Nitrate has not been detected above the USEPA Maximum Contaminant Level (MCL) of 10 milligrams per liter as N; however, nitrate has been found in some locations at levels that may indicate the effects of fertilizer application or effluent from septic systems.

Between June 7 and July 1, 1999, USGS personnel collected a total of 31 water-quality samples from wells completed in glacial deposits, the Pottsville Formation, the Cuyahoga Group, and the Berea Sandstone. All samples were analyzed for VOCs, sulfide, dissolved organic carbon, major ions, trace elements, alkalinity, total coliforms, and *Escherichia coli* bacteria. Fourteen of the samples also were analyzed for tritium.

Water-quality data were used to determine (1) suitability of water for drinking, (2) age of ground water, (3) stratigraphic variation in water quality, (4) controls on water quality, and (5) temporal variation in water quality.

Water from 16 of the 31 samples exceeded the Geauga County General Health District's standard of 0 colonies of total coliform bacteria per 100 milliliters of water. Esthetically based SMCLs were exceeded in the indicated number of wells for pH (8), sulfate (1), dissolved solids (3), iron (19), and manganese (18). Hydrogen sulfide was detected at or above the detection limit of 0.01 milligram per liter in 17 of the 31 water samples.

A range of water types was found among and within the four principal stratigraphic units. The waters can be categorized in three groups based on predominant anion type: bicarbonate-type waters, chloride-type waters, and sulfate-type waters.

Chloride-to-bromide ratio analyses indicate that water from 8 of the 31 wells is in some way affected by human activity. Five other samples were in a chloride-to-bromide ratio range that could indicate possible effects of human activity.

Ground-water-quality data from the current study were compared to data collected in 1986. Statistical analyses of data from the 16 wells that were sampled in both years did not indicate any significant changes that could be attributed to human activity.

INTRODUCTION

The population in Geauga County increased by 10.5 percent from 1990 to 1999 (U.S. Census Bureau, 2000). Greater residential development and population density brings greater potential for human effects on water quality (Ekchardt and Stackelberg, 1995; Thomas, 2000). This potential for water-quality changes is of critical concern in Geauga County, where 98 percent of the residents rely on ground water as their source of drinking water (U.S. Geological Survey, 1995). Most of the population (78 percent) is served by self-supplied domestic wells (U.S. Geological Survey, 1995); regular water-quality testing of such wells is not mandated by local, State, or Federal government regulations, which address only public water suppliers serving 25 or more people.

In addition, the condition of septic systems that are more than 20 years old may be a potential problem, especially where systems are not maintained by removal of solids from the septic tank about once every 3 years (Ohio State University Extension [no date]). Failure of septic systems can cause pollution that infiltrates to shallow ground water and (or) runs off to lakes and streams (Michigan State University Extension, 1998; Schwartz and others, 1998; Arnade, 1999). Because most wastewater in the county is treated by septic systems, the potential for effects on ground-water quality is considerable.

To address potential concerns about ground-water quality in Geauga County and to evaluate anthropogenic effects (that is, the effects of human activities) on ground-water resources, the USGS, in cooperation with the Geauga County Planning Commission and Board of County Commissioners, assessed water quality in the county in 1999 and compared these data to water-quality data collected by the

USGS in 1986 and to data collected by previous researchers.

Purpose and Scope

The purpose of this report is to review and briefly summarize nearly two decades of groundwater-quality data in Geauga County, describe the current (1999) status of ground-water quality in the county, and determine whether changes in water quality have occurred since wells were last sampled by USGS personnel in 1986. To obtain data on current ground-water quality, the USGS collected 31 groundwater samples from June 7 through July 1, 1999, from the glacial deposits, the Pottsville Formation, the Cuyahoga Group, and the Berea Sandstone. Results of the water-quality analyses are presented. The current status of water quality is examined in terms of suitability of water for drinking, ground-water age, stratigraphic variation in ground water, and anthropogenic influences on ground-water quality.

Acknowledgments

The authors and the Geauga County Planning Commission and Board of County Commissioners gratefully acknowledge the support from the Geauga County Water Resources Department and the City of Akron Public Utilities Bureau in this investigation. The authors also thank the 31 homeowners who allowed USGS personnel to collect water samples from their wells, as well as the Geauga County officials who provided geographic information systems (GIS) data regarding roads and land use. Appreciation is extended to Mike Bolis, who provided information on previous site-specific studies of ground-water quality in the county done by the Ohio Environmental Protection Agency.

DESCRIPTION OF STUDY AREA

Geauga County is in northeastern Ohio, east of the Cleveland metroplex (fig. 1). It encompasses an area of approximately 409 mi². The region consists of gently rolling hills, with local relief rarely more than 200 ft. Lowest and highest elevations in the county are about 860 ft (southeast of the village of Parkman) and about 1,360 ft above sea level (near villages of Chardon and Burton). Draining the county are the headwaters of the Chagrin, Cuyahoga, and Grand Rivers.

EXPLANATION

Ground-water quality site and well identification number

- ♦ GE-101 Glacial deposits
- GE-109 Pottsville Formation
- ▲ GE-120 Cuyahoga Group
- GE-103 Berea Sandstone

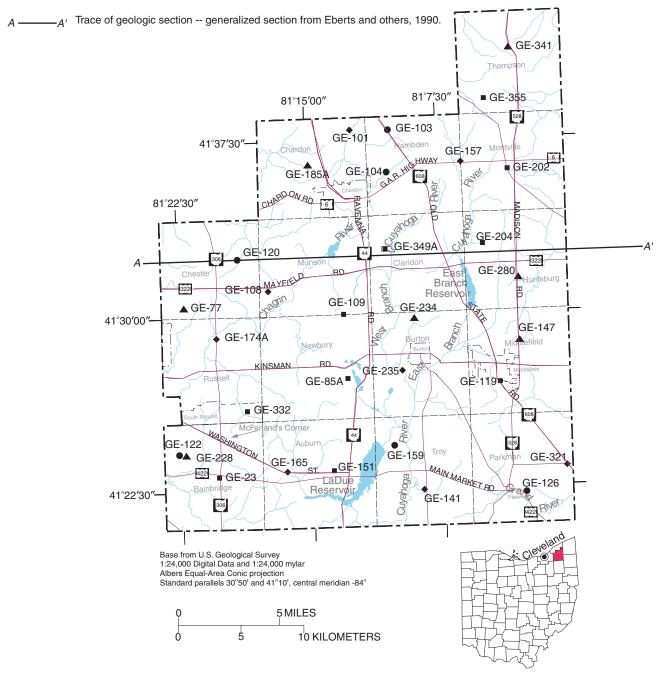


Figure 1. Location of wells sampled for water quality analysis in 1999, Geauga County, Ohio.

Average annual precipitation at the National Weather Service station in the Village of Chardon, Ohio, for the period 1945–99 was 45.74 in. Much of this precipitation is snowfall, with the annual average during 1945–99 being 102.8 in. as unmelted snowfall (Jon Burroughs, Midwest Climatic Data Center, written commun., 1999). This is the highest snowfall rate in Ohio (Harstine, 1991). Precipitation falls most heavily in the northern part of the county (Baker, 1964).

Water Use

Ground water is of great importance in Geauga County, as indicated by water-use data compiled by the USGS (1995) (table 1). These data show that, during 1995, self-supplied ground water for domestic use accounted for 73 percent of total ground-water use in the county and that self-supplied ground water was the source of drinking water for almost 80 percent of the population. Ground water that was publicly supplied (by utilities serving 25 people or more) for domestic use accounted for 7 percent of total ground-water use

and was the drinking-water source for 20 percent of the population.

These data indicate that only 20 percent of the county's population is safeguarded by mandatory periodic testing of water quality and safe drinking-water standards, which apply only to public-supply utilities as defined above. No periodic testing is required for private (self-supplied) domestic wells. The only requirement mandated by the State of Ohio and the Geauga County General Health District for a private well is that the well water be tested for total coliform bacteria when the well and the rest of the water system is initially installed. If a problem is later suspected, the well owner may voluntarily request testing by the Geauga County General Health District.

Land Use and Population

Land-use data for the years of 1975 and 1996 show that residential and commercial areas in Geauga County increased from 24,000 to 41,400 acres and from 800 to 2,800 acres, respectively (table 2). Forested lands increased in area from 105,000 to 139,000 acres, mostly because the 1996 analysts counted residential yards as forested area.

Table 1. Estimated water-use data for Geauga County, Ohio, 1995 [Modified from U.S. Geological Survey, 1995; Mgal/d, million gallons per day; --, not applicable]

Water-use category	Ground-water	Surface-water	Total		
	withdrawals, in Mgal/d	withdrawals, in Mgal/d	Water withdrawals, in Mgal/d	Population served	
Public-supplied domestic ^a	0.50	0.00	0.50	^b 16,850	
Self-supplied domestic ^c	4.95	.10	5.05	67,410	
Other ^d	1.37	.83	2.20		
Total water withdrawals	6.82	.93	7.75	84,260	

^aPublic-supplied domestic usage includes utilities serving 25 or more people. Withdrawals were estimated from the total water withdrawals by public water suppliers in Geauga County, as reported in the Water Withdrawal Facility Registration Program for 1995, Ohio Department of Natural Resources. Total withdrawals were multiplied by a U.S. Geological Survey derived coefficient of 35 percent for domestic use.

¹This precipitation value is the total of liquid and melted frozen precipitation.

^bPopulation served by water suppliers was estimated using a database called the Model State Information System—Active Community Public Water Supply, April 8, 1991, Ohio Environmental Protection Agency, adjusted on the basis of U.S. Department of Commerce 1995 census data.

^cSelf-supplied domestic use was estimated as the rural population (computed as the total population minus the number of people served by public suppliers) multiplied by 75 gallons per day per person.

^dIncludes commercial, livestock, irrigation, and public-supplied commercial and industrial use, as well as public use and distribution-system losses. Descriptions of estimation methodology are on file at the Columbus, Ohio, office of the U.S. Geological Survey.

Table 2. Land-use comparison between 1975 and 1996 for Geauga County, Ohio

[Land use data from Ohio Department of Natural Resources, Division of Real Estate and Land Mangement; modified by Geauga County Planning Commission]

	19	975	1996			
Land-use type	Area (acres)	Percentage of total land	Area (acres)	Percentage of total land		
Residential	24,000	9.2	41,400	15.9		
Commercial	800	.3	2,800	1.1		
Industrial	1,000	.4	1,100	.4		
Agricultural	63,400	24.3	51,500	19.7		
Recreational	2,900	1.1	2,400	.9		
Vacant	49,800	19.1	10,000	3.8		
Institutional	1,000	.4	2,700	1.0		
Forested	105,000	40.2	139,000	53.3		
Mined lands	700	.3	1,000	.4		
Water and marshes	12,400	4.8	9,100	3.5		

During this time, the area of lakes, rivers, streams, and marshes decreased from 12,400 acres to 9,100 acres, and the area of vacant land dropped from 49,800 acres to 10,000 acres (acreage extracted from land-use data furnished by the Geauga County Planning Commission, 1999; see figs. 2 and 3). Most of the urban area is in the western half of the county and the more agricultural area is in the eastern half of the county, as shown in figures 2 and 3.

According to the U.S. Census Bureau, the residential population for Geauga County in 1950 was 26,646 (U.S. Census Bureau, 1998). The number of people residing in Geauga County grew to 47,573 in 1960 and 62,977 in 1970. The population continued to grow at a steady rate of about 1 percent per year during 1970–99, when the total population reached 89,598. The townships of Chester, Russell, and Bainbridge and the southeast corner of Chardon Township are the most densely populated areas (fig. 4). Population growth has necessitated the installation of about 550 new domestic water wells and sewage-disposal systems in the county each year (Geauga County General Health District, 1997).

Hydrogeologic Setting

The bedrock surface in Geauga County consists of eroded sedimentary units dipping to the south at 10 to 20 ft/mi, overlain by glacial sediment from 3 to 400 ft in thickness (Baker, 1964). A detailed description of bedrock and glacial geology of Geauga County

is given by Baker (1964) and Eberts and others (1990). Glacial geology of the county is further described by Totten (1988). Directions of ground-water flow were studied by Nichols (1980), Eberts and others (1990), and Jagucki and Lesney (1995). Stratigraphy of the geologic units underlying the county is summarized in table 3. The water-bearing properties of each unit as described in table 3 indicates that the units primarily used for ground-water supply in the county are the glacial deposits, Pottsville Formation, Cuyahoga Group, and Berea Sandstone. A geologic section showing erosional features of the units is given in figure 5.

The Chagrin Shale, the Cleveland Member of the Ohio Shale, and the Bedford Shale (known collectively as pre-Berea sedimentary rocks) are the oldest units that are exposed in the study area. These units crop out along the sides and bottoms of valleys, but in most places they are completely covered by glacial deposits, which buried preglacial valleys. The pre-Berea units are poorly permeable, and wells completed in these units frequently have yields too low to meet the demands of domestic water supply (Baker, 1964).

The deltaic and shallow marine deposits known as the Berea Sandstone overlie the pre-Berea units. Although the Berea Sandstone underlies much of Geauga County, it is not used for water supply throughout most of the county because it is too deeply buried to be developed economically. The Berea Sandstone is used for water supply near areas where it crops out along the northern, eastern, and western edges of the county. Much of the water produced from

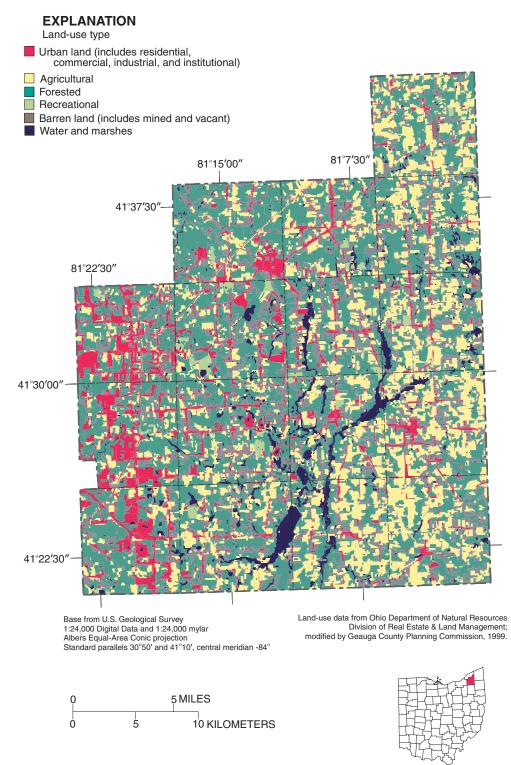


Figure 2. Land use in Geauga County, Ohio, 1975.

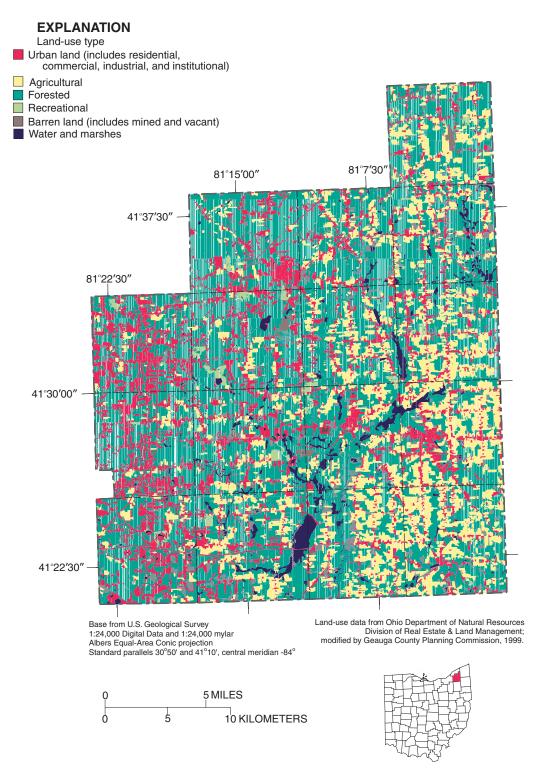


Figure 3. Land use in Geauga County, Ohio, 1996.

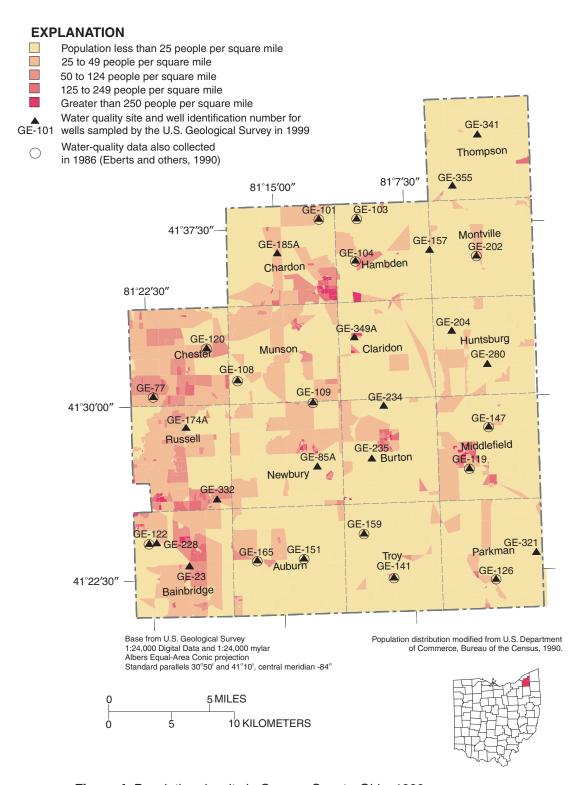


Figure 4. Population density in Geauga County, Ohio, 1990.

Table 3. Summary of stratigraphic units and associated water-bearing properties, Geauga County, Ohio

[Modified from Eberts and others, 1990; >, greater than]

System	Approximate rem Geologic unit maximum thickness (fee		Character of deposits	Water-bearing properties	
Quaternary (Pleistocene)	Glacial deposits	400	Clay, silt, sand, and gravel; deposited by ice and meltwater.	Locally productive aquifer.	
Pennsylvanian	Pottsville Formation: Homewood Sandstone Member Mercer Member Connoquenessing Sandstone Member Sharon Member	200	Sandstone; contains local channels of conglomerate and some shale where not removed by erosion.	Productive aquifer; most extensively developed aquifer in Geauga County.	
Mississippian	Cuyahoga Group: Meadville Shale Sharpsville Sandstone Orangeville Shale	250	Shale and sandstone; interbedded; fine grained.	Leaky confining unit on a regional scale; poorly productive aquifer on a local scale.	
Mississippian	Berea Sandstone	70	Quartz sandstone; relatively well sorted.	Productive aquifer; yields more water at shallow depth than where it is deeply buried.	
Mississippian and Devonian	Pre-Berea sedimentary rocks: Bedford Shale Cleveland Member of the Ohio Shale Chagrin Member of the Ohio Shale	>500	Shale	Poorly permeable; usually does not meet demands of domestic use.	

wells completed in the Berea Sandstone comes from flow through fractures (Baker, 1964).

Overlying the Berea Sandstone is the Cuyahoga Group. This group originated as interbedded, shallow marine shales and sandstones; and because of their poor permeability, they are treated as one hydrologic unit. The Cuyahoga Group is exposed widely, particularly in the eastern part of the county. Even though the unit is poorly productive, it is commonly used for domestic water supply where more permeable, shallower deposits are absent.

In areas where it has not been removed by erosion, the Pottsville Formation overlies the Cuyahoga Group. The Pottsville Formation caps the hilltops in the northern part of the county, underlies most areas in the southern part of the county, and is the most extensively developed aquifer in the county. The Pottsville Formation is divided, from oldest to youngest, into the Sharon Member (consisting of a conglomerate unit overlain by a shale unit), the Connoquenessing Sandstone, the Mercer Shale, and the Homewood Sandstone Members. Because of erosion, the Mercer Shale and Homewood Sandstone Members are absent in most areas of the county. The Connoquenessing Sandstone Member has also been eroded in the northern part of the county and thus is limited mostly to the southern half of the county (Baker, 1964).

Yields of wells completed in the Pottsville Formation are lower in the southern half of Geauga County than in the northern half. This difference in yield from south to north may be due to the relative thickness of the shale unit of the Sharon Member in southern Geauga County (which may limit recharge to the underlying conglomerate unit) and its thinness or absence in northern Geauga County (Baker, 1964).

Most of the bedrock in Geauga County is covered by unconsolidated glacial deposits that range in thickness from about 3 to 400 ft. Glacial deposits are used widely for domestic water supply where they contain large amounts of sand and gravel. The highest yielding wells that tap the glacial deposits are in buried glacial valleys that were filled with a mixture of clay, silt, sand, and gravel by glacial meltwater (Jagucki and Lesney, 1995). Buried-valley locations in the county are depicted in Eberts and others (1990). Confined ground water can be found where poorly permeable ice-lain silt and clay deposits overlie sand and gravel deposits. Wells that tap confined ground water (usually located near the base of hills) often flow without being pumped (Baker, 1964).

