

Prepared in cooperation with the Prairie Island Dakota Comm

Water Resources of the P Indian Reservation, Minn

Water-Resources Investigations Report 99-4069



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

Water Resources of the Prairie Island Indian Reservation, Minnesota, 1994-97

By Timothy K. Cowdery

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Prepared in cooperation with the Prairie Island Dakota Community

U.S. Department of the Interior

Bruce Babbitt, Secretary

U.S. Geological Survey

Charles G. Groat, Director

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Mounds View, Minnesota, 1999

For additional information write to:

District Chief

U.S. Geological Survey, WRD

2280 Woodale Drive

Mounds View MN 55112

Copies of this report can be purchased from:

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Conversion factors, vertical datum, and abbreviations

<u>Multiply inch-pound unit</u>	<u>By</u>	<u>To obtain metric unit</u>
acre	0.0407	hectare
cubic feet per day (ft ³ /d)	0.02832	cubic meters per day
foot (ft)	0.3048	meter
inch (in.)	2.54	centimeter
mile (mi)	1.609	kilometer
pound per pound	2.2046 x 10 ⁻⁶	microgram per kilogram
square mile (mi ²)	2.590	square kilometer
degrees Fahrenheit (°F)	(temperature °F - 32)/1.8	degrees Celsius

Sea level: In this report, sea level refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

<	Less than
>	Greater than
mg/L	Milligram per liter
µg/L	Microgram per liter
µm	Micrometer
pCi/L	Picocurie per liter
CFC	Chlorofluorocarbon
GL	Canadian Interim Sediment Quality Guideline's threshold effect level
HAL	U.S. Environmental Protection Agency's health advisory limit
MCL	U.S. Environmental Protection Agency's maximum contaminant level
NSP	Northern States Power (Company)
NWQL	U.S. Geological Survey's National Water-Quality Laboratory
PAH	Polycyclic aromatic hydrocarbon
QC	Quality control
SMCL	U.S. Environmental Protection Agency's secondary maximum contaminant level
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	Volatile organic compound

Water Resources of the Prairie Island Indian Reservation, Minnesota, 1994-97

By Timothy K. Cowdery

Abstract

This evaluation of the water resources on the Prairie Island Indian Reservation includes data collected from 8 surface-water sites and 22 wells during 1994–97 and historical data. The Mississippi River and the lakes and wetlands connected to it are separated from the Vermillion River and the lakes and wetlands connected to it by the surficial aquifer on Prairie Island and by Lock and Dam Number 3. These surface-water groups form hydrologic boundaries of the surficial aquifer. The aquifer is 130–200 feet thick, extends to bedrock (the Franconia Formation, which is also an aquifer), and is composed primarily of sand and gravel, but also contains thin, isolated lenses of finer-grained material. Flow in the surficial aquifer is normally from the Mississippi River to the Vermillion River (southwest). During spring snowmelt or heavy rains, a ground-water mound forms in the center of the study area and causes radial ground-water flow toward the surrounding surface waters.

Surface- and ground-water quality was generally similar, but the median ground-water nitrate concentration was 3.6-times greater than that for surface water. Water samples were dominated by calcium, magnesium, and bicarbonate ions, were usually oxygenated, and had a median dissolved solids concentration of 250 milligrams per liter (mg/L). Thirty-nine percent of ground-water samples showed evidence of anthropogenic nitrate. Most samples contained low concentrations of ammonia (less than 0.04 milligrams per liter as nitrogen). All 15 surface-water samples contained coliform or fecal streptococci bacteria, with 33 percent exceeding 100 colonies per milliliter. Two ground-water and two surface-water samples analyzed for trace metals contained natural concentrations except for one ground-water sample that contained 30 mg/L of lead (probably from a bullet). No volatile organic compounds were detected in 3 ground-water and 3 surface-water samples. Triazine herbicides and their degradation products were detected in one-half of the ground-water samples

at concentrations below 1 microgram per liter ($\mu\text{g/L}$) except for one sample at 3 $\mu\text{g/L}$. Wells with initially high concentrations of nitrate or triazines continued to have high concentrations throughout the study. Several polycyclic aromatic hydrocarbons and monoaromatic chemicals were detected at low concentration (less than 89 micrograms per kilogram) in 4 samples of 1993 Mississippi River flood sediments deposited in the study area.

Ground-water recharge dates based on chlorofluorocarbon (CFC) concentrations indicate that sampled ground water was young (less than 2 decades old) and that all tritium contained in samples from this study can be explained by atmospheric sources. Most historical tritium concentrations can also be explained by atmospheric sources through recharge from spatially and temporally constant precipitation and snowmelt. However, samples from three wells within 800 feet of the Prairie Island Nuclear Power Plant contained tritium at concentrations that cannot be explained by such atmospheric sources. These concentrations decline to that explainable by atmospheric sources within 800 feet of the wells. Many samples contained CFC-113 concentrations higher than that possible from equilibrium with the atmosphere. This CFC-113 contamination is presumably from Mississippi River recharge and complicated the recharge date estimates.

The only surface-water constituents exceeding U.S. Environmental Protection Agency drinking water standards was coliform or fecal streptococci bacteria, which was exceeded in all samples. Thirteen percent of ground-water samples exceeded the nitrate maximum contaminant level (MCL), but this is probably higher than the percentage of the aquifer exceeding the nitrate MCL because most of the wells sampled were shallow. Surface-water recharge to and ground-water discharge from the surficial aquifer influence the water quality in both the aquifer and the surrounding surface water. However, surface water probably influences ground-water quality more because of the greater amount of surface water flowing through the study area.

Introduction

The Prairie Island Indian Community is concerned about the sound management and conservation of its water resources. The 563-acre reservation is located near the southeast end of Prairie Island, in Goodhue County, Minnesota (fig. 1). Prairie Island is located within the Mississippi River Valley between the cities of Hastings and Red Wing, on the eastern border of Minnesota (fig. 1). Adjacent to the reservation on the southeast is the Prairie Island Nuclear Power Plant (fig. 2), owned and operated by Northern States Power Company (NSP).

The reservation is surrounded by rivers, lakes, and wetlands and is underlain by surficial and buried aquifers. Management of these water resources requires an understanding of the hydrologic systems on Prairie Island, both in terms of water movement and quality. Recent commercial and residential development on the reservation has increased the need for this understanding. Concerns of the Prairie Island Indian Community include changes in reservation water resources from frequent flooding of the island by the Mississippi River and from the power plant since it began operation in 1971.

The U.S. Geological Survey (USGS), in cooperation with the Prairie Island Indian Community, conducted a study of the surface- and ground-water resources of the Prairie Island Indian Reservation during 1994-97. The objectives of the study were to: 1) describe the hydrogeology of the surficial aquifer underlying the reservation, 2) describe the water quality of the surficial aquifer and the surface water on the reservation, and 3) describe the hydrologic and water-quality relations between ground water in the surficial aquifer and surface water on the reservation. This report presents the results of this study.

Approach

The study area consists of the southeastern one-third of Prairie Island, bounded on the west by the township line between ranges 15 and 16 west, on the northeast by the Mississippi River and the

lakes and wetlands connected to it (hereinafter, the Mississippi waters), and on the southwest by the Vermillion River and the lakes and wetlands connected to it (hereinafter, the Vermillion waters) (fig. 2). The geologic and hydrologic characteristics of the surficial aquifer on the Prairie Island Indian Reservation were determined from drilling and test boring logs from five sources: 1) 22 logs reported by commercial well drillers and archived by the Minnesota Geological Survey; 2) 28 logs from wells drilled for NSP; 3) 40 logs from borings drilled for NSP; 4) 6 logs from wells and borings drilled for the U.S. Army Corps of Engineers; and 5) 10 logs from wells drilled by the USGS for this study. The water-table surface, under various hydrologic conditions, was interpolated from water-level measurements at 10 wells and 9 staff gages throughout the study period. Water samples collected at 22 wells (15 observation, 6 domestic, and 1 public supply) and 8 surface-water sites at least once during 5 sampling periods characterized the quality of water resources. Table 1 lists the number of samples analyzed for each type of constituent during each sampling period. Four sediment samples collected in 1995 from material deposited on the island during the 1993 Mississippi River flood were used to assess soil contamination by organic compounds from flooding. Geologic, hydrologic, and water-quality data were combined to estimate ground-water/surface-water interaction, both in terms of water flow and quality.

Sampling Sites and Methods

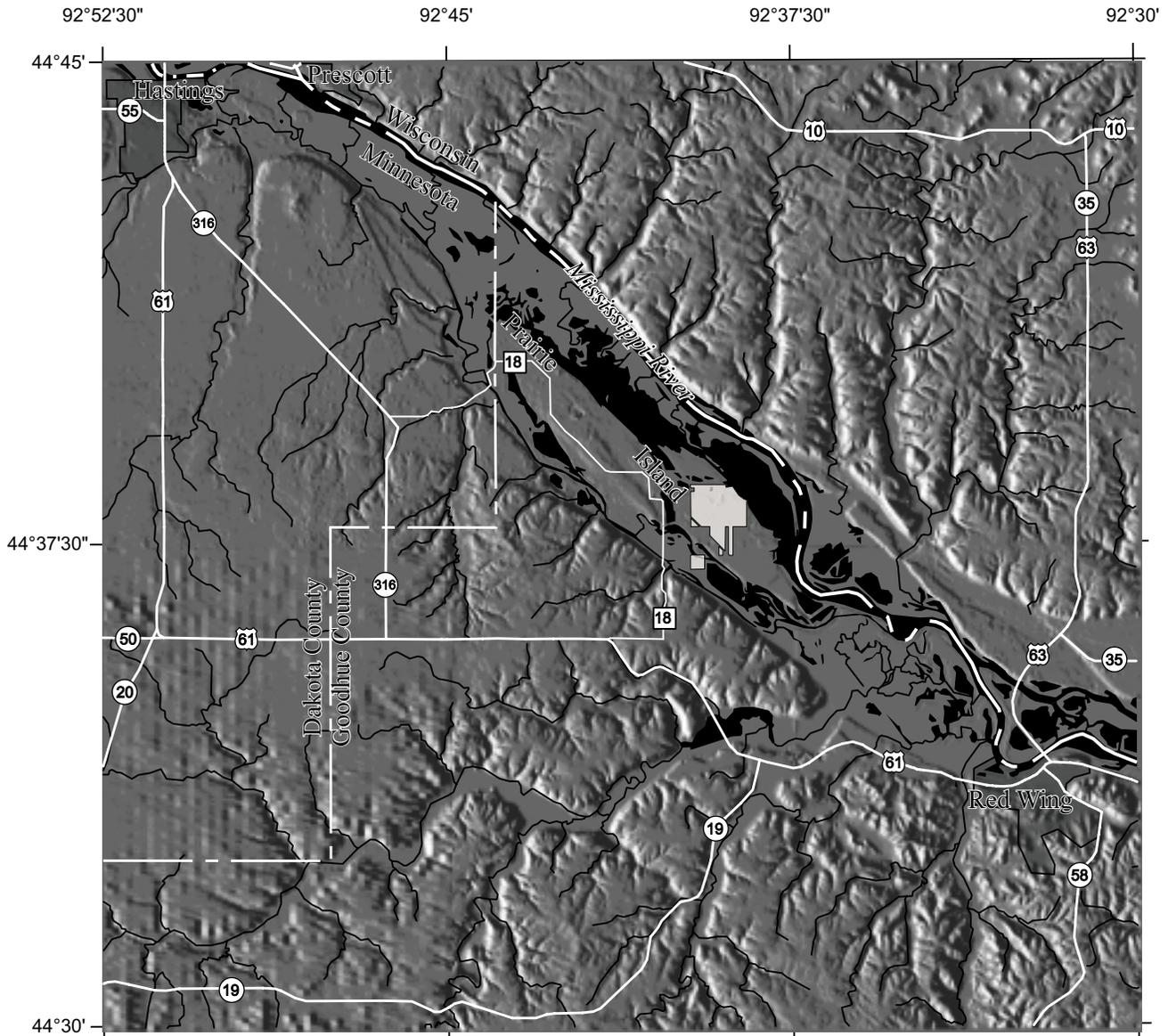
The ground-water and surface-water sites sampled for this study are shown in figure 2. When the study began, the eastern part of the study area contained shallow observation wells installed by NSP to monitor ground water near the power plant. The south-central part of the study area had domestic wells installed in the surficial aquifer. Most wells installed for this study were located in the northwestern part of the study area where few wells existed. Five NSP observation wells, 10 newly installed observation wells, and 6 domestic wells were used to describe water quality in the surficial aquifer. The Prairie Island Indian Community public-

water supply was also sampled to characterize its quality, although it draws water from a deeper bedrock aquifer.

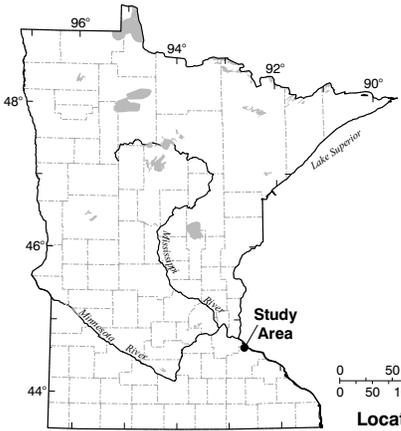
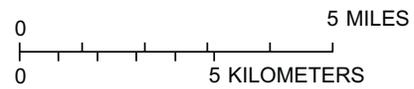
Reliable well construction and geologic data were available for all observation and public-supply wells sampled for this study. The median depth from the water table to the midpoint of the sampling interval for the 15 observation wells completed in the surficial aquifer was 3.00 ft. The median screen length was 4.43 ft. Almost no construction data were available for the 6 domestic wells. Other domestic wells completed in the surficial aquifer that have construction records are as deep as 100 ft and have screens as long as 20 ft. Therefore, the 6 domestic wells were likely completed deeper, with longer screens, than were the observation wells. All observation wells were constructed of 2 in.-diameter polyvinylchloride. Domestic wells were constructed of 2-4 in.-diameter steel, some of which is galvanized.

The quality of ground water sampled for this study is representative of near-surface water, which is most affected by recent land uses and surface-water interaction. Although sampled wells were completed throughout the upper one-half of the surficial aquifer, most were completed in the uppermost 6 ft of the aquifer.

Koterba and others (1995) detail the standard USGS methods used to sample wells for water quality in this study. All observation wells were sampled with a Keck submersible pump equipped with Teflon tubing. Domestic and public-supply wells were sampled using the pumps installed in the wells. Water was collected from these wells, either from an outside or a kitchen-sink tap, before being treated by a water softener. Major-ion, nutrient, and trace-metal samples were filtered with a 0.45- μm nitrocellulose filter using either the Keck pump or a peristaltic pump equipped with Tygon tubing. Triazine-herbicide samples were filtered in a similar manner using a 0.7- μm baked glass-fiber filter. Organic-carbon samples were filtered with a 0.45- μm silver metal filter using compressed nitrogen gas. Tritium and volatile-organic-compound (VOC) samples were not filtered. Chlorofluorocarbon (CFC) and dissolved-gas



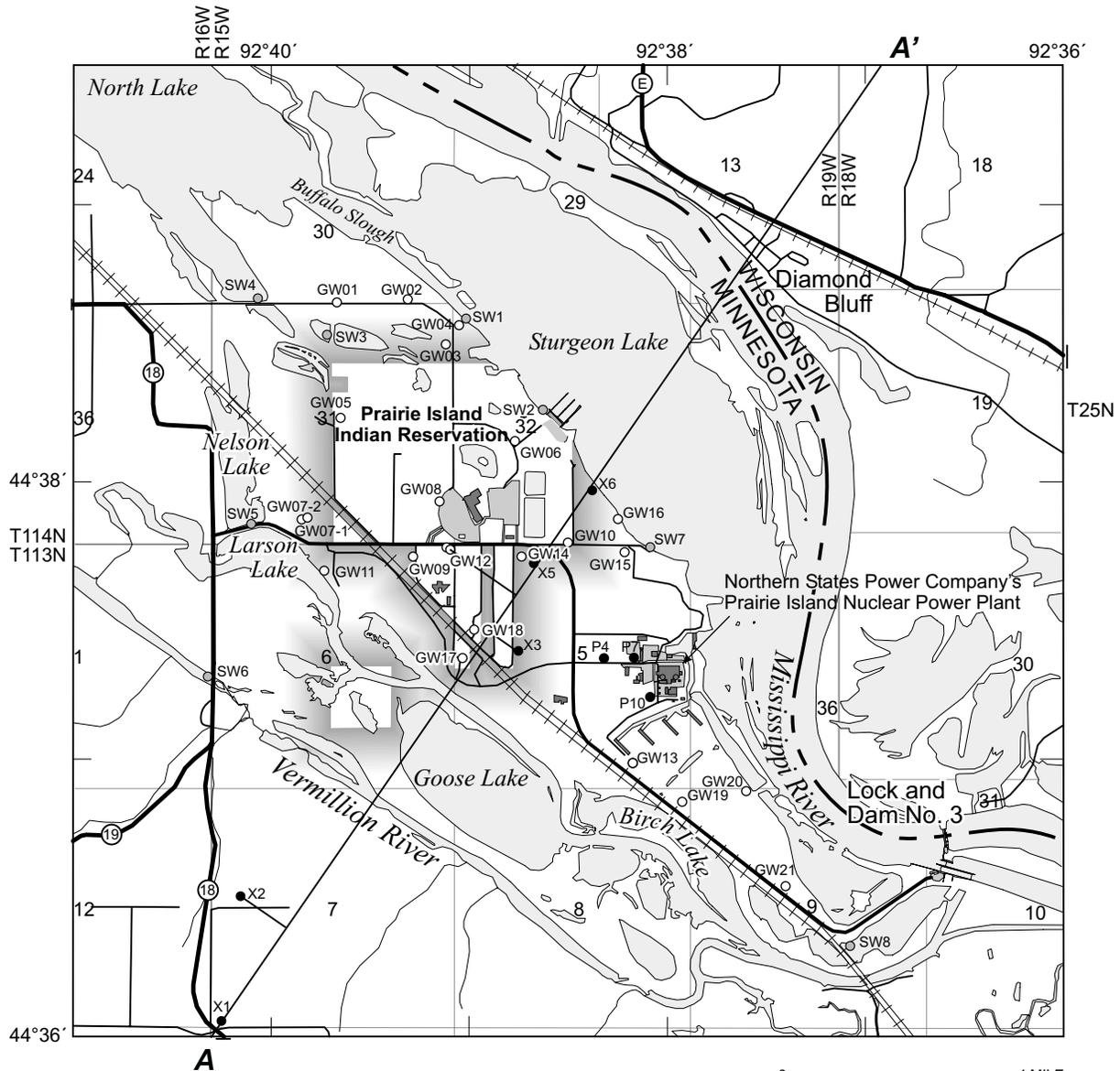
Base from U.S. Geological Survey digital data, 1:100,000, 1996.
 Projection Albers Equal Area, Standard parallels: 44°15'00" and 48°15'00",
 Central meridian-98°38'00", Latitude of projection's origin: 46°30'00".



