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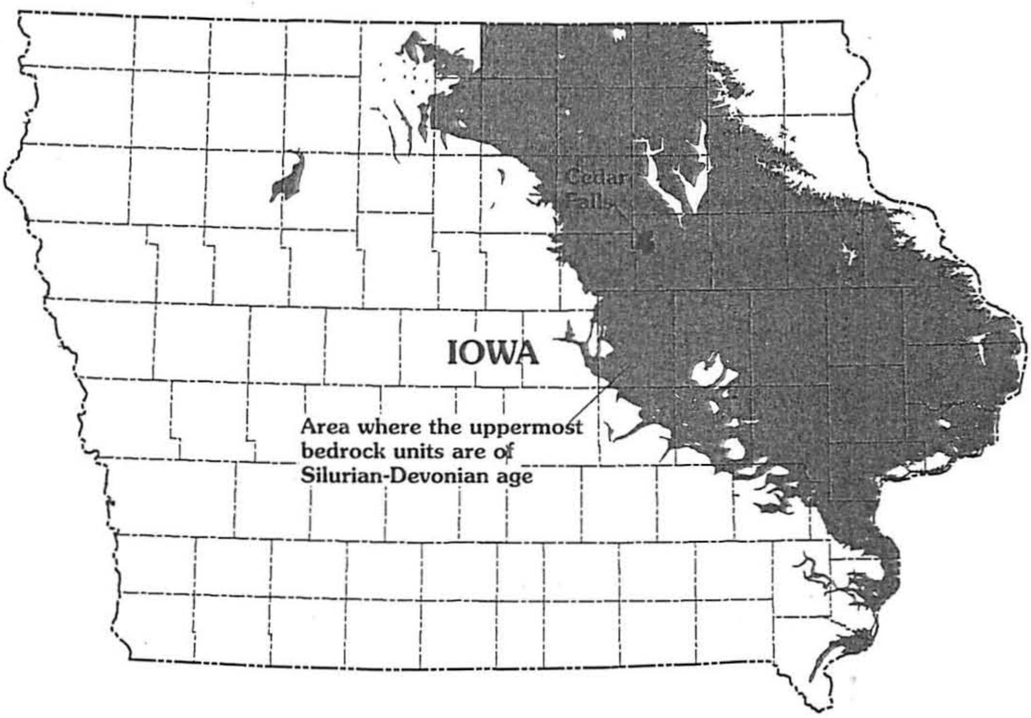
Water-Resources Investigations Report 99–4106



U.S. Department of the Interior
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Concentrations and Possible Sources of Nitrate in Water from the Silurian-Devonian Aquifer, Cedar Falls, Iowa

By BRYAN D. SCHAAP

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Iowa City, Iowa
1999

U.S. Department of the Interior
Bruce Babbitt, Secretary

U.S. Geological Survey
Charles G. Groat, Director

For additional information write to:

District Chief
U.S. Geological Survey
400 South Clinton St., Room 269
Iowa City, IA 52244

Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Building 810, Federal Center
Box 25286
Denver, CO 80225–0286

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CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

Multiply	By	To obtain
inch	2.54	centimeter
foot	0.3048	meter
mile	1.609	kilometer
square mile	2.590	square kilometer
gallon	3.785	liter
foot squared per day	0.0929	meter squared per day
cubic foot per year	0.02832	cubic meter per year
gallon per minute	0.06309	liter per second
short ton	0.9072	megagram

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows:

$$°F = 1.8°C + 32.$$

Abbreviated water-quality units used in this report: Chemical concentrations are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) and micrograms per liter (μg/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. Micrograms per liter is a unit expressing the concentration of chemical constituents in solution as weight (micrograms) of solute per unit volume (liter) of water. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

Per mil: A unit expressing the ratio of stable-isotopic abundances of an element in a sample to those of a standard material. Per mil units are equivalent to parts per thousand. Stable-isotopic ratios are computed as follows (Kendall and Caldwell, 1998):

$$\delta X = \left(\frac{R(\text{sample})}{R(\text{standard})} - 1\right) x 1{,}000,$$

where

X is the heavier stable isotope, and

R is the ratio of the heavier, less abundant stable isotope to the lighter stable isotope in a sample or standard.

The δ values for nitrogen stable-isotopic ratios discussed in this report are referenced to the following standard materials:

R	Standard identity and reference
nitrogen-15:nitrogen-14 (referred to as $\delta^{15}N$)	Standard atmospheric nitrogen, referenced to National Bureau of Standards, NBS-14 nitrogen gas (Fritz and Fontes, 1980, p. 16).

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.

Water year: The 12-month period October 1 through September 30. The water year is designated by the calendar year in which it ends. Thus, the year ending September 30, 1996, is called the "1996 water year."

Concentrations and Possible Sources of Nitrate in Water from the Silurian-Devonian Aquifer, Cedar Falls, Iowa

By Bryan D. Schaap

Abstract

Carbonate rocks of the Silurian-Devonian aquifer are the primary source of water for Cedar Falls, Iowa. A trend of increasing nitrate concentrations has been detected in samples from Cedar Falls water-supply wells 9 and 10, and 1998 nitrate concentrations were close to the U.S. Environmental Protection Agency's Maximum Contaminant Level of 10 milligrams per liter as nitrogen in drinking water. These wells are located in an area where the Silurian-Devonian aquifer is covered by 90 feet of alluvial and glacial deposits. A study to evaluate the concentrations and sources of nitrate in Cedar Falls water-supply wells 9 and 10 was conducted by the U.S. Geological Survey in cooperation with Cedar Falls Utilities.

Water-level measurements from a network of Silurian-Devonian observation wells in the Cedar Falls area were used to determine that ground-water flow in the Silurian-Devonian aquifer is generally from northwest to southeast and down the Cedar River Valley.

Water samples were collected from Cedar Falls water-supply wells 5, 9, and 10 and a domestic well in 1998. Chlorofluorocarbon analytical results indicate that time of recharge was the mid-1970's for water from Cedar Falls water-supply well 9. Tritium analytical results indicate that the time of recharge was after 1953 for water from all four sampled wells. Nitrogen isotope ratios in water from all four wells indicate that the primary source of nitrate in these wells is probably inorganic nitrogen fertilizer.

High nitrate concentrations in samples from Cedar Falls water-supply wells 9 and 10 are probably the result of nitrogen fertilizer applications in the area contributing recharge to the wells. Locally, the nitrate concentrations increase with depth, and the estimated time of recharge for the shallower well is later than the estimated time of recharge for the deeper wells. This suggests that the nitrate and water sampled in Cedar Falls water-supply wells 9 and 10 are moving along predominantly horizontal ground-water flow paths through the Silurian-Devonian aquifer. Land-use data from 1941 through 1994 indicate that increased nitrate concentrations observed in water from wells 9 and 10 are not the result of increased agricultural land use near the wells. Within 1 mile of the water tower between wells 9 and 10, the proportion of agricultural land has remained fairly stable since 1941.

Nitrogen fertilizer sales in Iowa have been higher in recent years than during the mid-1970's. This suggests that nitrate concentrations in water from well 9 may persist at present levels or could increase in future years if fertilizer use increases and if higher nitrate concentrations are directly related to higher nitrogen fertilizer use.

INTRODUCTION

Carbonate rocks of the Silurian-Devonian aquifer are the primary source of water for Cedar Falls, located in Black Hawk County, northeast Iowa (fig. 1) A trend of increasing nitrate concentrations has been detected in water samples collected from Cedar Falls water-supply wells 9 and 10 in northern Cedar Falls