Potentiometric-surface maps (figs. 6 and 7) constructed by Jagucki and Lesney (1995) indicate no major inflow of ground water to Geauga County from surrounding areas. Also, gain-loss studies done by the USGS in 1980 (unpublished data on file at the USGS

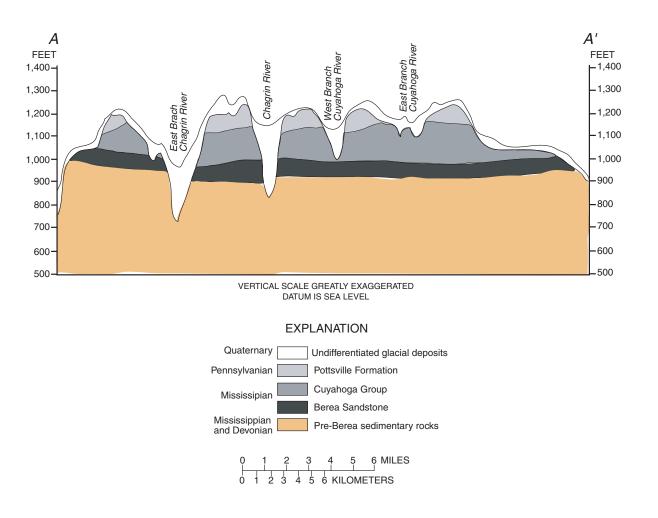


Figure 5. Generalized geologic section of Geauga County, Ohio (from Eberts and others, 1990). Trace of section *A-A'* is shown on figure 1.

office in Columbus, Ohio), show that the streams in the county are all gaining streams (that is, they receive discharge from ground-water sources rather than lose water to the ground-water system). Thus, virtually all ground water within the county originates as precipitation within the county. Most of the precipitation runs off into streams or is lost to the atmosphere through evaporation and (or) transpiration by plants. Pettyjohn and Henning (1979) used base-flow separation of stream hydrographs to estimate that 2 to 8 in. of precipitation per year reaches the water table in Geauga County.

In places where bedrock crops out or is covered only by glacial deposits, recharge occurs by infiltration of precipitation. Ground water in the surficial glacial deposits and Pottsville Formation generally flows from the uplands toward adjacent streams and buried valleys (fig. 6). Primary areas of ground-water dis-

charge include the Cuyahoga River, Chagrin River, and Grand River and their tributary streams (Jagucki and Lesney, 1995).

Where rocks of the Cuyahoga Group and the Berea Sandstone are covered by the Pottsville Formation, recharge occurs as downward flow through the overlying formation(s). The predominant direction of ground-water flow in the Cuyahoga Group is vertically downward from the Pottsville Formation to the Berea Sandstone (Eberts and others, 1990). Ground-water flow within the Berea Sandstone is principally horizontal and radial outward from Hambden and Claridon Townships (fig. 7). Water from the Berea Sandstone discharges to glacial deposits filling buried valleys that cut completely through the Berea Sandstone, such as are found in Chardon, Chester, Munson, and Russell Townships and along the western edge of

EXPLANATION

1250 — WATER-TABLE CONTOUR --Shows altitude of water table.
Dashed where inferred. Contour interval 50 feet.

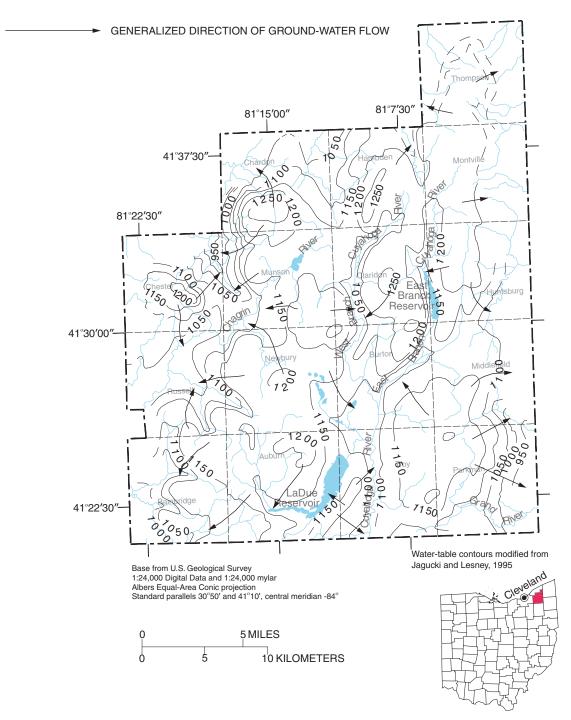


Figure 6. Ground-water levels and direction of flow in the Pottsville Formation and glacial deposits, Geauga County, Ohio, September 6-9, 1994.

EXPLANATION

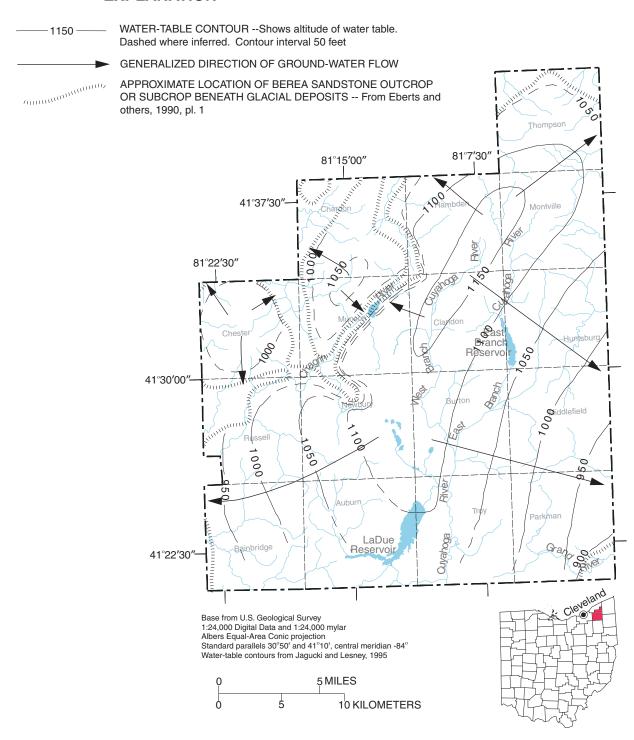


Figure 7. Ground-water levels and direction of flow in the Berea Sandstone, Geauga County, Ohio, September 6-9, 1994.

the county. Ground water also discharges from the Berea Sandstone at outcrop areas along the northern and eastern edges of the county (Jagucki and Lesney, 1995).

PREVIOUS STUDIES

Previous studies of ground-water quality in Geauga County have been done for various purposes and at various scales. These studies, when considered jointly with the data obtained from the current (1999) study, provide an extensive data base of ground-water quality in the county.

Baker and others (1989) completed a statewide study of nitrate in private wells that included data from 132 domestic wells in Geauga County. All samples were collected by well owners on the same day in June 1988 from a cold-water tap near the well. Well owners were instructed to run the tap for 3 minutes prior to sampling and to preferably select a tap that was not affected by any type of in-home water-treatment system. Samples were refrigerated between collection and analysis except while in transit to the laboratory. All 132 wells that were sampled in Geauga County contained nitrate concentrations below the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL)² of 10 mg/L as nitrogen (N). Nitrate concentrations of less than 0.3 mg/L assumed by the researchers to represent natural, background levels — were found in 75 of the 132 sampled wells in Geauga County. Concentrations from 0.3 to 3.0 mg/L were detected in 39 of the 132 sampled wells; according to Baker and others (1989) these values may or may not indicate anthropogenic effects. Concentrations of 3.0 to 10 mg/L were found in 18 of the 132 sampled wells and may indicate anthropogenic effects on water quality, such as fertilizer application to cropland and lawns, septic-system effluent, or proximity to feedlots.

Lesney (1992) examined the causes of spatial variability in ground-water chemistry in the glacial aquifers of the Cuyahoga River Basin, which is predominantly in Geauga, Portage, Summit, and Cuyahoga Counties. Thirty-four ground-water samples and 22 surface-water samples were collected from Novem-

ber 1987 to January 1988 as part of Lesney's study. These samples were analyzed for temperature, pH, specific conductance, Eh, major ions, alkalinity, nitrate, iron, manganese, and strontium. Lesney's data were combined with numerous ground-water-chemistry data from other locations in the Cuyahoga River Basin, obtained from unpublished Master's theses and USGS files. Ground-water data within the boundaries of Geauga County consisted of 12 samples from USGS files, as reported by Nichols (1980) and Eberts and others (1990), and 7 samples collected by Lesney from wells completed in the glacial deposits.

Lesney found that ground water in the glacial deposits of the upper Cuyahoga River Basin (which includes part of Geauga County) was relatively uniform, chemically unevolved water of calcium-magnesium bicarbonate type, with a low dissolved solids content (generally less than 350 mg/L). Lesney found that this water type was controlled by carbonate mineral equilibria and that the waters were undersaturated with respect to the minerals calcite and dolomite, owing to a lesser abundance of these minerals and shorter ground-water residence times in the upper basin than in the lower basin. In the lower Cuyahoga River Basin (which includes parts of Summit and Portage Counties), ground-water chemistry of the glacial deposits exhibited a wider range of water types and dissolved solids concentrations (143 to 2,077 mg/L). Waters in the lower basin generally were saturated or supersaturated with respect to calcite and dolomite. Lesney theorized that a combination of pyrite oxidation and gypsum dissolution, together with longer ground-water residence times in the lower basin, produced the calcium-magnesium sulfate waters found in the lower Cuvahoga River Basin. Sodium bicarbonatetype water found in the glacial deposits of the lower basin was attributed to discharge of sodium bicarbonate waters from the Cuyahoga Group, Berea Sandstone, and pre-Berea bedrock units along the margins of buried valleys. Sodium-chloride-type waters in the lower basin were thought to be caused by discharge of sodium chloride waters from Cuyahoga, Berea, and pre-Berea bedrock units and by infiltration of surface water that had been affected by runoff waters containing dissolved road salt.

Nichols (1980) sampled a total of 12 wells and 2 springs in Geauga County. Four samples collected in May and 10 samples collected in October 1978 were analyzed for major ions and nutrients at all sites. Trace metals were determined in samples from four wells.

²Maximum Contaminant Level (MCL) is the maximum permissible level of a contaminant in water delivered to any user of a public water system. MCLs are enforceable standards (U.S. Environmental Protection Agency, 2000).

The purpose of the study was to assess water quality in the most developed aquifers in the county. These data could serve as a baseline to determine the effects of future ground-water development. Nichols found that, of the constituents analyzed for, only 5 of 14 iron samples and 6 of 14 manganese samples exceeded OEPA water-quality standards (Nichols,1980). Nitrate concentrations in 12 of 14 samples were less than 0.3 mg/L as N, within the range that Baker and others (1989) considered to represent natural, background levels. The other two samples had concentrations of 0.36 and 2.4 mg/L. Elevated concentrations of barium and strontium (above background levels) were found in one well completed in the Berea Sandstone, which may indicate mixing with brines from deeper aquifers.

Eberts and others (1990) sampled 38 domestic and commercial wells in Geauga County in April and May 1986 to document background water quality in the glacial deposits, the Pottsville Formation, the Cuyahoga Group, and the Berea Sandstone. The samples were analyzed for fecal coliform and fecal streptococci bacteria; major ions; nutrients; the trace metals barium strontium and bromide; and phenols and methylene blue active substances (foaming agents). Like Nichols, Eberts found high iron and manganese concentrations to be widespread in the county. The USEPA Secondary Maximum Contaminant Level (SMCL)³ for iron of 300 µg/L (U.S. Environmental Protection Agency, 1988) was exceeded in 20 of 38 samples. The SMCL for manganese of 50 µg/L (U.S. Environmental Protection Agency, 1988) was exceeded in 15 of 38 samples. The highest proportion of exceedances was in water from the glacial deposits. where 7 of 8 samples had iron and manganese concentrations exceeding the SMCL.

Nitrate concentrations in 29 of 38 samples collected by Eberts and others (1990) were less than 0.3 mg/L as N, the concentration that Baker and others (1989) considered to represent natural, background levels. Of the 10 samples in which nitrate was detected, 9 were from the Pottsville Formation. The maximum concentration found was 6.0 mg/L as N, which is less than the USEPA MCL of 10 mg/L as N. Fecal coliform and (or) fecal streptococci bacteria were found in samples from 10 of the 38 wells tested,

at concentrations ranging from less than 1 colony per 100 milliliters (col/100 mL) to 6 col/100 mL. These bacteria were detected in all aquifers. Phenols and methylene blue active substances were present at very low concentrations (less than or equal to 4 μ g/L and 0.07 mg/L, respectively). Bromide/chloride mixing diagrams indicated that waters from at least 5 of the 38 wells sampled were affected by road salt; all five of these wells were completed in the Pottsville Formation. Bromide/chloride data also indicated that waters from at least 1 of the 38 wells was affected by oilfield brine.

Twelve of the wells that were sampled by Eberts and others (1990) had been sampled in 1978 (Nichols, 1980) or in 1980 (unpublished data on file at the USGS office in Columbus, Ohio). Eberts and others (1990) graphically compared the water-quality data from two studies by plotting constituent concentrations as a function of time. No appreciable long-term temporal variations in ground-water quality had occurred between 1978 and 1986.

Water-quality data for 62 wells in Chester Township were compiled by Jenkins (1987) from water-quality records from the Geauga County Board of Health, Ohio Environmental Protection Agency, the USGS, and a homeowner. The records examined reported a variety of analytes, but the major ions sodium, calcium, magnesium, chloride, bicarbonate, and sulfate were available in all the water-quality records. Jenkins noted anthropogenic effects on water quality, including high sodium and chloride concentrations in ground water at one location in southeastern Chester Township. Jenkins attributed the high concentrations to road deicing and (or) contamination from a salt-storage facility prior to 1981.

Richards (1981) analyzed ground-water quality in October 1979 and May 1980, in the South Russell Village area of Russell Township. Richards collected 21 surface-water samples and 29 ground-water samples from the glacial deposits, the Pottsville Formation, the Cuyahoga Group, and the Berea Sandstone. Samples were analyzed for water temperature, pH, specific conductance, alkalinity, chloride, nitrate, iron, sulfate, phosphate, silica, hardness, calcium, fluoride, sodium, and potassium. The pH of six samples from the Pottsville Formation was lower than 7.0 and, thus, outside the 7.0-10.5 range recommended by Ohio Environmental Protection Agency (1994). Acidic precipitation in the area combined with a short groundwater residence time was theorized as the origin of

³Secondary Maximum Contaminant Level (SMCL) is a nonenforceable, esthetically based standard set by the U.S. Environmental Protection Agency for public drinking water. SMCLs are established for constituents that can adversely affect the odor or appearance of water (U.S. Environmental Protection Agency, 2000).

low-pH waters from shallow wells in recharge areas of the Pottsville Formation. Nitrates at concentrations greater than 0.3 mg/L were found in 12 ground-water samples (most of which were from the Pottsville Formation); however, none exceeded the MCL of 10 mg/L (U.S. Environmental Protection Agency, 2000). The SMCL of 300 μ g/L for iron was exceeded in 14 of the 29 ground-water samples. No samples exceeded the SMCL of 250 mg/L for chloride. When comparing the ground-water quality of the four major stratigraphic units in the study area to surface-water quality at base flow conditions, Richards (1981) stated that the quality of the water from the Pottsville Formation most closely resembled that of surface water at base-flow conditions.

Macdonald (1987) analyzed 37 ground-water samples from wells in and adjacent to Russell Township in September and October 1985. Samples were from the four major water-bearing units in the area—the glacial deposits, the Pottsville Formation, the Cuyahoga Group, and the Berea Sandstone. Samples were analyzed for major ions and nutrients. Two of the 37 samples had high sodium and chloride concentrations; the SMCL of 250 mg/L for chloride was exceeded in both samples. Macdonald attributed these elevated concentrations to brine contamination. Two other nearby wells contained water with dissolved-solids concentrations that exceeded the SMCL of 500 mg/L. Macdonald also compared nitrate concentrations in wells from densely populated areas (greater than or equal to 10 houses clustered on lots of less than or equal to 1 acre) to those from sparsely populated areas (lots greater than or equal to 2 acres). Macdonald found that mean nitrate concentrations were statistically higher, at a 95-percent confidence level, in densely populated areas than in sparsely populated areas. All nitrate concentrations, however, were below the MCL of 10 mg/L as N.

Grasso (1986) compared the results of Macdonald's chemical analyses (1987) to those of Richards (1981) to determine whether water quality in the South Russell Village area was changing over time. A one-tailed *t*-test on the two groups of data indicated that the only ion concentration to increase significantly was phosphate; however, samples for the two studies were not collected from the same wells and were collected at different times of the year.

Water quality has been investigated in the county on a more site-specific scale by the Ohio Environmental Protection Agency (OEPA). Four principal

sites of ground-water contamination in Geauga County have been confirmed by the OEPA. A fifth site was investigated for possible manganese contamination, but the manganese was determined to be naturally occurring.

Three of the contaminated sites are in Bainbridge Township. Two sites, in the northern part of Bainbridge Township near McFarland's Corner (fig. 1), were identified in December 1987. These two sites cover about 285 acres and are separated by a groundwater divide. Since 1987, five separate plumes of contamination have been identified at these two sites, affecting both the Sharon Member of the Pottsville Formation and the Berea Sandstone. Three of the plumes contain trichloroethylene, one contains 1,1,1trichloroethane (TCA) and tetrachloroethylene (also known as perchloroethylene, PCE), and one contains benzene and PCE contamination. Benzene concentrations were found at approximately 10 times the MCL. and PCE concentrations in one well were more than 200 times the MCL. In 1996, a public water line that delivers water from Cuyahoga County was completed through the area; however, many of the public water supplies were not financially able to connect to the water line. A 1996 sampling effort also identified contamination in two residential wells and one publicsupply well to the east, beyond the public water line (Ohio Environmental Protection Agency, 1996a).

At a third site in the northwestern corner of Bainbridge Township, OEPA collected 51 ground-water samples from public water supplies and residential wells. The analysis of these samples confirmed the presence of diethyl ether, dichloroethane (DCA), and other volatile organic compounds (VOCs) (Ohio Environmental Protection Agency, 1984). In 1993, water lines were installed in the community to provide potable water to residents (Ohio Environmental Protection Agency, 1996b).

The fourth site of ground-water contamination is in Chester Township at the intersection of U.S. Highway 322 and State Route 306 (fig. 1). Ground water in this area has been affected by road-salt contamination (Ohio Environmental Protection Agency, 1991). The road-salt storage piles that were determined to be the source of the contamination in the late 1970s and early 1980s have since been underlain and covered. The ground water in the Sharon Member of the Pottsville Formation and the Berea Sandstone in the area also contains detectable concentrations of benzene, toluene, ethyl benzene, xylene, and other

chlorinated hydrocarbons. Leaking underground storage tanks at gas stations in the area and behind the police department building were removed or replaced with new tanks equipped with leak-detection systems, and monitoring wells were installed. No new wells may be drilled into the Sharon Sandstone in this area (Ohio Environmental Protection Agency, 1991), and investigation by OEPA is still ongoing.

A fifth site investigated by the OEPA for potential ground-water contamination was the Geauga Industries facility in Middlefield Township (Ohio Environmental Protection Agency, 1995). Groundwater samples were collected at three onsite production wells and 10 offsite residential wells and were analyzed for VOCs, semivolatile organic compounds (SVOCs), pesticides, polychlorinated biphenyls (PCBs), target analyte list metals, and strontium. In 10 the residential samples, the only water-quality problem noted was that manganese and iron concentrations exceeded the SMCLs for these constituents (50 and 300 µg/L, respectively) in 8 of the 10 samples. Manganese concentrations in several of the wells also exceeded the USEPA Removal Action Level (RAL)⁴ of 200 µg/L. The maximum manganese concentration in a residential well was 1,010 µg/L (Ohio Environmental Protection Agency, 1995).

A subsequent, expanded ground-water study (Bolas and Mohr, 1995) examined the occurrence of manganese in local ground water near the Geauga Industries site. Manganese concentrations in 28 residential wells west and south of the Village of Middlefield were determined. Most of the wells were completed in the Pottsville Formation. Manganese concentrations ranged from less than 10 µg/L to 4,060 µg/L. Bolas and Mohr concluded that elevated concentrations of dissolved manganese occur naturally in local pockets within the region and are not confined to areas immediately adjacent to the Geauga Industries facility. Areas of elevated manganese in ground water may be related to variations in (1) the manganese content of bedrock, (2) the manganese content of glacial deposits, (3) the geochemical properties of ground water, such as Eh and pH, and (4) the number of ironand manganese-reducing bacteria in the subsurface.

METHODS OF STUDY

The current study expanded on the previous work by determining whether the undesirable concentrations of water-quality constituents and the anthropogenic effects on water quality that were reported by other researchers have become more widespread and (or) greater in magnitude. The undesirable concentrations reported consistently throughout the studies include those for manganese and iron in ground water that commonly exceed the SMCL. Road salt and, less commonly, oil-field brines have been found to affect ground water. VOCs have been found in ground water at isolated locations that were affected by leaking underground storage tanks containing gasoline or solvents. Nitrate has not been not a widespread waterquality problem, and it has not been detected above the MCL of 10 mg/L as N; however, nitrate has been found in some locations at levels that may indicate anthropogenic effects on the aquifers from fertilizer application or effluent from septic systems.

The current study added an additional time point (after a gap of 11 years) to the temporal data reported by previous researchers. The most recent countywide water-quality sampling prior to this study that analyzed for a wide variety of water-quality constituents was that of Eberts and others (1990) in April and May 1986. The oldest water-quality data for the area were collected by Nichols (1980) in 1978. These two studies provide a good baseline for comparison with the current study because (1) 12 of the wells sampled by Nichols and Eberts and others were common to both studies, (2) many of the properties and constituents analyzed for were the same, (3) both studies analyzed for a broad set of indicators for major water-quality issues, (4) the same laboratory (USGS National Water Quality Laboratory) was used in both studies, and most analytical methods were the same and, therefore, are comparable, (5) both studies sampled waters from the four major aguifers in the county and, (6) the spatial distribution of samples across the county was good in both studies.