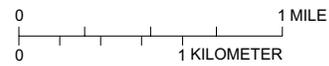
EXPLANATION

 Prairie Island Indian Reservation

Figure 1. Location of Prairie Island, Minnesota.



Base from U.S. Geological Survey digital data, 1:100,000, 1972
 Projection Albers Equal Area Standard parallels 44°15' and 48°15'
 Central meridian -98°38' Latitude of projection's origin 46°30'
 Minnesota Department of Transportation State of Minnesota Base Map '97
 Mankato State University Water Resources Center.



EXPLANATION

- A—A'** Trace of section—shown on figure 3
- Well at which water-quality samples were collected
- Surface-water site at which water-quality samples were collected
- Other well and line of projection of well onto trace of section
- Building
- Asphalt
- Reservation boundary

Figure 2. Location of Prairie Island Indian Reservation and study area.

Table 1. Number of samples collected by constituent group and date

[UW, University of Waterloo Environmental Isotope Laboratory, Waterloo, Ontario, Canada; VOCs, volatile organic compounds; CFC, chlorofluorocarbon]

Constituent group	Fall 1994	March 1995	May 1995	August 1995	August ¹ 1996	Laboratory reference ²	Analytical method reference
Ground-water samples							
Major ions	19	13	2		17	7, 146, 2750	Fishman, 1993
Nutrients	19	15	14	18	17	678 (455), 2752	Fishman, 1993
Organic carbon	10					114, 113	Wrenshaw and others, 1987
Triazine screen	19	13	15			immunoassay	Millipore Corporation, 1993
Tritium	11	7	18	18	17	1565, UW	
Trace metals	2					1043	inductively coupled plasma
VOCs	3					1390	Rose and Schroeder, 1995
CFC ages					14		Busenberg and Plumber, 1992
Dissolved gasses					14		Busenberg and Plumber, 1992
Surface-water samples							
Major ions	6				8	7, 146, 2701	Fishman, 1993
Nutrients	6	7			8	151, 2702	Fishman, 1993
Organic carbon	7				8	114, 2075	Wrenshaw and others, 1987
Bacteria	7				8	culture	Myers and Wilde, 1997
Triazine screen	7				8	immunoassay	Millipore Corporation, 1993
Tritium		7				1565, UW	
Trace metals	2					1043	inductively coupled plasma
VOCs	3					1390	Rose and Schroeder, 1995

¹Surface-water samples for this period were collected in May 1996

²Number is U.S. Geological Survey National Water-Quality Laboratory constituent group number

samples were collected only at observation wells using copper tubing on a Keck pump and were unfiltered. Major-ion and trace-metal samples were preserved with enough nitric acid to lower the pH to 2 standard units. Nutrient, triazine, and VOC samples were chilled from the time of sampling until analysis.

Surface-water samples were collected by filling Teflon bottles at the water surface. A peristaltic pump equipped with Tygon tubing delivered water for filtered samples (major ions, nutrients, trace metals, and triazines) from a filled bottle through the same type of filters used for ground-water samples. Dis-

solved-organic-carbon samples were filtered in the same way as ground-water samples. All surface-water samples were preserved and chilled in the same way as ground-water samples.

The USGS National Water-Quality Laboratory (NWQL) in Arvada, Colorado analyzed major-ion, nutrient, organic-carbon, trace-metal and VOC samples. Both the NWQL and the University of Waterloo Environmental Isotope Laboratory in Waterloo, Ontario, Canada, analyzed tritium samples. The USGS CFC Laboratory in Reston, Virginia analyzed CFC and dissolved-gas samples. The USGS laboratory in Mounds View, Minnesota

analyzed triazine and bacteria samples. Triazine samples were analyzed using a Millipore ENVR P00 00 immunoassay kit (Millipore Corporation, 1993).

Four sediment samples were collected on August 2, 1995 from alluvium deposited during the 1993 Mississippi River flood. These samples were wet-sieved with river water through a 2-millimeter nylon screen. Organic chemicals in sediment samples were analyzed by the NWQL using 3 methods. Gross carbon was analyzed using methods detailed in Wrenshaw and others (1987), organochlorine compounds were analyzed using gas chromatography and electron capture

(Foreman and others, 1995), and polycyclic aromatic hydrocarbons (PAHs) and other semivolatile compounds were analyzed using gas chromatography with mass spectrometry (Furlong and others, 1996).

Tritium concentrations in precipitation at the study area were estimated from two sources. Concentrations during 1952–87 were interpolated from the North American monitoring network (Michel, 1989a and b). Data from 1996 were collected by the Minnesota Department of Health (written commun., 1997) at Cedar Creek Natural Area, about 60 mi northwest of the study area. Tritium concentrations during 1987–96 were interpolated using the variability of the 6-month moving average of the data before and after this period.

In addition to 109 ambient water-quality samples collected, quality-control (QC) samples were collected at 8 sites. Table 2 lists the number, type, and results of the QC analyses. No constituents for which QC data were collected showed

evidence of contamination above the ambient concentrations measured. Replicate samples agreed within 2.6 percent mean relative difference (defined as average absolute value of $[(X_1 - X_2) / (X_1 + X_2)] \times 100$ for all replicate pairs) for samples not close to the reporting limit with the exception of nutrients in surface water (7 percent) and other constituents noted in table 2. Manganese and suspended organic carbon in surface-water replicates, and potassium, dissolved phosphorus, and lead in ground-water replicates were particularly variable. Both laboratories analyzed two replicate tritium samples collected in May 1995. One sample replicate set had concentrations within the precision error reported by the laboratories, but one set had a relative difference of 14 percent. This replicate set varied by 12 picocuries per liter (pCi/L), with the USGS NWQL reporting the lower concentration at 38 pCi/L. Concentrations of constituents with high variability (table 2) should be considered qualitative.

Acknowledgments

Shannon Smith, formerly of the U.S. Geological Survey, planned this study and conducted it from its inception until mid-1995. Thanks to Heather Westra and Amy Johnson of the Prairie Island Indian Community Environmental Department for their prompt and professional assistance in this study. Ms. Johnson collected much of the water-level data. Thanks also to Rajalakshmi Josiam and Alan Peterson of Northern States Power Company for their help in obtaining Northern States Power Company geological, water-level and water-quality data, and for their permission to sample Northern States Power Company observation wells. Thanks also to the U.S. Army Corps of Engineers, which supplied water-level and precipitation data from Lock and Dam Number 3, and to private well owners for permission to sample their wells. Without the cooperation of and help from this diverse group of people, this study would have been impossible. Thanks to Neil Plumber of the U.S. Geological Survey for help

Table 2. Quality control synopsis

[QC, quality control; SW, surface water; GW, ground water; ≤ less than or equal to; RL, reporting limit; mg/L, milligrams per liter; %, percent; <, less than]

QC sample type and purpose	Constituent	Ratio of samples ¹	Maximum concentration (for blanks), or mean relative difference ² (for replicates)
BLANKS (contamination from equipment, sampling, cleaning, and analysis)	major ions	1/65	•All ≤ RL except calcium (0.1 mg/L) and silica (0.07 mg/L)
	nutrients	2/104	•All ≤ RL except ammonia nitrogen (0.02 mg/L)
	organic carbon	1/22	•Dissolved: 0.8 mg/L
SW REPLICATES (accuracy, reproducibility)	major ions	1/14	•All ≤ 2.5% except iron (7%) and manganese (17%)
	nutrients	2/21	•All ≤ 7% except dissolved organic + ammonia nitrogen and orthophosphorus (both 17%, orthophosphorus near RL)
	organic carbon	1/12	•Dissolved: 1.7%. Suspended, 12%
	tritium	1/7	•4.2%
GW REPLICATES (accuracy, reproducibility)	major ions	3/51	•All < 2% except potassium (25%), bromide (33%, but near RL), and manganese (6%, but one sample near RL with high difference)
	nutrients	4/83	•All ≤ 2.6% except dissolved phosphorus (15.8%)
	organic carbon	1/10	•Dissolved: 5.8%
	trace metals	1/2	•All < 2% except lead (26%) and silver (33%, but near RL)
	tritium	14/71	•Waterloo Laboratory ³ : 3.7% (10.9% maximum); USGS/Waterloo Laboratory ³ : 9.5% (from 2 replicates)

¹Number of QC samples/number of water-quality samples

²Mean relative difference: average absolute value of $[(X_1 - X_2) / (X_1 + X_2)] \times 100$ for all replicate pairs

³University of Waterloo Environmental Isotope Laboratory, Waterloo, Ontario, Canada

interpreting the CFC age dates and to Mark Brigham, also of the U.S. Geological Survey, for help interpreting sediment organic-compound data.

Hydrogeology

Prairie Island is a group of low islands, lakes, and wetlands in the Mississippi River Valley (fig. 1). More than three-quarters of Prairie Island is <25 ft above the Mississippi River but it is as high as 65 ft above the river southwest of North Lake (fig. 2). The Mississippi River Valley in this area is 1–3 mi wide, bounded on each side by 360-ft-high bluffs consisting of flat-lying Paleozoic limestones and sandstones (fig. 3). The Mississippi River flows near the northeast bank of the valley, the Vermillion River flows near the southwest bank, and Prairie Island located between them. A channel joining the two rivers 1.2 mi west of the Goodhue-Dakota County line delimits the upstream end of the island and the confluence of the two rivers delimits the downstream end of the island.

Within the study area, ground water exists in bedrock and unconsolidated sand and gravel. The bedrock is primarily alternating layers of limestone and sandstone (fig. 3). The Prairie du Chien Group and Jordan Sandstone form one aquifer, which is separated from the underlying Franconia Formation (also an

aquifer) by the St. Lawrence Formation, which acts as a confining bed (Hoberg, 1972). The Mississippi River Valley is eroded through the upper three strata and more than 100 ft into the Franconia Formation. Ground-water flow in these aquifers is from the upland areas toward the axis of the Mississippi River Valley where it may discharge as springs in the river valley bluffs, or discharge upward into the unconsolidated sediments, which partially fill the valley. These unconsolidated sediments were the focus of the ground-water portion of this study.

The geologic processes that eroded the Mississippi River Valley and deposited the unconsolidated sediments within it reveal much about the hydrological characteristics of surficial aquifer. The following geologic history is based on an article by Carrie Patterson of the Minnesota Geological Survey (written commun., 1997). The Mississippi River Valley below Hastings, Minnesota was already a bedrock river valley before the onset of the last major cycle of glaciation (the Wisconsin glaciation), 60,000-12,000 years ago (Wright, 1972). During the peaks of this glaciation, an ice sheet more than 1 mi thick covered much of Canada and the northern United States. Meltwater from the entire southwestern side of this ice sheet flowed through the pre-existing Mississippi River Valley near the study area. When ice-sheet lobes termi-

nated close to the study area, outwash stream gradients were relatively steep and were capable of carrying more sediment than was supplied by the ice sheet. During this period, the outwash streams in the Mississippi River Valley eroded sand and gravel at the ice margin and deposited it in the valley further downstream near Prairie Island. This process proceeded until the slope of the river decreased and was in equilibrium with the sediment supply. As ice lobes retreated into central Minnesota, stream gradients decreased. Outwash streams braiding in the Mississippi River Valley eroded the unconsolidated sediments on which they flowed, increasing their gradients until they could carry their sediment supply. When western ice lobes retreated north of the continental divide in northern Minnesota, glacial Lake Agassiz was formed between the ice and the divide. Meltwater that flowed through Lake Agassiz deposited most of its sediment in the lake and relatively sediment-free water flowed through the Mississippi River Valley, eroded the unconsolidated sediments further, and re-excavated the valley (Dobbs and Mooers, 1991). Evidence of previous levels of sediment aggradation was left as the terraces now visible on the valley sides. These terraces record the highest elevation of sediment deposition before an ensuing period of erosion, but only some are preserved.

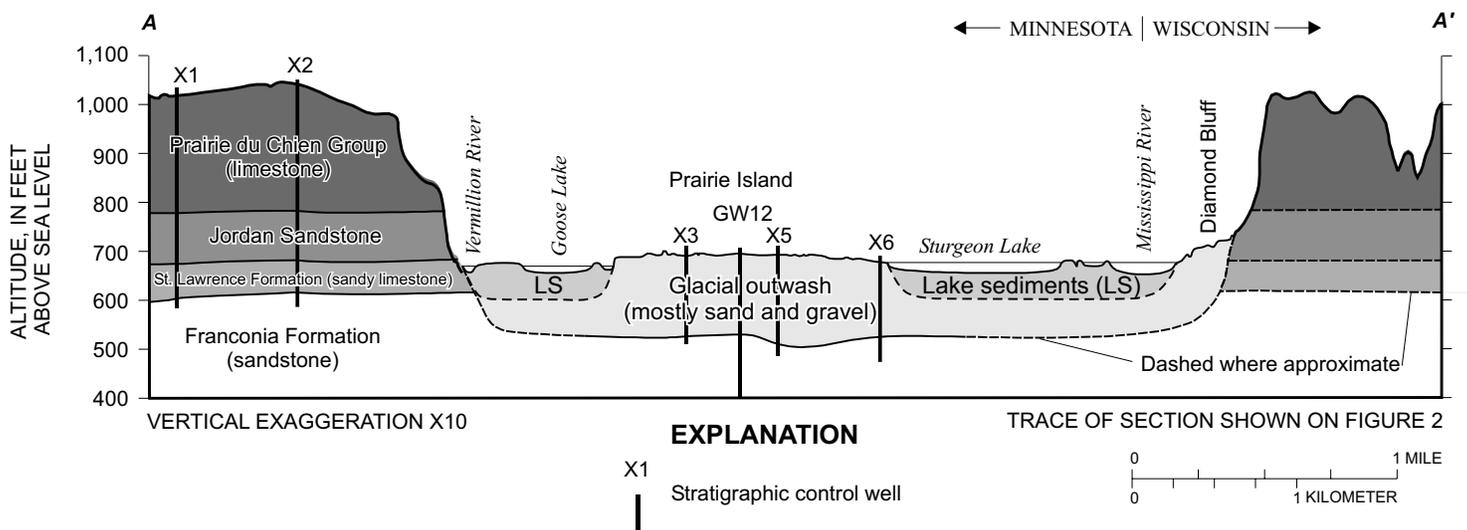


Figure 3. Geologic section across the Mississippi River Valley through Prairie Island, Minnesota.

Terraces are located at an elevation of about 820 ft on the Minnesota side and at elevations of 740 and 700 ft at Diamond Bluff on the Wisconsin side of the Mississippi River Valley. Another terrace near the study area at 720 ft also recorded sedimentation in this section of the river valley. A large area of the upstream part of Prairie Island, at an elevation of about 720 ft, may be a remnant of this terrace. Much of the eastern part of the island, containing the study area, has an elevation of about 700 ft and may be a remnant of the lowest terrace at Diamond Bluff. After Lake Agassiz drained for the last time about 9,200 years ago (Matsch, 1983), Prairie Island stood as a 90-ft high terrace mound within the Mississippi River Valley (Zumberge, 1952). Within the next 1,000-2,000 years, the Chippewa River delta, located 31 mi downstream of Lock and Dam Number 3, dammed the Mississippi River, forming Lake Pepin within the Mississippi River Valley. Initially, Lake Pepin extended upstream 15 mi further than Hastings, leaving the Prairie Island terrace a true island. Gradually, the upstream part of the lake filled with sediment and the upstream end of Lake Pepin came to be located 9 mi downstream of Prairie Island (Zumberge, 1952). This sedimentation left Prairie Island surrounded by the lakes and wetlands found today.

From this history, several features of the sand and gravel composing Prairie Island can be better understood. Glacial outwash sand and gravel deposited in the Mississippi River Valley are coarse grained, and generally well sorted because deposition occurred by braided, high-gradient glacial outwash streams capable of carrying all but their coarsest sediment load. Few fine-grained materials exist within these sediments. Fine-grained sediments (silt and clay), deposited in Lake Pepin after it formed, overlie the glacial outwash sands and gravels, and underlie most of the surface water surrounding Prairie Island. Hydraulic interaction between the surface water and ground water may be substantial near the land surface where logs from wells and test holes record that these fine-grained sediments are thin or absent. Among the sampled wells that have logs (16), the fin-

est material recorded is fine sand, in one log. Wells with logs that were not sampled show similar stratigraphy. Of 50 logs examined, 5 show thin layers of silty sand or finer sediments. Detailed logs from 33 borings located near or beneath the power plant (11 of which extended to bedrock) also show few, local layers of silty sand (extending < 65 ft horizontally). These logs also show that sand and gravel composes nearly all of the unconsolidated sediments from land surface to bedrock. A clay-rich layer is present immediately above the bedrock according to some logs, however.