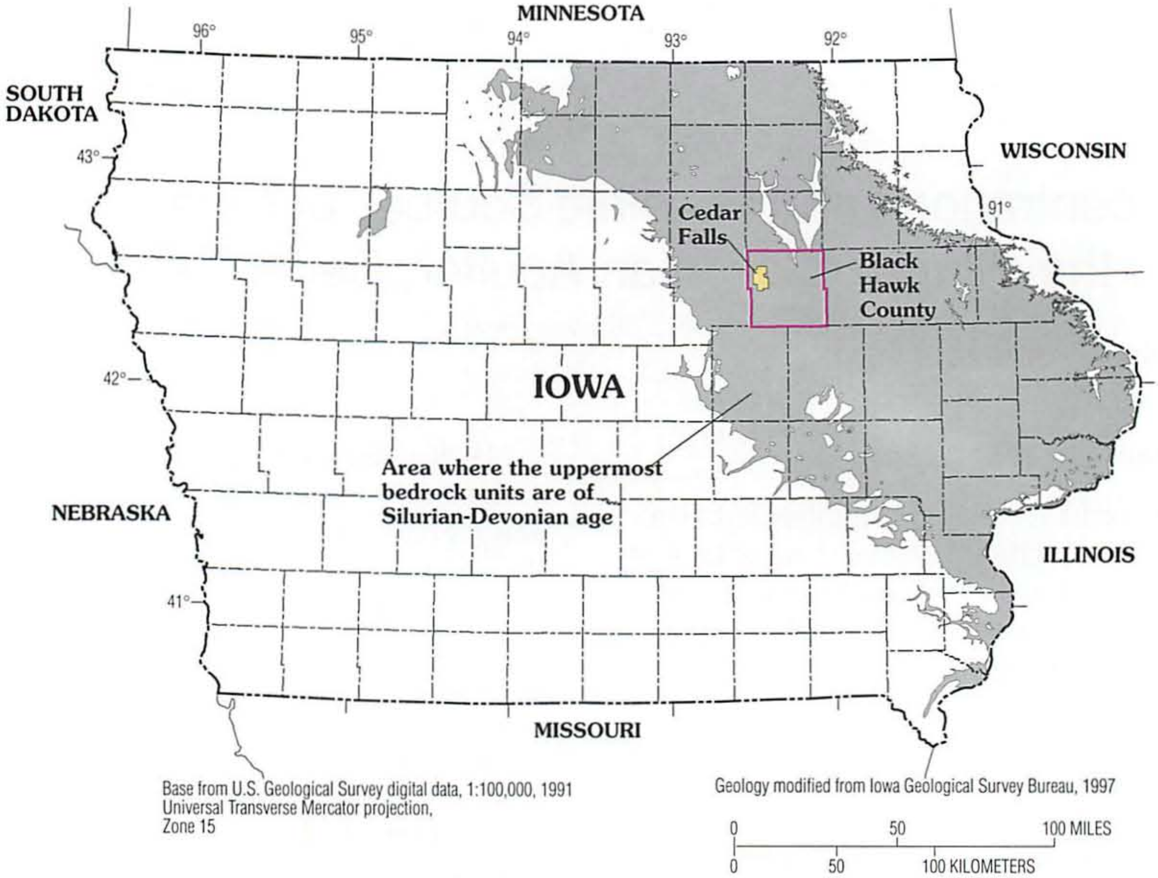


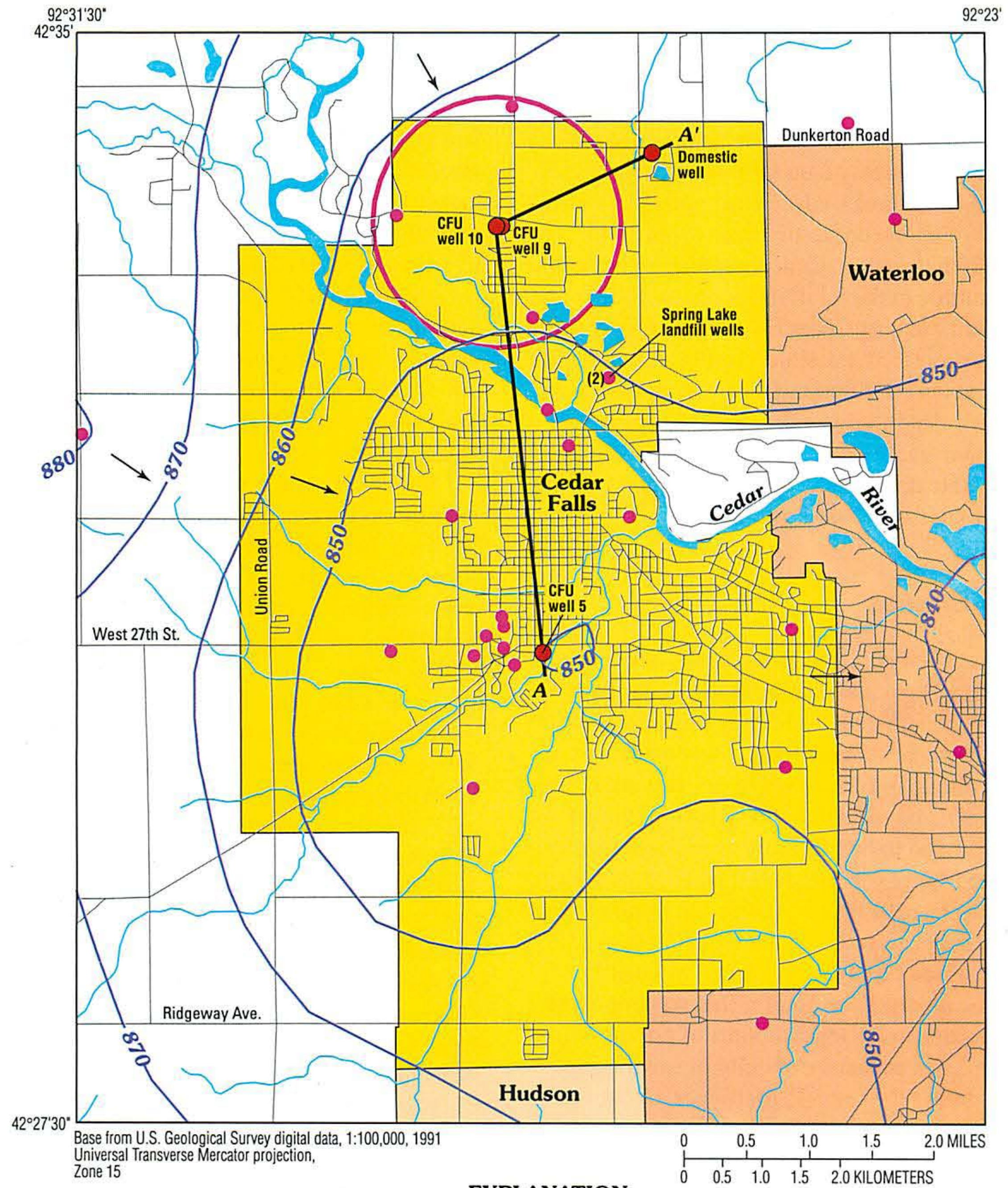
Figure 1. Location of Cedar Falls, Black Hawk County, Iowa, and area where uppermost bedrock units are of Silurian-Devonian age.

(fig. 2). When well 9 was drilled in 1975, the nitrate concentration was less than 4.0 mg/L (milligrams per liter). Samples from recent years have had nitrate concentrations greater than 8.0 mg/L, with some concentrations greater than or equal to 10 mg/L. Although nitrate concentrations in water from well 10 have generally been less than those in water from well 9, the trend of increasing values has also been observed (P. Mallinger, Cedar Falls Utilities, written commun., 1997). Nitrate concentrations greater than the Maximum Contaminant Level of 10 mg/L as nitrogen in drinking water (U.S. Environmental Protection Agency, 1996) are a concern for public health.

A study to evaluate the concentrations and sources of nitrate in water from Cedar Falls water-supply wells 9 and 10 was conducted by the U.S. Geological Survey (USGS) in cooperation with Cedar Falls Utilities. Information regarding the ground-water flow system was collected to help explain the occurrence of high nitrate concentrations in water from the wells. Identifying possible sources of the nitrate might be useful in relation to management practices that could improve water quality and allow continued use of Cedar Falls water-supply wells 9 and 10 without the addition of expensive treatment facilities. An improved understanding of the ground-water flow system, time of recharge, and the sources of the nitrate may indicate if the trend of increasing nitrate concentrations is likely to continue.

Purpose and Scope

The purpose of this report is to describe the study of concentrations and sources of nitrate in ground water from the Silurian-Devonian aquifer in Cedar Falls, Iowa. The study involved (1) developing an improved understanding of the ground-water flow system near Cedar Falls water-supply wells 9 and 10; (2) assessing water chemistry to determine nitrate concentrations, to identify possible sources (for example, nitrogen fertilizer or animal waste) of nitrate in ground water, and to estimate the time of recharge of ground water from wells 9 and 10; and (3) evaluating the trend



EXPLANATION

Incorporated areas

- Cedar Falls
- Waterloo
- Hudson
- Unincorporated

—870— **Generalized water-level contour**—Shows altitude at which water would have stood in tightly cased wells. Contour interval 10 feet. Datum is sea level

A———*A'* **Trace of hydrogeologic section shown in figure 3**

→ **Approximate direction of ground-water flow**

Boundary of area within 1 mile of Cedar Falls, Iowa, water-supply wells 9 and 10

CFU well 5 ● **Sampling site and name where water-quality samples were collected and water levels were measured**

(2)● **Observation well**—Number in parentheses ( ) indicates number of wells at that location if more than one well present

Figure 2. Location of wells sampled for water quality, the observation well network, and the generalized water-level contours of the Silurian-Devonian aquifer, April 24–May 8, 1998, Cedar Falls, Iowa.

toward larger nitrate concentrations as a factor in future management-practice considerations.

The scope of this report includes descriptions of the Silurian-Devonian aquifer and the ground-water flow system that are based on water-level measurements, and water-quality data from samples collected during 1998 from three Cedar Falls municipal water-supply wells and one domestic water-supply well completed in that aquifer. Concentrations and possible sources of nitrate in the Silurian-Devonian aquifer and historical land use near Cedar Falls water-supply wells 9 and 10 are described. Possible trends in future nitrate concentrations in the Silurian-Devonian aquifer near Cedar Falls water-supply wells 9 and 10, which are based on water-quality data collected by the USGS in 1998 and nitrate data provided by Cedar Falls Utilities for 1975 through 1998, are discussed.

Previous Studies

Little has been published specifically about nitrate in the Silurian-Devonian aquifer in the Cedar Falls area, even though there have been many reports written about nitrate in water of Iowa. Most studies have focused on nitrate in surface water (precipitation, rivers, and lakes), and the studies of nitrate in ground water have tended to be statewide or regional studies.

A limited study was conducted in 1995 by Cedar Falls Utilities in an effort to identify the source of the high nitrate concentrations. Zone-isolation tests of Cedar Falls water-supply well 9 failed to identify a limited vertical part of the aquifer that was contributing disproportionately large amounts of nitrate, but there may have been some difficulty in isolating specific zones during the tests (P. Mallinger, Cedar Falls Utilities, oral commun., 1997).