To examine current water-quality conditions and to determine changes in water quality since 1978 and 1986, the USGS sampled 31 domestic and commercial wells from June 7 through July 1, 1999. Well locations are shown in figure 1, and well records are summarized in table 4. The following criteria were used in selecting these wells:

⁴The RALs are drinking-water concentrations of compounds that are considered, along with other factors, in determining whether to provide alternate water supplies under Superfund removal authority.

- Resampling for Temporal Analysis Efforts were made to resample wells used in previous USGS studies (Nichols, 1980; Eberts and others, 1990) so that temporal changes in water quality could be assessed. Unfortunately, none of the 12 wells that were sampled in both 1978 and 1986 could be resampled because either (1) the well had been destroyed, (2) permission of the owner could not be obtained, or (3) the well was no longer in suitable condition for obtaining a representative water sample from the aquifer. Of the 26 additional wells that were sampled in 1986, 16 were resampled for the current study. Wells fitted with hand pumps were not resampled because of the difficulty of adequately sterilizing the drinking-fountain discharge fitting on the hand pump so that bacteria samples that were representative of the aquifer could be obtained. Wells sampled in both 1986 and 1999 are shown in figure 4.
- Spatial Distribution Approximately two wells were selected in each township to provide even spatial distribution of data within the county.
- Stratigraphic Distribution Wells completed in each of the primary stratigraphic units in the county were sampled in the quantities indicated: glacial deposits, 8 wells; Pottsville Formation, 10 wells; Cuyahoga Group, 7 wells; and Berea Sandstone, 6 wells. Only wells completed in a single stratigraphic unit were used.
- Flow-system Distribution Wells from recharge zones, discharge zones, and intermediate positions within the flow system were sampled. Flowpath position was determined by use of potentiometric-surface maps (figs. 6 and 7) from Jagucki and Lesney (1995).

Samples were collected from household spigots using the existing plumbing fixtures and well pumps. Well owners identified spigots that provided untreated water. USGS personnel were able to inspect the plumbing at 16 of the 31 sites to verify untreated spigot designations. At only two of the sites (GE-85A and GE-234) was it possible to bypass the pressure tank for sampling.

Upon arrival at a site, clean tubing was attached to the designated sampling spigot. The tubing contained three separate sampling ports—one made of Teflon for VOC sampling, one made of silicon for major-ion and trace-element sampling, and one that connected to a flowthrough chamber for measurement

of pH, specific conductance, temperature, and dissolved oxygen. The flowthrough chamber did not allow contact of the water with air prior to measurement. Even though all wells sampled were in regular use, water was pumped from the well before sampling to eliminate stagnant water that had been standing in the well bore, pressure tank, and pipes and to ensure that subsequent samples reflected the chemistry of water in the aquifer. Purging also helped to condition the sampling equipment and reduce turbidity caused by startup of the pump (Koterba and others, 1995). Purge volume was calculated as:

$$Vp = Vt + [\pi(r^2) \times (WellDepth - StaticLevel)]$$

where

Vp is purge volume, in cubic feet; Vt is pressure-tank volume, in cubic feet; r is inside radius of the well casing, in feet; WellDepth is depth of well from top of casing, in feet; and

StaticLevel is distance from the top of casing to the static water level, in feet.

A volume of water equal to 1.6 to 4.3 purge volumes was removed from each well prior to sampling. Sampling did not begin until successive measurements of pH, specific conductance, dissolved oxygen, and temperature had stabilized.

Before sampling, flow rate through the sampling tube was reduced to 0.1 gal/min, leaving discharge through other tubes at the purge rate. The water was allowed to discharge at the purge rate in an attempt to keep the pump from cycling off after the pressure tank was filled. This procedure also reduced the likelihood of backflow of water stored in adjacent plumbing lines.

VOC samples were collected in 40-mL vials by means of Teflon fill tubes; no headspace was allowed in the bottle (Koterba and others, 1995). Attempts were made to ensure that samples were not collected downwind of car exhaust or other VOC sources. At the one location with a noticeable hydrocarbon odor, an ambient VOC blank sample was collected. Sulfide was determined in the field on an unfiltered sample with a spectrophotometer, by use of the methylene blue method (Hach Company, 1989). Dissolved organic carbon (DOC) samples were filtered through a 0.45-µm silver filter. Other major-ion and trace-element samples were filtered through a 0.45-µm inline

Table 4. Physical characteristics of wells sampled in Geauga County, Ohio, June and July 1999

[LS, land surface; MP, measuring point.]

Well name Site ident	014-114-115-1	Site identifier Latitude	Longitude Towns	T	Township Land surface datum (feet)	MP height (feet above LS)	Aquifer	Open interval (feet below LS)	
	Site identifier			Township				Тор	Bottom
GE-23	412309081202400	41°23'09"	81°20'24"	Bainbridge	1,162	1.32	Pottsville	31	40
GE-77	413028081221000	41°30'28"	81°22'10"	Chester	1,140	2.07	Cuyahoga	80	155
GE-85A ^a	412716081125401	41°27'16"	81°12'54"	Newbury	1,220	2.23	Pottsville	72	140
GE-101	413757081122300	41°37'57"	81°12'23"	Chardon	990	.90	Glacial	48	48
GE-103	413755081101200	41°37'55"	81°10'12"	Hambden	1,158	.40	Berea	133	136
GE-104	413606081102100	41°36'06"	81°10'21"	Hambden	1,215	1.25	Berea	187	204
GE-108	413117081171900	41°31'06"	81°17'19"	Munson	1,120	.60	Glacial	132	132
GE-109	413005081130000	41°30'02"	81°13'02"	Munson	1,280	1.50	Pottsville	89	105
GE-119	412657081040500	41°26'58"	81°04'12"	Middlefield	1,185	1.50	Pottsville	21	79
GE-120	413230081190200	41°32'30"	81°19'02"	Chester	1,115	1.00	Berea	91	135
GE-122	412410081223900	41°24'10"	81°22'39"	Bainbridge	1,010	1.20	Berea	94	135
GE-126	412212081230100	41°22'12"	81°02'53"	Parkman	1,070	1.50	Berea	136	200
GE-141	412224081084300	41°22'24"	81°08'43"	Troy	1,118	.80	Glacial	53	53
GE-147	412845081030100	41°28'45"	81°03'01"	Middlefield	1,120	1.90	Cuyahoga	54	63
GE-151	412319081135000	41°23'19"	81°13'50"	Auburn	1,270	2.30	Pottsville	64.5	148
GE-157	413628081060500	41°36'28"	81°06'05"	Hambden	1,185	1.50	Glacial	36	36
GE-159	412442081102100	41°24'20"	81°10'21"	Troy	1,140	1.40	Berea	237	286
GE-165	412319081163000	41°23'19"	81°16'30"	Auburn	1,165	1.20	Glacial	56	56
GE-174A ^b	412907081202101	41°29'07"	81°20'21"	Russell	1,060	1.15	Glacial	85°	85 ^d
GE-185A	413630081145001	41°36'30"	81°14'50"	Chardon	1,260	.84	Cuyahoga	68.5	90
GE-202	413607081032500	41°36'07"	81°03'25"	Montville	1,247	1.60	Pottsville	51	74
GE-204	413256081045800	41°32'56"	81°04'58"	Huntsburg	1,230	.70	Pottsville	46	53
GE-228	412408081221500	41°24'08"	81°22'15"	Bainbridge	1,060	1.00	Cuyahoga	37	65
GE-234	412948081090000	41°29'48"	81°09'00"	Burton	1,170	1.33	Cuyahoga	40	80
GE-235	412733081094600	41°27'33"	81°09'46"	Burton	1,105	1.81	Glacial	46	51 ^e
GE-280	413127081025900	41°31'27"	81°02'59"	Huntsburg	1,145	1.45	Cuyahoga	62	162
GE-321	412318081003200	41°23'18"	81°00'32"	Parkman	925	2.25	Glacial	89	92 ^f
GE-332	412558081184200	41°25'58"	81°18'42"	Russell	1,180	1.14	Pottsville	48	104
GE-341	414121081030800	41°41'21"	81°03'08"	Thompson	1,267	2.00	Cuyahoga	72	120
GE-349A	413247081103301	41°32'47"	81°10'33"	Claridon	1,190	1.32	Pottsville	16.5 ^g	49.5
GE-355	413910081043900	41°39'10"	81°04'39"	Thompson	1,222	.60	Pottsville	63	71

^aWell GE-85A is near the former location of and is completed at a depth very similar to that of well GE-85, which was sampled in 1978.

^bWell GE-174A was redrilled 20 feet from the location of well GE-174, which was sampled in 1986. The new well is completed about 20 feet shallower in the same formation.

^c Estimated value based on the observation that other wells in the area that are completed in glacial deposits are constructed as open-ended wells.

^d Value reported by owner.

^e Slotted polyvinylchloride (PVC) well screen, 30 slot.

f Stainless steel well screen, 10 slot.

g Estimated value based on construction of adjacent well and the observation that other Pottsville wells in the area are cased through the glacial deposits and have an open hole through the Pottsville Formation.

nylon capsule filter. Trace-element samples were acidified to pH less than 2.0 by use of nitric acid to ensure that trace elements did not precipitate (Koterba and others, 1995). Alkalinity was determined in the field by means of the incremental titration method (Wilde and Radtke, 1998). Tritium samples and some majorion samples were unfiltered. No headspace was allowed in the tritium samples. Tritium samples were collected at each of the 31 wells, and 14 were later selected for analysis on the basis of the following criteria:

- representation of ground water from recharge, discharge, and mid-flowpath positions, as determined from potentiometric-surface maps (figs. 6 and 7) by Jagucki and Lesney (1995),
- spatial distribution of wells completed at various depths,
- representation of ground water from wells completed in the same formation but at locations having various degrees of stratigraphic confinement
- unexpected presence of total coliform bacteria and,
- location of the well along a simulated groundwater flowpath for which residence times were estimated by Eberts and others (1990). The calculated residence time could later be compared to the tritium-analysis results.

Water samples to be analyzed for total coliform and *Escherichia coli* (*E. coli*) were collected after the spigot had been wiped with ethanol, the ethanol had evaporated, and the spigot had been rinsed with sterile water. Bacteria samples were plated in the field, within 30 minutes of collection, using the membrane filtration method with MI agar (Brenner and others, 1993). Samples were incubated at 35°C for 24 hours, after which all blue colonies were counted as *E. coli* and all colonies that fluoresced under a blacklight were counted as total coliforms (Brenner and others, 1993).

All VOC, DOC, and nutrient samples were chilled to 4°C and were shipped overnight to the analyzing laboratory. A VOC screen was done at the USGS office in Columbus, Ohio, by means of a portable gas chromatograph with a heated column and a calibration library consisting of benzene at 3 μ g/L, trichloroethylene at 5 μ g/L, toluene at 3 μ g/L. Nutrients were determined by a water-quality laboratory at Heidelberg College in Tiffin, Ohio. All other properties and constituents were determined by the

USGS National Water Quality Laboratory in Denver, Colo.

The sampling equipment was cleaned between sites to eliminate cross-contamination of samples (Koterba and others, 1995). The sample tubing, filters, and glassware were disassembled and allowed to soak for at least 10 minutes in clean, colorless basins filled with a 0.1 percent solution by volume of nonphosphate detergent in deionized water. Parts were then scrubbed with a brush and rinsed three times with deionized water to remove detergent and particulates. The equipment used for VOC sampling was then rinsed three times with small amounts of methanol and allowed to air dry. When the VOC equipment was dry, it was wrapped with foil.

Bacteria-sampling equipment was rinsed three times with tap water and three times with deionized water and then was sterilized by soaking in a 1/250 dilution of household bleach and tap water for 30 minutes. The equipment was then dechlorinated by soaking in a sterile sodium thiosulfate solution for 5 minutes. After dechlorination, all parts were rinsed at least three times with sterile water. Open ends of tubing and equipment were covered with foil after sterilization.

Quality-assurance/quality-control samples, including field blanks, duplicate samples, and source-solution blanks, were collected for most analytes at the rate of 10 percent to ensure sample integrity and final quality of data. More stringent quality-assurance/quality-control procedures were applied to bacteria and VOCs. Types of quality-control samples and the method and frequency of collection are discussed in more detail in Appendix A.

GROUND-WATER QUALITY

Water-quality data were used to determine (1) suitability of water for drinking, (2) age of ground water, (3) stratigraphic variation in water quality, (4) controls on water quality, and (5) temporal variation in water quality.

Results of analyses of water-quality samples collected in Geauga County in 1999 are listed in table 5 (at back of report). A reference of regulatory drinking-water standards for each of the properties and constituents analyzed for in this study, along with possible sources and effects on ground water, is provided in table 6 (at back of report).

An examination of table 5 makes evident that samples from wells GE-119 and GE-159 contain unusually high concentrations of sodium and unusually low concentrations of calcium and magnesium when compared to other samples. GE-119 and GE-159 also have unusually low concentrations of hardness, iron, manganese, and strontium. This pattern indicates that these water samples were softened by ionexchange methods (Driscoll, 1986). Followup investigation revealed that water from well GE-119 was softened by a water-treatment system at the point sampled; however, no water-treatment devices were used on well GE-159; water in this well is softened by natural geochemical processes and has major ions in proportions that are comparable to those of certain water samples from the Berea Sandstone documented by Lesney (1992) and Richards (1981). Because of the water-treatment system installed on well GE-119, data from this well are omitted from subsequent discussions of sodium, hardness, calcium, magnesium, manganese, iron, and strontium.

Suitability of Water for Drinking

Because no regulatory standards apply to the chemical quality of domestic wells in Ohio, constituent concentrations documented during this study are compared to OEPA standards (Ohio Environmental Protection Agency, 1994) that are enforceable only for public water supplies that serve 25 or more people. The Geauga County General Health District's standard for total coliform bacteria in raw water from newly constructed wells also was used to assess suitability for drinking.

Bacteria. OEPA regulatory standards for total coliform bacteria, as listed in table 6, are established for public-supply wells that are sampled several times a month. Because samples for the current study were collected at only one time point, it is difficult to compare results to the OEPA drinking-water standards. The Geauga County General Health District standard for a newly constructed well is 0 total coliform colonies per 100 mL of water (Bob Wiesdak, Geauga County General Health District, oral commun., 1999). This standard is applicable to domestic wells. Using the criteria of the Geauga County General Health District, water from 16 of the 31 wells exceeded the health-based standard for total coliform. Coliform bacteria are indicator organisms. Some coliform bacteria can occur naturally in the soil, whereas others have a source related to the intestines of humans and other

warmblooded animals. The presence of coliform bacteria indicates a possibility, but not a certainty, that disease-causing organisms also may be present in the water because of contamination from human or other animal wastes. To confirm contamination by a fecal source, the water was analyzed for Escherichia coli (E. coli), a species in the total coliform group that originates in the intestines of humans and other warmblooded animals. E. coli were not detected in any of the wells sampled. Although the presence of E. coli would have confirmed contamination by a fecal source, the absence of E. coli does not rule out fecal waste as one possible source of the total coliform bacteria. The Geauga County General Health District recommends that private wells in which total coliforms or E. coli are detected should be disinfected, because a properly constructed well should not contain coliform bacteria.

Volatile Organic Compounds. The USGS analytical screening for VOCs detected no benzene, toluene, xylene, trichloroethylene, or tetrachloroethylene (also known as perchloroethylene) compounds at the detection limits defined in table 5, which are at or below the MCLs for these compounds. This absence of detections indicates that VOC contamination is not a widespread problem in the county; however, VOCs have rendered water unsuitable for drinking at specific locations identified in the "Previous Studies" section of this report (Ohio Environmental Protection Agency, 1984, 1991, 1996a, and 1996b). It should be noted that USGS personnel were able to bypass the pressure tank at only two of the sites sampled. VOCs would tend to volatilize from the water upon pressurization within the tank, so the results of the USGS analyses for VOCs may be erroneously low.

Nitrate and Nitrite. No samples in either the current study or in any of the investigations described in the "Previous Studies" section of this report exceeded the health-based standard for nitrate (MCL of 10 mg/L as N) in drinking water. The health-based MCL for nitrite (1 mg/L as N) also was not exceeded in the current study. (Nitrite concentrations were not determined separately from nitrate concentrations in the previous studies.)

Esthetic Considerations. Although the SMCL of 250 mg/L for chloride was not exceeded, esthetically based SMCLs were exceeded in the indicated number of wells for pH (8), sulfate (1), dissolved solids (3), iron (19), and manganese (18). Possible implications of not meeting each of these the SMCLs

are listed in table 6. Bolas and Mohr (1995) investigated complaints of high manganese concentrations in ground water of southeastern Geauga County, comparing manganese concentrations in 18 raw and treated water samples from domestic wells. They determined that, although manganese concentrations that exceed the SMCL (50 μ g/L) are common in Geauga County, most properly operating residential water-treatment systems were effective at reducing elevated manganese concentrations to below the esthetically based drinking-water standard.

Although there is no drinking-water standard for hydrogen sulfide (H_2S), its characteristic rotten-egg odor can make drinking water unpalatable. Hydrogen sulfide was detected in 17 of the 31 wells sampled at a detection limit of less than 0.01 mg/L, but it was listed as a chronic odor complaint by only 8 well owners. Hydrogen sulfide concentrations in water can be reduced by use of in-home ozonation systems (Melligan, 2000) or catalytic carbon filters (Brooks, 1998).

Hardness is a term associated with the interaction of water and soap and (or) the encrustations left when water is heated. Because the presence of calcium and magnesium causes most of the observed soap effects, hardness is computed from calcium and magnesium concentrations reported as an equivalent concentration of calcium carbonate (Hem, 1989, p. 158-159). The greater the hardness of the water, the more soap is consumed and the more mineral encrustation is left behind after heating. According to the hardness classification used for this study (table 6), 25 of the 31 samples were hard to very hard water. Only five samples were soft to moderately hard water. (The remaining sample, from well GE-119, was found to be artificially softened.)

Age of Ground Water

The age of ground water has implications for management of water resources. In terms of water supply, ground water that receives some component of modern recharge is being continuously renewed, and its use is potentially sustainable (Clark and Fritz, 1997). In terms of water quality, age of ground water is an indicator of susceptibility of an aquifer to human activities at or near land surface. Ground water that recharged the aquifer after about 1950 is more susceptible to near-surface contamination than older waters because "relatively little time has passed to allow for attenuation of contaminants in the subsurface, and because regulated chemicals have been introduced into

the environment in large quantities since the mid 1940's, following World War II" (Harlow and others, 1999).

Dating of 14 ground-water samples from Geauga County was done by use of tritium analyses (Michel, 1989; Clark and Fritz, 1999). Tritium, whose chemical symbol is ³H, is a radioactive isotope of hydrogen that is naturally produced in the Earth's atmosphere at low concentrations; however, large quantities of manmade tritium were released to the atmosphere from the early 1950s to the mid-1960s by the testing of nuclear weapons. Tritium concentrations increased two to three orders of magnitude with the onset of testing, peaking in 1963 (Michel, 1989). Tritium concentrations in precipitation began declining with the cessation of Soviet and American nuclear atmospheric testing in the mid-1960s. Concentrations of tritium in precipitation during calendar year 2000 at stations in Penola, Ga., and Shenandoah National Park, Va., ranged from 2.7 to 4.3 TU (Robert L. Michel, U.S. Geological Survey, written commun., 2001).

Other than radioactive decay, tritium is not significantly affected by geochemical reactions, so it is thus useful for dating ground water. Estimates of tritium concentration in precipitation that fell in northern Ohio from 1953 to 1983 (and subsequently entered the ground-water system) were made by Michel (1989). Given a half-life of tritium of 12.43 years (International Atomic Energy Agency, 1981), these estimated input concentrations were corrected for radioactive decay up to the time of ground-water sample collection (June and July 1999) and are shown in figure 8. For example, for a well yielding water recharged in 1963 that has not been mixed with waters recharged in other years, the tritium concentration would be 390 tritium units (TU) in a sample collected in 1999. Similarly, radioactive decay has reduced the tritium in waters recharged prior to 1953 to concentrations that are less than 1.8 TU in 1999.

In reality, a sample of ground water is most likely a mixture of several years of precipitation. Thus, only a qualitative interpretation of ground-water ages can be made. Ground-water samples with tritium concentrations less than the detection limit of 1.8 TU are considered to have reached the water table as recharge prior to 1953 or are mixtures of pre-1953 waters and recent recharge with a low tritium concentration. Such waters are referred to in subsequent paragraphs as "predominantly old waters." Waters with tritium con-

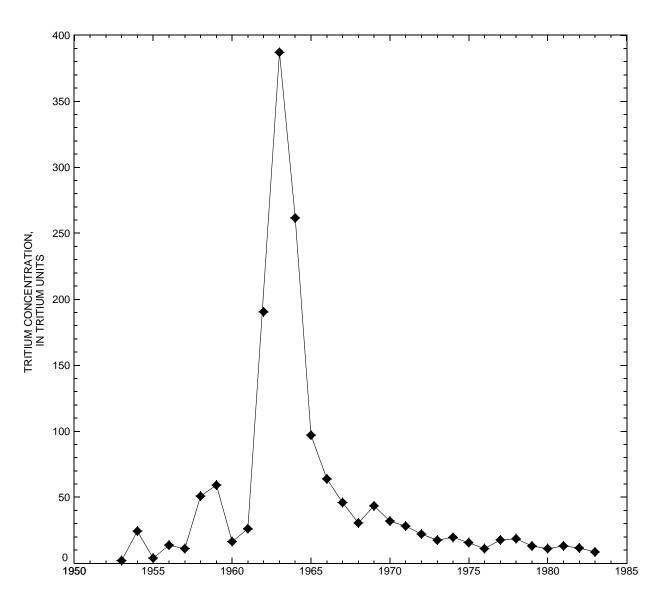


Figure 8. Estimated annual mean tritium concentration, corrected for radioactive decay through 1999, in precipitation that fell in northeastern Ohio, 1953 to 1983. (Tritium concentrations in original precipitation based on tritium deposition estimates by Michel, 1989.)

centrations greater than 1.8 TU are considered to have been recharged after 1953 or consist of a mix of waters containing a component of post-1953 recharge. These waters will be hereafter referred to as "predominantly young waters." The age determination of water with a tritium concentration of greater than 60 TU could be further narrowed to indicate that the water originated as recharge between 1962 to 1966 (fig. 8).