The glacial formation of the surficial aquifer beneath the study area and well and borehole data indicate that the aquifer is composed of well-sorted sands and gravels from the land surface to bedrock (130–200 ft). These sands and gravels contain a few, small, local, fined-grained lenses that are most numerous at the land and bedrock surfaces. Three boreholes drilled east of the power plant in the bed of the Mississippi River confirm that lake sediments overlie the aquifer beneath surface waters.

Surface waters near Prairie Island consist of rivers, lakes, and wetlands, most of which are interconnected. The surface waters can be divided into two groups, each associated with either the Mississippi or Vermillion Rivers. North and Sturgeon Lakes are connected to the Mississippi River in many places through channels called runs. Larson, Goose, and Birch Lakes are connected to the Vermillion River. Water levels in the lakes fluctuate with river stage. Some surface waters, such as Nelson Lake, are connected to both Mississippi River lakes and Vermillion River lakes through wetlands. During much of the year, most lakes have a current that is controlled by the slope of the river to which they are connected.

Lock and Dam Number 3, located about two-thirds mile above the confluence of the Mississippi and Vermillion Rivers, controls the water level and flow of the Mississippi River. Usually, the lock and dam keeps levels of the Mississippi waters higher than those of the Vermillion waters. This difference in water

level produces flow in Nelson Lake from north to south, at an angle to the direction of flow in both the Mississippi and Vermillion waters. During periods of high flow, water levels in both groups are nearly the same, and flow in nearly all lakes, wetlands, and rivers is down the axis of the Mississippi River Valley.

These surface waters form hydraulic boundaries of the ground-water system and substantially influence the flow of water in the surficial aquifer. Mississippi waters form the northeastern hydraulic boundary of Prairie Island (fig. 2). Vermillion waters form the southwestern hydraulic boundary. The aquifer receives recharge from and supplies discharge to the surface waters, although fine-grained bed sediments reduce the volumetric rate of flow between surface and ground water. The aquifer also receives recharge from infiltration of rain, snowmelt, and floodwater, and receives water from the underlying bedrock aquifers. Hydraulic head differences from the Eau Claire/Mt. Simon aquifer (stratigraphically beneath the Franconia Formation) to the surficial aquifer are more than 30 ft based on water levels in the reservation public-supply wells. This high vertical head gradient is related partly to the fact that Prairie Island is topographically low compared to the bluffs that bound the valley. Clay-rich materials separating the surficial and bedrock aquifers are noted in some drilling logs. If these materials are extensive, water movement to the surficial aquifer from beneath may be small despite the large head difference between aquifers.

Water leaves the surficial aquifer by discharging to surface waters, by evapotranspiration, or by withdrawal from wells. Within the study area, fewer than 50 active, low-capacity domestic wells are completed in the surficial aquifer. The Prairie Island Indian Reservation public-water supply, which withdraws water from the Eau Claire/Mt. Simon aquifer, has replaced the need for most domestic wells. The power plant uses at least 7 wells screened in the surficial aquifer for water supply. Two of these are 165-ft-deep, 10 in.-diameter wells and are the largest capacity wells (116,000 cubic feet per day (ft³/d) each).

The amount of water that discharges from the shallow ground water (the water table is generally 6–23 ft deep) to surface water and to the atmosphere is larger than the amount that discharges to wells. During July 1997, ground-water levels over a 2-mi² area containing the study area rose an average of about 2.6 ft following high rainfall (2.65 times the monthly median precipitation since 1949, U.S. Army Corps of Engineers, written commun.; 1997). Within one month, ground-water levels declined by one-half (1.3 ft). The water discharged from the aquifer during this period was about 700,000 ft³/d, assuming an aquifer porosity of 0.3. Assuming the average domestic well pumps 35 ft³/d, and the NSP plant wells pump at capacity, discharge from wells in the 2-mi² area totaled about 234,000 ft³/d, or less than one-third of the total aquifer discharge. The remaining ground water discharged to surface waters or the atmosphere.

Flow in the surficial aquifer is controlled by the elevation of the surface waters surrounding Prairie Island and by the amount of recharge (infiltration of rain, snowmelt, and floodwater) vertically from the land surface. Lock and Dam Number 3 maintains the Mississippi waters at a higher head than the Vermillion waters (hereinafter referred to as normal conditions) except during spring runoff and relatively long periods of rain (fig. 4). During normal periods, water in the surficial aquifer flows from the Mississippi waters southwest toward the Vermillion waters. Figure 5 shows the water table during normal conditions on February 9, 1995. Water upstream of the dam was > 6.5 ft higher than downstream. The head difference caused ground-water flow from northeast to southwest, across the island (flow is perpendicular to water-table contours in the direction of decreasing head). The flow direction in bedrock aquifers in the Mississippi River Valley is almost vertically upward. Because the flow direction in the surficial aquifer was from Mississippi waters toward Vermillion waters, it is likely that flow in the surficial aquifer was perpendicular to flow in the bedrock aquifers. Water-table slope increased from about 0.001 near

Mississippi waters to about 0.002 near the discharge area of Vermillion waters. The hydrographs in figure 4 show that the lock and dam usually keeps the elevation of Mississippi waters higher than the elevation of Vermillion waters. During these periods, ground-water levels gradually decrease from Mississippi water elevations on the northeast side of the island to Vermillion water elevations on the southwest side of the island. Therefore, the water table configuration shown in figure 5 is representative of normal conditions.

Rainfall during July 1997 (26.59 in.) was 2.65 times higher than normal, causing the water levels of both surface and ground water to rise, ground-water flow to change direction, and water-table slope (and therefore ground-water flow rate) to increase (fig. 6). By August 7, 1997 (fig. 6), vertical recharge to the surficial aquifer from the high rainfall in July produced a ground-water mound in the central part of the study area. Water levels in Mississippi and Vermillion waters differed by only 0.56 ft at the dam. Surface water elevations along transects across the Mississippi River Valley were about the same. All cross-island ground-water flow ceased because water levels in most areas of the aquifer were higher than those in the surface-waters surrounding the island. The ground-water mound caused water to flow radially outward from the central part of the study area. Water-table gradients northwest of the mound were lower than gradients southeast of the mound because surface-water levels, and hence ground-water levels near surface waters, were higher longitudinally up the Mississippi River Valley than down it. This gradient asymmetry caused more ground water to flow southeast from the mound than northwest from the mound.

During August 1997, near normal rainfall (10.80 in., 1.26 times the median monthly rainfall since 1949) returned to the area, and the stage of Vermillion waters began to decline. The water table on September 3, 1997 (fig. 7) is an intermediate configuration between the mound-dominated configuration of August 7 (fig. 6) and the surface-water-dominated configuration shown in figure 5. By September 3, a larger head differ-

ence (3.38 ft) between the Mississippi and Vermillion waters at the dam recurred. Flow from the ground-water mound on the island caused water levels at well GW08 to decline 1.39 ft, eliminating flow to the northwest. A remnant of the mound (now a ridge) still existed, although it had shifted to the east. The normal ground-water flow direction to the southwest was recurring because of the increasing head difference between the Mississippi and Vermillion waters.

Analysis of these water-table-surface maps reveals three characteristics of recharge and flow in the surficial aquifer. First, surface waters recharge the aquifer through lake sediments and, in the absence of vertical recharge, surface-water levels control ground-water-flow direction and rate. Second, during periods of high rainfall or snowmelt, the aquifer can be recharged from the land surface so rapidly that ground-water levels rise higher than surface-water levels, creating a ground-water mound in the central part of the study area. When this mound exists, ground water flows radially away from it. Rapid recharge and lack of significant overland flow result from the coarse grain size of the surficial aquifer. Finally, surface-water levels and recharge alone explain the water-table configurations observed. This implies that any movement of water from bedrock aquifers to the surficial aquifer must be relatively evenly distributed.

Water Quality and Organic Compounds in Sediment

The connection of the surficial aquifer with the surrounding surface water produces ground and surface water of similar quality. In general, ground- and surface-water samples had low concentrations of dissolved solids and were dominated by calcium, magnesium, and bicarbonate ions (fig. 8) (median dissolved solids concentration from ground-water samples was 261 milligrams per liter (mg/L), and from surface-water samples was 249 mg/L). Most ground-water samples contained dissolved oxygen, but 7 wells usually produced water with little

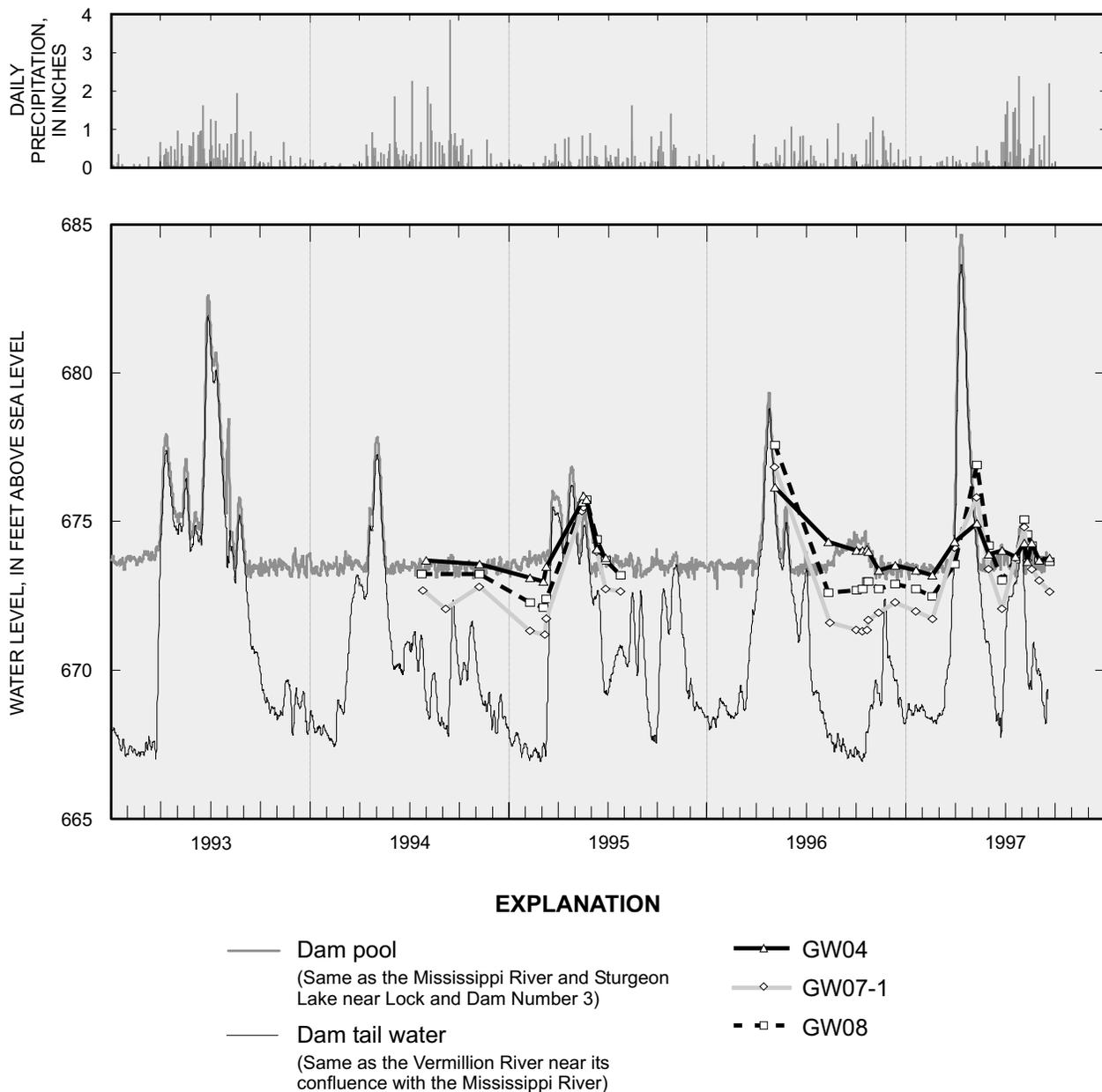


Figure 4. Surface- and ground-water hydrographs and precipitation, 1993–97.

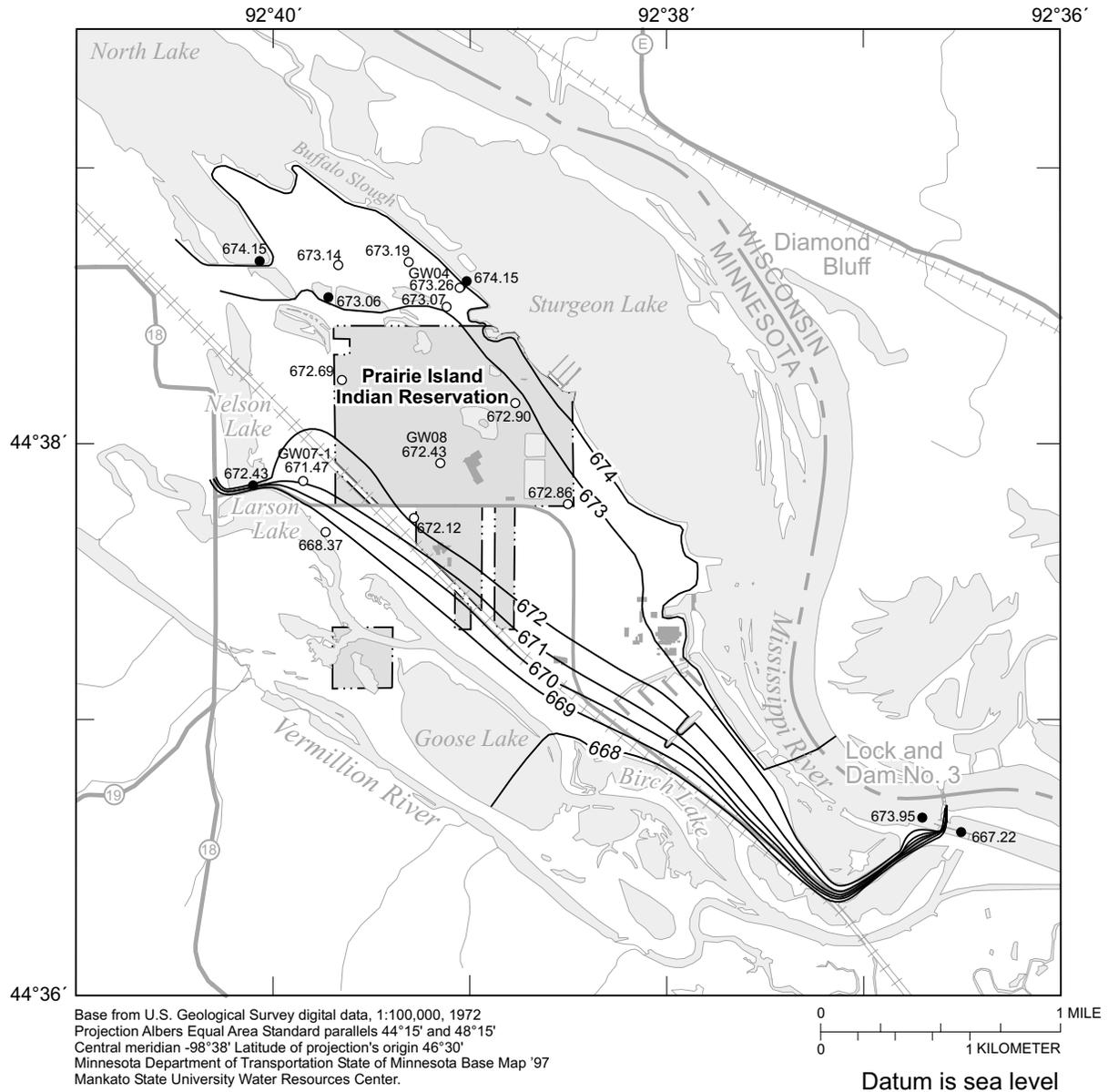
or no dissolved oxygen (0.5 mg/L or less from wells GW04, 12, 15, 16, 19, 20, and 21). Surface-water samples were compositionally more similar to each other than were ground-water samples. The greater variability among ground-water samples may result from the greater number of wells sampled over a longer time period (ground water, 21 wells; surface water, 7 sites). Surface water is also generally better mixed than ground water, possibly lowering its variability. Surface-water samples from the lake sites (SW3 and

SW5) were slightly higher in magnesium and lower in calcium concentrations than were samples from river or ground-water sites.

All wells sampled were completed in the surficial aquifer except GW12, which was completed in the Eau Claire-Mount Simon aquifer. With the exception of samples from GW07-1, samples from GW12 had the highest sodium and chloride concentrations (fig. 8). High sodium and chloride concentrations in water from the Eau Claire-Mount Simon aquifer

result from the long time this water had been in contact with the aquifer material (Hem, 1989). Ground-water flow paths (and therefore, travel times) in the Eau Claire-Mount Simon aquifer are longer than those in the surficial aquifer because the areal extent of the Eau Claire-Mount Simon aquifer is hundreds of times larger.