A study by Libra and others (1985) of the Devonian aquifer in Floyd and Mitchell Counties to the north of Cedar Falls along the Cedar River found that nitrate detections were associated with shallow bedrock wells. This study also suggested that high nitrate concentrations in water sampled from deeper bedrock wells may be the result of local inputs from agriculture drainage wells.

A study of the carbonate aquifers in Linn County and adjacent counties to the southeast of Cedar Falls along the Cedar River found that the Silurian-Devonian aquifer tends to have small concentrations of nitrate except where hydraulically connected to the overlying Quaternary aquifer (Wahl and Bunker, 1986).

A study of ground-water quality in the eastern part of the Silurian-Devonian and Upper Carbonate aquifers in the Eastern Iowa Basins of Iowa and Minnesota found that nitrate concentrations were significantly higher in water from two subsets of wells. One subset of wells containing water with higher nitrate concentrations consisted of those wells completed in aquifers not overlain by 100 feet or more of Quaternary-age deposits or a bedrock confining unit. The other subset of wells containing water with higher nitrate concentrations consisted of those wells where the sampled water was recharged after 1953 (Savoca and others, 1999).

Kolpin and others (1997) examined data from the Iowa ground-water-quality monitoring program from 1982–95. No significant statewide temporal trends in either the frequency of detection or median nitrate concentrations in ground water were found, even after considering well subsets on the basis of depth and aquifer type.

From water year 1982 through water year 1996, more than 400 untreated water samples were collected from municipal water-supply wells completed in the Silurian-Devonian aquifer as part of the Iowa ground-water-quality monitoring program, which is conducted cooperatively by the Iowa Geological Survey Bureau, the University of Iowa Hygienic Laboratory, and the USGS. The median nitrate concentration of those samples was 0.10 mg/L as nitrogen, which might be considered an approximate background nitrate level for Silurian-Devonian wells in Iowa. The median well depth for all Silurian-Devonian samples was 205 feet (Schaap and Linhart, 1998).

Horick (1984) described the Silurian-Devonian aquifer in Iowa. His report includes maps of aquifer thickness, water quality, and potential water movement.

Acknowledgments

The author gratefully acknowledges several members of the Iowa Geological Survey Bureau who provided valuable information regarding the geology of the Cedar Falls area. P.E. VanDorpe and B.J. Bunker were helpful in retrieving information from data bases, and B.J. Witzke offered guidance regarding interpretation of the geologic data.

Many public, corporate, and private well owners made water-level measurements or allowed access for the USGS to make water-level measurements. Shawver Well Company provided driller's logs.

Several members of the USGS provided technical advice for this study. C. Kendall responded to several inquiries regarding interpretation of the nitrogen isotope data. G.C. Casile, E. Busenberg, and L.N. Plummer used their expertise to assist with the collection of the chlorofluorocarbon samples and to help interpret the time of recharge.

HYDROGEOLOGY

The ground-water flow system near Cedar Falls water-supply wells 9 and 10 is affected by the subsurface geology, the capacity of the geologic units to store and transmit water, and the locations and rates of recharge to and discharge from the aquifer. Figure 3 shows a hydrogeologic section that is based on driller's logs (P. Mallinger, Cedar Falls Utilities, written commun., 1998) and geologic logs (Iowa Geological Survey Bureau, 1999). The trace for the section goes through Cedar Falls water-supply well 5, Cedar Falls water-supply well 10, and a domestic well. Cedar Falls water-supply well 9 is not shown in figure 3 because of space considerations, but wells 9 and 10 are located within 160 feet of each other, were drilled the same year, and have very similar construction characteristics. Driller's logs for wells 5, 9, and 10 identify lithologic units in terms such as "sand," "clay," or "limestone," so the uppermost report of limestone was assumed to be the top of the Devonian-age bedrock. Geologic samples from these wells were not delivered to Iowa Geological Survey Bureau, so geologic logs are not available for these wells. At these locations, the contact between the Devonian-age rocks and the Silurian-age rocks was estimated on the basis of identified or estimated Devonian-Silurian contacts in nearby wells. This is discussed in more detail in the following paragraphs. The top of the Devonian-age bedrock at the domestic well was estimated by assuming that the

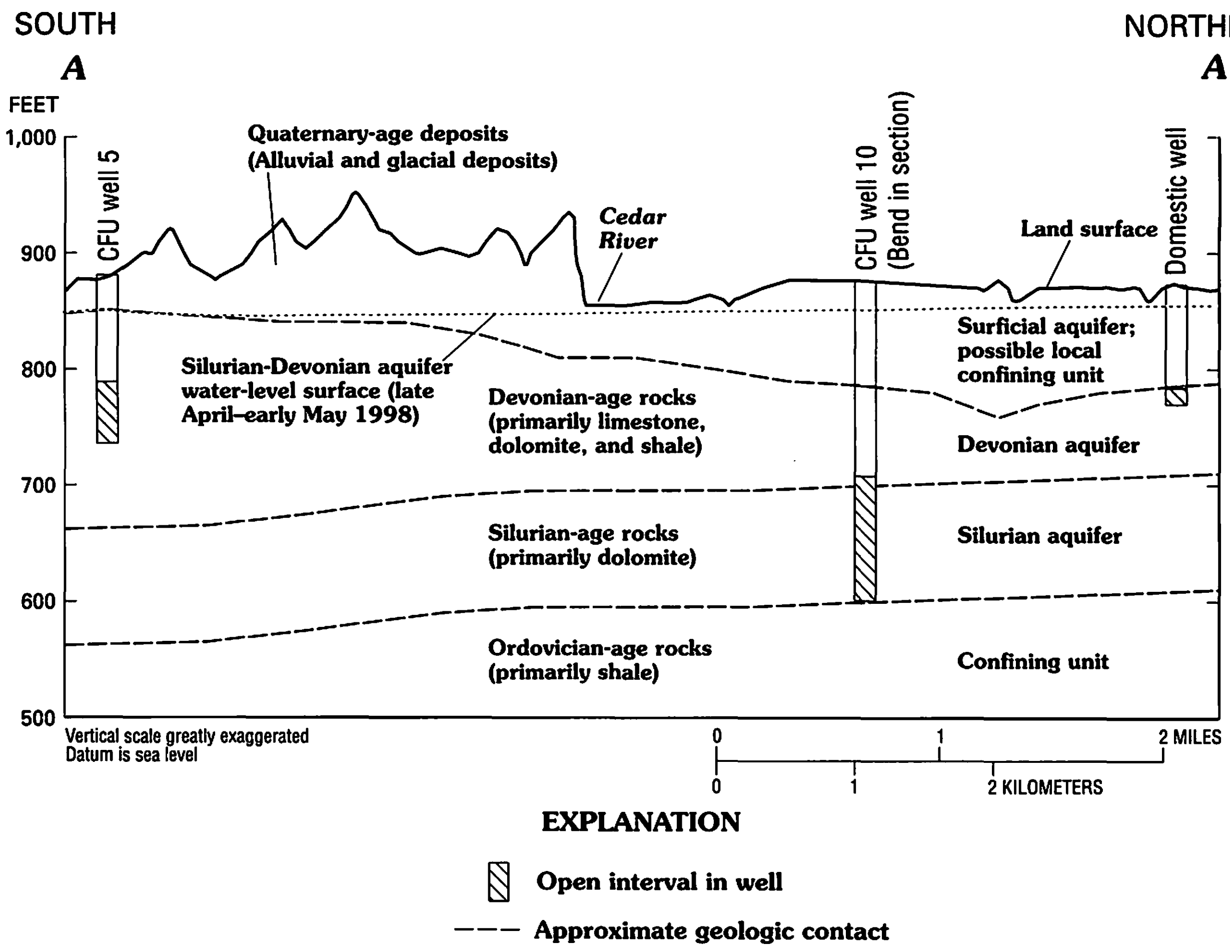


Figure 3. Hydrogeologic section *A–A'*, Cedar Falls, Iowa.

bottom of the casing was 2 feet into the bedrock, which was common for other domestic wells in the area for which driller's logs were available. For wells 5, 9, and 10, and the domestic well near the northeast end of the trace, specific information, such as well depth and depth to bedrock, is listed in table 1.

The surficial aquifer system consists of Quaternary-age alluvial and glacial deposits less than 150 feet thick (fig. 3). The permeability of the alluvial and glacial deposits may be quite variable, both vertically and horizontally. The glacial deposits in Iowa are rich in clay, which means that in some locations they may have lower permeability (Olcott, 1992) than "sand" and "coarse sand" units described in the driller's logs for Cedar Falls water-supply wells (P. Mallinger, Cedar Falls Utilities, written commun., 1997). These deposits may provide limited protection against contaminants in surface water and shallow ground water from leaching to the underlying bedrock units (Hallberg and others, 1996).

The uppermost bedrock unit consists of Devonian-age rocks. Flow between weathered and fractured limestone near the top of the Devonian-age rocks to the underlying rocks of Silurian age may be restricted by intervening Devonian-age limestone, dolomite, and shale that are unweathered and less fractured. The Devonian-age rocks unconformably overlie the Silurian-age rocks and consist primarily of limestone, dolomite, and shale, but locally include minor amounts of sandstone (Witzke and others, 1988). In the Cedar Falls area, the total thickness of the Devonian-age rocks is approximately 50 to 200 feet.