Results of tritium analyses are given in table 5 and are plotted as a function of depth in figure 9. Most waters are predominantly young. Because all young waters contained tritium at concentrations greater than

1.8 TU and less than 60 TU, age of these waters could not be refined beyond a qualitative post-1953 recharge date.

Only three wells (GE-108, GE-120, and GE-202) yielded predominantly old waters. This category included the only sample from the Berea Sandstone (GE-120) that was dated. In the vicinity of GE-120, the Berea is overlain by 78 ft of glacial deposits and 13 ft of Cuyahoga Group. The sample from GE-202 was the only water collected from a location where the shale unit of the Sharon Member is present as the uppermost unit of the Pottsville Formation. Although

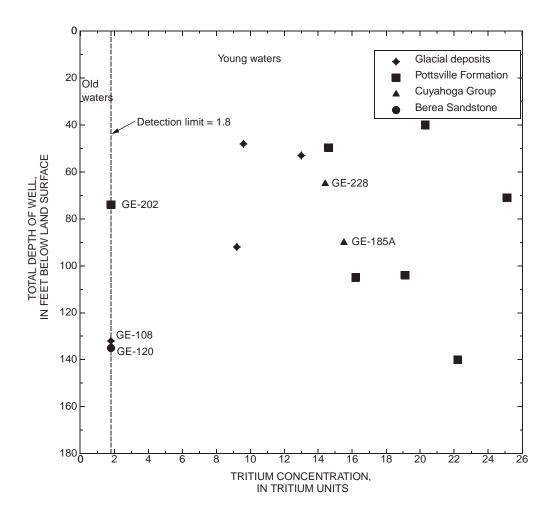


Figure 9. Tritium concentrations in ground water and well depth in Geauga County, Ohio, June and July 1999. (Definitions of old and young waters are given on p. 21)

Pottsville waters were predominantly old at GE-202, samples that were collected from other locations where the Pottsville Formation is not capped by the shale unit were predominantly young—even where the total depth of the well was greater than that of GE-202 (fig. 9).

The glacial waters that were tested for tritium also were predominantly young, with the exception of the sample from well GE-108. The predominantly old age for this well water is problematic. Well GE-108 is relatively deep (132 ft), and the open interval is overlain by 83 ft of clay. Yet, chloride and dissolved solids concentrations in water from this well are low compared to those at other wells (table 5), indicating a short residence time rather than the long one that is indicated by the low tritium concentration. The presence of bacteria in GE-108 also indicates a mixing

with recent recharge. One factor contributing to the low tritium concentration in this well may be its location in a buried valley. The valley formed by erosion through the Pottsville Formation, Cuyahoga Group, Berea Sandstone, and into the pre-Berea bedrock units, and the valley has since been filled with glacial deposits. Eberts and others (1990) and Jagucki and Lesney (1995) determined that waters from the bedrock units discharge into this buried valley. Mixing of young water originating in the glacial deposits with old, deep bedrock water might dilute the tritium concentration at GE-108 to less than 1.8 TU, especially if the water originating from the glacial deposits is very recent (post-1987) recharge with a low tritium concentration.

Two samples of water from the Cuyahoga Group were chosen for analysis. One sample (GE-185A) is

from a location where the shale is overlain by 35 ft of Pottsville Formation, and recharge to the Cuyahoga Group occurs as precipitation seeping through this overlying bedrock. The second sample (GE-228) was collected from an area where the Cuyahoga Group is the uppermost bedrock unit and is overlain by only 9 ft of clay. Waters from both wells, GE-185A and GE-228, were classified as predominantly young.

The tritium data agree with the residence times estimated by Eberts and others (1990) by use of a three-dimensional, steady-state flow model in conjunction with a particle-tracking program. The residence time associated with each simulated flowpath indicates the number of years it would take for a particle of water to travel the entire length of the groundwater flowpath, beginning when the water particle reaches the water table and ending when the water particle discharges to a stream. Approximate residence times estimated by Eberts and others for simulated flowpaths in the Pottsville Formation and (or) the glacial deposits ranged from 15 to 170 years. Residence times for flowpaths in the Berea Sandstone ranged from 70 to 4,800 years.

Among the sites for which samples were dated, three of the wells completed in the Pottsville Formation (GE-85A, GE-109, and GE-349A) lie roughly along three separate ground-water flowpaths simulated by Eberts and others (1990). Eberts and others determined ground-water residence times for the three relevant flowpaths to be 50, 40, and 15 years, respectively. Because wells GE-85A, GE-109, and GE-349A intercept the simulated flowpaths about three-quarters to one-half of the way along the length of the simulated flowpath, one would expect to find water ages that are three-quarters to one-half of the computed residence times (that is, no more than 37.5 years). One would expect waters of this age to be tritiated and classified as predominantly young waters. Tritium dating does, in fact, show the waters from these wells to be predominantly young.

The dating results signify that waters of the glacial deposits, Pottsville Formation, and Cuyahoga Group are all part of the active hydrologic cycle. Thus, as stated previously, waters withdrawn from these stratigraphic units for water supply can be replenished (at least in part), but their quality may be susceptible to influence of human activity.

Stratigraphic Variation in Water Quality

Stratigraphic variation in chemical composition of ground water can be examined by use of a trilinear diagram (fig. 10). This type of trilinear diagram is constructed by converting concentrations of anions and cations to milliequilavents per liter (meg/L) and plotting relative percentages of the major cations on the lower left equilateral triangle and the major anions on the lower right equilateral triangle (Hem, 1989). Each corner on the triangles represents 100 percent of a particular type (or types) of ions. The cation and anion compositions are then projected along a line parallel to the outer edge of the equilateral triangles until the cation and anion projections intersect on a third, diamond-shaped diagram. Plotting of the data in this way makes evident some characteristics of the waters and some constraints that must be considered in interpreting the geochemical evolution of the waters.

Several characteristics need to be considered when interpreting figure 10:

- 1. The data do not plot as distinct groupings by stratigraphic unit. In fact, a range of water types can occur within a single unit.
- 2. The data can be divided into three groups on the basis of predominant anion type:
 - a. Most waters, regardless of aquifer, are dominated by the bicarbonate anion. These bicarbonate-type waters have quite a range of cation types, from calciumdominated waters (predominantly from the glacial deposits and Pottsville Formation) to mixed calcium-magnesiumsodium waters (including waters from every unit except the Pottsville Formation), to sodium-dominated waters. The sodium bicarbonate waters were found at two locations—wells GE-321 (glacial) and GE-159 (Berea).
 - b. The second group of waters are those that would be considered chloride-type waters or waters of mixed anion type (mixtures of chloride, bicarbonate, and sulfate). For the purposes of this report, both types of water will be referred to as chloride-type waters. The four samples in this category (GE-23, 228, 341, and 349A) have at least 45 relative percent chloride, and all are from the Pottsville Formation or the Cuyahoga Group. Cation types in this group are a mixture of calcium, magnesium, and

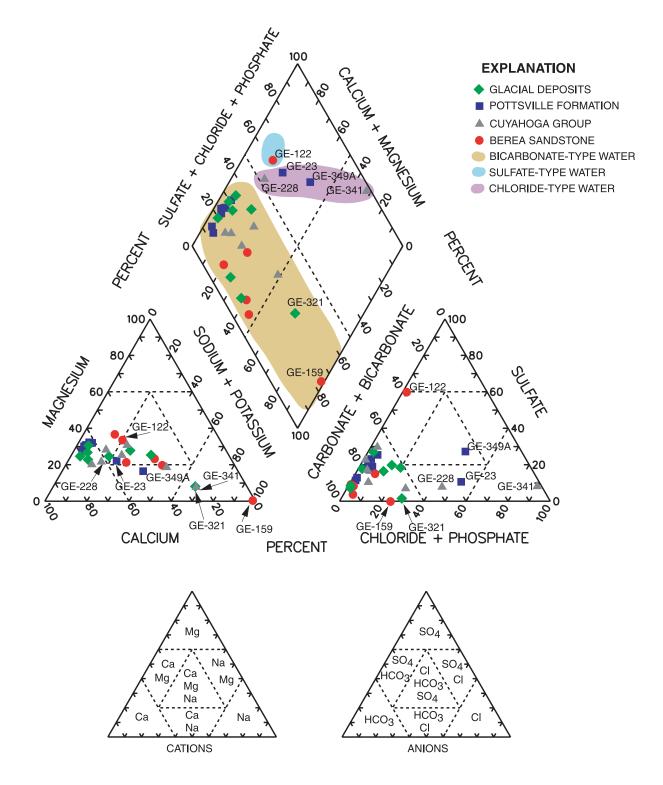


Figure 10. Trilinear diagram of chemical differences in stratigraphic units showing major cation and anion percentages for samples collected in Geauga County, Ohio, June and July 1999.

- sodium, except for GE-341, which is dominated by sodium.
- c. The third type of water is dominated by the sulfate anion. The only sample in this category is GE-122 from the Berea Sandstone, which has approximately 60 relative percent sulfate and would be classified as a calcium-magnesium-sulfate-type water.

The significance of the three types of waters will be discussed in "Controls on Water Quality."

Another visual method for examining differences in water chemistry between the four main stratigraphic units is the use of boxplots (fig. 11). The boxplots allow visual comparison of median concentration, interquartile range (the distribution of the data that lie between the 75th percentile and the 25th percentile), and total range of measured values. Statistical tests (a nonparametric Kruskall-Wallis analysis of variance followed by Tukey's t-test) also were done on each constituent grouped by stratigraphic unit, to determine whether differences were statistically significant at the 95-percent confidence interval (SAS Institute, 1990). Boxplots showing no statistically significant difference between units are indicated by a common letter (such as "A") in figure 11. Boxplots showing a statistically significant difference between units are indicated by a different letter and are referred to as having "significantly different" concentrations in subsequent discussions.

As with the trilinear diagram, the boxplots indicate more similarities than differences between the chemistry of the four stratigraphic units. No statistically significant differences in constituent concentrations between units were found for calcium. magnesium, sulfide, sulfate, chloride, bromide, silica, and manganese. Neither are there significant differences in specific conductance or concentrations of dissolved oxygen, total coliform, hardness, dissolved solids, or organic carbon. The absence of statistical difference is due in part to a large interquartile range as is evident on some of the boxplots. A large interquartile range represents variability in constituent concentration between sampling locations within a stratigraphic unit. Variability of constituent concentrations in the Cuyahoga and Berea waters likely is caused by the varying degrees of stratigraphic confinement of these units. For instance, in some places the full stratigraphic column as shown in table 3 is present, and recharging water must filter through all of these units before making its way to the lower bedrock aquifers. In other locations, the upper bedrock units have been removed by erosion (fig. 5), and recharge waters flow only through the glacial deposits before reaching the Cuyahoga Group or the Berea Sandstone.

In all stratigraphic units, the Geauga County General Health District standard for total coliform in domestic wells was exceeded in at least one location, as well as the SMCLs for iron and manganese. Notable chemical characteristics shown by the boxplots are discussed below for each unit.

Glacial Deposits. Waters of the glacial deposits generally are anoxic; dissolved oxygen concentrations were at or below the detection limit of 0.1 mg/L in seven of the eight samples collected from wells completed in the glacial deposits. Even though the glacial deposits are the uppermost stratigraphic unit in the area and thus might be expected to be oxygenated, well construction in this unit is such that water enters the well only at the bottom of the well. Well screens are not typically used in glacial wells in the area; and because the glacial sediments are unconsolidated, an unscreened hole does not remain open. Therefore, the depth to the top of the open interval for glacial wells, as shown in figure 12, is equal to the total depth of the well (table 4).

Total coliform concentrations are highly variable in the glacial deposits, and include the highest concentration found (120 col/100 mL), as well as the greatest median concentration (6 col/100 mL). Another unusually high constituent concentration, noted as an outlier on the boxplot, is a sodium concentration of 120 mg/L from well GE-321. Chloride concentrations at this well are discussed later in the "Anthropogenic Effects" section of this report. Iron concentrations in six out of eight glacial water samples exceed the SMCL.

Pottsville Formation. Waters from the Pottsville Formation are unique in various ways. First, dissolved oxygen, nitrate, and total coliform concentrations in the Pottsville Formation exhibit a wide range of values and elevated concentrations relative to the other stratigraphic units, although differences are not always statistically significant. The Pottsville Formation has the highest median concentration of dissolved oxygen (0.8 mg/L) and nitrate (0.3 mg/L as N) among the four stratigraphic units. Of the six locations at which nitrate was detected in this study, five were in the Pottsville Formation. Part of the reason for elevated dissolved oxygen and nitrate con-

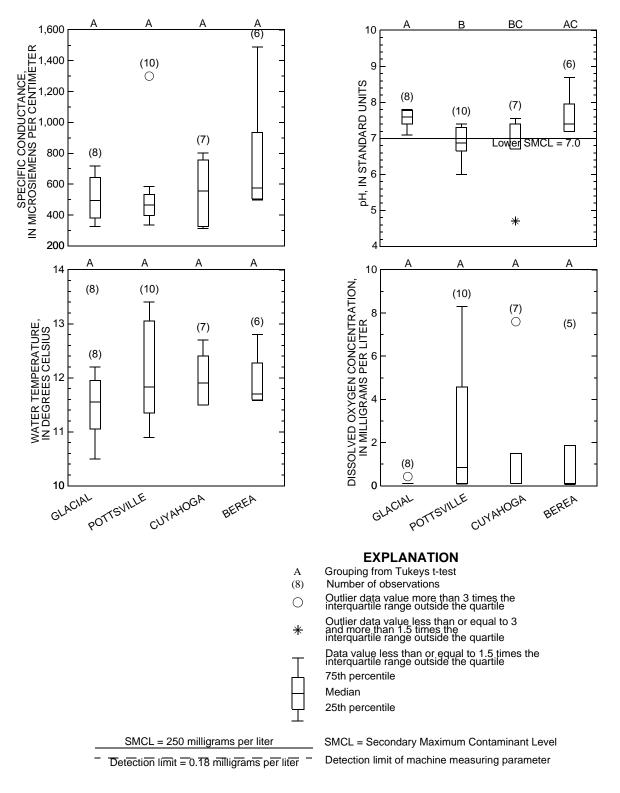


Figure 11. Boxplots of chemical constituents delineated by stratigraphic unit for the 1999 sampling in Geauga County, Ohio. (Sample GE-119 not included in boxplots where constituent concentrations are affected by artificial water-softening system. Results of Tukey's t-test are represented as letters, and concentrations with at least one letter in common do not differ significantly at the 95-percent

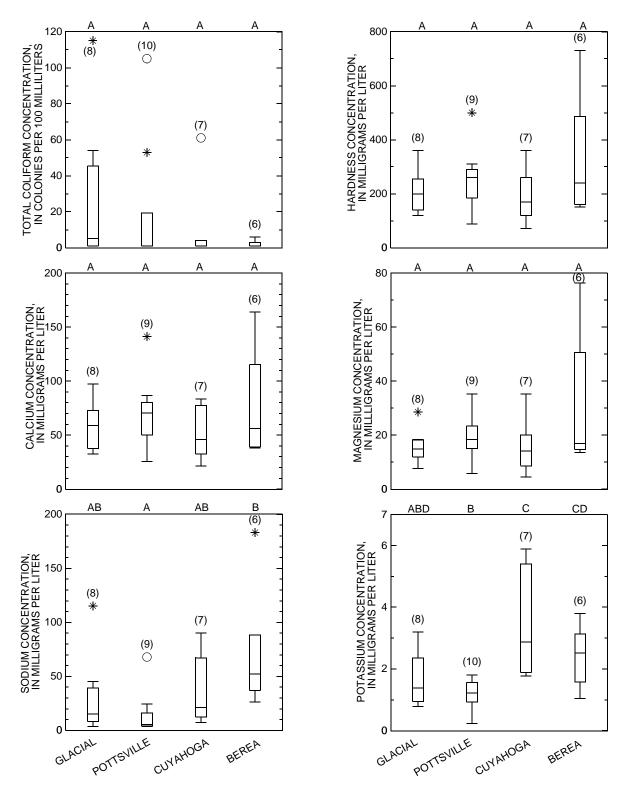


Figure 11. Boxplots of chemical constituents delineated by stratigraphic unit for the 1999 sampling in Geauga County, Ohio —Continued.

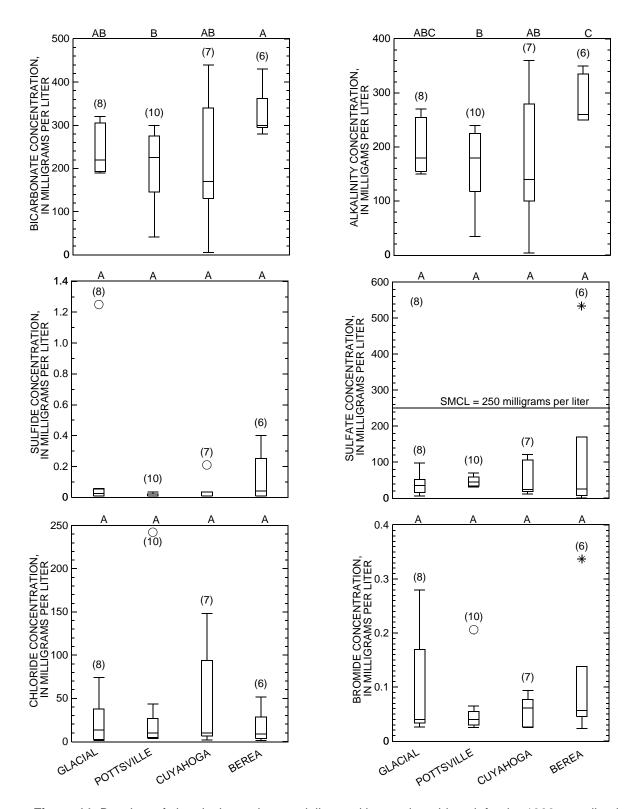


Figure 11. Boxplots of chemical constituents delineated by stratigraphic unit for the 1999 sampling in Geauga County, Ohio —Continued.

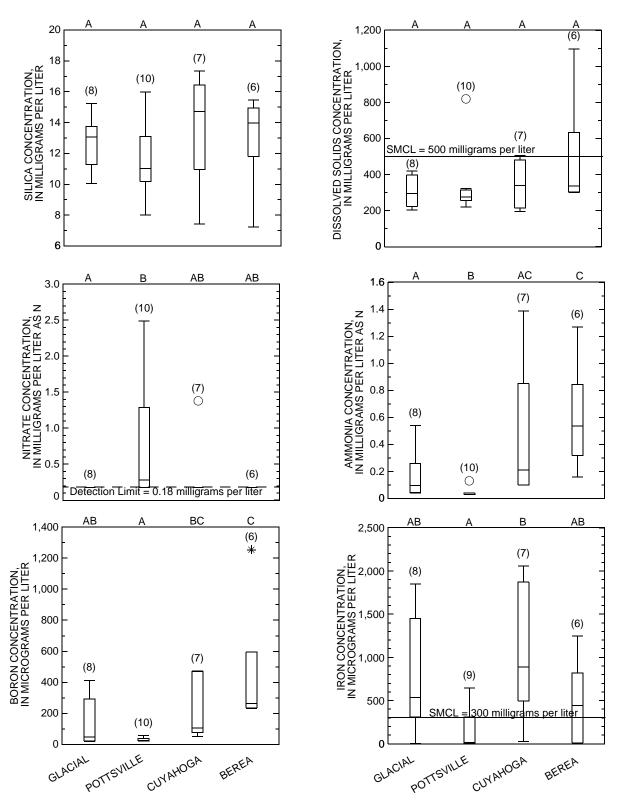


Figure 11. Boxplots of chemical constituents delineated by stratigraphic unit for the 1999 sampling in Geauga County, Ohio —Continued.

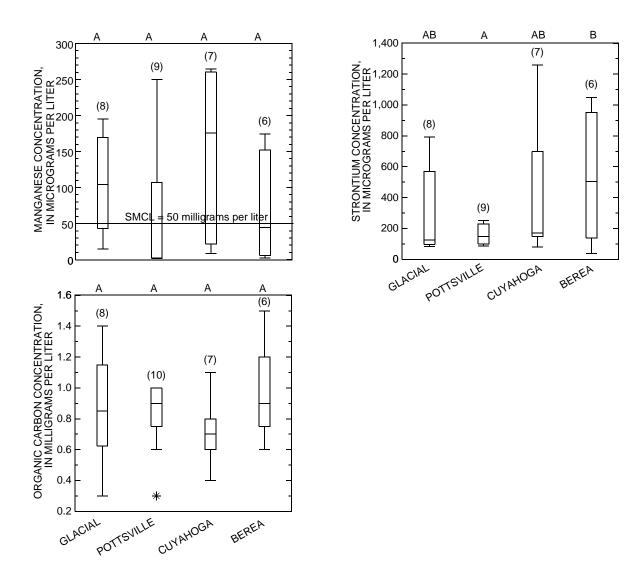


Figure 11. Boxplots of chemical constituents delineated by stratigraphic unit for the 1999 sampling in Geauga County, Ohio —Continued.