Samples from observation well GW07-1 also contained relatively high sodium, chloride, and nitrate concentrations (fig. 8). This well is screened at the water table (well depth 15 ft). Samples



EXPLANATION

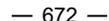
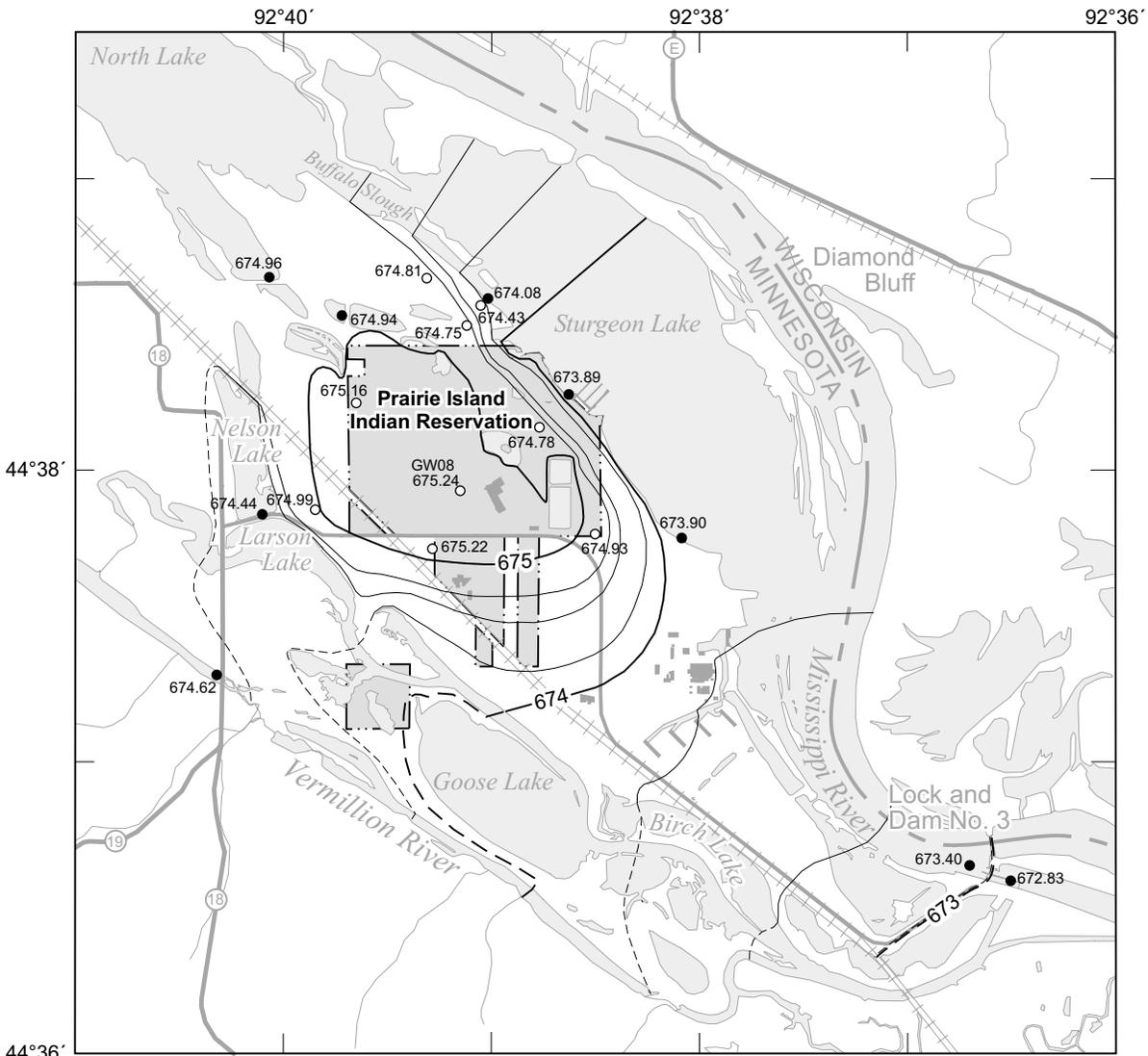
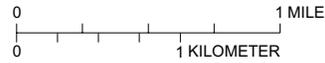
-  Reservation
-  — 672 — Water table contour—
Contour interval 1 foot
-  ^{672.69} Well and water-level elevation
-  ^{674.15} Surface-water site and water-level elevation
-  Building

Figure 5. Normal water-table surface, February 9, 1995.



Base from U.S. Geological Survey digital data, 1:100,000, 1972
 Projection Albers Equal Area Standard parallels 44°15' and 48°15'
 Central meridian -98°38' Latitude of projection's origin 46°30'
 Minnesota Department of Transportation State of Minnesota Base Map '97
 Mankato State University Water Resources Center.

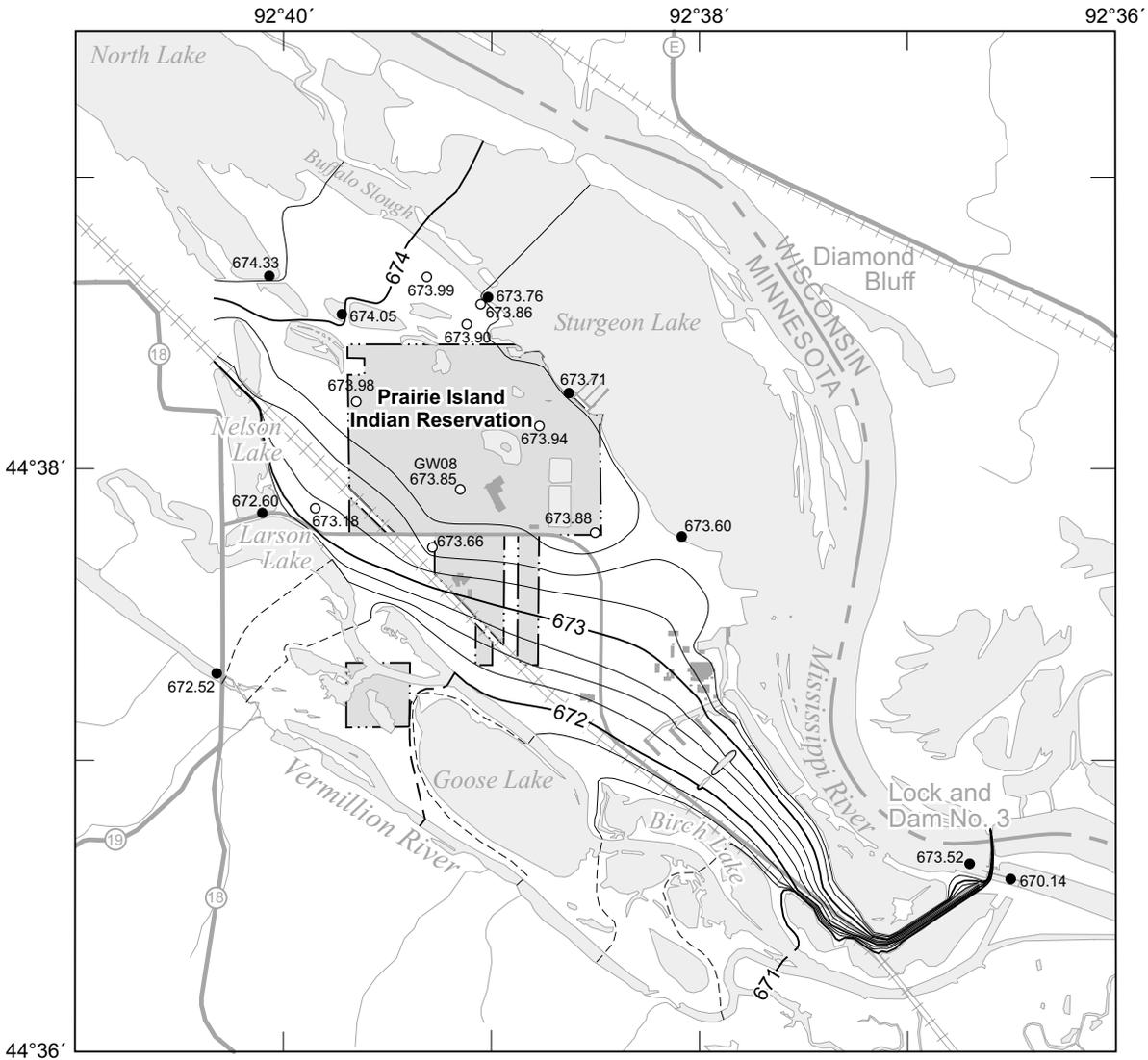


Datum is sea level

EXPLANATION

- Reservation
- 674 Water table contour. Dashed where approximate—Contour interval 0.25 foot
- 674.81 Well and water-level elevation
- 674.94 Surface-water site and water-level elevation
- Building

Figure 6. Water-table surface, August 7, 1997, following high rainfall.



Base from U.S. Geological Survey digital data, 1:100,000, 1972
 Projection Albers Equal Area Standard parallels 44°15' and 48°15'
 Central meridian -98°38' Latitude of projection's origin 46°30'
 Minnesota Department of Transportation State of Minnesota Base Map '97
 Mankato State University Water Resources Center.

0 1 MILE
 0 1 KILOMETER
 Datum is sea level

EXPLANATION

- Reservation
- 673 Water table contour. Dashed where approximate—Contour interval 0.25 foot
- 673.94 Well and water-level elevation
- 672.60 Surface-water site and water-level elevation
- Building

Figure 7. Water-table surface, September 3, 1997, about one month after high rainfall ended.

from the deeper, domestic well GW07-2, (well depth, 85 ft), located about 100 ft horizontally from well GW07-1, had a major-ion composition similar to samples from other wells screened in the surficial aquifer. This indicates that ground water in the surficial aquifer containing high concentrations of sodium, chloride, and nitrate may be localized. The high concentrations of sodium, chloride, and nitrate ions at this well may have come from agricultural activities (Delin and others, 1995) or septic systems.

Multiple samples (2–4 per well) were collected at 17 wells for this study; variability existed in major-ion concentrations at each well through time. Variability was measured by maximum relative percent difference, $[(C_{\text{maximum}} - C_{\text{minimum}}) / (C_{\text{maximum}} + C_{\text{minimum}})] \times 100$, where C is the concentration in a sample from a well. Among the ions that make up most of the dissolved solids in a sample (calcium, magnesium, bicarbonate, sulfate, and silica), median variability ranged from 5 to 15 percent. Among major ions with lower concentrations

(chloride, fluoride, sodium, iron, and manganese) median variability was higher, ranging from 11 to 54 percent.

Manganese concentrations show an unusual spatial pattern. Manganese was analyzed in samples from most wells 3 or 4 times during the study. Concentrations ranged from < 1 to 160 micrograms per liter ($\mu\text{g/L}$) in all samples except those from wells GW04, 16, 20, and 21. In these wells, manganese concentrations ranged from 1,600 to 3,000 $\mu\text{g/L}$ (more than one order of magnitude higher). All

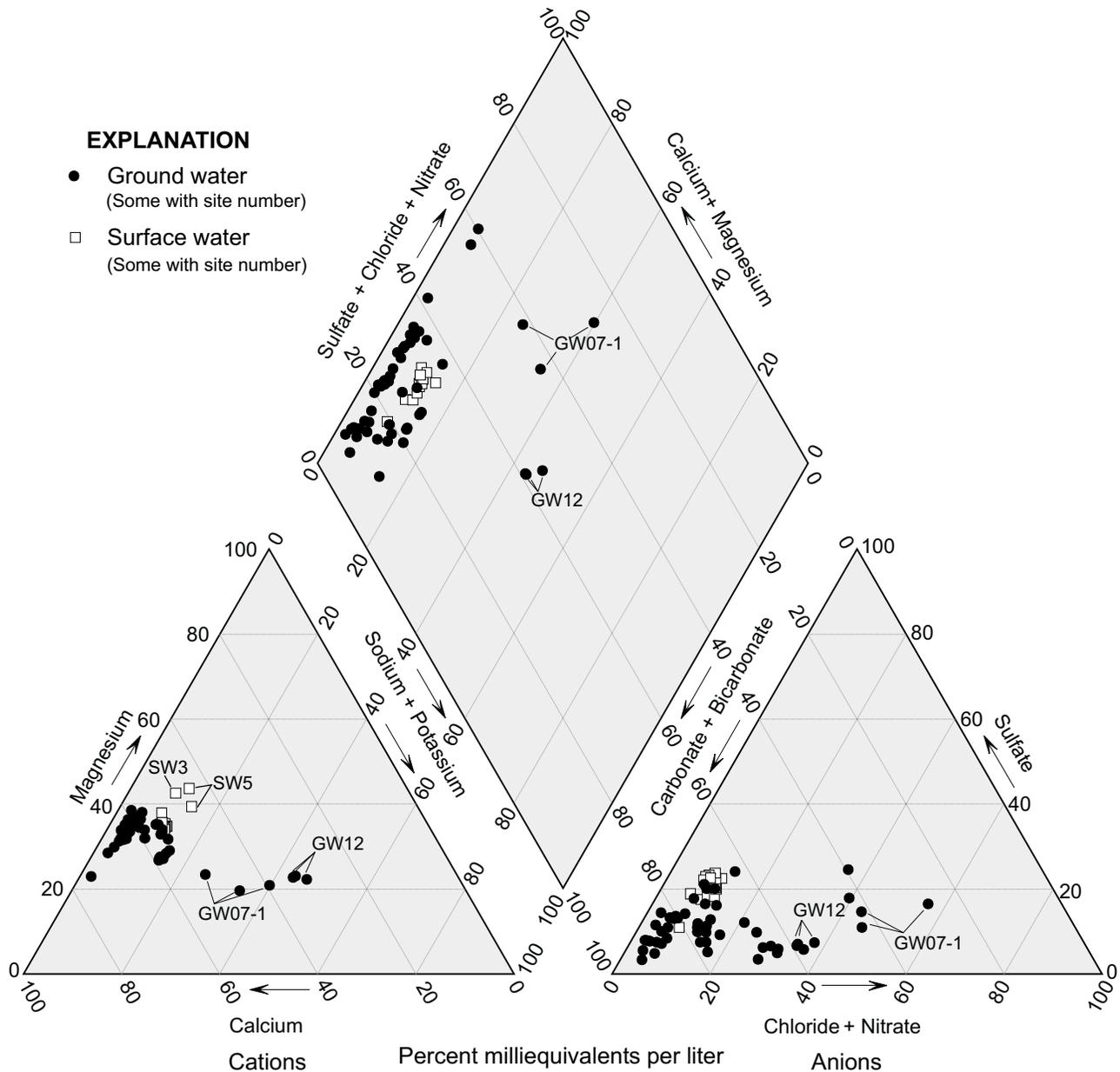


Figure 8. Major ionic composition of water, 1994–96.

samples from the four wells with high manganese concentrations had < 0.6 mg/L dissolved oxygen. Two wells were observation wells open at depths < 3 ft below the water table and two were domestic wells probably open at depths > 40 ft below the water table. The four wells with high manganese concentrations are within 300 ft of Mississippi waters, which usually recharge the aquifer. Samples from Mississippi waters contained manganese concentrations from 5 to 150 µg/L, excluding one concentration of 850 µg/L, which is too low to account for the manganese concentrations in these four wells. Hem (1989) notes that high manganese concentrations in ground waters have been reported in wells designed to induce recharge from rivers, a

situation analogous to the high-manganese wells on Prairie Island.

Nutrients, Organic Carbon, and Bacteria

Unlike major ion concentrations, considerable differences in nutrient and organic carbon concentrations existed between surface- and ground-water samples. Generally, nitrate concentrations were higher and organic-nitrogen and carbon concentrations lower in ground-water than surface-water samples (fig. 9, table 3). The median nitrate concentration for ground-water samples was 3.6-times greater than that for surface-water samples. Ammonia, nitrite, and orthophosphorus concentrations were low (< 0.3 mg/L, as nitrogen (-N) for ammonia

and nitrate and as phosphorus (-P) for orthophosphorus) and were similar between surface- and ground-water samples (table 3).

Madison and Brunett (1984) reviewed nitrate concentrations across the United States and concluded that ground waters with concentrations > 3 mg/L-N contain some anthropogenic nitrate and water with concentrations > 10 mg/L-N contains substantial amounts of anthropogenic nitrate. In the study area on Prairie Island, 27 percent of ground-water samples (22 of 83) had nitrate concentrations that ranged from 3 to 10 mg/L-N. Twelve percent (10 samples) exceeded 10 mg/L-N. Most wells with high nitrate concentrations were located in the central part of the study area (wells GW06, 07-1, 08, 10,

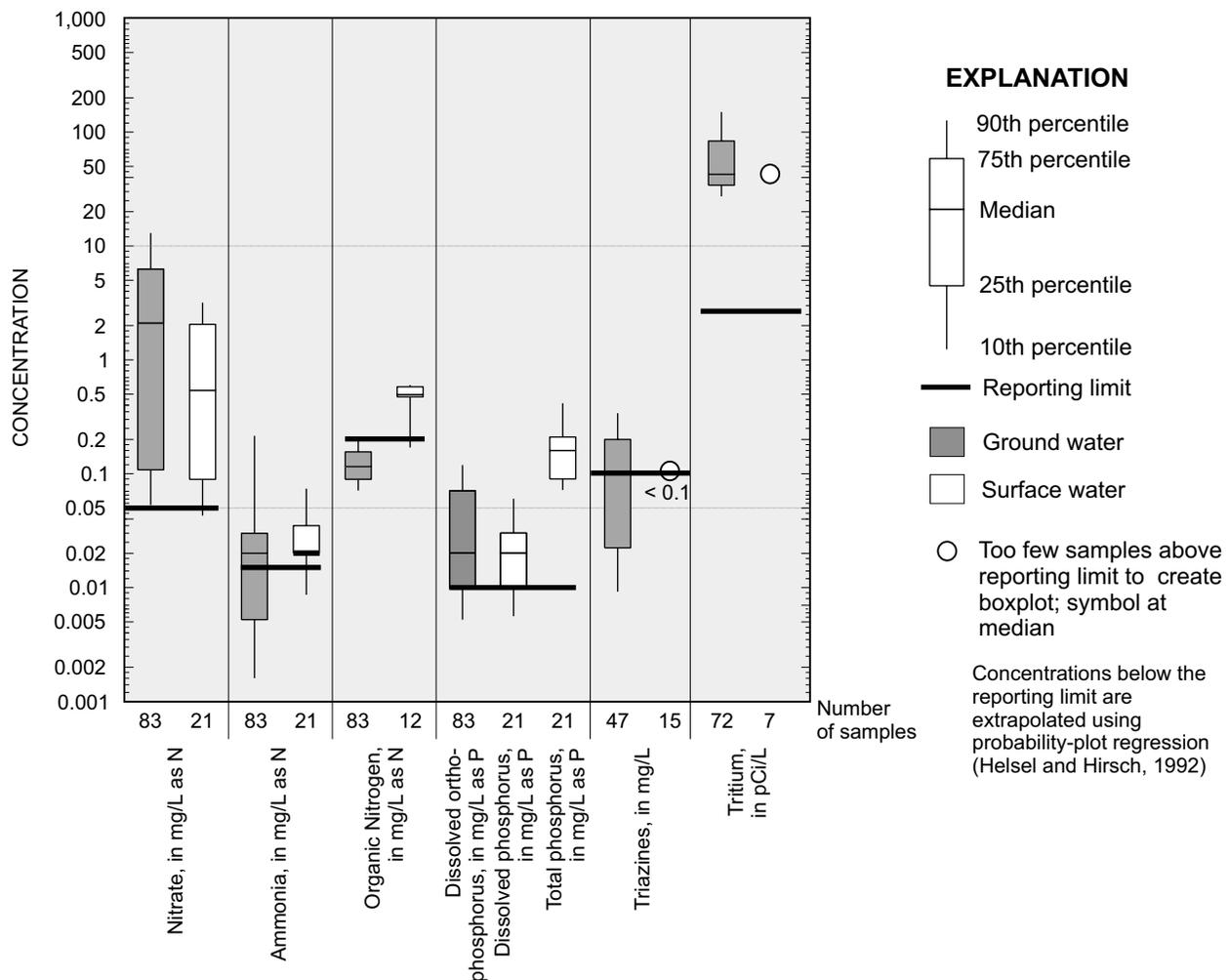


Figure 9. Nutrient, triazine, and tritium concentrations, 1994–96.