The Silurian-age rocks consist primarily of dolomite with minor chert (Iowa Geological Survey Bureau, 1999). The upper surface of Silurian-age rocks shown in figure 3 was estimated by using nearby geologic logs from the Iowa Geological Survey Bureau (1999). Most wells in Cedar Falls and the surrounding area are completed in large-yielding rocks of Devonian age, so in some locations the Silurian-Devonian contact was estimated by assuming constant thicknesses for two Devonian-age units, the Eagle Center Member and the Wapsipinicon Group, which were often identified in the geologic logs. The Eagle Center Member is a distinctive interval of argillaceous and generally laminated dolomite with considerable amounts of chert (Witzke and others, 1988). Some wells were drilled through the Eagle Center Member, through the fossiliferous Devonian-age rocks which disconformably overlie the Wapsipinicon Group, and into the Wapsipinicon Group, which is distinguished by its laminated limestone and dolomite with few

Table 1. Sampling-site information, nitrogen sources, and estimated time of recharge as indicated by water-chemistry samples collected April 29, 1998, Cedar Falls, Iowa

[CFU, Cedar Falls Utilities; CFC, chlorofluorocarbon]

Sampling-site name (fig. 2)	Sampling-site number	Well depth (feet)	Depth to bedrock (feet)	Hydro-geologic unit	Indicated nitrate source[1]	Time of recharge: CFC estimate[2]	Time of recharge: Tritium estimate[3]
CFU well 5	423042092265801	145	30	Devonian aquifer	Nitrogen fertilizer	Inconclusive	Post-1953
CFU well 9	423341092273001	275	90	Silurian-Devonian aquifer	Nitrogen fertilizer	Mid-1970's	Post-1953
CFU well 10	423341092273301	275	90	Silurian-Devonian aquifer	Nitrogen fertlizer	Early 1970's	Post-1953
Domestic well	423411092260401	103	87	Devonian aquifer	Nitrogen fertilizer	Mid-1980's	Post-1953

[1]Based on information in Kendall (1998).

[2]E. Busenberg, U.S. Geological Survey, written commun., 1998.

[3]Based on information in Freeze and Cherry (1979).

fossils (Witzke and others, 1988). The Silurian-Devonian contact was estimated to be 130 feet below the top of the Eagle Center Member and 50 feet below the top of the Wapsipinicon Group. Outside of Cedar Falls, the top of the Silurian-age rocks was identified in some of the geologic logs, and this information was considered in estimating the top of the Silurian-age rocks.

The uppermost Ordovician-age rocks consist of the Maquoketa Formation (shale, dolomite, and limestone), which is a regional confining unit in eastern Iowa (Olcott, 1992). The upper surface of the Ordovician-age rocks shown in figure 3 was calculated by assuming that the Silurian-age rocks are 100 feet thick in this area. This thickness is based on information from geologic logs of a few widely scattered wells more than 6 miles from Cedar Falls water-supply wells 9 and 10.

The carbonate rocks of Devonian and Silurian age commonly are considered to be one hydrologic unit because they are often in hydraulic connection. Silurian-age rocks were usually the primary source of water for wells completed in this unit in Iowa, so the unit became known as the Silurian-Devonian aquifer (Horick, 1984). The Silurian-Devonian aquifer consists of two primary water-bearing units, the Devonian aquifer and the Silurian aquifer. The Silurian-Devonian aquifer is absent in extreme northeastern Iowa and is more than 700 feet thick in southwestern Iowa (Horick, 1984). In the Cedar Falls area, the Silurian-Devonian aquifer is estimated to be about 150 to 300 feet thick. Many wells in the Black Hawk County area are open to Devonian-age and Silurian-age rocks, so even if there was no natural hydraulic connection, the construction of these wells created a connection.

In this report, all wells open to either Devonian-age or Silurian-age rocks, or both, are considered to be Silurian-Devonian aquifer wells. Some of these wells are known to be screened in only Devonian-age rocks, and they may be described more specifically as Devonian-aquifer wells. Those wells known to be screened in only Silurian-age rocks may be described more specifically as Silurian-aquifer wells. For example, the three sampling sites shown in figure 3 are all considered to be Silurian-Devonian aquifer wells. However, well 5 and the domestic well are open only to Devonian-age rocks, and they are described more specifically as Devonian-aquifer wells (table 1).

Transmissivity of the Silurian-Devonian aquifer is highly variable, depending on the degree of interconnection between the joints, fractures, and bedding planes. Transmissivity is greatest, about 360,000 feet squared per day, in areas where the Silurian-Devonian aquifer is the uppermost bedrock unit and is overlain by the surficial aquifer system, as is the case in northeastern Iowa. Transmissivity may be about 1,200 feet squared per day where the aquifer is confined (Olcott, 1992).

A network of observation wells open to the Silurian-Devonian aquifer in Cedar Falls and the surrounding area was established as part of an ongoing study to determine the areas contributing recharge to the Cedar Falls water-supply wells. The location of those observation wells comprising the central part of the network is shown in figure 2. Horizontal position (latitude-longitude) of the wells was determined using a global positioning system, and reference to the National Geodetic Vertical Datum of 1929 (sea level) was determined, as necessary, using a combination of global positioning system and conventional surveying techniques. Ground-water levels were measured by various organizations (municipalities, businesses, and so forth) or the USGS once from April 24, 1998, through May 8, 1998, with more than 85 percent of the water levels measured during April 27–29, 1998. This water-level information was used to create a generalized water-level map for an area that extends several miles in all directions from the Cedar Falls municipal boundary (fig. 2). The generalized water level is the altitude at which water would have stood in tightly cased wells.

The generalized water-level contours in figure 2 indicate that, in Cedar Falls, ground-water flow in the Silurian-Devonian aquifer is generally from northwest to southeast and down the Cedar River Valley. Both figures 2 and 5 (in a later section of the report) show this general trend of potential ground-water movement around Cedar Falls wells 9 and 10. The map showing generalized water-level contours constructed for this study is very similar, in shape and magnitude, to the potentiometric-surface map constructed by Horick (1984) in 1980 for this part of the Silurian-Devonian aquifer.

Water-level data from two observation wells at the former Spring Lake landfill (fig. 2) suggest that vertical ground-water movement is generally from the surficial aquifer to the Silurian-Devonian aquifer. The two wells were located within a few feet of each other, and the water level in the observation well completed in the surficial aquifer was higher than the water level in the observation well completed in the Silurian-Devonian aquifer.

CONCENTRATIONS OF NITRATE

Water samples were collected from wells 5, 9, and 10 and a domestic well (fig. 2) on April 29, 1998, and a second time from the domestic well on June 26, 1998 (table 2). The samples were analyzed for physical properties, dissolved solids, major ions, nutrients (including nitrate), metals, tritium, nitrogen isotopes, and chlorofluorocarbons (CFCs). Analytical results for tritium and CFCs were used to estimate the time of recharge of the water and presumably the time when the nitrate also entered the ground-water system. The nitrogen isotopes in the nitrate were analyzed to identify the possible sources of the nitrate.

Selection of the wells was based on accessibility and the potential to provide information about the possible sources of nitrate in the Silurian-Devonian aquifer in the Cedar Falls area. Well 5 was selected for sampling because of historically lower nitrate concentrations than in water from well 9 (P. Mallinger, Cedar Falls Utilities, written commun., 1998). The domestic well was selected to sample a shallower part of the Silurian-Devonian aquifer near wells 9 and 10 (fig. 3). Like wells 9 and 10, the domestic well is located in an area where the Silurian-Devonian aquifer is covered by about 90 feet of alluvial and glacial deposits (table 1).

Sample Collection and Analysis

Onsite measurements of physical properties (specific conductance, pH, water temperature, and dissolved oxygen) were conducted at the time of sample collection. Samples were collected after the well had been pumping for several minutes and physical properties had stabilized. At wells 5, 9, and 10, the addition of chlorine and fluoride was discontinued before pumping began, and onsite tests were used to determine that the water was free of the chlorine routinely added as treatment. At the domestic well, discharge from the outdoor hydrants was maintained during sampling so that the pump had to run continuously and provide water that had just been removed from the aquifer rather than water that had been stored in the pipes or pressure tank of the home's water system.

Major cations and anions, nutrients, and metals were analyzed at the USGS National Water-Quality Laboratory in Arvada, Colorado. Nitrogen isotopes were analyzed by Global Geochemistry in Canoga Park, California. Tritium was analyzed by a University of Miami laboratory in Miami, Florida. CFCs and dissolved gases were analyzed at a USGS research laboratory in Reston, Virginia.

Two types of quality-assurance samples were evaluated for the well 9 sampling site to assess the validity of the analytical results. A duplicate sample was collected to investigate the precision of the analytical results and to check sample handling onsite and in the laboratory. The duplicate sample would be expected to have the same concentrations as the primary sample within the limits of the analytical methods. A set of field blank samples was collected to determine possible sources of contamination during transportation, collection, or processing of samples. The results from these quality-assurance samples (table 2) indicate good precision for the analytical methods and that no significant contamination was introduced during sample handling.

Nitrate Concentrations

The minimum reporting level for nitrite plus nitrate as nitrogen was 0.10 mg/L. In all samples, nitrite concentrations were less than the minimum reporting level. Therefore, nitrite plus nitrate as nitrogen is referred to as nitrate throughout this report. Nitrate concentrations for this study are reported in table 2.