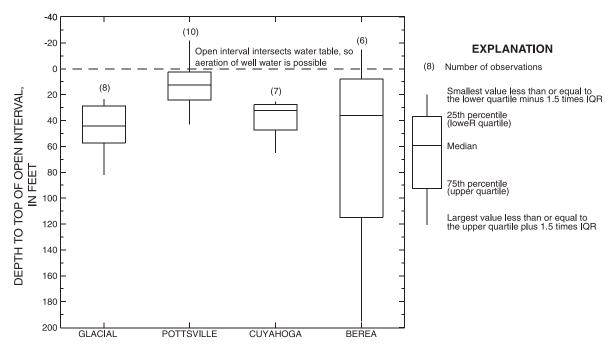


Figure 12. Boxplots of the distance from the water table to the top of the open interval, by stratigraphic unit, for ground-water samples collected in Geauga County, Ohio, 1999. (IQR refers to the interquartile range.)

centrations is that the top of the open interval in the Pottsville wells is much nearer the water table than the top of the open interval in the other three units (fig. 12). Unusually high total coliform concentrations were found in the Pottsville Formation at wells GE-332 and GE-23

(100 col/100 mL and 53 col/100 mL, respectively). Elevated concentrations of dissolved oxygen, nitrate, and total coliform are indicative of recently recharged waters.

Second, less variation is found in this formation than in the other three units for specific conductance, sodium, potassium, sulfide, sulfate, chloride, bromide, dissolved solids, ammonia, boron, iron, and strontium. Low values of specific conductance and dissolved solids generally indicate that ground water was recently recharged and has not had much time to interact with the aquifer minerals. The low variability and concentrations of ammonia, iron, and sulfide can be explained in that the waters generally are oxygenated, and these constituents either precipitate or change to another form in the presence of oxygen. The low variability of the other constituents relative to the Cuyahoga and Berea waters likely results because the Pottsville Formation is the uppermost bedrock unit

and is not affected by varying degrees of stratigraphic confinement as are waters in the Cuyahoga Group and Berea Sandstone.

The median value of pH in the Pottsville waters is below the SMCL range required by OEPA (1994) for drinking waters. Richards (1981) previously noted this problem in the area of South Russell Village and attributed the low pH values in the Pottsville to a combination of acidic precipitation and short ground-water residence times. Because short ground-water residence times do not allow for much dissolution of carbonate minerals from the aquifer materials, one result is minimal neutralization of acidic recharge from precipitation.

Cuyahoga Group. Waters of the Cuyahoga Group are noteworthy mainly for their great variability in concentrations of various constituents (sodium, potassium, bicarbonate, alkalinity, chloride, silica, ammonia, iron, and strontium). As stated previously, erosion of the Pottsville Formation in some areas has left the Cuyahoga overlain only by thin glacial deposits in some areas and by as much as 200 ft of Pottsville Formation in other areas. Eberts and others (1990) found that variation in chemical concentration in the Cuyahoga Group was related to the length of the open

interval of the well, the hydraulic conductivity of the open interval, and the presence of overlying permeable glacial deposits.

Like the Pottsville waters, some Cuyahoga waters have a pH less than the lower limit of 7.0 required by OEPA (1994) for drinking water. The lowest pH found in any stratigraphic unit was in the Cuyahoga Group—a pH of 4.7 at well GE-341. Median iron and manganese concentrations in the Cuyahoga Group both exceed the respective SMCLs.

Berea Sandstone. Ground water within the Berea Sandstone can be distinguished from that of the other units on the basis of median constituent concentrations. Median concentrations of sodium, bicarbonate, alkalinity, ammonia, boron, and strontium in the Berea Sandstone are greater than those in the other three units and are significantly greater than those of the Pottsville Formation. The highest specific conductance and concentrations of hardness, calcium, magnesium, sulfate, and dissolved solids were found in ground-water samples from the Berea Sandstone. High concentrations of dissolved solids are consistent with the longer ground-water residence times in the Berea (70 to 4,800 years relative to residence times in the Pottsville Formation of 15 to 170 years, as estimated by Eberts and others (1990)), which would allow for greater dissolution of aquifer minerals by ground water.

Data collected from wells completed in the Berea Sandstone contain some outliers. Well GE-159 contains more sodium (180 mg/L), bromide (0.34 mg/L), and boron (1,250 mg/L) than was found in any other ground-water sample. The only sample to exceed the SMCLs for sulfate and dissolved solids is from the Berea Sandstone (well GE-122).

Controls on Water Quality

In the preceding section, depth to top of the open (or sampling) interval was noted to affect concentrations of dissolved oxygen, nitrate, and iron. Concentrations of various constituents that were different at a statistically significant level between the Pottsville Formation and the Berea Sandstone were attributed to differences in the length of ground-water residence time. Other factors affecting the differences in ground-water chemistry, as noted in figures 10 and 11, are discussed in the following paragraphs. Effects that are examined include geochemical processes and anthropogenic effects.

Geochemical Processes. Geochemical processes can explain the evolution of the three water types grouped by dominant anion (bicarbonate-, sulfate-, and chloride-type waters), as shown in figure 10. One type of geochemical interaction between ground water and aquifer material is the dissolution and precipitation of minerals. Most waters in Geauga County are bicarbonate-type waters, with the dominant cations being calcium or calcium and magnesium. Dissolution of the carbonate minerals calcite and (or) dolomite is likely the process controlling the evolution of this water type. The glacial tills are one source of carbonate minerals in the area. Totten (1988) indicates that surficial tills in Geauga County are predominantly Hiram and Kent Tills. These tills contain more dolomite (3 to 10 percent by weight) than calcite (0.8 to 4.5 percent by weight) (Ford, 1987; Szabo, 1987).

As shown in figure 10, various samples of bicarbonate-type water contain greater than 20 relative percent sodium. A common process by which sodium is increased in bicarbonate water in aquifers containing abundant clay minerals is dissolution of carbonate minerals combined with cation exchange (Eberts and others, 1990; Lesney, 1992). Cation exchange is a process in which calcium and magnesium ions are removed from solution and replaced by sodium ions on exchangeable sites in clay minerals. As the reaction proceeds, the ratio of calcium ions to sodium ions remaining in solution decreases.

Marine shales, such as the Cuyahoga Group, contain both an abundance of clay minerals and sodium ions on cation-adsorption sites in the clays, a result of the original deposition of the clays in saltwater. Previous researchers (Eberts and others (1990) and Lesney (1992)) attributed sodium bicarbonate waters in the Cuyahoga Group and Berea Sandstone to cation exchange in the Cuyahoga Group, where the waters subsequently leaked downward into the Berea Sandstone. Data from the current study support the assumption that cation exchange is occurring in these stratigraphic units, because ratios of calcium to sodium are much lower for the Cuyahoga Group and Berea Sandstone (mean ratios of 1.5 and 0.79, respectively) than for the glacial deposits and Pottsville Formation (mean ratios of 3.6 and 6.1, respectively). Indeed, the samples collected from wells completed in the Berea Sandstone that contain the greatest proportion of sodium ions are also the only two wells where the Berea Sandstone is overlain by the Cuyahoga Group. Well GE-120, a mixed-cation bicarbonate

water, is overlain by 13 ft of shale, and well GE-159, a sodium bicarbonate water, is overlain by 168 ft of shale.

Sodium bicarbonate-type water would be the end product of cation exchange over a long residence time. Although the current study found no waters from the Cuyahoga Group that are of the sodium bicarbonate type, other researchers (Eberts and others (1990) and Lesney (1992)) have found sodium bicarbonate water at some locations in the Cuyahoga Group. In the current study, sodium bicarbonate water was detected in well GE-159, which is completed in the Berea Sandstone in an area overlain by extensive shale deposits, and sodium bicarbonate water was also detected in well GE-321, in the glacial deposits. Well GE-321 has a total depth of 92 ft, and the open interval is overlain by 14 ft of clay and 45 ft of clayey sand interbedded with 30 ft of sand and gravel. The cation exchange in this area may occur as water flows past adsorption sites on the clays. Alternatively, waters already softened by cation exchange may discharge from the Berea Sandstone into the glacial deposits of the buried valley in which GE-321 is located.⁵

The calcium-magnesium sulfate-type water (fig. 10) of well GE-122 may have evolved from dolomite dissolution by sulfuric acid. This is one process by which Lesney (1992) explained the evolution of calcium-sulfate-type water in glacial deposits of the lower Cuyahoga River Basin. Sulfuric acid is produced by the oxidation of pyrite (Nordstrom, 1982). Pyrite in unoxidized glacial deposits of northeastern Ohio has been reported by Sitler (1963). Pyrite oxidation causes carbonate minerals that are present in the aguifer materials to dissolve. Dissolving dolomite would release calcium, magnesium, sulfate, and bicarbonate to ground water. Dolomite dissolution by sulfuric acid, if allowed to proceed over a period of tens to hundreds of years, will produce calcium-magnesium sulfate-type waters (Eberts and George, 2000; Lesney, 1992).

Although waters from GE-122 were not dated, waters from this well likely have a long residence time. Well GE-122 is completed in the Berea Sandstone at the western edge of the county. A comparison of well location (fig. 1) with ground-water flowpaths in the Berea Sandstone (fig. 7) shows that GE-122 lies

at the end of a long flowpath, near a discharge area for the Berea Sandstone. The residence time along such a flowpath would be on the order of 1,000 years, according to estimates by Eberts and others (1990). In areas upgradient from GE-122, the Berea is overlain by shales of the Cuyahoga Group that are as much as 200 ft thick (Eberts and others, 1990). Cation exchange would be likely in such a setting. The calcium to sodium ratio of water at GE-122 is 2.9, well below the mean ratio of 6.1 for Pottsville waters that are unaffected by ion exchange.

The third type of water shown in figure 10 is chloride-type water or water of mixed anion type (mixtures of chloride, bicarbonate, and sulfate). Such waters are found in four samples (GE-23 and GE-349A from the Pottsville Formation and GE-228 and GE-341 from the Cuyahoga Group). Chloride-type waters probably are the result of road salt and, in some cases, domestic sewage. Evidence supporting this conclusion is discussed in the "Anthropogenic Effects" section of this report.

Anthropogenic Effects. Constituents that were analyzed for during this study and that can have anthropogenic sources (table 6) include nitrate, bacteria, boron, VOCs, organic carbon, and chloride. No VOCs were detected during this study, and organic carbon concentrations were less than the 3 to 4 mg/L that may indicate the presence of hydrocarbons in ground water from sources such as leaking petroleum tanks or landfill leachate (Hem, 1989).

Nitrate

Of the 31 samples from the current study, six had nitrate concentrations greater than 0.3 mg/L as N. Baker and others (1989) consider nitrate concentrations from 0 to 0.3 mg/L to represent background concentrations in Ohio (that is, concentrations that largely are unaffected by human activity). According to Baker and others (1989), concentrations of nitrate greater than 0.3 mg/L may represent anthropogenic effects. As shown in figure 13, all six nitrate detections were found at depths of less than 95 ft. Sample depth in this context refers to distance, in feet, from land surface to the top of the screened or open interval in the well. Five of the six wells in which nitrate was detected are completed in the Pottsville Formation.

Three common anthropogenic sources of nitrate in ground water are large-scale feedlots, agricultural fertilizers, and leaking septic systems. Commercial feedlots are not prevalent in Geauga County, and much of the agricultural land in Geauga County is main-

⁵The presence of a buried valley at this location is based on drillers' logs of wells GE-321 and nearby well GE-126 compared to geologic sections from Eberts and others (1990).

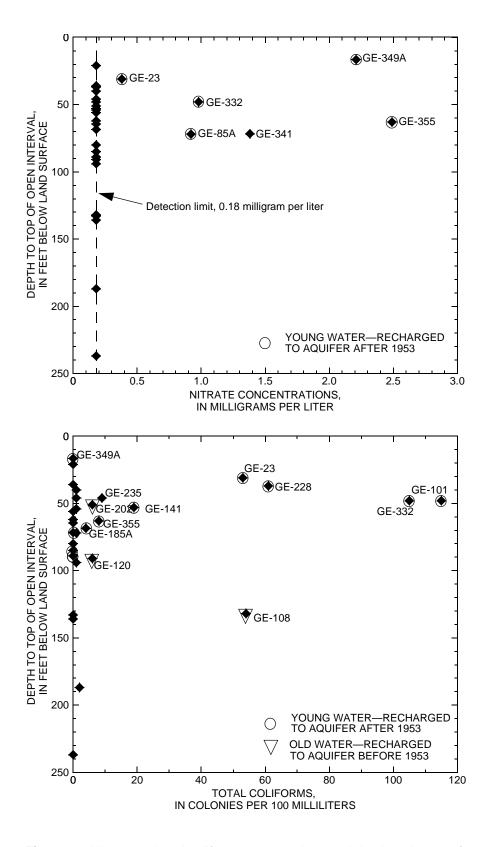


Figure 13. Nitrate and total coliform concentrations and depth to the top of the open interval from land surface for ground-water samples collected in Geauga County, Ohio, 1999.

tained by small family operations and does not rely on large inputs of chemical fertilizer. Therefore, leaking septic systems are the most likely source for nitrate in ground water at concentrations above background levels. Most residents in the county rely on domestic septic systems to treat their wastewater. Leaking septic systems, in addition to elevating nitrate concentrations, can cause elevated concentrations of total coliforms, *E. coli*, boron, sodium, and chloride in ground water (table 6).

Total coliform bacteria

Supporting the idea of possible contamination from septic systems in the county is that total coliforms were detected in 16 of the 31 samples (52 percent) from the current study. This detection rate of 52 percent greatly exceeds the total coliform detection rate of 20 percent documented by Francy and others (2000) for 143 ground-water samples collected in five regions of the United States (including part of northern Ohio). Francy and others found a relation between the presence of septic systems on the property near the sampling site and the detection of coliforms; however, the relation was not statistically significant.

Total coliforms are plotted as a function of depth in figure 13. Five of the six samples with total coliform concentrations greater than 10 col/100 mL are from wells with depths less than 55 ft from land surface to the top of the open interval. Water from these five wells all were categorized as young by tritium dating. The presence of coliforms in waters dated as old (GE-202, GE-120, and GE-108) is problematic because the lifespan of bacteria in the subsurface is considerably shorter than the age of these waters. As stated previously, old waters are considered to have recharged the aquifer before 1953. Bacteria survival times in the subsurface are on the range of days to years and are dependent on temperature, microbial activity, moisture content, pH, salt species and concentrations, soil properties, bacterium type, organic matter, and hydraulic conditions (Yates and Yates, 1988). The presence of total coliforms in old waters can be explained by either (1) the mixing of old waters with septic-system-affected young waters in such small amounts that the tritium concentrations of the mixture were not appreciably changed, or (2) introduction of bacteria into the distribution system from recent plumbing activities or some other type of intrusion. Because GE-108 is in glacial deposits in a buried valley that receives discharge from Cuyahoga Group,

Berea Sandstone, and pre-Berea formations, this water may be a mixture of old and young waters.

Although nitrate, boron, and chloride are possible indicators of septic-system leakage (table 6), concentration of total coliforms in the current study does not correlate with nitrate, boron, or chloride concentration, as determined by use of nonparametric correlation techniques (Spearman's rho = 0.21, -0.18, and -0.03, respectively). If nitrate and total coliforms in ground water are due to septic-system effects, concentrations would be expected to be greater in more densely populated areas. Macdonald (1987) found that mean nitrate concentrations were statistically higher at wells in densely populated areas than at wells in sparsely populated areas near South Russell Village. The current study found a moderate correlation between nitrate concentration and population density (Spearman's rho =0.61) but a poor correlation between total coliform concentration and population density (Spearman's rho = -0.10).

Chloride-to-bromide ratios

Two other anthropogenic effects on ground-water quality in Geauga County are road salting (Jenkins, 1987; Eberts and others, 1990; Lesney, 1992) and oil-field-brine disposal (MacDonald, 1987; Eberts and others, 1990). The county receives, on average, more than 100 in. of snowfall each year, so use of road salt to keep the roads clear is a common practice.

One technique to identify sources of chloride in ground water is the comparison of weight ratios of chloride and bromide concentrations in a sample (Whittemore, 1988; Knuth and others, 1990; Davis and others, 1998). Chloride and bromide are useful indicators because they are both (1) highly soluble, (2) minimally affected by adsorption to sediment once dissolved in water, (3) not altered by oxidation-reduction reactions, and (4) not found in high concentrations in common rock-forming minerals with the exception of evaporite minerals such as halite (NaCl) (Feth, 1981). Differences in ratios of chloride to bromide occur because bromide is even more soluble in water than chloride is (Davis and others, 1998). As seawater evaporates, halite (NaCl) in the residual water becomes saturated and precipitates (crystallizes) first, leaving a residual brine⁶ in which bromide has concentrated. If this halite (either as a natural rock salt

⁶Brine is defined as water having a dissolved-solids concentration greater than 100,000 mg/L (Eberts and others, 1990).

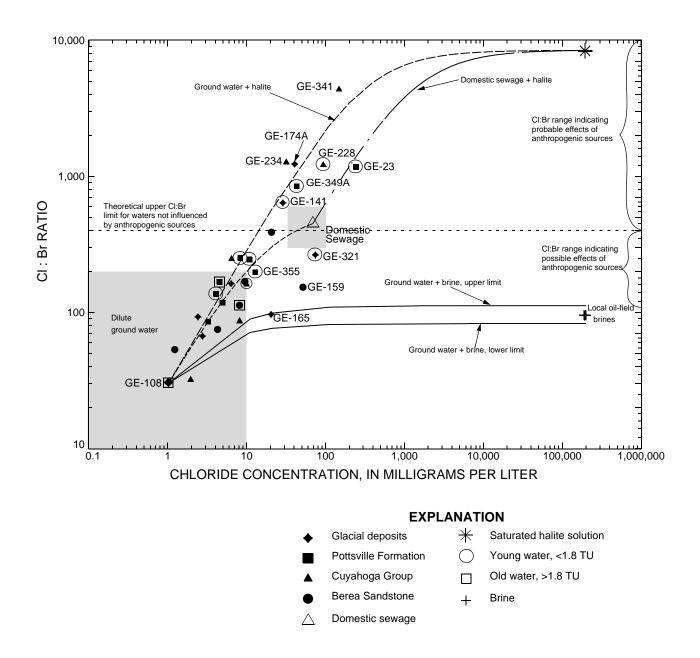


Figure 14. Binary mixing curves for chloride to bromide (CI:Br) ratios, Geauga County, Ohio, 1999. (Halite end-member from Knuth and others, 1990; domestic sewage end-member from Davis and others, 1998, and Peavy, 1978; brine end-member from Eberts and others, 1990.)

deposit or as halite applied as road salt) is subsequently dissolved in freshwater, the water will become enriched in chloride relative to bromide and will thus have a high chloride-to-bromide (Cl:Br) ratio. Residual brines, which can be found in deep aquifers as fossil water that was trapped at the time of rock deposition, will be enriched in bromide relative to chloride and will have a much lower Cl:Br ratio (Davis and others, 1988). Such residual brines often are brought to land surface as a by-product of oil-and-gas production.

Simple binary mixing curves (fig. 14) were prepared, following methods described in Whittemore (1988), to show how the Cl:Br ratio of dilute ground water would change with the addition of increasing amounts of three concentrated solutions: saturated halite solution, oilfield brine, and domestic sewage. These solutions, as well as the dilute, unaffected ground water, are referred to as "end-members" because they represent the starting and stopping points of the possible mixing process.

The sample from well GE-108 was chosen as the dilute ground water end-member because it had the lowest Cl:Br ratio and the lowest chloride concentration. Water from this well also contains no detectable tritium; thus, this water has a component of old water that recharged the aquifer prior to 1953. The Cl:Br ratio of the brine end-member was estimated as the mean of three samples of brine collected by Eberts and others (1990) from local oil and gas wells. The Cl:Br ratio of the saturated halite solution was computed as the mean of three samples of road salt applied in northeastern Ohio (collected by Knuth and others, 1990).

The Cl:Br ratio of the domestic sewage endmember was selected as the midpoint of the range (300-600) reported by Davis and others (1998), based on limited analyses of urban sewage from England and the United States. The chloride concentration of the sewage end-member was estimated as the midpoint of the range (37-101 mg/L) reported by Peavy (1978; cited in Canter and Knox, 1986).

Mixing curves were calculated by use of the following mixing equation (Whittemore, 1988):

$$C_{mix} = (C1 \times V) + C2(1 - V),$$

where

 C_{mix} is the concentration of bromide (or chloride) in the mixture,

C1 is the concentration of bromide (or chloride) in the first end-member water,

C2 is the concentration of bromide (or chloride) in the second end-member water, and V is the volume fraction of the first end-member

Upper and lower limits were added to the ground water plus brine mixing curve by adding 15 percent to the end-member value to account for natural variation and analytical error.

water.