Table 3. Nutrient, organic carbon, and bacteria statistics

[mg/L, milligrams per liter; N, nitrogen; P, phosphorus; C, carbon; #, number of samples; col/mL, colonies per milliliter; blank, analysis not done]

Constituent	Units	Ground-water samples			Surface-water samples		
		#	Median	Range	#	Median	Range
Dissolved nitrate	mg/L as N	81	1.95	< 0.05–30	17	0.53	< 0.05–3.24
Dissolved ammonia	mg/L as N	83	0.02	< 0.015–1.7	21	0.02	< 0.015–0.27
Dissolved organic nitrogen	mg/L as N	83	< 0.2	< 0.2–0.3	12	0.50	0.08–0.60
Orthophosphorus ¹	mg/L as P	83	0.02	< 0.01–0.27	21	0.02	< 0.01–0.13
Dissolved nitrite	mg/L as N	81	< 0.01	< 0.01–0.03	17	0.015	< 0.01–0.07
Organic carbon ²	mg/L as C	10	1	0.2–10	14	12	7–34
Coliform bacteria	col/mL				15	19	< 1–220
Fecal streptococci bacteria	col/mL				15	23	2–1800

¹Ground water: dissolved. Surface water: total

²Ground water: dissolved. Surface water: total, 8 samples of which are a summation of suspended and dissolved

11, 17, 18). Fourteen percent of surface-water samples (3 of 21) contained nitrate concentrations > 3 mg/L-N (3.4 mg/L-N maximum). The relatively low concentrations of nitrate in samples from wells near Mississippi waters and in surface waters suggest that much nitrate in ground water at concentrations >4 mg/L-N entered the aquifer in recharge from the land surface and is related to land use.

Variation of nitrate concentrations from a given well tended to be higher than the variation of major-ion concentrations. Two to five nitrate samples were collected at each of 19 wells throughout the study period. Variation of nitrate concentrations from a single well ranged from < 0.07 to 7.91 mg/L-N. The median variation for the 19 wells was 0.97 mg/L-N and the median maximum relative difference was 32 percent.

Eighty-nine percent of samples (17 of 19) collected during fall 1994 (August 2–November 10) and all 17 samples collected during August 1996 contained ammonia concentrations above the reporting limit of 0.015 mg/L-N. Only 33 to 39 percent of samples collected during the three 1995 sampling periods were above this reporting limit. Samples from wells GW04, 12, 20, and 21 contained consistently higher concentrations of ammonia (0.09–1.7 mg/L-N) than those from all other wells (< 0.015–0.04 mg/L-N).

Samples from these wells were usually anoxic, which is consistent with the presence of ammonia (a non-oxidized form of nitrogen). Samples from three of the high-ammonia wells (GW12 excluded) also contained higher organic nitrogen concentrations than those from other wells, and one well (GW20) contained orthophosphorus concentrations (0.13–0.27 mg/L-P) at least twice as high as samples from other wells (< 0.01–0.08 mg/L-P).

Wetzel (1983) reported that the concentration of total phosphorus in eutrophic lakes generally ranges from 0.03 to 0.10 mg/L-P. In the study area on Prairie Island, 13 percent of ground-water samples (11 of 83) and 35 percent of surface-water samples (6 of 17) had orthophosphorus in excess of this concentration. Orthophosphorus composes nearly all phosphorus in ground water but accounts for only some phosphorus in surface water. Lakes with total phosphorus concentrations > 0.1 mg/L-P are categorized as hypereutrophic. Substantial algal growth is likely in hypereutrophic surface waters because phosphorus is usually the limiting nutrient in lakes (Wetzel, 1983). Five percent of all ground-water and 18 percent of all surface-water samples had orthophosphorus concentrations in excess of 0.10 mg/L-P. Sixty-seven percent of surface water sam-

ples exceeded total phosphorus concentrations of 0.10 mg/L-P.

Coliform and fecal-streptococci bacteria were analyzed in 15 surface-water samples (table 3) and were generally found at low concentrations (10 samples <100 col/mL). Four samples had coliform-bacteria concentrations <10 col/mL. Two samples had coliform concentrations >100 col/mL and three other samples had streptococci concentrations >100 col/mL. All 15 samples contained at least one of these bacteria.

Trace Metals, Volatile Organic Compounds, and Triazine Compounds

Two ground- and two surface -water sites (GW04, GW06, SW1, SW5) were sampled for both trace metals and volatile organic compounds (VOCs). One additional surface-water site and one additional ground-water site (SW7, GW12) were also sampled for VOCs. Although these four trace-metal and six VOC samples (tables 4 and 5) provide an indication of the concentration of these substances in water, the small number of samples cannot adequately characterize the water resource. No VOCs were detected in any samples. Trace metal concentrations in all samples were below U.S. Environmental Protection Agency (USEPA) drinking

Table 4. Trace metals in surface and ground water

[All concentrations are in micrograms per liter. <, less than; MCL, maximum contaminant level; HAL, lifetime adult health advisory level (U.S. Environmental Protection Agency, 1997)]

Metal	MCL (except as indi- cated) ¹	HAL	Site			
			GW04	GW06	SW1	SW5
Arsenic	50		< 1	< 1	< 1	< 1
Barium	2000	2000	49	18	58	37
Beryllium	4		< 0.5	< 0.5	< 0.5	0.6
Cadmium	5	5	< 1	< 1	< 1	< 1
Chromium	100	100	< 5	< 5	< 5	< 5
Cobalt			< 3	< 3	< 3	< 3
Copper	1300		< 10	< 10	< 10	< 10
Iron	¹ 300		51	8	23	850
Lead	0		30	< 10	< 10	< 10
Lithium			< 4	< 4	6	< 4
Manganese	¹ 50		1600	5	22	7
Mercury	2	2	< 0.1	< 0.1	< 0.1	< 0.1
Molybdenum		40	< 10	< 10	< 10	10
Nickel	140	100	< 10	< 10	< 10	< 10
Silver	¹ 100	100	< 1	< 1	< 1	< 1
Strontium		17,000	120	110	230	56
Vanadium			< 6	< 6	< 6	< 6
Zinc	¹ 5000	2000	4	4	< 3	< 3

¹Secondary maximum contaminant level, set primarily for aesthetic reasons

water maximum contaminant levels (U.S. Environmental Protection Agency, 1997) and appear natural (Hem, 1989), except for the lead concentration in the sample from well GW04 (30 µg/L, table 4). A recent study of 30 ground-water samples in the Twin Cities metropolitan area just north of this study area found no lead concentration above 1 µg/L (Andrews and others, 1998) suggesting that the lead concentration in sample GW04 is not natural. The high lead concentration may be contamination during sampling or analysis, may have been introduced from flood sediments, or may be from a lead bullet (several wells were destroyed by gunfire during the study).

Triazine compounds are herbicides and degradation products of these herbicides. Triazine herbicides are widely used, particularly on cornfields. The compounds are relatively long lived and are commonly found in surface and ground water in areas where corn is grown (Barbash and Resek, 1996; Larson and others, 1997). In this study, triazine compounds were analyzed by an immunoassay method (Millipore Corporation, 1993), which detects the entire class of compounds at a concentration > 0.1 µg/L. The most common triazine compounds include atrazine, cyanazine, and simazine. A total of 15 surface-water samples were analyzed for triazine compounds—7 samples during fall 1994 and 8 samples dur-

ing August 1996. Only one sample (SW2) taken during fall 1994 contained a concentration of triazines above the reporting limit. A total of 47 ground-water samples were analyzed for triazine compounds during fall 1994, March 1995, and May 1995. Table 6 details the distribution of triazine concentrations in ground-water samples. All but one concentration (well GW01, March 1995, 3 µg/L) were < 1 µg/L. All 15 samples collected in May 1995 contained low concentrations (0.1–0.5 µg/L) of triazine compounds. The May samples were collected shortly after the period when triazines are generally applied to crops. The even distribution of low triazine concentrations in ground water across the study

Table 5. Volatile organic compounds analyzed for in surface and ground water

[None of these compounds were detected in the 6 samples analyzed. All concentrations are in micrograms per liter, with a reporting limit of 3 micrograms per liter, except as indicated¹. MCL, maximum contaminant level; HAL, lifetime adult health advisory level (U.S. Environmental Protection Agency, 1997)]

Compound	MCL	HAL	Compound	MCL	HAL
Methylchloride		3	Propene, <i>cis</i> -1,3-dichloro-		
Methylbromide		10	Propene, <i>trans</i> -1,3-dichloro-		
Methylenechloride	5		Benzene,	5	
Methane, bromochloro-		10	Benzene, chloro		
Methane, dibromo-			Benzene, <i>o</i> -chloro-		
Chloroform	100		Benzene, bromo-		
Bromoform	100		Benzene, 1,3-dichloro-		600
Methane, dichlorobromo-			Benzene, 1,4-dichloro-	75	
Methane, dichlorodifluoro-		1000	Benzene, 1,2,3-trichloro-		
Methane, chlorodibromo-	100		Benzene, 1,2,4-trichloro-	70	
Carbontetrachloride	5		Benzene, 1,2,4-trimethyl-		
Methane, trichlorofluoro-			Benzene, 1,3,5-trimethyl-		
Ethane, chloro-			Benzene, ethyl-	700	
Ethane, 1,1-dichloro-			Benzene, <i>n</i> -butyl-		
Ethane, 1,2-dichloro-			Benzene, <i>sec</i> -butyl-		
Ethane, 1,2-dibromo-			Benzene, <i>tert</i> -butyl-		
Ethane, 1,1,1-trichloro-	200		Benzene, <i>n</i> -propyl-		
Ethane, 1,1,2-trichloro-	5		Benzene, isopropyl-		
Ethane, 1,1,1,2-tetrachloro-		70	Toluene	1000	
Ethane, 1,1,2,2-tetrachloro-			Toluene, <i>o</i> -chloro-		100
Vinyl chloride	2		Toluene, <i>p</i> -chloro-		100
Ethene, 1,1-dichloro-	7		Toluene, <i>p</i> -isopropyl-		
Ethene, <i>cis</i> -1,2-dichloro-	70		Xylene	10,000	
Ethene, <i>trans</i> -1,2-dichloro-	100		Styrene	100	
Ethene, trichloro-	5		Naphthalene		20
Ethene, tetrachloro-	5		Freon 113		
Propane, 1,2-dichloro-	5		Hexachlorobutadiene	50	
Propane, 1,3-dichloro-			Ether, methyl <i>tert</i> -butyl-		20–200
Propane, 2,2-dichloro-			Ether, 2-chloroethylvinyl		
Propane, 1,2,3-trichloro-		40	Acrolein ¹		
Propane, dibromochloro-	0.2		Acrylonitrile ¹		
Propene, 1,1-dichloro-					

¹Reporting limit for these compounds: 20 micrograms per liter, not analyzed at surface-water sites

Table 6. Triazine concentrations in ground water

[All concentrations are in micrograms per liter (µg/L); <, less than; RL, reporting limit (0.1 µg/L)]

	Fall 1994	March 1995	May 1995
Number of samples	19	13	15
Number of detections	5	4	15
Median concentration	< 0.1	< 0.1	0.1
Median concentration in samples above RL	0.2	0.3	0.1
Maximum concentration	0.9	3	0.5

area suggests that the herbicides were probably applied to crops outside the study area. The triazines in the May samples may have been deposited from the atmosphere or may have resulted from continuous recharge of Mississippi waters containing low concentrations of triazine compounds. Water from wells with the highest concentrations (GW01, 06, and 08) always contained detectable triazines. Wells with the highest concentrations (GW01, 02, 06, 08, and 16) were located on the northeast side of the island with the exception of well GW08. This pattern suggests that the cause of higher herbicide concentrations may be surface-water recharge. At certain times of the year, surface-water triazine concentrations can be higher than those measured in ground water in this study (J. Fallon, U.S. Geological Survey, oral commun., 1998). Water from wells located down gradient usually contained very low triazine concentrations, indicating dilution or degradation along flow in the aquifer.

Tritium Concentrations and Sources

Tritium, a radioactive isotope of hydrogen, composes part of water itself and is not a substance dissolved in it. Tritium in water in the study area has three possible sources. First, it is naturally and continually produced in the upper atmosphere by cosmic ray bombardment and is present in precipitation in the study area at concentrations of 16–48 pCi/L (Davis and others, 1985). Second, tritium was produced by atmospheric nuclear-device testing from the early 1950's through the mid 1960's. This testing greatly increased tritium concentrations in the

atmosphere and in precipitation from 1953 through the mid 1980's. At its peak in 1964, the tritium concentration in precipitation in southeastern Minnesota was 14,400 pCi/L (Michel, 1989a, b). Finally, tritium is produced at the Prairie Island Nuclear Power Plant as part of normal operations. Planned releases of tritium from this plant to the Mississippi River have occurred regularly since it began operation in 1971 (Jeffery Berrington, Northern States Power Company, oral commun., 1996). When the water level in the Mississippi River is higher than water levels in the aquifer, it is possible for tritium from any of these sources to enter the aquifer.

Tritium decays with a half-life of 12.43 years. For the purposes of comparison in this report, all tritium concentrations have been adjusted for radioactive decay to August 14, 1996. Ground water that originated as precipitation before atmospheric nuclear-device testing began now has a tritium concentration of < 3 pCi/L. Ground water that originated as precipitation during the peak tritium concentration in 1964 now has a concentration of 2,265 pCi/L. Determination of the sources of tritium in ground water require the accurate estimate of the date when ground water originated as precipitation. Analysis of CFC concentrations in ground water can provide an accurate recharge date, and makes it possible to determine if natural sources and nuclear-device testing account for all tritium in a ground water sample.

Tritium Concentrations

Since November 1989, NSP has monitored tritium concentrations in

ground and surface water at 50 sites: 5 surface water sites, 20 observation wells, 7 production wells, 16 domestic wells, and 2 springs. There were 59 sampling periods at these sites between November 1989 and June 1997, although at no time were all sites sampled concurrently nor was any site sampled all 59 times. Two laboratories analyzed tritium concentrations in these samples. Teledyne Isotopes Midwest Laboratory, Northbrook, Illinois, analyzed samples during November 1989–July 1994 with a reporting limit of about 190 pCi/L. Thereafter, University of Waterloo's Environmental Isotope Laboratory analyzed samples with a reporting limit of 19 pCi/L. The maximum tritium concentration measured was 1,676 pCi/L at a 24-ft-deep observation well located within 650 ft of the power plant main building (NSP well P10, sampled October 14, 1994). During May–July 1996, 46 of the 59 sites were sampled for tritium. The median concentration of this synoptic sampling was 95 pCi/L, the mean concentration was 128 pCi/L, and the maximum concentration was 611 pCi/L (again from well P10).

An analysis of these NSP data compared tritium concentration trends in well samples to the tritium concentration trend in precipitation to estimate the recharge date. This analysis concluded that tritium in precipitation, both natural and from nuclear-device testing, most reasonably explains the tritium in most of these samples. Tritium concentrations in water from three wells located within about 800 ft of the power plant (P4, P7, and P10) cannot be explained by tritium concentrations in recharge from relatively spatially and temporally constant precipitation because concentrations do not generally

decrease during 1989–97. Concentrations in these wells are characterized by a relatively high range (158–1,676 pCi/L) and high variability (51–76 percent relative difference). These relatively high concentrations are quite localized and appear to be diluted in the aquifer very near the power plant because samples from wells < 800 ft down gradient contained tritium concentrations similar to that of present precipitation. One possible explanation for the tritium concentrations in these wells is that variations in ground-water-flow rate and direction near these wells cause samples to be of variable age and, therefore, to contain tritium concentrations that does not covary with precipitation tritium concentrations. This flow variation could result from variable recharge from precipitation and floods, or from variable flow upward from bedrock aquifers. Tritium trends in ground water will match trends in precipitation only where there is a relatively constant source and amount of flow to an aquifer. If it exists, such variable flow would probably be present at all wells in the study area, however. Another possible explanation is that some of the tritium in these wells is tritium periodically released from the power plant. The tritium concentration of all NSP samples collected since November 1989 have been less than concentrations possible from rainfall from the 1960s, however. Without knowing recharge dates for the water samples from P4, P7, and P10, the possibility that the power plant may contribute some tritium to the ground water near these wells cannot be excluded.