POSSIBLE SOURCES OF NITRATE

Nitrogen occurs as two stable isotopes, ^{15}N and ^{14}N, and the ratio ^{15}N:^{14}N is reported relative to a standard, in per mil. (See page IV for further description of notation, standards, and units.) The $\delta^{15}N$ can provide information on sources of the nitrogen in nitrate. Atmospheric sources and microbial decay of organic matter in soil may contribute small amounts of nitrate to the Silurian-Devonian aquifer, but the relatively high concentrations of nitrate indicate that most of the nitrate probably is derived from some combination of (1) inorganic nitrogen fertilizers and (2) human and other animal wastes. Inorganic nitrogen fertilizers, such as urea, ammonium nitrate, and potassium

Table 2. Results of analysis of water-chemistry samples collected from Cedar Falls water-supply wells 5, 9, and 10, and a domestic well, April 29 and June 26, 1998, Cedar Falls, Iowa

[Number in parentheses is the U.S. Geological Survey Water Data Storage and Retrieval System parameter code. µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than method minimum reporting level; --, not available; $CaCO_3$, calcium carbonate; CFU, Cedar Falls Utilities; $\delta^{15}N$, a measure of the difference between the ratio of nitrogen-15 to nitrogen-14 in the sample and standard atmospheric nitrogen, see page IV for details]

			Physical properties					
Sampling-site name (fig. 2)	Sampling-site number	Date of sample collection (1998)	Specific conductance (µS/cm) (00095)	pH, water, whole field (standard units) (00400)	Water temperature (degrees Celsius) (00010)	Dissolved oxygen (mg/L) (00300)	Alkalinity (laboratory) total (mg/L as $CaCO_3$) (90410)	Dissolved solids, residue at 180 degrees Celsius (70300)
CFU well 5	423042092265801	April 29	631	7.1	11.5	2.4	239	368
CFU well 9	423341092273001	April 29	531	7.4	10.5	2.2	210	313
(duplicate)	423341092273001	April 29	--	--	--	--	210	312
(blank)	423341092273001	April 29	--	--	--	--	1.7	<10
CFU well 10	423341092273301	April 29	499	7.3	10.5	3.7	213	294
Domestic well	423411092260401	April 29	482	7.4	11.0	.8	188	285
	423411092260401	June 26	485	7.3	14.0	.2	--	--
(duplicate)	423411092260401	June 26	--	--	--	--	--	--

	Major ions								
Sampling-site name (fig. 2)	Calcium, dissolved (mg/L as Ca) (00915)	Magnesium, dissolved (mg/L as Mg) (00925)	Sodium, dissolved (mg/L as Na) (00930)	Potassium, dissolved (mg/L as K) (00935)	Sulfate, dissolved (mg/L as SO4) (00945)	Chloride, dissolved (mg/L as Cl) (00940)	Fluoride, dissolved (mg/L as F) (00950)	Bromide, dissolved (mg/L as Br) (71870)	Silica, dissolved (mg/L as SiO_2) (00955)
CFU well 5	83	21	14	1.8	35	31	0.21	0.06	13
CFU well 9	70	21	5.4	1.1	21	12	.15	.06	18
(duplicate)	78	21	5.5	1.2	20	12	.17	.06	20
(blank)	<.02	<.004	<.10	<.10	1.1	<.10	<.10	<.01	<.10
CFU well 10	65	20	4.8	1.1	18	8.8	.20	.05	16
Domestic well	69	17	3.6	1.3	30	9.9	<.10	.05	15
	--	--	--	--	--	--	--	--	--
(duplicate)	--	--	--	--	--	--	--	--	--

Table 2. Results of analysis of water-chemistry samples collected from Cedar Falls water-supply wells 5, 9, and 10, and a domestic well, April 29 and June 26, 1998, Cedar Falls, Iowa—Continued

Sampling site name	Nutrients					
	Nitrite nitrogen, dissolved (mg/L as N) (00613)	Nitrite plus nitrate nitrogen, dissolved (mg/L as N) (00631)	Ammonia nitrogen, dissolved (mg/L as N) (00608)	Ammonia plus organic nitrogen, dissolved (mg/L as N) (00623)	Phosphorus, dissolved (mg/L as P) (00666)	Phosphorus, dissolved, orthophosphate (mg/L as P) (00671)
CFU well 5	<0.01	4.1	<0.02	<0.10	0.02	0.04
CFU well 9	<.01	8.5	<.02	<.10	.04	.06
(duplicate)	<.01	8.6	<.02	<.10	.05	.06
(blank)	<.01	<.05	<.02	<.10	<.01	<.01
CFU well 10	<.01	6.5	<.02	<.10	.02	.04
Domestic well	--[1]	--[1]	--[1]	--[1]	--[1]	--[1]
	<.01	.14	.16	.11	<.01	<.01
(duplicate)	<.01	.22	.16	<.10	<.01	<.01

Sampling-site name (fig. 2)	Metals		Tritium, total (picocuries per liter) (07000)	δ ^{15}N (per mil) (82690)
	Iron, dissolved (µg/L as Fe) (01046)	Manganese, dissolved (µg/L as Mn) (01056)		
CFU well 5	<10	<4	31	8.2
CFU well 9	<10	<4	52	5.1
(duplicate)	<10	<4	51	5.3
(blank)	<10	<4	--	--
CFU well 10	<10	<4	44	5.2
Domestic well	900	68	50	5.4
	--	--	--	--
(duplicate)	--	--	--	--

[1] U.S Geological Survey National Water-Quality Laboratory (NWQL) analytical results were rejected due to conflict with analytical results from the University of Iowa Hygienic Laboratory (UHL) for a nitrate and bacteria sample collected coincidentally. NWQL analytical results for the June 26, 1996, nutrients samples were in agreement with the UHL analytical results.

nitrate, are produced by the fixation of nitrogen gas from the atmosphere, and they generally have $\delta^{15}N$ values from -4 to +4, although some fertilizers have $\delta^{15}N$ values from -8 to +7 (Kendall, 1998). Nitrate derived from human and other animal wastes generally has $\delta^{15}N$ between +10 and +20 (Kendall, 1998). Denitrification, which is a multiple-step process associated with the reduction of nitrate, causes the $\delta^{15}N$ values of the remaining nitrate to increase exponentially (Kendall, 1998), and $\delta^{15}N$ values from nitrogen fertilizers can become more like those associated with human and other animal wastes. The detection of nitrogen dioxide in the water-quality samples indicates that the reduction of nitrate is taking place in the Silurian-Devonian aquifer near the wells sampled for this study (E. Busenberg, U.S. Geological Survey, written commun., 1998). The nitrogen isotope samples collected during the study had $\delta^{15}N$ values from 5.1 to 8.2 (table 2), which indicates that the primary source of nitrate in the sampled wells probably is inorganic nitrogen fertilizers. The nitrogen isotope ratio for water from well 5 was higher than for water from the other three wells, and this higher ratio may indicate that a larger percentage of the nitrate in water from well 5 is derived from human and other animal wastes.

Water from the shallowest of the four wells had the lowest nitrate concentration, and water from the deepest of the wells had the highest nitrate concentrations. This suggests that nitrate is moving along predominantly horizontal ground-water flow paths, entering the Silurian-Devonian aquifer at some distance from well 9. If nitrate had been moving along predominantly vertical ground-water flow paths near well 9, this pattern of the lowest nitrate concentrations in water from the shallowest of the wells and the highest nitrate concentrations in water from the deepest of the wells could have been caused by a period of higher nitrogen inputs in the past followed by a period of lower nitrogen inputs more recently. If this had occurred, the 1975–98 nitrate concentrations observed in water from the deeper wells would have been observed in water from the shallower wells in the past. However, predominantly agricultural land use and historical nitrogen fertilizer sales, discussed later in the report, indicate higher rather than lower nitrogen inputs are more likely to have occurred recently within the contributing area of wells 9 and 10.

Time of Recharge

Time of recharge can be estimated using several methods that make use of the fact that water exposed to the Earth's atmosphere contacts natural and synthetic constituents. The time when this water was isolated from the Earth's atmosphere by moving into the ground-water zone (becoming recharge) can be estimated by measuring the concentrations of those constituents.

CFCs are synthetic volatile organic compounds that have been produced since the 1930's for use in refrigerants, aerosols, and cleaning agents. CFCs eventually are released to the atmosphere where they may become part of the water cycle in the form of precipitation and can be used for estimating the time of recharge for water that entered the ground-water zone after 1940. To estimate the time of recharge to ground water, the CFC concentration in the sample is divided by the appropriate Henry's Law constant to give the partial pressure of the CFC compound in air at the time the sample was last in contact with the atmosphere. The Henry's Law constants are temperature dependent, so an estimate of recharge temperature is needed. The recharge temperature is the temperature at the base of the unsaturated zone and can be estimated from dissolved gas (nitrogen to argon) ratios or from long-term air temperature records for the area. The calculated partial pressure then is compared with the atmospheric concentration curves that define the temporal trend in CFC concentrations in air since 1940 to determine the time of recharge of the sample. Time-of-recharge estimates using the CFC technique that is based on CFC-11, CFC-12, and CFC-113, may be accurate to within a few years under ideal conditions for water recharged during the last 30 years (Plummer and Busenberg, 1993).