The shaded area designated as dilute ground water in figure 14 is based on Cl:Br ratios reported by Davis and others (1998) and on chloride concentrations reported by Jones and Sroka (1997). Davis and others (1998) reported that shallow ground water, unaffected or only minimally affected by dissolution of halite, generally has a Cl:Br ratio of 100 to 200. Davis and others (1998) also reported that Cl:Br ratios of atmospheric precipitation are generally between 50 and 150, with ratios highest near the coast and decreasing inland. Jones and Sroka (1997) estimated that shallow wells in Ohio that were unaffected by halite dissolution had chloride concentrations less than 10 mg/L. The water samples tritium dated as old and the other samples in the shaded area at the lower lefthand corner of the plot (fig. 14) have ratios consistent with dilute, shallow ground water originating as precipitation and unaffected or only minimally affected by the dissolution of halite. Where the limits of the dilute ground-water area (as drawn) cross the mixing curves, waters contain less than 0.01 percent saturated halite solution, less than approximately 15 percent domestic sewage, and less than 0.01 percent oilfield brine

Mixing of potable ground water with oilfield brines is not a widespread problem in the county (fig. 14). Localized problems are present, however. Only one well from the current study, GE-165, falls along the mixing curve between dilute ground water and brine (volume of brine is 0.01 percent, or 100 ppm). This well is completed in glacial deposits. Eberts and others (1990) sampled another well (GE-105, Hambden Township, completed in Cuyahoga Group) that was not analyzed during the current study with Cl:Br ratios indicative of mixing with oilfield brine. Eberts also sampled three additional wells to investigate homeowner complaints of brine contamination. These three wells had Cl:Br ratios consistent with ground water affected by a mixture of oilfield or residual brine and halite. Well GE-159 (Berea), from the current

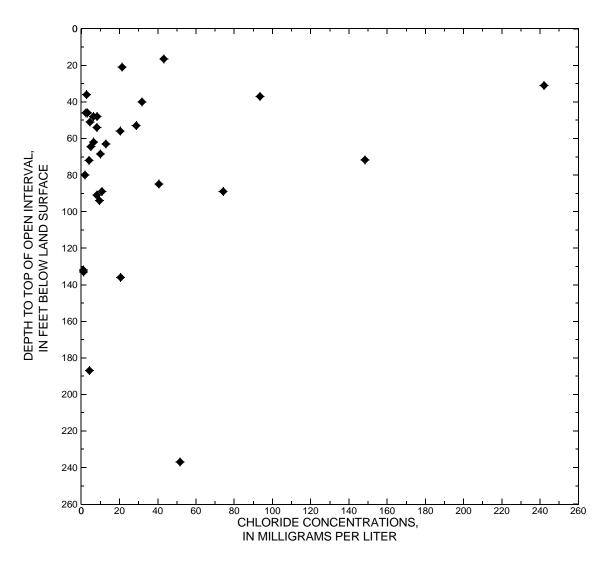


Figure 15. Chloride concentrations and depths of wells sampled in Geauga County, Ohio, 1999.

study, may represent such a mixture. Well GE-321 (glacial) may represent a mixture of dilute ground water, domestic sewage, and oilfield or residual brine. Although the young water from this well completed in glacial deposits plots very near the range of Cl:Br ratios and chloride concentrations in domestic sewage, well GE-321 contains no detectable nitrate or total coliform frequently associated with sewage.

Other wells outside of the "dilute ground water" area lie near or between the mixing lines of dilute ground water with either halite or domestic sewage. In Geauga County, halite is found only in salt deposits at

great depth (about 2,100 ft below land surface). Because ground-water flow through the Cuyahoga Group is predominantly downward and because a graph of chloride concentration in ground water and depth shows that concentrations are generally higher near land surface (fig. 15), halite in these waters must originate from anthropogenic sources rather than as upflow of deep waters that have previously seeped through the deep salt deposits. Anthropogenic sources of halite could be road salt or the high-chloride-content water produced during the regeneration of watersoftening systems. The water used for regenerating the

water softening system is often discharged to septic systems, storm drains, or ditches (Thomas, 2000). Domestic sewage in Geauga County would enter the ground-water system by way of malfunctioning septic systems.

The cutoff for what are considered "dilute ground waters" is rather subjective, so no definitive statements can be made regarding anthropogenic effects on waters that have Cl:Br ratios between 200 and 400. When Cl:Br ratios fall within this range, other factors can be evaluated to determine anthropogenic effects. For example, ground water containing greater than the background concentration of 0.3 mg/L of nitrate may have been affected by human activities (Baker and others, 1989). This criterion can be applied to well GE-355, where a nitrate concentration of 2.5 mg/L indicates possible anthropogenic effects but the Cl:Br ratio of 217 does not definitively point to anthropogenic sources.

Waters having Cl:Br ratios greater than 400 and plotting near or between the mixing lines are considered to have been affected by anthropogenic sources such as road-salt application or leakage from septic systems. No samples from the Berea Sandstone fall into this range, but each of the three other formations have at least one sample that are within the range. The age of waters in this category, if known, are young. Wells plotting to the right of the "ground water + halite" mixing curve (GE-23, GE-141, GE-228, GE-349A) contain total coliform bacteria, consistent with input from a domestic sewage source. Well GE-349A also contains 2.2 mg/L of nitrate, also consistent with a sewage source. Waters plotting just to the left of the "ground water + halite" line in the Cl:Br range of probable anthropogenic effects (GE-174A, GE-234, GE-341) contain no total coliform bacteria. Association of bacteria with road-salt sources would not be expected. Only well GE-341 in this group contains detectable nitrate concentrations. Nitrate in this well could come from runoff of dissolved fertilizer.

Samples whose Cl:Br ratios indicate effects of road salt are indicated in figure 16, which shows chloride concentrations and of distance from the sampled well to the road. A nonparametric correlation analysis of these data shows that chloride concentration is moderately correlated to distance of the well from the road (Spearman's rho = -0.48, p = 0.0067).

In summary, leaking septic systems are a possible source of nitrogen at concentrations greater than background (0.3 mg/L). These concentrations were

found in 6 of the 31 samples, predominantly in those from the Pottsville Formation. The presence of total coliform bacteria in 16 of the 31 samples provides additional evidence that septic-system wastes may be affecting ground water, particularly in the glacial deposits and Pottsville Formation. Ratios of chloride to bromide indicate that dilute ground water, domestic sewage, and road salt may be mixing in four locations, possibly more; however, conclusive evidence of sewage in ground water is precluded by the absence of E. coli in ground water and the absence of correlations of total coliform concentrations to nitrate, boron, and chloride concentration.

Road salt was found to affect ground-water quality in a total of eight samples from wells completed in the glacial deposits, Pottsville Formation, and Cuyahoga Group. Ratios of chloride to bromide for the samples indicate that they are mixtures of dilute ground water with (1) a halite (salt) solution, or (2) domestic sewage and halite (as indicated in the preceding paragraph). Chloride concentration in ground water is somewhat inversely correlated to distance of the well from the road.

Of the anthropogenic inputs affecting groundwater quality as noted above, only total coliform bacteria are present at concentrations that exceed a healthbased drinking-water standard and thereby diminish the suitability of ground-water for drinking. Influences of road salt and sewage in well GE-23 contribute to the exceedance of the esthetically based SMCL for dissolved solids at this location.

Temporal Variations in Water Quality

Two of the many reasons that changes in water quality can occur over time are (1) effects of human activities, and (2) increased pumping of an aquifer, which may begin to draw water from different sources (such as leakage from other aquifers, water from deeper zones, and induced infiltration of surface water). To determine whether water quality has changed over time in Geauga County, wells that were previously sampled by USGS personnel in 1978 (Nichols, 1980) and in 1986 (Eberts and others 1990) were considered for resampling.

Reasons why the 1978 and 1986 data provide a good baseline for comparison with current data were discussed previously (in the "Methods of Study" section). The main limitation of the use of these data as a baseline is the impermanence of wells. (This also is a limitation of the current study.) Because ground-water

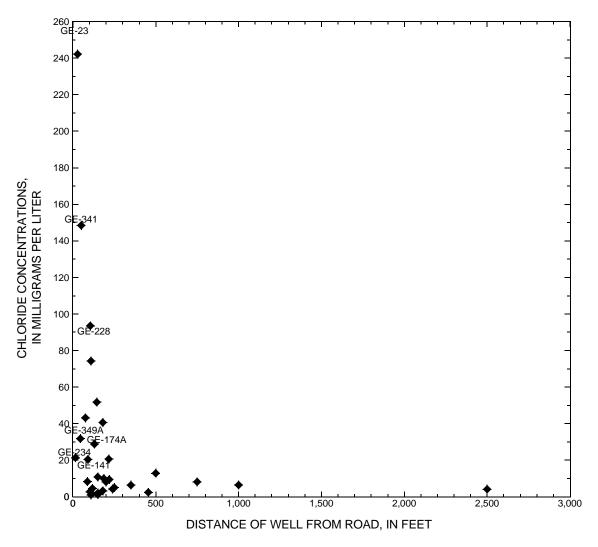


Figure 16. Chloride concentration and distance of well from road for samples collected in Geauga County, Ohio, 1999. (Labeled data poits are samples having a CI: Br ratio as shown in figure 14 that indicates effects of road salt.)

flowpaths in the county are localized (fig. 6), the best comparisons over time are from the same wells.

Although every effort was made to resample as many of the same wells as possible, only 16 of the wells that were sampled in 1986 could be resampled for the current study and none of the wells sampled in 1978 could be resampled. The number of resampled wells was limited because many of the wells that were sampled in previous years were either destroyed, were fitted with hand pumps from which a representative sample could not be obtained, or were inaccessible because new property owners would not allow the

USGS to sample the well in 1999. The 16 wells that were sampled in both 1986 and 1999 were plotted on a population-density map (fig. 4), and none of the wells falls in an area where the population exceeds 250 people per square mile. Therefore, this limited data set reflects temporal variation in the quality of the water from rural areas, but it is probably not a good representation of the temporal variation caused by human activity in the villages of Geauga County where population density exceeds 250 people per square mile. The only way to obtain reliable, comparable data documenting changes in water quality caused by long-term

population growth would be to install and maintain monitoring wells in areas subject to growth. Temporal comparisons could not be made in some townships (fig. 4).

Six constituents detected in both 1986 and 1999 are likely affected by inputs such as road salt, septic leakage, and fertilizer: potassium, ammonia, sulfate, chloride, sodium, and bromide. Bacteria and nitrate data, which also are indicative of changes in human inputs, could not be used in the analysis of temporal variation in ground-water quality. (Bacteria data from the two years were not comparable; fecal coliform bacteria and fecal streptococci bacteria, which were analyzed for in 1986, no longer have an associated regulatory standard; therefore, the 1999 samples were analyzed for bacteria that are currently regulated by OEPA. Wells in which nitrate was detected in 1986

could not be resampled in 1999, and wells in which nitrate was detected in 1999 were all wells that had not been previously sampled.) Boxplots and basic statisticsof the six constituents, grouped by year, are shown in figure 17 and listed in table 7. The boxplots and basic statistics did not reveal any significant changes over time that could be attributed to anthropogenic sources.

For a more robust analyses of the data, two statistical tests were done, a standard two-sample *t*-test and a nonparametric Wilcoxon Rank Test. The two statistical analyses were done on pH, dissolved oxygen, specific conductance, all the major ions, iron, manganese, strontium, and bromide. At a 95-percent confidence level, none of these water-quality characteristics demonstrated a significant difference from 1986 to 1999.

Table 7. Summary ground-water-quality statistics for waters from 16 wells sampled in 1986 and 1999, Geauga County, Ohio

[Abbreviations: <, less than. Standard p-value is the value given for a standard *t*-test with the hypothesis that the mean of the two samples are the same, assuming a normal distribution. The Wilcoxon p-value uses the same hypothesis but does not assume a normal (Gaussian) distribution]

	Minimum	Maximum	Mean	Standard p-value	Wilcoxon p-value
Potassium 1986	0.1	6.4	2.24	0.89	0.92
Potassium 1999	.2	5.9	2.16		
Ammonia 1986	.03	1.4	.37	.85	.88
Ammonia 1999	<.03	1.4	.41		
Sulfate 1986	.90	660	90.6	.82	.86
Sulfate 1999	.14	535	79.2		
Chloride 1986	.80	53	9.49	.49	.29
Chloride 1999	1.0	52	12.7		
Sodium 1986	3.40	190	47.8	.84	.93
Sodium 1999	3.4	180	44.4		
Bromide 1986	<.015	.34	.074	.94	.95
Bromide 1999	.02	.34	.076		

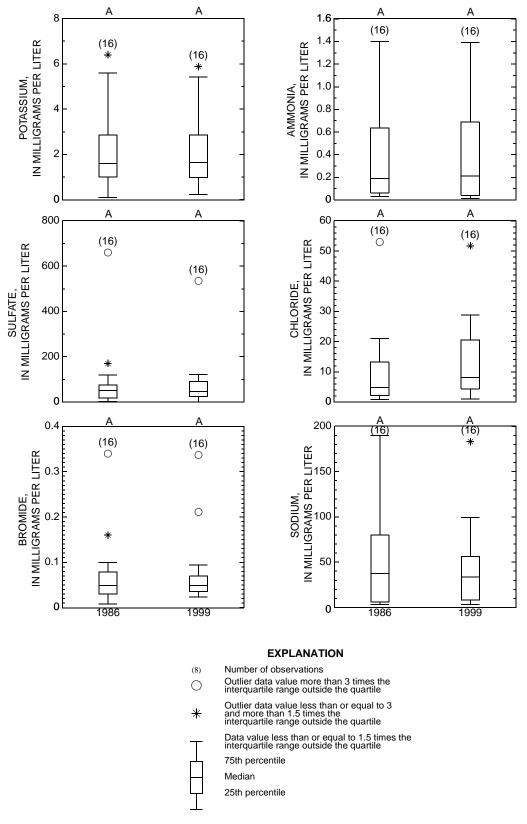


Figure 17. Boxplots of chemical constituents at 16 wells sampled in 1986 and 1999, Geauga County, Ohio. (Results of Tukey's *t*-test are represented as letters, and concentrations with at least one letter in common do not differ significantly at the 95-percent level.)

SUMMARY AND CONCLUSIONS

In 1995, Geauga County residents used 6.82 Mgal/day of ground water. Ground water is the primary source of drinking water for almost 80 percent of the population of Geauga County. To address potential concerns about quality of ground water in Geauga County and to evaluate what effect human activities have on ground-water resources, the USGS, in cooperation with the Geauga County Planning Commission and Board of County Commissioners, assessed water quality in the county in 1999 and compared these data to water-quality data collected by the USGS in 1986 and to data collected by other previous researchers.

Previous studies of ground-water quality in the county (Ohio Environmental Protection Agency, 1996a, 1996b, 1995, 1991, and 1984; Bolas and Mohr, 1995; Lesney, 1992; Eberts and others, 1990; Baker and others, 1989; Jenkins, 1987; Macdonald, 1987; Grasso, 1986; Richards, 1981; Nichols, 1980) have been done for various purposes and at various scales. These studies, when considered jointly with the data obtained from the current study, provide an extensive data base on ground-water quality in Geauga County. The effects reported consistently throughout the studies include manganese and iron concentrations in ground water that often exceed the Secondary Maximum Contaminant Level. Road salt and, less commonly, oil-field brines have been found to affect ground water. Volatile organic compounds (VOCs) have been found in ground water at isolated locations that were affected by leaking underground storage tanks containing gasoline or solvents. Nitrate has not been a widespread ground-water-quality problem and has not been detected above the Maximum Contaminant Level (MCL) of 10 mg/L as N; however, nitrate has been found in some locations at concentrations that may indicate effluent from septic systems or the effects of fertilizer application.

To gather information on the current quality of the ground water, the USGS collected 31 samples from domestic and commercial wells between June 7 and July 1, 1999, using standard field techniques. Samples were obtained from the four primary stratigraphic units used as water supply in the county: glacial deposits, the Pottsville Formation, the Cuyahoga Group, and the Berea Sandstone. All samples were analyzed for VOCs, sulfide, dissolved organic carbon, major ions, trace elements, alkalinity, total coliform and *Escherichia coli* bacteria. Fourteen of the samples

were also analyzed for tritium. Water-quality data were used to determine (1) suitability of water for drinking, (2) age of ground water, (3) stratigraphic variations in ground-water quality, (4) controls on the quality of the water, and (5) changes in ground-water quality since 1986.

Suitability of water for drinking was determined by comparing constituent concentrations documented during this study to Ohio Environmental Protection Agency drinking-water standards for public water supplies and to standards of the Geauga County General Health District. No samples contained nitrate at concentrations above the MCL of 10 mg/L as N. Neither were benzene, toluene, trichloroethylene, tetrachloroethylene, and xylene detected at concentration limits set at levels less than or equal to the MCLs for these constituents.

Esthetically based SMCLs were exceeded in the indicated number of wells for pH (8), sulfate (1), dissolved solids (3), iron (19), and manganese (18). More importantly, water from 16 of the 31 samples exceeded the Geauga County General Health District's standard for newly constructed wells of 0 colonies of total coliform bacteria per 100 mL of water. The detection rate of 52 percent for total coliforms greatly exceeding the total coliform detection rate of 20 percent documented by Francy and others (2000) for 143 groundwater samples collected in five regions of the United States. The presence of total coliforms indicates that disease-causing organisms also may be in the water because of contamination from human or other animal wastes; however, contamination by sewage could not be confirmed because Escherichia coli bacteria, an indicator of fecal contamination, was not detected in any of the water samples.

Fourteen ground-water samples were qualitatively dated by use of tritium analyses. Most waters were considered to contain a component of water that was young, having reached the water table as precipitation after 1953. The young waters included two samples from the Cuyahoga Group—one at a location where the Cuyahoga Group is the uppermost bedrock unit and the other at a location where recharge is through the overlying Pottsville Formation. Three wells yielded old waters that recharged the water table prior to 1953. This category included the only sample from the Berea Sandstone (GE-120) that was dated, as well as the only water collected from the Pottsville at a location where the shale unit of the Sharon Member is present (GE-202). The third sample of old water was

obtained from well GE-108, which is completed in the glacial deposits of a buried valley that receives discharge from the Cuyahoga Group and the Berea Sandstone. Waters at this location likely represent a mixture of old bedrock waters and young waters with a relatively low tritium concentration. The tritium data agree, to the extent that they could be compared, with the residence times estimated by Eberts and others (1990) by use of a three-dimensional, steady-state flow model in conjunction with a particle-tracking program.

Variation in chemical composition of ground water by stratigraphic unit was evaluated by plotting major ions concentrations of the four principal stratigraphic units on a trilinear diagram. The data do not plot as distinct groupings by stratigraphic unit. A range of water types can occur within a single unit.

Ground waters in Geauga County can be categorized in three groups on the basis of predominant anion type: bicarbonate-type waters, sulfate-type waters, and chloride-type water. Most waters, regardless of aquifer, are dominated by the bicarbonate anion. These bicarbonate-type waters contain a wide range of cation types. Bicarbonate-type waters dominated by the calcium- and calcium-magnesium cations are formed by dissolution of the carbonate minerals calcite and dolomite.

Bicarbonate-type waters that include sodium as a major cation are found in every stratigraphic unit except the Pottsville Formation. These sodiumenriched waters are formed when calcium- or calciummagnesium bicarbonate-type waters undergo cation exchange, a geochemical process in which calcium and magnesium ions produced by carbonate dissolution are removed from solution and replaced by sodium ions on exchangeable sites in clay minerals. As the reaction proceeds, the ratio of calcium ions to sodium ions remaining in solution decreases. Data from the current study support the idea that cation exchange is occurring in the Cuyahoga Group, with waters subsequently leaking downward into the Berea Sandstone. Calcium-to-sodium ratios are much lower for the Cuyahoga Group and Berea Sandstone (ratios of 1.5 and 0.79, respectively) than for the Pottsville Formation (6.1). Calcium-to-sodium ratios for the glacial deposits (3.6) are between the ratios for the Pottsville Formation and the deeper bedrock units (Cuyahoga Group and Berea Sandstone), because glacial deposits in buried valleys likely consist of calcium-bicarbonate-type waters that are mixing with

sodium-bicarbonate-type waters that discharge from the Berea Sandstone and Cuyahoga Group into the buried valley.

The only calcium-magnesium-sulfate-type water was obtained from well GE-122 in the Berea Sandstone. This water was likely formed by oxidation of pyrite and concurrent dissolution of dolomite over a period of tens to hundreds of years.

Chloride-type waters were found in four samples (GE-23, 228, 341, and 349A). These waters from the Pottsville Formation and Cuyahoga Group were formed by inputs of road salt and, in some cases, domestic sewage. This origin is supported by ratios of chloride to bromide for these samples. Chloride-to-bromide ratios indicate that four additional non-chloride-type waters also are affected by road salt. Chloride concentration of ground water is somewhat inversely correlated to distance of the well from the road (Spearman's rho = -0.48, p = .0067).

Leaking septic systems are a possible source of nitrogen at concentrations greater than background (0.3 mg/L). These concentrations were found in 6 of the 31 samples. Ratios of chloride to bromide indicate mixing of dilute ground water, domestic sewage, and road salt at four of the sample locations, perhaps more. The detection of total coliforms in 16 of the 31 samples further supports the idea that fecal wastes may be affecting county ground waters, although the absence of E.coli in the waters that were sampled precluded a definitive statement regarding contamination by sewage. Evidence of sewage in ground water is further complicated by the absence of correlation between concentration of total coliforms and nitrate, boron, and chloride concentration, as determined by use of nonparametric correlation techniques (Spearman's rho = 0.21, -0.18, and -0.03, respectively).