Additional tritium samples were collected during this study to better characterize tritium concentration in water. Twenty-one of the 22 wells sampled for other chemicals were sampled for tritium one to five times during 1994–96. Tritium concentrations in these 71 samples ranged from < 1 to 550 pCi/L, and have a median of 43 pCi/L. Forty-three samples (61 percent) contained tritium concentrations between 26 and 54 pCi/L. Concentrations in this range could result from current natural atmospheric tritium production. If the water is older, however, other sources must have contributed tritium. Seven wells produced 23 samples

(32 percent) with concentrations higher than 54 pCi/L. These samples contain more than one source of tritium, regardless of their age. Seven surface-water sites were sampled for tritium on August 1, 1995. Concentrations ranged from 13 to 84 pCi/L, but the range drops to 34–46 pCi/L by excluding the samples with the highest and lowest concentrations. The tritium concentrations of all samples collected for this study have been below concentrations possible from rainfall from the 1960s. Because the 14 ground-water samples collected in August 1996 were also analyzed for CFC concentrations, recharge-date and tritium-source estimates are possible.

Chlorofluorocarbon Recharge Dates

Accurate age dating of shallow ground water is possible by measuring CFC concentrations (Busenberg and Plummer, 1992). CFCs (or Freons) are man-made chemicals that were used since the 1930's in refrigeration and plastics, and as aerosol propellants. As use increased, so did the concentrations in the atmosphere, and therefore, in precipitation and ground water. Atmospheric CFC concentrations and Henry's law can be used to calculate the atmospheric component of CFC concentration in ground water at a given time, elevation, and temperature. Conversely, a date of recharge can be calculated to within 1–2 years by analyzing CFC concentrations in ground water, and from recharge elevation and recharge temperature. This analysis assumes that the CFCs in ground water have not undergone degradation and that all CFCs come from the atmosphere. In the usually well-oxygenated conditions of shallow ground water, CFCs are relatively stable. Recharge temperature and CFC degradation can both be estimated by measuring the concentrations of certain other dissolved gasses in ground water (oxygen, nitrogen, argon, and methane). Because nitrogen and argon are at relatively constant concentrations in the atmosphere, Henry's law can be used to estimate recharge temperature from their relative concentrations. Concentrations of oxygen and methane describe the oxidation-reduction state of ground water and warn of reducing conditions that can

degrade CFCs. Three CFCs (CFC-11, CFC-12, and CFC-113) were measured in each sample analyzed for CFCs. In water under reducing conditions, each CFC will degrade at a different rate, resulting in recharge dates from each CFC that do not agree. If such degradation occurs, the precision and reliability for the CFC recharge date for that sample is reduced.

Contamination by non-atmospheric CFCs is another possible source of error with this dating method. In the following discussion, the word "contamination" refers specifically to CFCs from non-atmospheric sources and implies nothing about the purity or health effects of the water sampled. CFC use in metropolitan areas is substantial and therefore, wastewater from these areas can contain high CFC concentrations. CFC contamination of ground water is possible considering that the treated wastewater from large metropolitan areas enter the Mississippi River upstream of the study area and that Mississippi waters recharge the surficial aquifer. As with CFC degradation, CFC contamination is apparent if recharge dates based on different CFCs are inconsistent, or if CFC concentrations are above those possible in the atmosphere.

During August 1996, 14 ground-water samples were collected from observation wells previously sampled and were analyzed for tritium, dissolved gas, and CFCs to determine how much of the tritium concentration in the sample came from natural sources and nuclear-device testing (hereinafter, atmospheric sources) during recharge. A recharge temperature was estimated for a sample based on concentrations of dissolved nitrogen and argon. Next, a recharge date or range of dates was estimated using the estimated recharge temperature and the CFC concentrations in the sample. Then, the expected tritium concentration in a sample was determined, based on the atmospheric tritium concentration at the time of recharge. To account for the range of water ages intercepted by an average well screen 3 ft in length, the 6-month running average of tritium concentrations in the atmosphere (figs. 10 and 11) was used to determine the expected tritium concentration in a sample. Finally, the tritium con-

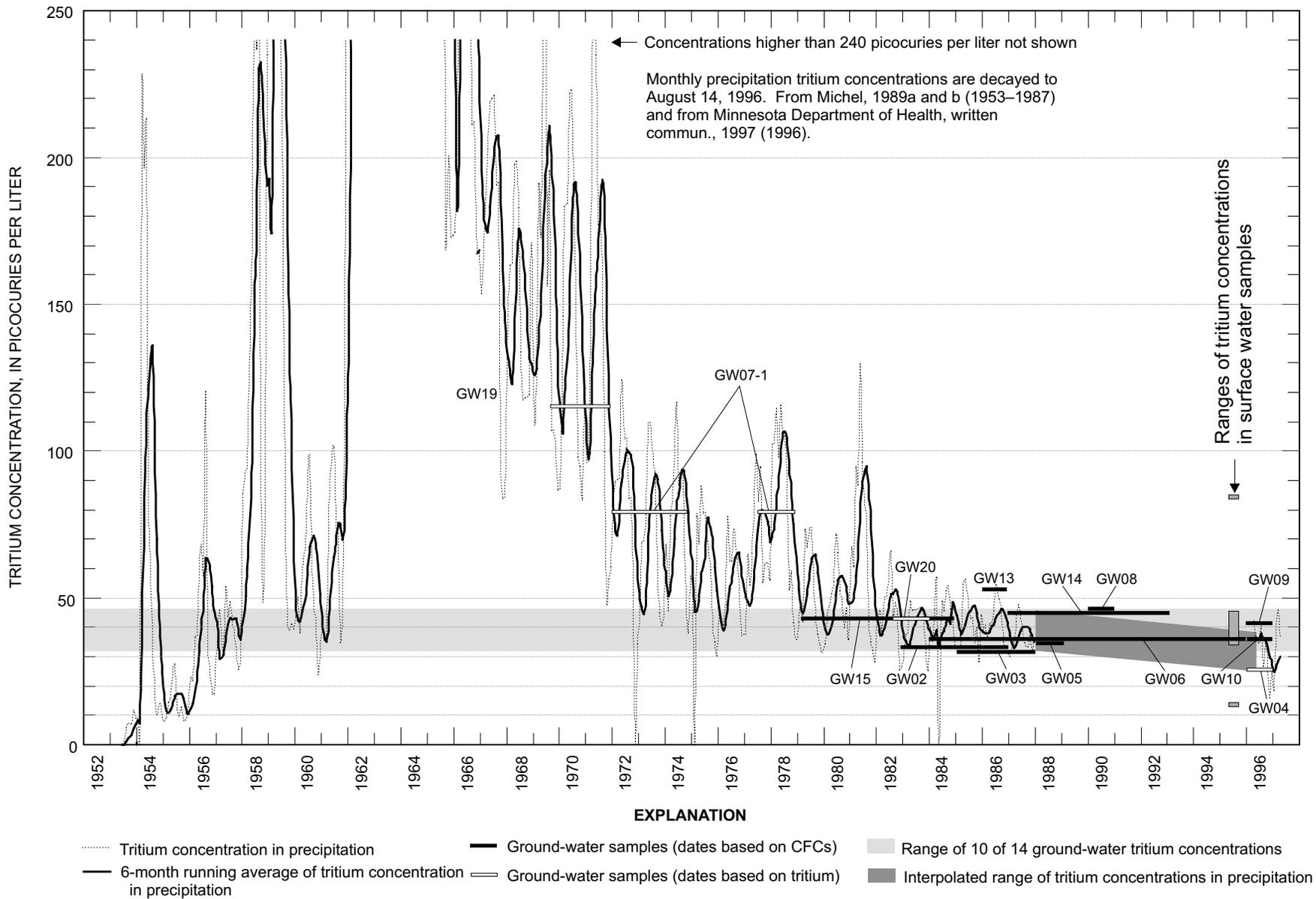


Figure 10. Precipitation and ground-water tritium concentrations and ground-water chlorofluorocarbon recharge dates, 1953–97.

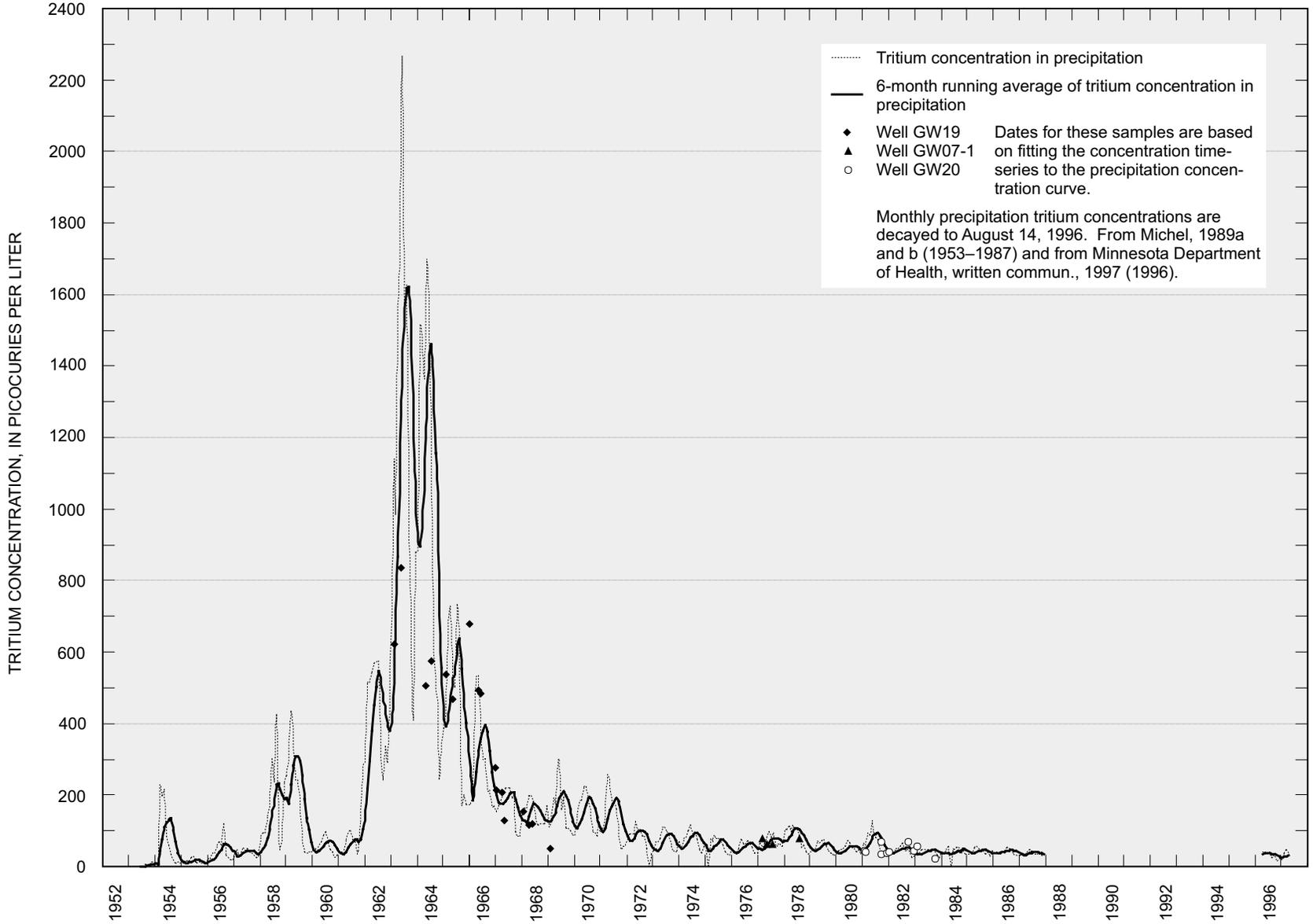


Figure 11. Tritium concentrations in precipitation, 1953–97 and selected ground-water samples, 1991–97.

centration measured in a sample was compared to the expected tritium concentration. If these concentrations agreed, all tritium in the sample was attributed to atmospheric sources.

Despite several complications, calculated recharge temperatures of the samples ranged from 46 to 59 degrees Fahrenheit (°F), excluding two samples that degassed. One dissolved-gas sample bottle leaked, causing the sample to gain dissolved gasses (GW15, 15.99 mg/L excess air, table 7). At least two samples degassed during sampling (GW19 and 20, low argon concentrations, table 7). All but one sample (GW05) had excess air, that is, gas concentrations beyond equilibrium. Excess air was probably gaseous air trapped in the aquifer and pumped out with the sample water. The calculated recharge temperature range is reasonable considering that the sampled water is a mixture of all water surrounding a 3 ft (or longer) well screen. The ground water composing a sample likely recharged in pulses, each pulse at a different temperature, over some period. A median recharge temperature of 52°F was used to calculate recharge dates for the two samples that degassed.

CFC concentrations in all samples appear to have been contaminated or degraded to some degree (noted for each sample in table 7. See the appendix for a detailed discussion). CFC concentrations in four samples (GW04, 07-1, 19, and 20) were so altered that a CFC recharge date estimate was impossible. The two highest and the lowest tritium concentrations of the 14 samples analyzed for CFCs are among the four altered samples. The recharge dates for these four samples (table 7) are based on tritium concentration and sample depth assuming all tritium came from atmospheric sources. Although no independent assessment about tritium sources is possible for these samples, the tritium they contain is reasonably explained by atmospheric sources.

CFC recharge dates for the remaining 10 samples ranged over 18 years (1979 to 1996), although 5 of these were in the last 6 years. Samples from the two deepest wells (GW14 and 15, about 30-ft deep)

were the oldest. Tritium concentrations in 9 of the 10 samples range from 31 to 47 pCi/L (light-grey band, fig. 10), within the range of current natural rainfall. The measured tritium concentrations in all 10 samples were within the range of expected tritium concentration based on the CFC recharge dates. This concurrence indicates that all tritium in these samples had atmospheric sources. The appendix contains detailed discussion of the CFC recharge dates and expected tritium concentration estimates for all 14 samples.

Organic Compounds in Sediment

The Mississippi and Vermillion Rivers occasionally flood low-lying areas, leaving alluvial deposits. The 1993 Mississippi River flood deposited fine-grained sediments along the north and east sides of the study area. A sample of these flood sediments was collected at four locations (SW1, 2, 4, and 7, fig. 2) near the water's edge on August 2, 1995 to determine if semivolatile and chlorinated organic compounds transported from upstream were deposited. The samples were analyzed for gross carbon, organochlorine pesticides, polycyclic aromatic hydrocarbons (PAH), monoaromatic compounds, and other semivolatile organic compounds (table 8). Samples from SW1 and 4 contained 3–4 times more total carbon than did samples from the other two sites, probably reflecting the more sheltered conditions of North Lake and Buffalo Slough. Floodwaters probably flowed more slowly here, permitting the deposition of less-dense, fine-grained organic matter. About 50 to 90 percent of the carbon in all samples was organic carbon.

Most of the compounds detected in sediments belong to the PAH or monoaromatic classes and were found in all samples (table 8). Samples from SW1 and 4 contained nearly twice as many detected PAH and monoaromatic compounds as did the other two samples. In all samples together, 17 out of 26 PAHs and 8 out of 21 monoaromatic compounds were detected, but only 2 and 3 compounds in each class, respectively, were present at concentrations high enough to quantify

accurately. Compounds with the highest concentrations were the monoaromatic phthalate esters (plasticizers used in industry). Only 1 of 31 organochlorine pesticides (hexachlorobenzene, estimated at 12 µg/kg) was detected in one sample (SW7). The sample from site SW1 was the only sample containing any other organic compounds, with 4 out of 16 detected at concentrations below the reporting limit.

The concentrations of these semivolatile and chlorinated organic compounds in sediment samples were low. Two guidelines developed from toxicity literature provide benchmarks with which to evaluate concentrations, for 14 of the 95 compounds analyzed. Long and Morgan (1991) determined 10th- and 50th-percentile concentrations that were found to adversely affect aquatic organisms. No concentration in the samples exceeded those guidelines. Also, the Canadian government is developing draft sediment contaminant benchmarks called the Canadian Interim Sediment Quality Guidelines (Brigham and others, 1997; Canadian Council of Ministers of the Environment, 1995). Three PAH concentrations in the sample from SW1 and one in the sample from SW4 exceeded the threshold effect level (GL) (table 8), but none exceeded the probable effect level. The threshold effect level is defined as “the concentration below which adverse effects are expected to occur rarely” (Canadian Council of Ministers of the Environment, 1995). The probable effect level is “the level above which adverse effects are predicted to occur frequently” (Canadian Council of Ministers of the Environment, 1995). None of the 4 concentrations exceeding the GL did so by more than 47 percent (15 µg/L maximum). Three of these exceedences were estimated below the reporting limit and, therefore, quantifiably unreliable. Only 4 of the 11 PAHs with a GL were analyzed with a reporting limit above that GL.