Time of recharge also can be estimated on the basis of the concentration of tritium in ground water. Tritium is a hydrogen isotope that is produced naturally in the Earth's outer atmosphere, but the amount of tritium in the atmosphere increased dramatically during above-ground thermonuclear weapons testing in the 1950's and 1960's. Water that entered the ground-water zone prior to nuclear testing contains little or no tritium, and water recharged during or after nuclear testing contains detectable concentrations of tritium (Freeze and Cherry, 1979). Relative time-of-recharge estimates from tritium analyses are useful in separating ambiguities and confirming results from CFC-based time-of-recharge estimates.

The results of the time-of-recharge estimates are given in table 1. The CFC-based results were inconclusive for water from well 5, but they indicate that the time of recharge for the water samples collected from wells 9, 10, and the domestic well was the mid-1970's, the early 1970's, and the mid-1980's, respectively (E. Busenberg, U.S. Geological Survey, written commun., 1998). For these wells, the estimated time of recharge for the shallower, domestic well is later than the estimated time of recharge for the deeper, Cedar Falls water-supply wells 9 and 10. The estimated time of recharge for the well 9 sample was based on CFC-11 analytical results (years 1975.5, 1975.0, and 1975.5) and CFC-12 analytical results (years 1977.5, 1977.0, and 1978.0). The three values in parentheses are the analytical results for three separate samples collected at the same time from each well. No time-of-recharge estimates that were based on CFC-113 concentrations were made for this sample due to interference with other constituents in the water (E. Busenberg, U.S. Geological Survey, written commun., 1998). The estimated time of recharge for the well 10 sample was based on CFC-11 analytical results (years 1972.0, 1972.0, and 1976.0) and CFC-12 analytical results (years 1973.5, 1973.5, and 1978.0). As with well 9, no time-of-recharge estimates that were based on CFC-113 concentrations were made due to interference with other constituents in the water sample (E. Busenberg, U.S. Geological Survey, written commun., 1998). The estimated time of recharge for the domestic well sample was based on CFC-12 analytical results (years 1986.5, 1987.5, and 1986.0). Time of recharge estimates that were based on CFC-11 and CFC-113 analytical results were disregarded due to problems with degradation of these compounds (E. Busenberg, U.S. Geological Survey, written commun., 1998). For all four sampled wells, the tritium results indicate that time of recharge for most of the water was after 1953, which agrees with the CFC-based estimates.

Land Use Near Cedar Falls Water-Supply Wells 9 and 10

If the large nitrate concentrations found in water from Cedar Falls water-supply wells 9 and 10 are associated with nitrogen fertilizer use in the past, then examination of historical land use in the area may be useful in indicating potential source areas. U.S. Department of Agriculture aerial photographs from 1941, 1952, and 1970 were obtained from the University of Iowa Map Library (Iowa City) and scanned to obtain high-resolution electronic images. The location of the images were established using a geographic information system (GIS). Cedar Falls Utilities provided digital images of 1994 aerial photography supported by Black Hawk County (fig. 4). The geographic coordinates were provided with the digital images so that the GIS could be used to make direct comparisons between images from different years.

The area contributing recharge to wells 9 and 10 was estimated using the calculated fixed radius method (U.S. Environmental Protection Agency, 1987). This method, which is also described in a draft copy of the Iowa Wellhead Protection Plan Guidance Document (Iowa Department of Natural Resources, written commun., 1997), assumes that water being withdrawn from a well is from a cylinder, and the equation for calculating r, the radius of that cylinder, is:

$$r = \sqrt{\frac{Qt}{\pi n H}}, \qquad (1)$$

where Q = pumping rate of the well, in cubic feet per year;
t = time of travel to the well, in years;
n = aquifer porosity; and
H = open interval, in feet.

For the purposes of this estimate, the pumping rate of the well was assumed to be 56,934,900 gallons per year or approximately 7,610,000 cubic feet per year, the combined pumpage of wells 9 and 10 during 1996, a recent year with high combined pumpage (P. Mallinger, Cedar Falls Utilities, oral commun., 1999). The time of travel was assumed to be 25 years, an approximate average of the CFC-based time-of-recharge estimates for the two wells (table 1). The aquifer porosity was assumed to be 0.05, the high end of a range of porosity values specified in the draft copy

EXPLANATION

Boundary of area within 1 mile of the water tower between Cedar Falls water-supply wells 9 and 10

Water tower between Cedar Falls water-supply wells 9 and 10

Figure 4. Composite of 1994 aerial photographs of the area near water-supply wells 9 and 10, Cedar Falls, Iowa.

of the Iowa Wellhead Protection Plan Guidance Document (Iowa Department of Natural Resources, written commun., 1997) for common fractured limestone and dolomite. The open interval was assumed to be 108 feet, the approximate average of the open intervals of wells 9 and 10. Using these assumptions, the radius of the cylinder was calculated to be 3,349 feet.

The radius of the area contributing recharge was assumed to be 5,280 feet or 1 mile in an effort to make sure that the area studied for land-use changes would be at least as large as the area contributing recharge estimated using the calculated fixed-radius method. The area contributing recharge estimated by a ground-water flow model is unlikely to have a circular shape because of aquifer heterogeneity within the fractured carbonate rocks of the Silurian-Devonian aquifer and regional hydraulic gradients.

A GIS was used to establish a point at the water tower, midway between wells 9 and 10, and generate a 1-mile-radius circle centered at the water tower. Within that circle, areas of four different land-use categories (agricultural, undeveloped, urban, and open water) were delineated. For the purposes of this study, agricultural lands were considered to be those areas used for crop or livestock production where nitrogen fertilizer or animal waste might have been applied. Farmsteads and building sites were not included. Undeveloped lands included those areas, such as parks, wooded areas along rivers, and recreational areas around lakes, that did not fit into the other three categories. Urban lands are defined as those areas used for commercial, industrial, or residential purposes. The open-water category includes bodies of water, such as lakes, rivers, and wetlands that were clearly visible on the aerial photographs.

Figure 5 shows the location of the water tower and the delineation using the four land-use types interpreted from the 1994 aerial photographs. The generalized water-level contours indicate that around wells 9 and 10, ground water in the Silurian-Devonian aquifer generally flows from northwest to southeast.

The fraction of the total cumulative areas for each land-use category in 1941, 1952, 1970, and 1994 are summarized in figure 6. Figure 6 shows that within 1 mile of the water tower between wells 9 and 10, the amount of agricultural land has decreased steadily from about 69 percent of the total area in 1941 to about 49 percent in 1994. During this same time, the undeveloped areas increased from about 20 to 23 percent, the urban area increased from about 10 to about 24 percent, and the open water area increased from about 1 to about 4 percent of the total area.

The relative proportion of agricultural land upgradient within 1 mile of the water tower (approximately the area in figure 5 where the water-level altitude is greater than 852 feet) has remained fairly stable since 1941. This suggests that the increased nitrate concentrations observed in water from wells 9 and 10 are not the result of increased agricultural land use near the wells.

IMPLICATIONS FOR FUTURE NITRATE CONCENTRATIONS

Figure 7 shows generally increasing nitrogen fertilizer sales in Iowa from 1945 through 1997 (John Sawyer, Iowa State University, written commun., 1998) and the generally increasing nitrate concentrations in water from well 9 from 1975 through 1998 (P. Mallinger, Cedar Falls Utilities, written commun., 1999). To show relative concentrations in relation to the fertilizer sales data, the nitrate concentrations in water from well 9 also are plotted at the respective estimated times of recharge (fig. 7). The 22-year time difference between the time of sample collection and the estimated time of recharge is based on the CFC results for the sample collected on April 29, 1998 (table 1). Over the years, the elapsed time between the time of recharge and when the water sample was collected may have been less or more than 22 years and may have been affected by many factors, including pumping rates of individual wells, development of the aquifer, and water-level changes in the aquifer.

Assuming that nitrogen fertilizer sales are directly related to nitrogen fertilizer use, and the trend of annual nitrogen fertilizer use in the area contributing recharge to well 9 is similar to statewide use, figure 7 may indicate why nitrate concentrations in water from well 9 have been increasing over time and may help estimate trends in future nitrate concentrations. For example, a sample collected in 1984 had a nitrate concentration of 3.0 mg/L and an estimated time of recharge of 1962 when nitrogen fertilizer sales totaled about 164,000 tons in Iowa. A sample collected in 1997 had a nitrate concentration of 8.8 mg/L and an estimated time of recharge of 1976 when nitrogen fertilizer sales totalled about 747,000 tons in Iowa. From 1976 through 1997, annual nitrogen fertilizer sales in Iowa have totalled at least 840,000 tons per year, except during the Payment-In-Kind program year of 1983, and the annual nitrogen fertilizer sales in Iowa averaged more than 968,000 tons per year. This average is nearly 30 percent more than the 1975 usage rate and may indicate that nitrate concentrations in water from well 9 may persist at present levels or could increase in future years if fertilizer use increases and if higher nitrate concentrations are directly related to higher nitrogen fertilizer use.