Water-quality data from the current study were also compared to data collected in 1986. The 1986 study is a good baseline for comparison with the current study because (1) many of the properties and constituents analyzed for were the same, (2) a broad set of indicators for major water-quality issues was analyzed, (3) the same laboratory (U.S. Geological Survey National Water Quality Laboratory) was used, and most analytical methods were the same and, therefore, are comparable, (4) waters from the four major stratigraphic units in the county were analyzed, and (5) the study had good spatial distribution of samples across the county. The main limitation of the use of the 1986 study as a baseline is that the wells used are imperma-

nent. (This is also a limitation of the current study). Only 16 of the wells that were sampled in 1986 could be resampled for this study because many of the wells were either destroyed, had hand pumps from which a representative sample could not be obtained, or were inaccessible because new property owners would not allow the USGS access to the well in 1999.

Statistical analyses of the 16 wells that were sampled in both 1986 and 1999 did not indicate any significant temporal changes in water quality (at a 95-percent confidence interval). Because none of the 16 wells were in an area where the population exceeds 250 people per square mile, conclusions from statistical analyses of the data set are applicable to temporal variation in the quality of the water from rural areas, but are probably not applicable to temporal variation caused by anthropogenic effects in the villages of Geauga County where population density exceeds 250 people per square mile.

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Table 5. Chemical characteristics of water samples collected in Geauga County, Ohio, June and July 1999

[Well locations are shown in figure 1; Abbreviations: <, less than; μ S/cm, microsiemens per centimeter; col/100 mL, colonies per 100 milliliters; *E.coli*, *Escherichia coli*; mg/L, milligrams per liter; μ g/L, micrograms per liter; TU, tritium units; one TU = 3.24 picocuries per liter; --, not analyzed; NEG, negative detection; boldface type in the station name indicates that water-quality data also were collected in 1986 (Eberts and others, 1990). Footnotes at end of table.]

Station name	Date	Water level, depth below land surface (feet)	Depth of well, total (feet)	Specific conductance (µS/cm)	pH, water, whole, field (standard units)	Temperature, water (degrees Celsius)	Oxygen, dissolved (mg/L)	Coliform, total, water unfiltered (col/100 mL)	E. coli, water, unfiltered (col/100 mL)	Hardness, total (mg/l as CaCO ₃)
-				(GLACIAL DEP	OSITS				
GE-101	06/24/99	24.39	48	665	7.1	11.4	0.1	120	<1	360
GE-108	06/28/99	49.92	132	326	7.8	11.8	.1	54	<1	130
GE-141	06/15/99	9.55	53	502	7.4	11.2	.4	19 ^a	<1	260
GE-157	06/23/99	8.53	36	485	7.6	12.0	.1	<1	<1	170
GE-165	06/08/99	10.72	56	427	7.4	10.5	.1	<1	<1	210
GE-174A	06/14/99	29.13	85	574	7.7	12.2	.1	<1	<1	240
GE-235	06/21/99	13.49	51	365	7.6	11.0	.1	9 ^a	<1	190
GE-321	06/22/99	31.21	92	719	7.8	11.7	.1	<1	<1	120
				РОТ	TSVILLE FOR	MATION				
GE-23	06/29/99	18.20	40	1300	6.9	13.0	1.3	53	<1	500
GE-85A	06/15/99	64.89	140	334	6.8	12.3	6.4	1 ^a	<1	170
GE-109	06/15/99	76.66	105	511	7.4	12.0	.1	<1	<1	270
GE-119 ^b	06/17/99	14.77	79	449	6.3	13.2	.1	<1	<1	.2
GE-151	06/08/99	86.26	148	431	7.3	11.4	.4	<1	<1	230
GE-202	06/22/99	30.28	74	514	7.3	11.7	.1	6 ^a	<1	270
GE-204	06/30/99	11.56	53	479	6.8	11.5	.1	<1	<1	260
GE-332	06/14/99	35.06	104	418	6.8	13.4	3.8	100	<1	200
GE-349A	07/01/99	25.59	49.5	338	6.0	11.2	8.3	1 ^a	<1	88
GE-355	06/30/99	19.88	71	586	7.0	10.9	4.0	8 ^a	<1	310
				(CUYAHOGA G	ROUP				
GE-77	06/08/99	42.53	155	803	7.4	12.1	.1	<1	<1	360
GE-147	06/16/99	6.72	63	757	7.6	11.9	.1	1 ^a	<1	220
GE-185A	06/28/99	36.74	90	325	6.7	11.7	.1	4 ^a	<1	150
GE-228	06/30/99	4.70	65	605	7.0	12.4	.1	61	<1	260
GE-234	06/21/99	14.70	80	313	7.4	11.5	.4	<1	<1	120
GE-280	06/22/99	34.42	162	383	7.0	11.5	7.6	<1	<1	170
GE-341	06/23/99	6.81	120	556	4.7	12.7	1.5	<1	<1	72
				E	BEREA SANDS	TONE				
GE-103	06/24/99	91.19	136	543	7.2	11.8	.1	<1	<1	240
GE-104	06/23/99	98.67	204	507	7.7	11.6	.1	<1	<1	170
GE-120	06/29/99	105.91	135	497	7.4	12.1	.2	6 ^a	<1	150
GE-122	06/07/99	63.80	135	1490	7.2	11.6	.1	1 ^a	<1	730
GE-126	06/17/99	120.65	200	608	7.4	11.6	.1	<1	<1	240
GE-159	06/16/99	41.77	286	749	8.7	12.8	6.9°	1ª	<1	7

Table 5. Chemical characteristics of water samples collected in Geauga County, Ohio, June and July 1999 — Continued

[Well locations are shown in figure 1; Abbreviations: <, less than; μ S/cm, microsiemens per centimeter; col/100 mL, colonies per 100 milliliters; *E.coli*, *Escherichia coli*; mg/L, milligrams per liter; μ g/L, micrograms per liter; TU, tritium units; one TU = 3.24 picocuries per liter; --, not analyzed; NEG, negative detection; boldface type in the station name indicates that water-quality data were also collected in 1986 (Eberts and others, 1990). Footnotes at end of table.]

Station name	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)	Potassium, dissolved (mg/L as K)	Bicarbonate, water, field (mg/L as HCO ₃)	Carbonate, water, field (mg/L as CO ₃)	Alkalinity, water, field (mg/L as CaCO ₃)	Sulfide, total (mg/L as S)	Sulfate, dissolved (mg/L as SO ₄)
				GLACI	AL DEPOSITS				
GE-101	97	29	8.1	1.7	320	0	270	1.2	97
GE-108	33	12	21	1.4	190	0	150	.06	14
GE-141	75	18	8.2	1.1	220	0	180	.05	53
GE-157	41	17	45	3.2	290	0	240	<.01	19
GE-165	63	13	9.0	.9	200	0	170	.01	37
GE-174A	67	18	23	2.6	220	0	180	<.01	52
GE-235	55	12	3.4	.8	190	0	150	<.01	34
GE-321	37	7.7	120	1.4	310	0	260	.04	5.7
				POTTSVII	LLE FORMATION				
GE-23	140	35	68	1.6	290	0	240	<.01	68
GE-85A	45	15	4.0	1.2	150	0	120	<.01	38
GE-109	70	22	5.6	1.0	260	0	210	<.01	47
GE-119 ^b	.06	.03	99	.2	130	0	110	.02	70
GE-151	62	17	3.5	.9	200	0	160	<.01	44
GE-202	72	23	7.8	1.6	300	0	240	.02	32
GE-204	74	18	4.5	1.2	250	0	200	.04	31
GE-332	55	15	5.0	1.4	180	0	150	.03	53
GE-349A	26	5.8	24	1.8	42	0	34	<.01	35
GE-355	87	24	5.9	.9	270	0	220	<.01	55
					HOGA GROUP				
GE-77	84	35	46	5.9	440	0	360	<.01	110
GE-147	55	20	90	5.4	340	0	280	.02	120
GE-185A	46	8.7	7.5	2.9	170	0	140	<.01	19
GE-228	77	17	21	1.8	170	0	140	.21	24
GE-234	33	10	15	3.2	130	0	100	.01	12
GE-280	46	14	12	1.9	200	0	160	.04	36
GE-341	21	4.6	67	2.4	5	0	4	<.01	20
					SANDSTONE				
GE-103	56	25	26	2.9	340	0	270	<.01	27
GE-104	40	16	50	2.7	300	0	250	.01	23
GE-120	38	14	57	2.4	300	0	250	<.01	10
GE-122	160	76	55	3.8	430	0	350	.07	530
GE-126	66	17	41	1.8	300	0	250	.20	48
GE-159	1.8	.54	180	1.0	280	60	330	.40	.1

Table 5. Chemical characteristics of water samples collected in Geauga County, Ohio, June and July 1999 — Continued

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Station name	Chloride, dissolved (mg/L as Cl)	Bromide, dissolved (mg/L as Br)	Silica, dissolved (mg/L as SiO ₂)	Solids, residue at 180 degrees Celsius, dissolved (mg/L)	Nitrogen, nitrate, dissolved (mg/L as N)	Nitrogen, nitrite, dissolved (mg/L as N)	Nitrogen, ammonia, dissolved (mg/L as N)	Nitrogen, ammonia + organic, dissolved (mg/L as N)	Phosphorus, dissolved (mg/L as P)
				GLACL	AL DEPOSITS				
GE-101	6.4	0.04	15	420	< 0.18	< 0.02	0.13	0.188	< 0.02
GE-108	1.0	.03	13	207	<.18	<.02	.26	.266	<.02
GE-141	29	.04	11	306	<.18	<.02	.04	<.005	<.02
GE-157	2.7	.04	14	283	<.18	<.02	.54	.482	<.02
GE-165	20	.21	10	272	<.18	<.02	.04	<.005	<.02
GE-174A	41	.03	11	330	<.18	<.02	.06	<.005	<.02
GE-235	2.4	.03	13	203	<.18	<.02	.05	.117	<.02
GE-321	74	.28	13	418	<.18	<.02	.25	.208	<.02
				POTTSVIL	LE FORMATIC	N			
GE-23	240	.21	15	820	.38	<.02	.03	<.005	<.02
GE-85A	4.1	.03	12	220	.92	<.02	.03	<.005	<.02
GE-109	11	.04	12	286	<.18	<.02	.04	<.005	<.02
GE-119 ^b	21	.02	11	283	<.18	<.02	<.03	<.005	<.02
GE-151	5.0	.04	10	267	<.18	<.02	.04	<.005	<.02
GE-202	4.5	.03	16	312	<.18	<.02	.13	.099	<.02
GE-204	3.2	.04	11	265	<.18	<.02	<.03	<.005	<.02
GE-332	8.3	.03	9.4	266	.98	<.02	.04	<.005	<.02
GE-349A	43	.05	8.0	231	2.2	<.02	<.03	<.005	<.02
GE-355	13	.06	11	321	2.5	<.02	<.03	.014	<.02
				CUYAH	HOGA GROUP				
GE-77	2.0	.06	17	507	<.18	<.02	1.4	1.19	<.02
GE-147	8.1	.09	15	480	<.18	<.02	.85	.786	<.02
GE-185A	10	.06	15	213	<.18	<.02	.20	.145	<.02
GE-228	93	.08	15	361	<.18	<.02	.10	<.005	<.02
GE-234	32	.02	11	194	<.18	<.02	.36	.335	<.02
GE-280	6.4	.03	16	260	<.18	<.02	.21	.233	<.02
GE-341	150	.03	7.4	338	1.4	<.02	.10	<.005	<.02
					SANDSTONE				
GE-103	1.2	.02	15	318	<.18	<.02	.37	.376	<.02
GE-104	4.3	.06	13	302	<.18	<.02	.70	.654	<.02
GE-120	8.1	.07	15	301	<.18	<.02	.65	.487	<.02
GE-122	9.5	.06	13	1100	<.18	<.02	1.3	1.27	.02
GE-126	21	.05	15	354	<.18	<.02	.16	<.005	<.02
GE-159	52	.34	7.2	479	<.18	<.02	.42	.330	<.02

Table 5. Chemical characteristics of water samples collected in Geauga County, Ohio, June and July 1999 —Continued

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Station name	Phosphorus, ortho, dissolved (mg/L as P)	Boron, dissolved (μg/L as B)	Iron, dissolved (μg/L as Fe)	Manganese, dissolved (μg/L as Mn)	Strontium, dissolved (μg/L as Sr)	Tritium, total (TU)	Tritium precision estimate (TU)	Carbon, organic, dissolved (mg/L as C)	Volatile organic compounds, screen (µg/L) ^d
				GLACIAL DE	EPOSITS				
GE-101	< 0.01	49.5	1600	120	250	9.6	±1.4	1.0	NEG
GE-108	<.01	167	440	34	680	<1.8	±1.0	.6	NEG
GE-141	<.01	27.3	890	200	110	13.0	±1.4	.7	NEG
GE-157	<.01	336	290	15	790			1.0	NEG
GE-165	<.01	18.3	1900	180	84			.3	NEG
GE-174A	<.01	46.1	<10	120	140			1.2	NEG
GE-235	<.01	19.8	630	72	100			.7	NEG
GE-321	<.01	413	360	92	96	9.2	±1.4	1.4	NEG
				POTTSVILLE FO	ORMATION				
GE-23	.01	36.5	10	2 ^e	220	20.3	±1.8	1.0	NEG
GE-85A	<.01	21.5	<10	<3	100	22.2	±2.0	.6	NEG
GE-109	.02	25.9	300	110	250	16.2	±1.6	.9	NEG
GE-119 ^b	<.01	25.0	18	6	<1			.9	NEG
GE-151	<.01	26.0	310	96	96			.3	NEG
GE-202	<.01	45.6	640	100	230	<1.8	±1.0	.8	NEG
GE-204	.01	22.2	170	250	160			1.0	NEG
GE-332	<.01	21.5	<10	<3	100	19.1	±1.8	.9	NEG
GE-349A	<.01	56.5	15	<3	88	14.6	±1.6	.8	NEG
GE-355	.01	21.8	<10	<3	150	25.1	±2.0	1.0	NEG
				CUYAHOGA	GROUP				
GE-77	<.01	471	890	22	1300			.7	NEG
GE-147	<.01	473	490	9	700			1.1	NEG
GE-185A	.01	107	2100	190	160	15.5	±1.6	.7	NEG
GE-228	.02	75.6	1900	180	150	14.4	±1.6	.6	NEG
GE-234	<.01	335	560	69	260			.4	NEG
GE-280	<.01	86.5	1800	260	170			.8	NEG
GE-341	<.01	50.8	28	260	81			.7	NEG
				BEREA SANI	OSTONE				
GE-103	<.01	231	680	174	920			1.0	NEG
GE-104	<.01	375	310	7	640			.8	NEG
GE-120	<.01	256	9e	25	360	<1.8	±1.0	.8	NEG
GE-122	<.01	273	1200	63	1000			.6	NEG
GE-126	<.01	238	570	140	170			1.1	NEG
GE-159	<.01	1250	<10	2 ^e	37			1.5	NEG

^a Estimated count based on a non-ideal colony count. An ideal colony count, necessary for accurate enumeration, is greater than or equal to 20 and less than or equal to 80 colonies per filter.

^b Although efforts were made to collect untreated water that would be representative of the aquifer, the high sodium concentration and unusually low concentrations of hardness, calcium, magnesium, iron, manganese, and strontium suggest that this water sample was artificially softened by ion-exchange methods.

^c Anomalously high dissolved oxygen concentration. Dissolved oxygen increased after 45 minutes of purging, but all other field parameters remained stable.

^d Samples were screened by means of a portable gas chromatograph with a heated column and a calibration library consisting of benzene at 3 μ g/L, trichloroethylene at 5 μ g/L, toluene at 3 μ g/L, perchloroethylene at 5 μ g/L, and xylene at 13 μ g/L. NEG means not detected at stated levels.

^e Estimated values are lower than the lowest calibration standard but higher than the detection limit of the machine.

Table 6. Concentration limits defined by primary and secondary public drinking-water regulations and implications for domestic water use and ground-water geochemistry for selected properties and chemical constituents in water samples collected in Geauga County, Ohio, June and July, 1999

[USEPA, U.S. Environmental Protection Agency; OEPA, Ohio Environmental Protection Agency; MCL, Maximum contaminant level; SMCL, Secondary maximum contaminant level; DWEL, Drinking water equivalent level; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; CaCO₃, calcium carbonate; TU, tritium units; mL, milliliters; *E. coli, Escherichia coli*; >, greater than. MCLs, SMCLs based on standards set by the Ohio Environmental Protection Agency (1994) and DWELs are based on standards set by the U.S. Environmental Protection Agency (2000). Geochemical implications of each water property as they relate to this study are modified from Dumouchelle and others (1993), the discussion of natural water chemistry given by Hem (1989) and Driscoll (1986), and a discussion of bromide/chloride ratios given by Davis and others (1998).]

Constituent or property	Concentration limits and water-use implications	Implications for ground-water geochemistry
Specific conductance, μS/cm	Regulatory standards not established with respect to drinking water.	Proportional to total ionic concentration in solution. May be used to distinguish between different water types in an aquifer
pH, standard units	The SMCL requires values between 7.0 and 10.5. Values outside this range may be corrosive to metal well casings and pipes, creating costly replacement problems. A pH below 6.5 can generate health-related problems by dissolving small quantities of trace metals such as lead, especially in a house built before lead solder was banned in 1987.	General measure of the acidity or alkalinity of a water sample. One of the most important properties with respect to regulating the transport of metals, organics, and other dissolved constituents in ground water. Also controls dissolution-precipitation reactions in the aquifer.
Temperature, degrees Celsius	Regulatory standards not established with respect to drinking water.	Needed for speciation and saturation-state calculations. Can be used to identify recharge-discharge zones.
Dissolved oxygen, mg/L	Regulatory standards not established with respect to drinking water.	Atmospheric oxygen dissolves in shallow ground water, and its presence at concentrations exceeding 0.5 mg/L indicates oxidizing conditions. Oxygen reacts with organic matter, nitrate, ferrous iron, or sulfidebearing minerals and is quickly removed from the aquifer. The presence of dissolved oxygen in deep parts of an aquifer indicates rapid recharge rates or a lack of oxidizable material (organic matter, sulfide minerals) in aquifer rocks and sediments.
Total coliform bacteria, colonies/100 mL	The MCL states that for systems with more than 40 samples per month no more than 5 percent of the samples can be total coliform-positive. For water systems that collect fewer than 40 samples per month, no more than one sample can be total coliform-positive. All total coliform-positive samples must be retested for fecal coliforms.	Total coliform bacteria are indicator organisms that, when present, indicate that there is a possibility, but not a certainty, that disease-causing organisms may also be present in the water due to contamination from human or animal wastes. Coliform bacteria can also occur naturally in the soil, so their presence does not necessarily indicate a sewage-contamination problem or imminent health risk.
E. coli bacteria, colonies/100 mL	The MCL states that there can be no <i>E.coli</i> or other fecal coliforms in a well.	One species of bacteria in the total coliform group that originates only in the intestines of warm-blooded animals and humans. The presence of <i>E.coli</i> indicates that sewage wastes or other fecal material are present in the water.
Hardness, mg/L as CaCO ₃	Upon heating and evaporation, hard water precipitates carbonate mineral deposits, scale, and crusts on pipes, hot water heaters, boilers, and cooking utensils. Also causes increased soap consumption. Dufor and Becker (1964) give the following hardness classification:	Hardness is caused by high concentrations of calcium, magnesium, and to a lesser extent, strontium. Waters with hardness values greater than 200 or 300 mg/L usually are associated with carbonate- or gypsum-containing materials.
	Hardness range (mg/L of CaCO ₃) 0 - 60 Soft 61 -120 Moderately hard 121 -180 Hard More than 180 Very hard	
Calcium, dissolved mg/L	Regulatory standards not established with respect to drinking water. Major contributor to hardness and scale formation.	In carbonate-bearing aquifers, is derived from the dissolution of calcite or dolomite and in some instances, gypsum. Concentrations of calcium usually are regulated by equilibria with carbonate minerals such as calcite. Carbonate equilibria are, in turn, largely controlled by pH and the partial pressure of CO_2 .
Magnesium, dissolved mg/L	Regulatory standards not established with respect to drinking water. Contributes to hardness and scale formation. At high concentrations (>125 mg/L) may cause laxative effects, especially to transient users.	In carbonate-bearing aquifers, is derived from the dissolution of magnesium-bearing calcite or dolomite.

Table 6. Concentration limits defined by primary and secondary public drinking-water regulations and implications for domestic water use and ground-water geochemistry for selected properties and chemical constituents in water samples collected in Geauga County, Ohio, June and July, 1999 —Continued

[USEPA, U.S. Environmental Protection Agency; OEPA, Ohio Environmental Protection Agency; MCL, Maximum contaminant level; SMCL, Secondary maximum contaminant level; DWEL, Drinking water equivalent level; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; CaCO₃, calcium carbonate; TU, tritium units; mL, milliliters; *E. coli, Escherichia coli*; >, greater than. MCLs, SMCLs based on standards set by the Ohio Environmental Protection Agency (1994) and DWELs are based on standards set by the U.S. Environmental Protection Agency (2000). Geochemical implications of each water property as they relate to this study are modified from Dumouchelle and others (1993), the discussion of natural water chemistry given by Hem (1989) and Driscoll (1986), and a discussion of bromide/chloride ratios given by Davis and others (1998).]