Water-Resource Implications

The analysis of data for this study has implications for water resources on the

Table 7. Tritium, dissolved gasses, and chlorofluorocarbons in ground water and associated information, August 1996
 [BLS, below land surface; BWT, below water table; CFC, chlorofluorocarbon; pCi/L, picocuries per liter; mg/L, milligrams per liter; °F, degrees Fahrenheit; ft, feet]

Well	Estimated recharge date	Date basis	CFC contaminated	CFC degraded	Tritium pCi/L	Expected tritium ¹ pCi/L	Oxygen, field mg/L	Oxygen, laboratory mg/L	Methane mg/L	Recharge temperature °F	Argon mg/L	Excess air mL	Nitrogen gas mg/L	Nitrate as nitrogen mg/L	Water level, BLS ft	Screen top, BWT ft	Well depth, BLS ft	Screen length ft
GW02	1983–1987	CFC-11 and 12 range	113		33	30–55	4.0	2.26	0.00	47	0.74	2.89	21.21	2.3	8.15	0.77	13.92	4.42
GW03	1985–1988	CFC-11 and 12 range	113		31	30–55	6.1	3.82	0.00	46	0.74	1.93	20.67	0.35	6.96	0.44	12.4	4.42
GW04	1996	Tritium concentration, sample depth		ALL	26	18–40	< 0.1	0.04	5.80	55	0.73	6.05	22.72	0.05	4.03	1.96	10.99	4.42
GW05	1988	CFC-12, CFC-11 trend flat	113		34	30–45	6.5	4.03	0.00	46	0.71	0.04	18.78	0.16	5.70	0.76	11.46	4.42
GW06	1984–1996	CFC-11 and 12 range	113		35	30–55	1.8	1.20	0.00	55	0.70	4.37	21.09	5.9	11.43	0.82	17.25	4.42
GW07-1	1972–1974, 1977–1978	Tritium concentration, sample depth	ALL ³		79	40–110	7.4	4.54	0.00	49	0.71	1.82	19.71	30	10.85	-0.30	15.55	4.42
GW08	1990	CFC-12	113, 11		47	30–45	6.1	3.84	0.00	53	0.70	3.28	20.47	6.9	12.90	0.99	18.89	4.42
GW09	1996	CFC-11 and 12 concurrence	113		41	18–40	9.5	6.69	0.00	54	0.68	2.56	19.57	2.5	17.50	-0.36	22.14	4.42
GW10	1996	CFC-12, CFC-11 trend flat	113		35	18–40	10.4	6.27	0.00	55	0.66	1.70	18.48	8.1	13.85	-0.51	18.34	4.42
GW13	1986	CFC-11	113, 12		54	30–55	3.9	1.92	0.50	59	0.67	4.07	20.14	2.2	18.34	-3.8	24.5	10
GW14	1987–1992	CFC-11 and 113 range	12		45	30–45	11.6	7.95	0.00	49	0.79	6.54	24.44	0.87	13.29	14	30	3
GW15	1979–1984	CFC-11 and 113 range, leak in gas sample	12		43	28–130	< 0.1	0.15	0.00	56	0.89	15.99	32.52	0.88	4.42	25	32.3	3
GW19	1970–1972	Tritium concentration and gas loss	113	ALL	115	98–210	< 0.1	0.06	17.80	² 71	0.56	1.86	16.10	0.07	20.68	28	52	3
GW20	1976–1982	Tritium concentration and gas loss, sample depth	113	ALL	43	35–70	0.2	2.85	4.00	² 107	0.52	9.02	19.52	0.28	6.90	-3	14	10

¹Tritium concentration expected for the estimated recharge date

²Loss of dissolved gasses in aquifer or sampling resulted in low argon concentrations and unrealistically high recharge temperatures, and possible loss of CFCs, resulting in excessively early recharge dates

³Assumed contaminated because CFC concentrations inconsistent with high tritium concentrations

Table 8. Organochlorine, polycyclic aromatic hydrocarbon, and other semivolatile organic compounds in flood deposits (particle sizes less than 2 millimeters)

[All concentrations are in dry weight; code, U.S. Geological Survey parameter code; GL, Canadian Interim Sediment Quality Guideline threshold effect level; <, less than, E, estimated concentration (between detection and reporting limits)]

Code	Name	Site name:	Sample				GL
			SW1	SW2	SW4	SW7	
		Site number:	99500564	99500562	99500560	99500558	
Total carbon, in grams per kilogram							
49270	carbon, inorganic		1.4	0.6	5.6	1.6	
49272	carbon, organic + inorganic		12	3.5	14	3.2	
49271	carbon, organic		11	2.9	8.4	1.6	
Organochlorine pesticides and polychlorinated biphenols (PCBs), in micrograms per kilogram							
49319	aldrin		< 1.00	< 1.00	< 1.00	< 1.00	
49343	benzene, hexachloro-		< 0.750	< 1.00	< 1.00	E 4.10	
49320	chlordane, <i>cis</i> -		< 1.00	< 1.00	< 1.00	< 1.00	
49321	chlordane, <i>trans</i> -		< 1.00	< 1.00	< 1.00	< 1.00	
49322	chloroneb		< 5.00	< 5.00	< 5.00	< 5.00	
49324	DCPA		< 5.00	< 5.00	< 5.00	< 5.00	
49325	DDD, <i>o, p'</i> -		< 1.00	< 1.00	< 1.00	< 1.00	
49326	DDD, <i>p, p'</i> -		< 1.00	< 1.00	< 1.00	< 1.00	3.54
49327	DDE, <i>o, p'</i> -		< 1.00	< 1.00	< 1.00	< 1.00	
49328	DDE, <i>p, p'</i> -		< 1.00	< 1.00	< 1.00	< 1.00	1.42
49329	DDT, <i>o, p'</i> -		< 2.00	< 2.00	< 2.00	< 2.00	
49330	DDT, <i>p, p'</i> -		< 2.00	< 2.00	< 2.00	< 2.00	16.71
49331	dieldrin		< 1.00	< 1.00	< 1.00	< 1.00	
49332	endosulfan I		< 1.00	< 1.00	< 1.00	< 1.00	
49335	endrin		< 2.00	< 2.00	< 2.00	< 2.00	
49341	heptachlor		< 1.00	< 1.00	< 1.00	< 1.00	
49342	heptachlor epoxide		< 1.00	< 1.00	< 1.00	< 1.00	
49338	α -hexachlorocyclohexane		< 1.00	< 1.00	< 1.00	< 1.00	
49339	β -hexachlorocyclohexane		< 1.00	< 1.00	< 1.00	< 1.00	
49344	isodrin		< 1.00	< 1.00	< 1.00	< 1.00	
49345	lindane		< 1.00	< 1.00	< 1.00	< 1.00	

Table 8. Organochlorine, polycyclic aromatic hydrocarbon, and other semivolatile organic compounds in flood deposits (particle sizes less than 2 millimeters)--Continued

[All concentrations are in dry weight; code, U.S. Geological Survey parameter code; GL, Canadian Interim Sediment Quality Guideline threshold effect level; <, less than, E, estimated concentration (between detection and reporting limits)]

Code	Name	Site name:	Sample				GL
			SW1	SW2	SW4	SW7	
		Site number:	99500564	99500562	99500560	99500558	
49347	methoxychlor, <i>o, p'</i> -		< 5.00	< 5.00	< 5.00	< 5.00	
49346	methoxychlor, <i>p, p'</i> -		< 5.00	< 5.00	< 5.00	< 5.00	
49348	mirex		< 1.00	< 1.00	< 1.00	< 1.00	
49316	nonachlor, <i>cis</i> -		< 1.00	< 1.00	< 1.00	< 1.00	
49317	nonachlor, <i>trans</i> -		< 1.00	< 1.00	< 1.00	< 1.00	
49318	oxychlorane		< 1.00	< 1.00	< 1.00	< 1.00	
49459	PCBs, total		< 50	< 50	< 50	< 50	
49460	pentachloroanisole		< 1.0	< 1.0	< 1.0	< 1.0	
49349	permethrin, <i>cis</i> -		< 5.00	< 5.00	< 5.00	< 5.00	
49350	permethrin, <i>trans</i> -		< 5.00	< 5.00	< 5.00	< 5.00	
49351	toxaphene		<200	<200	<200	<200	
Polycyclic aromatic hydrocarbons, in micrograms per kilogram							
49429	acenaphthene		< 50	< 50	< 50	< 50	¹ 46.9
49428	acenaphthylene		E 15	< 50	< 50	E 12	
49434	anthracene		E 19	< 50	E 16	< 50	¹ 74.8
49461	anthracene, dibenz(a,h)		< 50	< 50	< 50	< 50	¹ 6.22
49435	anthracene, 2-methyl-		< 50	< 50	< 50	< 50	
49436	benz(a)anthracene		E 37	< 50	E 21	E 17	31.7
49389	benzo(a)pyrene, 1-methyl-		E 47	< 50	E 34	< 50	31.9
49458	benzo(b)fluoranthene		E 49	< 50	E 41	E 40	
49397	benzo(k)fluoranthene		E 47	< 50	E 20	E 17	
49408	benzo[g,h,i] perylene		< 50	E 29	E 28	< 50	
49450	chrysene		E 38	E 28	E 19	E 14	57.1
49466	fluoranthene		63	E 24	E 34	E 25	111
49399	fluorene, 9H-		E 10	< 50	E 9.0	< 50	¹ 21.2
49398	fluorene, 1-methyl-9H-		< 50	< 50	< 50	< 50	
49390	indeno(1,2,3-c,d)pyrene, 1-methyl-		< 50	< 50	E 24	< 50	

Table 8. Organochlorine, polycyclic aromatic hydrocarbon, and other semivolatile organic compounds in flood deposits (particle sizes less than 2 millimeters)--Continued

[All concentrations are in dry weight; code, U.S. Geological Survey parameter code; GL, Canadian Interim Sediment Quality Guideline threshold effect level; <, less than, E, estimated concentration (between detection and reporting limits)]

Code	Name	Site name:	Sample				GL
			SW1	SW2	SW4	SW7	
			Site number: 99500564	99500562	99500560	99500558	
49402	naphthalene		< 50	< 50	< 50	< 50	¹ 34.6
49948	naphthalene, 2-ethyl-		< 50	< 50	< 50	< 50	
49403	naphthalene, 1,2-dimethyl-		< 50	< 50	< 50	< 50	
49404	naphthalene, 1,6-dimethyl-		< 50	< 50	< 50	< 50	
49406	naphthalene, 2,6-dimethyl-		E 11	< 50	E 9.0	< 50	
49405	naphthalene, 2,3,6-trimethyl-		< 50	< 50	< 50	< 50	
49409	phenanthrene		E 17	< 50	< 50	< 50	41.9
49411	phenanthrene, 4H-cyclo-penta(d,e,f)-		E 16	< 50	E 13	< 50	
49410	phenanthrene, 1-methyl-		E 16	< 50	< 50	< 50	
49387	pyrene		59	E 22	E 29	E 22	53
49388	pyrene, 1-methyl-		E 35	< 50	E 29	< 50	
Monoaromatic compounds, including nitrated, chlorinated, and phenolic compounds and phthalate esters, in micrograms per kilogram							
49443	azobenzene		< 50	< 50	< 50	< 50	
49438	benzene, 1,2,4-trichloro-		< 50	< 50	< 50	< 50	
49441	benzene, <i>m</i> -dichloro-		< 50	< 50	< 50	< 50	
49439	benzene, <i>o</i> -dichloro-		< 50	< 50	< 50	< 50	
49442	benzene, <i>p</i> -dichloro-		< 50	< 50	< 50	< 50	
49444	benzene, nitro-		< 50	< 50	< 50	< 50	
49446	benzene, pentachlor- nitro-		< 50	< 50	< 50	< 50	
49451	cresol, <i>p</i> -		E 29	< 50	E 31	< 50	
49422	cresol, 4-chloro-, <i>m</i> -		< 50	E 19	< 50	< 50	
49413	phenol		E 21	< 50	E 15	E 14	
49424	phenol, C8-alkyl-		< 50	< 50	< 50	< 50	
49467	phenol, <i>o</i> -chloro-		< 50	< 50	< 50	< 50	
49426	phthalate, bis(2-ethyl hexyl)-		E 81	60	E 89	E 52	
49427	phthalate, butylbenzyl		52	52	E 48	E 46	
49381	phthalate, di- <i>n</i> -butyl		54	58	52	E 49	

Table 8. Organochlorine, polycyclic aromatic hydrocarbon, and other semivolatile organic compounds in flood deposits (particle sizes less than 2 millimeters)--Continued

[All concentrations are in dry weight; code, U.S. Geological Survey parameter code; GL, Canadian Interim Sediment Quality Guideline threshold effect level; <, less than, E, estimated concentration (between detection and reporting limits)]

Code	Name	Site name:	Sample				GL
			SW1	SW2	SW4	SW7	
		Site number:	99500564	99500562	99500560	99500558	
49383	phthalate, diethyl		E 16	E 19	E 15	E 14	
49384	phthalate, dimethyl		E 8.0	< 50	E 7.0	E 8.0	
49382	phthalate, di- <i>n</i> -octyl		< 50	< 50	< 50	< 50	
49395	toluene, 2,4-dinitro-		< 50	< 50	< 50	< 50	
49396	toluene, 2,6-dinitro-		< 50	< 50	< 50	< 50	
49421	xyleneol, 3, 5-		< 50	< 50	< 50	< 50	
Heterocyclic compounds and polycyclic aromatic hydrocarbon derivatives, in micrograms per kilogram							
49430	acridine		< 50	< 50	< 50	< 50	
49437	anthraquinone, 9, 10-		E 33	< 50	< 50	< 50	
49468	benzo(c)cinnoline		< 50	< 50	< 50	< 50	
49391	biquinoline, 2, 2'-		< 50	< 50	< 50	< 50	
49449	carbazole		E 33	< 50	< 50	< 50	
49394	isoquinoline		< 50	< 50	< 50	< 50	
49407	naphthalene, 2-chloro-		< 50	< 50	< 50	< 50	
49392	quinoline		< 50	< 50	< 50	< 50	
49393	phenanthridine		< 50	< 50	< 50	< 50	
49452	thiophene, dibenzo-		E 13	< 50	< 50	< 50	
Other base-neutral-acid extractable organic compounds, in micrograms per kilogram							
49454	ether, 4-bromophenyl phenyl-		< 50	< 50	< 50	< 50	
49455	ether, 4-chlorophenyl phenyl-		< 50	< 50	< 50	< 50	
49400	isophorone		< 50	< 50	< 50	< 50	
49401	methane, bis(2-chloroethoxy)-		< 50	< 50	< 50	< 50	
49433	diphenylamine, N-nitroso-		E 32	< 50	< 50	< 50	
49431	di- <i>n</i> -propylamine, N-nitroso-		< 50	< 50	< 50	< 50	

¹No freshwater guide exists; reported value is a marine sediment guideline

Prairie Island Indian Reservation in three respects. First, water-quality influences the uses of water resources, particularly its use as drinking water. Second, land uses in the study area can affect ground-water quality directly, and surface-water quality indirectly, through ground-water discharge. Third, manipulation of the levels of Mississippi waters for transportation at Lock and Dam Number 3 affects water quality. By maintaining levels in Mississippi waters artificially high for much of the year, the interaction between surface water and ground water is changed, thereby inducing changes in both ground- and surface-water quality.

Drinking-Water

Quality requirements for drinking water are the most stringent of water-quality standards, and thus are conservative standards against which to evaluate water-quality data from this study. Since

the Prairie Island Indian Community established a public drinking water supply from the Eau Claire-Mt. Simon aquifer in 1992, most reservation residents and guests do not drink water from the surficial aquifer. However, some households, both within and outside of the reservation, still rely on this aquifer for drinking water. The USEPA has established drinking water standards and health advisories for some of the constituents sampled in water in this study (U.S. Environmental Protection Agency, 1997). USEPA promulgates two levels of drinking water standards. Maximum contaminant levels (MCLs) are the enforceable limits that public supplies cannot exceed. Secondary MCLs (SMCLs) are non-enforceable guidelines regarding mostly aesthetic qualities of water. Several categories of non-enforceable health advisory limits (HALs) also exist. The most stringent of the HALs is the lifetime adult advisory, which is defined as “the concentration of

a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects over a lifetime of exposure, with a margin of safety”. Excluding trace metals and VOCs, table 9 lists the sampled constituents for which standards and advisories exist and the degree to which water on the reservation exceeded those levels.

Among the constituents in table 9, surface-water samples exceeded the pH SMCL in 6 of 22 samples and the bacteria MCL in all 15 samples. Water from one well (GW06) exceeded the pH SMCL, water from 2 wells (including the public supply at GW12) exceeded the sodium lifetime adult health advisory, and water from 3 wells (14 percent of the 22 wells sampled) exceeded the nitrate MCL of 10 mg/L-N. Twelve percent of the 81 ground-water samples contained nitrate concentrations over the MCL. Triazine concentrations in one sample from well

Table 9. U.S. Environmental Protection Agency drinking-water standards and health advisories

[Standards and health advisories from U.S. Environmental Protection Agency (1997) and Code of Federal Regulations (1996 for tritium); MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HAL, long-term adult health advisory limit; SW, surface-water samples; GW, ground-water samples; mg/L, milligrams per liter; N, nitrogen; µg/L, micrograms per liter; pCi/L, picocuries per liter; col/mL, colonies per milliliter]

Constituent	Unit	MCL	SMCL	HAL	Ratio of samples above MCL, SMCL, or HAL	
					SW	GW
pH			6.5–8.5		¹ 6/22	4/86 (4/5 at well GW06)
Total dissolved solids	mg/L		500		0/14	0/51
Sodium	mg/L			² 20	0/14	6/51 (3/3 each at wells GW07-1 and 12)
Sulfate	mg/L	500	250		0/14	0/51 (MCL), 0/51 (SMCL)
Chloride	mg/L		250		0/14	0/51
Fluoride	mg/L		2		0/14	0/51
Nitrate	mg/L as N	10			0/21	10/81 (5/5 at well GW07-1, 4/5 at well GW10, 1/2 at well GW18)
Nitrite	mg/L as N	1			0/18	0/81
Ammonia	mg/L as N			³ 30	0/21	0/83
Triazines	µg/L	3 (atrazine) 4 (simazine)			0/15	1/47 (1/2 at well GW01)
Tritium	pCi/L	⁴ 20,000			0/7	0/71
Total bacteria ⁵	col/mL	0	0		15/15	

¹All higher than 8.5

²Drinking water equivalent level for a 70 kilogram adult (guidance)

³Lifetime for a 70 kilogram adult

⁴Assuming that all man-made radiation comes from tritium

⁵Coliform and fecal streptococci

GW01 equaled the atrazine MCL and exceeded the simazine MCL. It is unlikely, however, that the entire triazine concentration in this sample was either atrazine or simazine, but rather a combination of several triazine herbicides and their degradation products (Lindgren and Landon, in press). Therefore, it is unlikely that either of these standards was exceeded. The USEPA has no standards for summed contaminants. No water samples from the study area exceeded the radioactivity standard because of tritium concentrations.