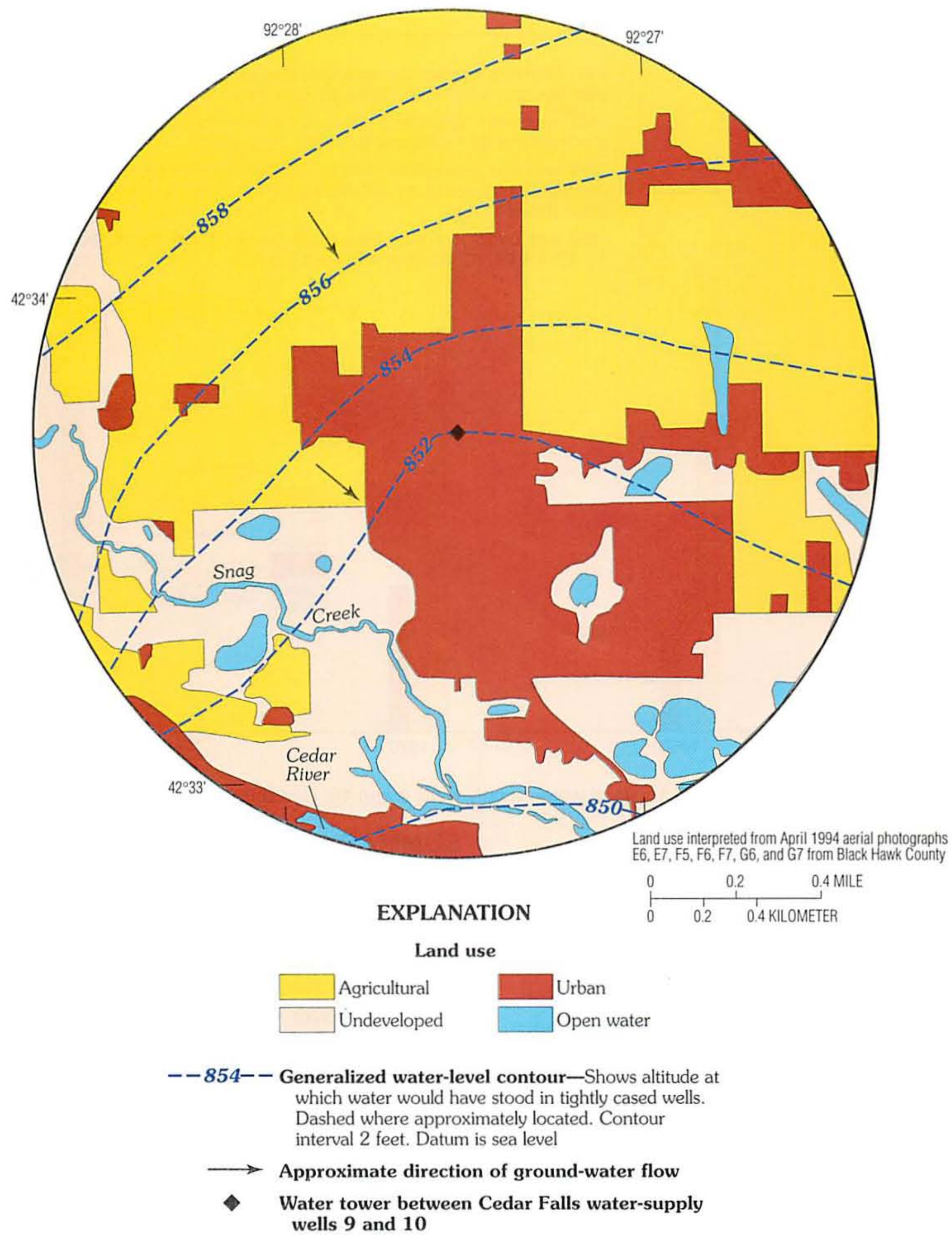


Figure 5. 1994 land use with 1 mile of water-supply wells 9 and 10, Cedar Falls, Iowa, and generalized water-level contours in the Silurian-Devonian aquifer, April 24–May 8, 1998.

Regression was used to describe a relation, with $r^2=0.52$, between annual nitrogen fertilizer sales in Iowa and nitrate concentrations in water from well 9, 22 years later (fig. 8). This relation indicates that annual nitrogen fertilizer sales of about 903,000 tons are associated with nitrate concentrations 22 years later of 10 mg/L, the Maximum Contaminant Level of nitrate as nitrogen (U.S. Environmental Protection Agency, 1996), in water from well 9. In 17 of the 22 years from 1976 through 1997, annual nitrogen fertilizer sales in Iowa have exceeded 903,000 tons (John Sawyer, Iowa State University, written com-

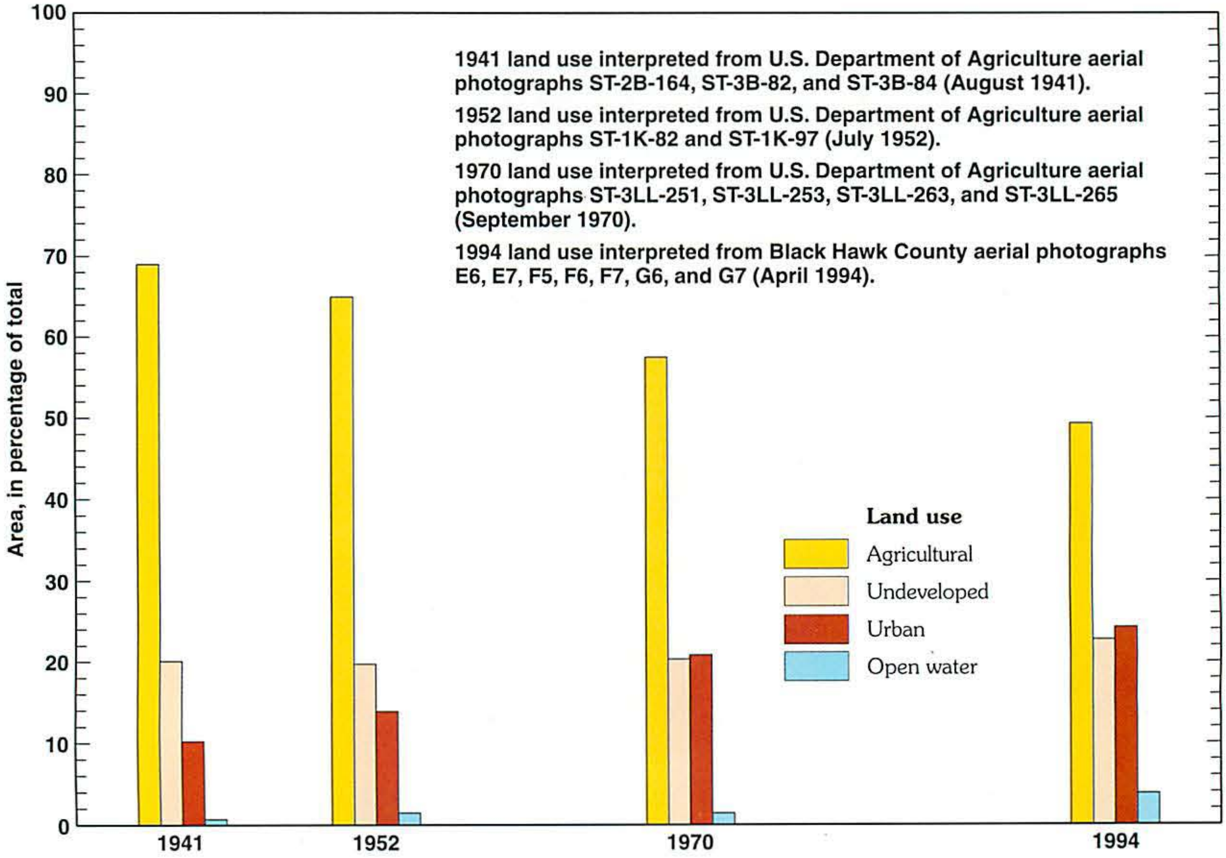


Figure 6. Historical land use within 1 mile of water-supply wells 9 and 10, Cedar Falls, Iowa.

mun., 1998). The regression relation appears to reinforce the qualitative assessment of the trends seen in figure 7, which led to the suggestion that nitrate concentrations in water from well 9 could persist at present levels or increase in future years.

The area contributing recharge to well 9 is assumed to be within 1 mile of the well. Well 9 is open to the fractured carbonate rocks of the Silurian-Devonian aquifer, and the area contributing recharge could be much larger and more complex in shape because of preferential flow in multiple zones and regional hydraulic gradients. More information about local aquifer characteristics, chemical processes affecting nitrate, the time of travel through the unsaturated zone, and the ground-water flow system near wells 9 and 10 would improve understanding of the sources of nitrate and providing information pertinent to evaluating management practices. Controlling the source of the nitrate may be difficult, and measures taken today might not have the desired effect for many years.