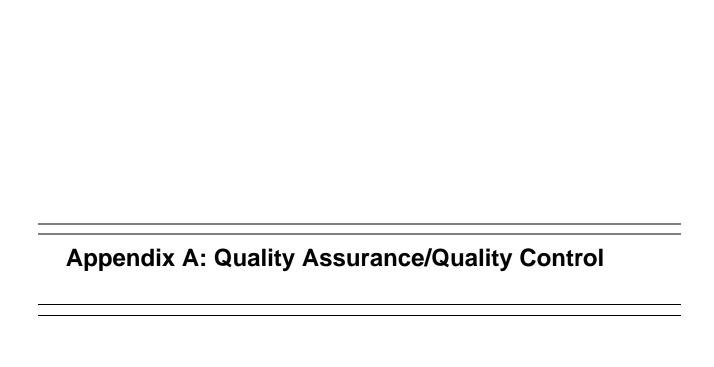
Constituent or property	Concentration limits and water-use implications	Implications for ground-water geochemistry
Sodium, dissolved mg/L	Regulatory standards not established with respect to drinking water, but is listed on the USEPA Drinking Water Contaminant Candidate List (CCL) as a Research Priority.	May be derived from the dissolution of sodium-bearing aluminosilicate minerals (such as albitic feldspar), or halite (NaCl) present in evaporite deposits. In carbonate aquifers, high sodium concentrations are often indicative of the effects of human activities such as road deicing, leaking septic tanks, or the disposal of brine pumped from oil wells.
Potassium, dissolved mg/L	Regulatory standards not established with respect to drinking water. No health or esthetic implications for the range of concentrations found in this study.	Typically derived from the dissolution of potassium-bearing aluminosilicate minerals (such as potassic feldspar or micas). Concentrations typically are low because of the low reactivity of the potassium-bearing silicate minerals and the incorporation of potassium in clay minerals such as asillite (a common mineral in glacial-till deposits).
Bicarbonate, mg/L as HCO ₃	Regulatory standards not established with respect to drinking water.	Major contributor to alkalinity (see below). Is derived from the dissolution of carbonate minerals by carbonic acid (H ₂ CO ₃).
Carbonate, mg/L as CO ₃	Regulatory standards not established with respect to drinking water.	Minor contributor to alkalinity (see below).
Alkalinity, mg/L as CaCO ₃	Regulatory standards not established with respect to drinking water. No health or esthetic implications for the range of concentrations found in this study. Alkalinity is a measure of the capacity of a water to neutralize acid.	In carbonate-bearing aquifers, almost all alkalinity results because of the presence of the bicarbonate ion (HCO_3 °). Minor contributors to alkalinity include the carbonate (CO_3 ² °) and hydroxide (OH°) ions.
Sulfide, total mg/L as S	Regulatory standards not established with respect to drinking water. Most people can smell the rotten-egg odor of hydrogen sulfide at a concentration of only 0.5 mg/L in cold water.	This form of sulfur is formed by sulfate-reducing bacteria that live in water that has a high sulfate content and the absence of oxygen. Under oxidizing conditions the sulfide can be converted back to sulfate.
Sulfate, dissolved mg/L as SO ₄	The SMCL is 250 mg/L. Combines with calcium to form scale in water heaters and boilers. At concentrations exceeding 500-600 mg/L, imparts a bitter taste and may cause laxative effects in some individuals.	Derived from the dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) or the oxidation of sulfide minerals such as pyrite (FeS_2). Stable under oxidizing conditions; however, under reducing conditions can be converted to hydrogen sulfide.
Chloride, dissolved mg/L	The SMCL is 250 mg/L. At concentrations greater than 250 to 400 mg/L, imparts a salty taste to water depending on individual tolerance. High concentrations are corrosive to most metals.	Derived from the dissolution of halite. Is a rare constituent of non-evaporite rocks. High concentrations imply inputs of brines of natural origin or anthropogenic sources such as road salt or the disposal of brine pumped from oil wells.
Bromide, dissolved mg/L	Regulatory standards not established with respect to drinking water.	Derived from precipitation, dissolution of evaporites, or intrusion of brine from compacting clays. The ratio of chloride to bromide can be used to evaluate the origin of dissolved salts in ground water.
Silica, dissolved mg/L	Regulatory standards not established with respect to drinking water.	Used to evaluate controls on silica concentration.
Dissolved solids, residue at 180°C		Proportional to dissolved ion concentrations. Like specific conductance, may be used to distinguish between different water types in an aquifer.
Nitrate, dissolved mg/L as N	At concentrations greater than the MCL of 10 mg/L as N, can cause "Blue baby syndrome" (methemoglobinemia) in infants under six months - life threatening without immediate medical attention.	Presence of nitrate indicates oxidizing conditions in the aquifer. Elevated concentrations are indicative of anthropogenic sources of nitrate (fertilizer, septic tank leakage) and indicate that the aquifer is vulnerable to infiltration of surface drainage.
Nitrite, dissolved mg/L as N	At concentrations greater than the MCL of 1 mg/L as N, can cause "Blue baby syndrome" (methemoglobinemia) in infants under six months - life threatening without immediate medical attention.	Nitrite is unstable in oxidizing conditions and is an intermediate product in the reduction of nitrate to ammonia. Is an indicator of pollution through disposal of sewage or organic waste from a nearby source.

Table 6. Concentration limits defined by primary and secondary public drinking-water regulations and implications for domestic water use and ground-water geochemistry for selected properties and chemical constituents in water samples collected in Geauga County, Ohio, June and July, 1999 —Continued

[USEPA, U.S. Environmental Protection Agency; OEPA, Ohio Environmental Protection Agency; MCL, Maximum contaminant level; SMCL, Secondary maximum contaminant level; DWEL, Drinking water equivalent level; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; µg/L, micrograms per liter; CaCO₃, calcium carbonate; TU, tritium units; mL, milliliters; *E. coli, Escherichia coli*; >, greater than. MCLs, SMCLs based on standards set by the Ohio Environmental Protection Agency (1994) and DWELs are based on standards set by the U.S. Environmental Protection Agency (2000). Geochemical implications of each water property as they relate to this study are modified from Dumouchelle and others (1993), the discussion of natural water chemistry given by Hem (1989) and Driscoll (1986), and a discussion of bromide/chloride ratios given by Davis and others (1998).]

Constituent or property	Concentration limits and water-use implications	Implications for ground-water geochemistry
Ammonia, dissolved mg/L as N	No health or esthetic implications for the range of concentrations found in this study.	Aqueous ammonia is unstable in oxidizing conditions. May also be an indicator of pollution through disposal of sewage or organic waste.
Ammonia + organic nitrogen, dissolved mg/L as N	No health or esthetic implications for the range of concentrations found in this study.	Also called "Total Kjeldahl Nitrogen." Organic species of nitrogen are unstable in aerated water. An indicator of pollution through disposal of sewage or organic waste from a nearby source.
Phosphorus, dissolved mg/L	No health or esthetic implications for the range of concentrations found in this study.	Although a common minor element in most rocks, readily soluble forms are rare. Mobility in subsurface is low due to its ready adsorption by common metal oxide minerals.
Orthophosphorus, dissolved mg/L as P	No health or esthetic implications for the range of concentrations found in this study.	The most thermodynamically stable of the P ⁵⁺ forms of phosphorus. Is an indicator of pollution from laundry wastewater, commercial cleaning wastes, or from sewage. Elevated concentrations also can indicate that the aquifer is vulnerable to infiltration of surface drainage containing fertilizer from agricultural areas.
Boron, dissolved mg/L	Regulatory standards not established with respect to drinking water. No health or esthetic implications for the range of concentrations found in this study. Boron is essential for plant nutrition but is toxic to some plants at high concentrations.	Concentration of boron is not affected by adsorption, precipitation or dissolution reactions. It can therefore be used as a chemical tracer. Boron is present in high concentrations in most landfill leachate. Is also present in laundry detergent, and its presence in ground water can indicate contamination from leaking septic systems.
Iron, dissolved μg/L	The SMCL is 300 µg/L. At concentrations exceeding the SMCL, iron contributes to staining of fixtures, utensils, and laundry. Higher concentrations form reddish-brown sediment and water-line deposits. At concentration greater than 1,800 µg/L the water has a metallic taste (Fetter,1980, p. 355).	General redox indicator. Dissolved-iron concentrations are below detection limits in oxygenated waters at near-neutral conditions. Under more reducing conditions, dissolved iron concentrations may exceed several milligrams per liter.
Manganese, dissolved $\mu g/L$	The SMCL is 50 µg/L. At concentrations exceeding the SMCL, manganese may cause dark-brown or black staining of fixtures, utensils, and laundry.	Concentrations controlled by various oxide and oxy-hydroxide mineral equilibria. Dissolution of manganese-oxide coatings on glacial aquifer material under reducing conditions is a likely source of dissolved manganese.
Strontium, dissolved µg/L	USEPA health advisory guidance (DWEL) is 20 mg/L.	Derived from the dissolution of calcite or dolomite in which Sr has replaced Ca in trace amounts, the carbonate mineral strontianite, or the sulfate mineral celestite. Elevated concentrations in ground water may indicate contamination by fertilizer and pesticide. Can also be used as an indicator of the origin of dissolved salts in ground water.
Tritium, total TU	Regulatory standards not established. No health or esthetic implications for the range of concentrations found in this study.	Radioactive isotope of hydrogen introduced into the atmosphere in large quantities during the period of atomic bomb testing in early 1950's and 1960's. Used to estimate approximate recharge age of ground water; to examine ground-water flowpaths; and to examine contributions to the glacial deposits from bedrock formations.
Dissolved organic carbon, mg/L	Regulatory standards not established. No health or esthetic implications for the range of concentrations found in this study.	Concentrations greater than 3-4 mg/L are unusual for ground water and may indicate the presence of hydrocarbon compounds derived from human activities and vulnerability of the aquifer to surface drainage. Present at high concentrations in landfill leachate and in ground water affected by petroleum spills or leaks.
Volatile organic carbon ^a	Health—MCLs are as follows: benzene, 5 μ g/L; trichloroethylene, 5 μ g/L; toluene, 1 mg/L; tetrachloroethylene, 5 μ g/L; and xylene, 10 mg/L.	Indicate the presence of hydrocarbon compounds derived from human activities and vulnerability of the aquifer to surface drainage. Present in ground water affected by petroleum spills or leaks.

^aSamples were screened using a portable gas chromatograph with a heated column and a calibration library consisting of benzene at 3 μ g/L, trichloroethylene at 5 μ g/L, toluene at 3 μ g/L, tetrachloroethylene at 5 μ g/L, and xylene at 13 μ g/L.



APPENDIX A: QUALITY ASSURANCE/ QUALITY CONTROL

Quality assurance/quality control (QA/QC) samples, including field blanks, duplicate samples, and sourcesolution blanks, were collected for most analytes at the rate of 10 percent to ensure sample integrity and final quality of data. Duplicate samples were collected to assess the reproducibility of the sample-collection procedures and laboratory and (or) field determination of constituent concentration, as well as to provide the data user with a measure of variability (Francy and others, 1998). Duplicate samples were collected immediately after the environmental sample from the same well by use of the same equipment and field methods. A total of three duplicate samples (one per week) were collected for analysis of the same constituents as the environmental samples. The exception was tritium, for which only one duplicate sample was analyzed. Duplicate samples were collected at sites where surrounding land use, well depth, and (or) housing density indicated that nitrate, VOCs, and (or) bacteria might be detected. These samples were collected at wells GE-119, GE-165, and GE-349A. The tritium duplicate sample was collected at a site where a detectable concentration of tritium in ground water also was expected. (Because two sample vials were sent to the laboratory for each VOC sample, the laboratory technician could run additional VOC duplicates if VOCs were detected at other well locations.)

A total of three field blanks were collected to identify bias caused by contamination from equipment, supplies, and ambient environmental conditions (Francy and others, 1998). The field blanks were collected at the same locations as the duplicate samples. After the environmental samples and duplicate samples had been collected and the equipment had been decontaminated, deionized water was gravity-fed through the sample tubing. For filtered samples, a peristaltic pump was used to provide enough pressure to push the water through the filter. A portion of the water was collected and preserved for chemical analysis of major ions, trace metals, and nutrients. Field blanks for VOCs were collected by use of organic-free water. This water was gravity-fed through the Teflon sample tubing. Blanks for dissolved organic carbon (DOC) were gravity-fed through the silicon sample tubing. The first 200 mL of water was discarded, and the subsequent water was forced through the DOC

stainless steel filter cartridge by use of nitrogen gas. No blanks were analyzed for tritium.

A total of two bottles of organic-free water were used in the process of preparing VOC and DOC field blanks. When each of these bottles was opened, an unfiltered sample of the water was poured immediately into a sample container and was sent to the NWQL for DOC analysis to verify that the source water used to prepare the equipment blanks was organic free. These two samples are referred to as source-solution blanks (Francy and others, 1998).

More stringent QA/QC procedures were applied to bacteria. For bacteria samples, the sterility of the buffer water and the sterilization techniques for the membrane-filtration equipment were tested by processing an equipment blank before each water sample was filtered.

Additional QA/QC methods to ensure sample integrity and final quality of data for VOC analyses were used as detailed by Parnell (1995). Each day before sample analysis, an instrument blank and syringe blank were run, followed by a calibration run. The instrument blank checked for a flat baseline signifying that no VOCs remained in the internal column of the gas chromatograph. The syringe blank ensured that the syringe used to deliver the samples to the gas chromatograph was free of VOCs and was also used to identify the resultant air peak on the chromatogram. At the end of the day, another instrument blank was run. To assess recovery bias of VOCs and variability in relation to different ground-water matrices, one water sample from the glacial deposits and one sample from the Cuyahoga Group was spiked in the USGS Columbus, Ohio, laboratory with known concentrations of the VOCs of interest and was analyzed 24 hours later to simulate field holding times. To assess loss or degradation of VOCs during sample collection and shipping, one spike was prepared per week of field work from organic-free water fortified with known concentrations of the VOCs of interest, was retained with the samples until the time of shipment, and then submitted to the Columbus, Ohio, laboratory. To identify contamination from migration of VOCs into the samples from the air, a trip blank of organic-free water was put in the same type of vial used for the environmental samples and kept with the VOC sample vials before and after sample collection. One trip blank was included in each shipment of VOC samples to the laboratory. At one sampling site (GE-77) where the faucet was in the garage and the air smelled of oil and paint,

an ambient air blank was collected to determine potential contamination of the environmental sample from conditions in the sampling environment (Francy and others, 1998). The ambient air blank was prepared at the sample-collection site by pouring organic-free water into a VOC vial and sending it to the laboratory in Columbus for analysis.

Quality-control data are listed in table A1. Out of a total of 83 comparisons of duplicate analyses, 71 had a relative percent difference that was less than 5 percent. Only 11 comparisons had relative percent differences that were greater than 5 percent; these are shown in bold type in table A1. The ratios computed with these problem values would still be reliable enough to determine water types and would not alter the determination of whether a constituent exceeded water-quality standards. The variability in NO₃ concentrations in sample GE-349A is not enough to affect the classification as to whether the nitrate detected reflects anthropogenic influence or is indicative of background concentrations. Chloride-to-bromide ratios determined using duplicate values with a relative percent difference greater than 5 percent still plot very near the original points on the Cl:Br diagram and would not affect interpretations of the source of salinization in these samples.

Blank values were compared to all values for each constituent shown in table 5. In most cases, concentrations detected in the blanks are much less than concentrations in the environmental samples, often by 2 or more orders of magnitude. In no case is the concentration value in the blank large enough to substantially affect the concentration of the constituent in the environmental sample.

Quality-control data for VOCs are not shown in table A1 because no VOCs were detected in any environmental sample or duplicate sample. Similarly, the instrument, syringe, field, trip, and ambient air blanks all contained no detectable VOCs. Calibration runs showed that the gas chromatograph was working properly, and spikes compared well with the calibration run, showing little if any qualitative loss or degradation of VOCs during sample collection and shipping. Matrix spikes also compared qualitatively well with the calibration run, indicating no recovery bias of VOCs and variability in relation to different groundwater matrices.

No bacteria were detected in any of the equipment blanks, an indication that equipment, supplies, and ambient environmental conditions did not bias the bacteria analyses in any way. Colonies that fluoresced but were small and green were not counted.

Table A1. Chemical characteristics of selected quality-control samples collected in Geauga County, Ohio, June and July 1999

[Well locations are shown in figure 1; Abbreviations: <, less than; col/100 mL, colonies per 100 milliliters; mg/L, milligrams per liter; μ g/L, micrograms per liter; TU, tritium units; one TU = 3.24 picocuries per liter; --, not analyzed; boldface type indicates relative differences of 5 percent or greater]

Station name	Date	pH, water, whole, lab (standard units)	Coliform, total, water , unfiltered (col/100 mL)	E. coli, water, unfiltered (col/100 mL)	dissolved	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)
GE-119	6-17-1999	6.3	<1	<1	0.06	0.03	99
GE-119 DUP	6-17-1999	6.3	<1	<1	.06	.03	100
GE-165	6-8-1999	7.5	<1	<1	63	13	9
GE-165 DUP	6-8-1999	7.5	<1	<1	62	13	8.9
GE-349A	7-1-1999	6.6	1	<1	26	5.8	24
GE-349A DUP	7-1-1999	7.0	1	<1	27	6	25
GE-119 BLANK	6-17-1999	7.3	<1	<1	.01 ^a	<.004	.05 ^a
GE-165 BLANK	6-8-1999	8.1	<1	<1	.09	.004	.03 ^a
GE-349A BLANK	7-1-1999	7.1	<1	<1	.02	$.002^{a}$	<.06
GE-165 SOURCE	6-8-1999						
GE-349A SOURCE	7-1-1999						

Table A1. Chemical characteristics of selected quality-control samples collected in Geauga County, Ohio, June and July 1999—Continued

[Well locations are shown in figure 1; Abbreviations: <, less than; col/100 mL, colonies per 100 milliliters; mg/L, milligrams per liter; ug/L, micrograms per liter; TU, tritium units; one TU = 3.24 picocuries per liter; --, not analyzed; boldface type indicates relative differences of 5 percent or greater]

Station name	Potassium, dissolved (mg/L as K)	water, field (mg/L as	•	Alkalinity, water, field (mg/L as CaCO ₃)	Sulfide, total (mg/L as S)	Sulfate, dissolved (mg/L as SO ₄)	Chloride, dissolved (mg/L as Cl)
GE-119	0.2	130	0	110	0.02	70	21
GE-119 DUP	.2	130	0	110		70	23
GE-165	.9	200	0	170	.01	37	20
GE-165 DUP	.9	200	0	170	.01	37	20
GE-349A	1.8	42	0	34	<.01	35	43
GE-349A DUP	1.8	40	0	30	<.01	35	43
GE-119 BLANK	<.1					<.1	<.1
GE-165 BLANK	<.1					<.1	<.1
GE-349A BLANK	<.1					<.1	<.1
GE-165 SOURCE							
GE-349A SOURCE							

Station name	Bromide, dissolved (mg/L as Br)	Silica, dissolved (mg/L as SiO ₂)	Solids, residue at 180 degrees Celsius, dissolved (mg/L)	Nitrogen, nitrate, dissolved (mg/L as N)	Nitrogen, nitrite, dissolved (mg/L as N)	Nitrogen, ammonia, dissolved (mg/L as N)	Nitrogen, ammonia + organic, dissolved (mg/L as N)	Phosphorus, dissolved (mg/L as P)
GE-119	0.02	11	283	< 0.18	< 0.02	< 0.03	< 0.005	< 0.02
GE-119 DUP	.03	10	287	<.18	<.02	<.03	<.005	<.02
GE-165	.21	10	272	<.18	<.02	.04	<.005	<.02
GE-165 DUP	.21	10	282	<.18	<.02	.04	<.005	<.02
GE-349A	.05	8.0	231	2.2	<.02	<.03	<.005	<.02
GE-349A DUP	.06	8.2	223	2.4	<.02	<.03	<.005	<.02
GE-119 BLANK	<.01	<.05	<10	<.18	<.02	<.03	<.005	<.02
GE-165 BLANK	<.01	<.05	<10	<.18	<.02	.03	<.005	<.02
GE-349A BLANK	<.01	.05	<10	<.18	<.02	.03	.034	<.02
GE-165 SOURCE								
GE-349A SOURCE								

Table A1. Chemical characteristics of selected quality-control samples collected in Geauga County, Ohio, June and July, 1999— Continued

[Well locations are shown in figure 1; Abbreviations: <, less than; col/100 mL, colonies per 100 milliliters; mg/L, milligrams per liter; ug/L, micrograms per liter; TU, tritium units; one TU = 3.24 picocuries per liter; --, not analyzed; boldface type indicates relative differences of 5 percent or greater]

Station name	Phosphorus, ortho, dissolved (mg/L as P)	Boron, dissolved (μg/L as B)	Iron, dissolved (μg/L as Fe)	Manganese, dissolved (μg/L as Mn)	Strontium, dissolved (μg/L as Sr)	Carbon, organic, dissolved (mg/L as C)	Tritium, total (TU)
GE-119	< 0.01	25.0	18	6	<1	0.9	
GE-119 DUP	<.01	22.5	21	6	<1	.8	
GE-165	<.01	18.3	1900	180	84	.3	
GE-165 DUP	<.01	19.0	1800	180	83	.3	
GE-349A	<.01	56.5	15	<3	88	.8	14.6
GE-349A DUP	<.01	59.8	19	2 ^a	88	.8	14.6
GE-119 BLANK	.01	8.5a	<10	<3	<1	<.1	
GE-165 BLANK	<.01	10.4 ^a	<10	<3	<1	<.1	
GE-349A BLANK	<.01	10.8 ^a	6 ^a	<3	<1	<.1	
GE-165 SOURCE						<.1	
GE-349A SOURCE						.2	

^aEstimated values are lower than the lowest calibration standard but higher than the detection limit of the machine.