Of the 18 trace metals analyzed in water samples for this study, 15 have either a drinking-water standard or lifetime adult HAL or both (MCL: 9, SMCL: 4, lifetime adult HAL: 9, table 4). The lead concentration (30 µg/L) from one sample at well GW04 exceeded the MCL of 0 µg/L. This lead may be from aquifer sediments, flood sediments, contamination from sampling, or from a lead bullet in the well casing. Because the concentration of lead common in glacial outwash is lower than that measured in this sample, the aquifer sediments can be eliminated as a source of the lead. Of the 63 VOCs analyzed in water for this study, 34 have either a drinking-water standard or lifetime adult HAL (23 with an MCL; 11 with a lifetime adult HAL; table 5). None of these standards or advisories was known to be exceeded, as there were no detections of VOCs in the study samples. Reporting limits (3 µg/L) were higher than the standards for vinyl chloride (2 µg/L) and dibromochloropropane (0.2 µg/L), so it is not known if these two standards were exceeded.

Surface-water samples from the study area exceeded USEPA standards for coliform or fecal streptococci bacteria (no bacteria), as all samples contained one of these bacteria. Surface-water samples did not exceed standards for the chemicals analyzed. Filtering or bacterial decontamination would render the surface water potable. Water samples from the surficial aquifer were usually potable and of good quality; however, 13 percent of wells (3 wells) consistently produced samples containing concentrations of nitrate above the MCL. Two of these were observation

wells screened at the water table and the third was a domestic well, probably of shallow depth. Deeper wells usually have lower nitrate concentrations because the water is older. Older water was recharged before fertilizer was extensively used. Also, any nitrate that may have been in water that reached the water table has had longer to degrade (Cowdery, 1997). Consumption of water from some shallow surficial-aquifer wells poses health risks, particularly for infants (who are susceptible to acquired methemoglobinemia caused by chemicals such as nitrate).

Land-Use Effects

Land uses within the study area consist of residences, a resort and casino, agriculture, and nuclear power generation. Because residences occupy a small area and the resort and casino is a fairly new land use, these land uses may have had relatively small influences on the water quality observed in this study. A sewage lagoon recently built near the center of the study area receives wastewater from these land uses and may influence ground-water quality in the future. Sewage from residential and resort and casino land uses and fertilization from agricultural land use have the potential to increase both nitrate and sodium concentrations in the underlying ground water (Delin and others, 1995). Samples from well GW07-1 consistently had the highest concentrations of nitrate (all samples higher than 20 mg/L-N) and sodium (35-50 mg/L) among surficial aquifer wells. This well is one of two sampled that was near an agricultural field and a residential septic system. The estimated tritium-based recharge date for this well is older than 1979, so concentrations in these samples reflect land uses that occurred prior to that year.

Samples from well GW10 also had nitrate concentrations near 10 mg/L-N (8.1-16 mg/L-N), but had much lower sodium concentrations (2.2-2.5 mg/L) than well GW07-1. The only obvious source of nitrate near this well is the reservation sewage lagoon. The CFC recharge date for this well is 1996, indicating that samples from this well are modern. High nitrate concentrations in

samples from well GW10 suggest that nitrate from the sewage lagoon may be leaking to the surficial aquifer. If this were the case, however, one would also expect to find higher sodium concentrations than were measured in water from well GW10.

The main water-quality concern related to the power plant is tritium production. In samples for which CFC ground-water-recharge dates were determined, atmospheric sources can explain the tritium concentrations in the samples. Further, by comparing historical tritium concentrations at NSP observation wells to tritium concentrations in precipitation over time, reasonable recharge dates can be estimated and most historical tritium concentrations can also be explained by atmospheric sources alone. Three wells located near the power plant contain tritium concentrations that cannot be explained by atmospheric sources alone. Tritium concentrations in these wells may result from variations in ground-water-flow rate and direction near these wells, or from power-plant releases of tritium. Ground water in the area of these three wells appears to be diluted in the aquifer very near the plant because samples from wells < 800 ft down gradient did not have high tritium concentrations.

Effects of Surface-Water/Ground-Water Interaction on Water Quality

The flow between ground water and surface water documented herein implies that ground water and surface water have an influence on the water quality of each other. Both surface water and shallow ground water have their origin in precipitation, which contains fairly low concentrations of dissolved chemicals. Chemical concentrations increase as rain runoff or snowmelt flows across the land surface into lakes and rivers. Therefore, land use throughout their entire surface-water basins influences the chemical concentrations in the Vermillion and Mississippi Rivers. These land uses may be as far away as several hundred miles from the study area. Chemical concentrations also increase as rain runoff or snowmelt recharges the surficial aquifer through the

unsaturated zone; in this way, land use within the study area influences the chemical composition of surficial ground water. Dissolution of aquifer materials and subsurface flow from bedrock aquifers can also affect the chemical composition of surficial ground water, generally increasing the concentrations of major ions and some trace metals. It is possible that the different mechanisms influencing surface and ground waters could produce differences in water quality between surface waters and ground waters.

Based on the rapid change in ground-water flow directions in the surficial aquifer between June and August 1997, chemical distinction between surface and ground water is continually blurred by mixing. In the winter of 1996–97, surface water likely recharged the surficial aquifer on the Mississippi River side of Prairie

Island, and ground water discharged on the Vermillion River side (fig. 5). During the spring snowmelt, a recharge mound probably formed on the island, with ground water discharging to all surface waters from the mound. By May or June, Vermillion waters had declined 3 ft lower than Mississippi waters and the “normal” cross-island flow system was recurring. When high rainfall occurred in July, the ground-water mound reformed on the island, resulting in radial flow and discharge to surface waters in all directions (fig. 6), probably similar to the spring flow system. By August, the normal cross-island flow system was recurring (fig. 7). Each of these flow-system changes involved changes in flow direction and rate that varied throughout the study area. Flow direction reversed on the Mississippi River side of Prairie Island, while the magnitude of the

ground-water gradient (and hence flow rate) changed on the Vermillion River side of the island.

Throughout the aquifer, water from surface-water recharge flowed with water recharged through the unsaturated zone and probably began mixing by dispersion. The relative amounts of ground water recharged through these two sources is unknown and is probably highly variable, dependent on the weather and flood history of each year. The similar quality of surface and ground water suggests that recharge from surface water is probably the dominant pathway. The volumetric rate of water flow in the aquifer is small compared to that in the surface-water system. Thus, ground-water discharge is probably too small to substantially affect surface-water quality in the study area.

Summary

Stratigraphic, water-level and water-quality information gathered in and around the Prairie Island Indian Reservation during 1994–97 was supplemented with historical data to form the basis of an evaluation of the water resources of the Prairie Island Indian Community. The reservation occupies a small part of southeastern Prairie Island, a glacial outwash remnant in the Mississippi River Valley between Hastings and Red Wing, Minnesota. The Mississippi River and the lakes and wetlands connected to it form the northeastern boundary of the island. The southwestern boundary is the Vermillion River and the lakes and wetlands connected to it. Lock and Dam Number 3 and Prairie Island separate these surface-water groups. The stages of these surface-water groups determine flow and influence water quality in the surficial aquifer. The surficial aquifer is 130–200 ft thick, composed of sand and gravel, but also contains thin, isolated lenses of finer-grained material. The aquifer extends from the land surface to bedrock (the Franconia Formation), which is also an aquifer.

Flow in the surficial aquifer is controlled primarily by the stage difference created by Lock and Dam Number 3 between the two surface-water groups. During much of the year, the dam produces stage differences of 3–6 ft, causing Mississippi waters to recharge the aquifer. This ground water flows toward the Vermillion waters (southwest) where it discharges. During snowmelt or very rainy periods, a ground-water mound forms on the island through recharge from the land surface. This mound causes ground water to flow radially away from it, discharging to surrounding surface waters.

The quality of both surface and ground water is similar because of the hydraulic connection between these waters. Samples were collected at 8 surface-water sites and 22 wells (most of which were observation wells screened at or near the water table) during 5 periods throughout the study. Water samples were dominated by calcium, magnesium, and bicarbonate ions, were usually oxygenated, and had median dissolved solids concentrations of about 250 mg/L. Generally, nitrate concentrations were higher and organic carbon concentration lower in ground water samples than in surface-water samples. Thirty-nine percent of all ground-water samples contained nitrate at a concentration of at least 3 mg/L-N and 12 percent contained at least 10 mg/L-N indicating substantial anthropogenic nitrogen content. Only 14 percent of all surface-water samples contained at least 3 mg/L nitrate nitrogen, with a maximum concentration of 3.4 mg/L-N. The median nitrate concentration for ground-water samples was 3.6-times greater than that for surface-water samples. Wells with relatively high nitrate concentrations in 1994 tended to have high concentrations throughout the study period. Samples from 17 wells contained ammonia at very low concentrations (< 0.04 mg/L-N), while samples from 4 wells that produced anoxic water contained higher concentrations, as high as 1.7 mg/L-N. Five percent of ground-water and 18 percent of surface-water samples contained at least 0.10 mg/L phosphorus. Water with phosphorus concentrations in this range may contribute to algal growth in surface waters. All 15 surface-water samples contained coliform or fecal-streptococci bacteria above the reporting limit with five of these exceeding 100 col/mL.

Trace metal concentrations in 2 ground-water and 2 surface-water samples were at natural levels and below drinking water standards except 1 ground-water sample that contained a high

lead concentration. This well may have been contaminated with a lead bullet. No VOCs were detected in the 3 ground-water and 3 surface-water samples collected. Triazine herbicides and their degradation products were detected in one-half of the ground-water samples at concentrations below 1 µg/L except for one sample at 3 µg/L. Only 1 of 15 surface-water samples contained triazine compounds at a concentration above the reporting limit. This distribution, combined with the low triazine use in the study area, indicates that the triazine source is outside the study area. Wells with the highest triazine concentrations contained triazines whenever sampled.

Ground-water recharge dates estimated from chlorofluorocarbon (CFC) concentrations indicate that most shallow ground-water samples are young (< 2 decades old) and that tritium contained therein is from atmospheric sources. Most historical tritium samples also contained concentrations that can be explained by atmospheric concentrations. Three observation wells within 800 ft of the Prairie Island Nuclear Power Plant contained tritium at concentrations above that explainable by recharge from spatially and temporally constant precipitation and snowmelt, but these concentrations are low (158–1,676 pCi/L) and did not persist down gradient in the aquifer. Many ground-water samples contained CFC-113 concentrations higher than that possible from atmospheric equilibrium. Presumably this CFC-113 contamination is from Mississippi River recharge containing CFC-113 from upstream treated wastewater. This contamination and some samples with CFC degradation complicated recharge-date estimation

and increased date uncertainty. Sediments deposited on the island during the 1993 Mississippi River flood contained low concentrations of several semivolatile and chlorinated organic compounds (< 89 micrograms per kilogram), most of which belonged to the polycyclic aromatic hydrocarbon and monoaromatic chemical classes.

Surface water contained no constituent except bacteria above a U.S. Environmental Protection Agency drinking water standard. All surface-water samples contained some bacteria, yielding it unfit to drink untreated. Thirteen percent of ground-water samples exceeded the nitrate maximum contaminant level of 10 mg/L-N, posing health risks, particularly for infants. Because most wells sampled were shallow, however, the percentage of the aquifer contaminated with nitrate is probably < 13 percent. Land uses that could account for high nitrate concentrations include agricultural fertilization, leaking septic systems, or a leaking sewage lagoon. These nitrate sources were confirmed in some samples by the covariance of nitrate and chloride.

Surface-water recharge to and ground-water discharge from the surficial aquifer influence the water quality of both ground water and surface water. Because the amount of water flowing through the surface-water system is probably much greater than that flowing through the ground-water system, surface-water quality probably influences ground-water quality to a larger degree.

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Appendix

This section records the rationale for recharge dates estimated from CFC concentrations in 14 ground-water samples collected in the study area in August 1996. This section also examines the concurrence of atmospheric tritium concentrations at the time of estimated recharge with the measured tritium concentration in the sample, to determine tritium sources. CFC concentrations higher than that possible from atmospheric equilibrium are noted as contamination. Samples are examined in groups containing similar contamination or degradation problems.

Recharge dates for water samples from wells GW02, 03, 06, and 09 are based on the range of dates estimated from CFC-11 and 12 because these samples were contaminated with CFC-113. Because concentrations of CFC-113 are very low in the atmosphere (< 80 parts per trillion; E. Busenberg, U.S. Geological Survey, written commun., 1997), contamination of ground water or samples by this Freon occurs easily. Surface water contaminated with CFC-113 from upstream wastewater sources may have recharged the surficial aquifer. The estimated recharge dates for these four samples range from 1983 to 1996.

Recharge dates for samples from wells GW05 and 10 are based solely on CFC-12. These samples were also contaminated with CFC-113. CFC-11 concentrations in these samples are consistent with the recharge dates derived from CFC-12 concentrations. However, CFC-11 concentrations were not used to estimate recharge dates for GW05 and 10, because during the recharge period for these samples, concentrations of CFC-11 began to stabilize in the atmosphere and dates based on this Freon are imprecise. Recharge dates for GW05 and 10 are 1988 and 1996 respectively.

Recharge dates for samples from wells GW14 and 15 are based on the range of dates estimated from CFC-11 and 113 because they were contaminated with CFC-12. Samples from wells GW08 and GW13 were contaminated with CFC-

113. The sample from GW08 was also contaminated with CFC-11 and the sample from GW13 was also contaminated with CFC-12. Therefore, the recharge date of 1990 for the sample from GW08 is based solely on CFC-12 and the date of 1986 for the sample from GW13 is based solely on CFC-11. The recharge dates based on only one CFC (GW05, 08, 10, and 13) are less reliable than those based on two CFCs (GW02, 03, 06, 09, 14, and 15).

Tritium concentrations in water samples from these 10 wells are within the variability of tritium concentrations in precipitation at the time of estimated recharge. However, because the samples were collected from wells with screen lengths of 3–6 ft (median: 4.43 ft), these samples are composites of water with a range of ages and tritium concentrations. These composites probably include water that varies in age about 6–12 months, considering that recharge to the surficial aquifer caused the water table to fluctuate between 4.3 and 6.6 ft during 1994–97 (fig. 4). Use of the 6-month running average of tritium concentration in precipitation (fig. 10) accounts for this composite effect. In such composites, estimated recharge dates will be later than the average recharge date because CFC concentrations in precipitation had been increasing exponentially until the late 1990's (E. Busenberg, U.S. Geological Survey, written commun., 1997). Therefore, the CFC recharge dates in figure 10 may be later than the actual recharge dates because of screened-interval mixing. Three of the 10 samples (GW08, 09, and 13) plot slightly above the range (< 10 pCi/L) of the 6-month running average of precipitation tritium concentration. Given the uncertainties in the precipitation-tritium-concentration interpolation, recharge temperatures, CFC contamination, and well-screen mixing, however, the sample tritium concentrations in these 10 samples can be fully explained by precipitation concentrations at the CFC-estimated date of recharge.

A CFC recharge date could not be estimated for the remaining 4 samples (GW04, 07-1, 19, and 20). In water from wells GW04 and 19, dissolved oxygen

was not detected in the field and methane concentrations were above 5 µg/L, indicating reducing conditions so severe that CFC degradation is likely. Evidence that degradation occurred in water from wells GW04 and 19 includes recharge dates that are highly disparate (more than 30 years) using different CFCs. The waters from wells GW19 and 20 show evidence of degassing (low argon concentration) during sampling, which could also reduce the concentrations of CFCs. The water from GW20, while containing some oxygen, had 4 µg/L methane, also suggesting CFC degradation.

Tritium concentrations in the water from well GW04 were the lowest sampled (26 pCi/L). A recharge date of 1996 for this sample is reasonable because of the low tritium concentration and the shallow depth of the well (10.99 ft). Tritium concentrations in water from well GW19 were the highest sampled (115 pCi/L). Assuming that all tritium in these samples was from precipitation, this water could only have been recharged during 5 short (< 1 month) periods during the mid 1950's–61 or during 1970–71. These recharge dates are reasonable because of the well's depth (screen top depth: 28 ft below the water table). Well GW19 was sampled for tritium 13 times between 1991–97 by NSP and 4 times during this study. The concentrations in the well decreased from 837 to 115 pCi/L. This decline (black diamonds, fig. 11) fits the precipitation tritium concentration curve well and implies a recharge date of 1968 for the August 1996 sample from well GW19.

The August 1996 sample from well GW20 was contaminated with CFC-113 and appears to have degassed during sampling, based on the low argon concentration. Although the recharge date estimated from both CFC-11 and 12 is 1958, this date is probably too early considering degassing and CFC degradation. The estimated date is also too early considering that the screen of well GW20 intersected the water table, sampling water from only the upper several feet of the aquifer. Ten tritium samples with concentrations greater than the reporting limit were collected at well GW20 during

1994–97 by the USGS (4 samples) and NSP (6 samples). These tritium concentrations are most consistent with a recharge date of 1982, but the actual recharge date may be in the 1976–82 range (white circles, fig 11).

Although there is no evidence of CFC contamination, estimated recharge dates from each CFC concentration do not agree in water from well GW07-1 (dates span 1986–96). Further, the tritium concentration (79 pCi/L) exceeds the precipitation tritium concentrations throughout that period. Either the CFC dates are cor-

rect and the sample contains additional tritium from the power-plant, or the tritium concentration is from atmospheric sources and the sample is contaminated with CFCs. The latter possibility is most plausible because well GW07-1 is located up gradient from the power plant in all water-table configurations observed during this study. A realistic water-table configuration could not cause ground-water flow from the power plant to the well. Further, because most other ground-water samples show clear evidence of CFC contamination, it is likely that this sample

was also contaminated, but not to the degree that the contamination is obvious. Well GW07-1 was sampled for tritium four times during 1995–96 by the USGS. Assuming that all tritium in the sample was derived from atmospheric sources, a recharge date in the periods of 1972–74, 1977–78, and 1981 is possible. A recharge date of 1978 is most likely (black triangles, fig. 11) considering the match with precipitation tritium concentrations and the shallow depth of the sample below the water table (0–4.12 ft).