SUMMARY

Carbonate rocks of the Silurian-Devonian aquifer are the primary source of water for Cedar Falls, located in Black Hawk County, northeast Iowa (fig. 1). A trend of increasing nitrate concentrations has been detected in water samples collected from Cedar Falls water-supply wells 9 and 10, and 1998 nitrate concentrations were close to the U.S. Environmental Protection Agency's Maximum Contaminant Level of 10 mg/L as nitrogen in drinking water. These wells are located in an area where the Silurian-Devonian aquifer is covered by 90 feet of alluvial and glacial deposits. A study to evaluate the concentrations and sources of nitrate in water from wells 9 and 10 was conducted by the U.S. Geological Survey in cooperation with Cedar Falls Utilities. Water-chemistry samples were collected from municipal water-supply wells 5, 9, and 10, and a domestic well. These samples were analyzed for physical properties, dissolved solids, major ions, nutrients, trace elements, tritium, nitrogen isotopes, and

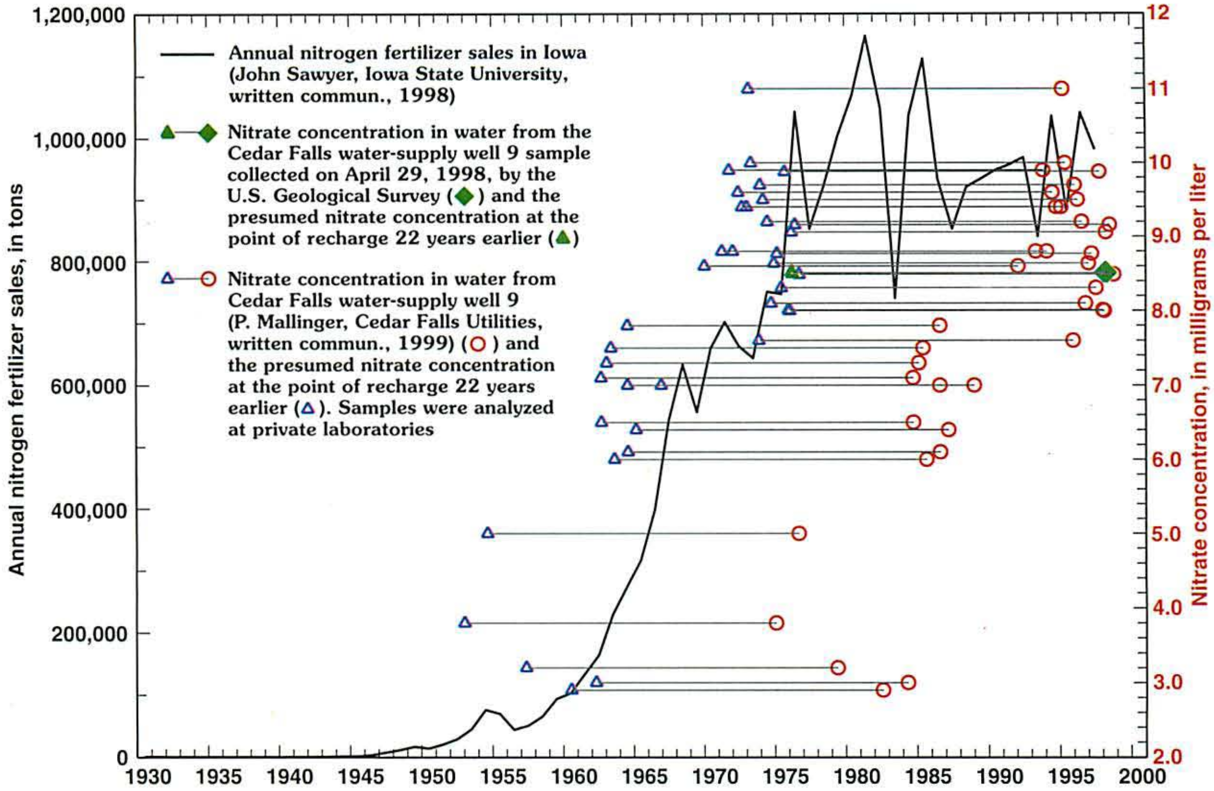


Figure 7. Annual nitrogen fertilizer sales in Iowa, nitrate concentrations in water from Cedar Falls water-supply 9, and estimated time of recharge, 1930–98.

chlorofluorocarbons (CFCs). The nitrogen isotopes were used to identify possible sources of the nitrate, and the tritium and CFC results were used to estimate the time of recharge of the sampled water.

In this report, all wells open to Devonian-age rocks or Silurian-age rocks, or both, were considered to be Silurian-Devonian wells. In the Cedar Falls area, the Silurian-Devonian aquifer is estimated to be about 150 to 300 feet thick. Transmissivity of the Silurian-Devonian aquifer is highly variable, depending on the degree of interconnection between the joints, fractures, and bedding planes.

A network of Silurian-Devonian observation wells in Cedar Falls and the surrounding area was established as part of an ongoing study to determine the areas contributing recharge to the Cedar Falls water-supply wells. Water-level information from these wells was used to construct a map of generalized water-level contours that shows that ground water in the Silurian-Devonian aquifer generally flows from northwest to southeast and down the Cedar River Valley.

CFC analytical results indicate that time of recharge was the mid-1970s for water from Cedar Falls water-supply well 9. Tritium analytical results indicate that the time of recharge was after 1953 for water from wells 5, 9, 10, and the domestic well.

On the basis of nitrogen isotope analysis, the high nitrate concentrations in water from wells 9 and 10 probably are the result of nitrogen fertilizer applications in the area contributing recharge to the wells. Locally, the nitrate concentrations increase with depth, and the estimated time of recharge for the shallower well is later than the estimated time of recharge for the deeper wells. This suggests that the nitrate is moving along predominantly horizontal ground-water flow paths through the Silurian-Devonian aquifer.

Land-use data from 1941 through 1994 indicate that increased nitrate concentrations observed in water from wells 9 and 10 are not the result of increased agricultural land use near the wells. Within 1 mile of the water tower between wells 9 and 10, the proportion of agricultural land has remained fairly stable since 1941.

Nitrogen fertilizer sales in Iowa have been higher in recent years than during the mid-1970's. This suggests that nitrate concentrations in water from well 9 may persist at present levels or could increase in future years if fertilizer use increases and if higher nitrate

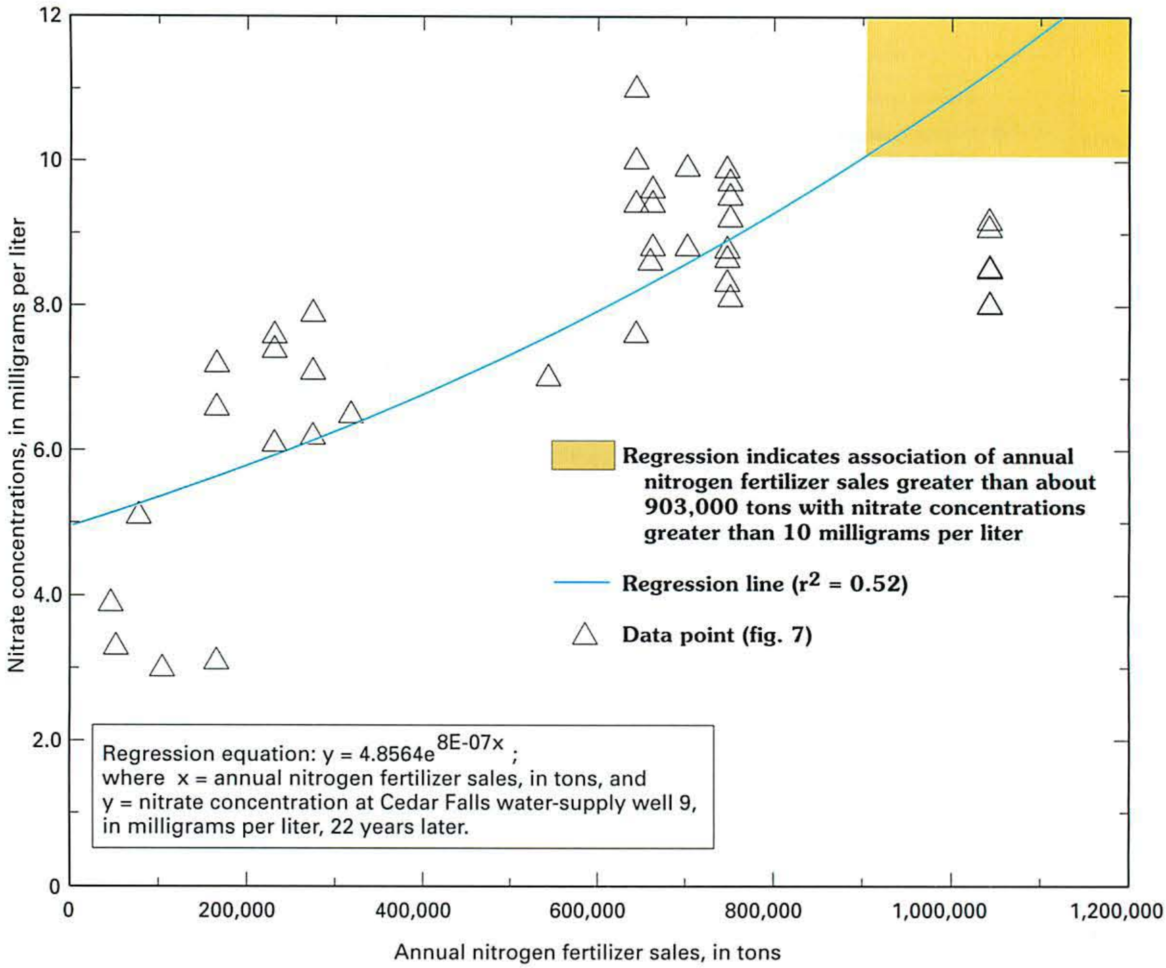


Figure 8. Regression of annual nitrogen fertilizer sales in Iowa and nitrate concentrations in water from water-supply well 9, Cedar Falls, Iowa, 22 years later.

concentrations are directly related to higher nitrogen fertilizer use.

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