

MINNESOTA DEPARTMENT OF NATURAL RESOURCES

Technical Appendix to Part B

**REGIONAL HYDROGEOLOGIC ASSESSMENT
OTTER TAIL AREA, WEST-CENTRAL MINNESOTA**

REGIONAL HYDROGEOLOGIC ASSESSMENT SERIES RHA-5

PART A

(Published separately by the Minnesota Geological Survey)

Plate 1, Surficial geology

Plate 2, Quaternary stratigraphy

PART B

Plate 3, Surficial hydrogeology

Plate 4, Geologic sensitivity to pollution of near-surface ground water

Technical Appendix, Water chemistry and residence time



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GLOSSARY

- age dating** – Expressing the age of water in years by measuring radioactive elements (e.g., tritium and carbon-14) and their decay products.
- aquifer** – Geologic material capable of yielding a usable quantity of water to a well.
- buried aquifer** – A confined or unconfined aquifer covered by at least 10 feet of low-permeability sediments in a Quaternary setting.
- carbon-14** – A radioactive isotope of carbon (^{14}C) with a half-life of 5,730 years; used for age-dating.
- carbonate rock** – Rock containing the carbonate anion and consisting chiefly of carbonate minerals such as calcite and dolomite.
- contamination** – Degradation of natural water quality as a result of human activity.
- discharge** – The volume of water flowing through a given cross section in a given time period.
- drinking water standards** – National Primary Drinking Water Standards issued by the Environmental Protection Agency for public water systems. The standards establish maximum contaminant levels for several inorganic and organic substances that could pose a health risk. Secondary standards list maximum contaminant levels for substances that affect taste, odor, and staining. For current standards, see www.epa.gov/safewater/standards.html.
- Eh** – Redox potential using a hydrogen scale. The “E” means electromotive force and “h” means hydrogen scale.
- electrical conductivity** – The ability of a substance to conduct an electrical charge.
- fractures in till** – Secondary porosity in till produced by weathering.
- hardness** – A measurement of the property of water that causes formation of insoluble residue when the water is used with soap. It is primarily the sum of concentrations of calcium and magnesium ions.
- hydraulic conductivity** – A measure of the ease with which a fluid flows through porous geologic material.
- kettle lake** – A lake in a depression in glacial drift formed by the melting of an isolated ice block.
- map polygon** – A cartographic feature used to represent an area. A polygon has attributes that describe it.
- model** – A system of postulates, data, or inferences presented as a simulation or representation.
- parameter** – A physical property or set of physical properties whose values determine the characteristics of something.
- permeability** – A measure of the ability of a geologic unit to transmit fluids.
- pollution sensitivity** – The general potential for ground water to be contaminated.
- recharge** – 1. The entry of water into the saturated zone at the water-table surface, together with the associated flow away from the water table within the saturated zone. 2. The entry of water into an aquifer.
- recharge (ground water) area** – Area at or near the land surface through which water moves to replenish an aquifer or other ground-water resource.
- residence time** – 1. The time water has been underground; the time elapsed from when water left the atmosphere until it is discharged from the ground-water system. 2. The time water resides in a lake.
- saturated zone** – The portion of the subsurface in which all voids and cracks in geologic materials are completely filled with water.
- stable isotopes** – Isotope of an element that does not decay. Isotopes of oxygen (^{16}O and ^{18}O) and hydrogen (^1H and ^2H) are examples of stable isotopes used to understand the sources of water or the processes that have affected the water.
- static water level** – The level to which water will rise in an unpumped well that is open to a single aquifer.
- surficial aquifer** – A water-table aquifer in sediment that is exposed at the land surface.
- travel time** – The time required for water or a contaminant to move from a source at the land surface to an aquifer or other target.
- unsaturated** – Voids and cracks in geologic materials are not completely filled with water.
- water-table aquifer** – The uppermost aquifer that has a water table; more generally, an unconfined aquifer.

WATER CHEMISTRY AND RESIDENCE TIME

by
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INTRODUCTION

This appendix describes regional water movement, water types and quality, lakes and interaction with ground water, ground-water residence time, and sensitivity map preparation. Data sources included water-level measurements and chemistry analyses of water samples from wells and lakes in the Otter Tail study area. A glossary at the end of the appendix defines terms used on the plates and in the appendix. The study area is bounded by 46° to 47° latitude and 95° to 96° longitude in west-central Minnesota and includes most of Becker and Otter Tail counties and parts of Douglas, Grant, Todd, Wadena, and Hubbard counties. The plates and appendix provide information that is useful for planning and environmental protection efforts.

Glacial deposits provide the framework for the hydrogeology of this study area. Sediment texture information from Plate 1 of Part A and information on topography were integrated into four hydrogeologic settings: hummocky moraine (map units cs, cd, cm, os, od, om, lgs, lgt, lgd, lgm, ugs, ugd, and ugm), ground moraine (map units cg and cw), collapsed outwash (map units oo, op, lgo, lgp, ugo, and ugp), and outwash plain (map units cc, oow, oc, lgow, lgc, ugc, and ha).

Glacial melting and the subsequent collapse of sediments produced the hummocky moraine setting characterized by high topographic relief and unsorted materials. Typical sediment textures in this setting include sandy loam, loam, and loam to clayey loam. Water scoured or overriding ice eroded the underlying tills of the ground moraine forming drumlins in much of this setting. The rolling, low-relief topography in the ground moraine setting consists of sandy loam sediments. Surficial sands and gravels deposited by broad meltwater streams characterize the collapsed outwash and outwash plain settings. Subsequent melting of buried ice blocks formed the depressions, many now occupied by lakes, which are typical of the collapsed outwash setting.

REGIONAL WATER MOVEMENT

Permeability and topography of sediments influence ground-water movement. Water-level information and chemistry analyses were compared with hydrogeologic setting and well depths to evaluate this influence.

Regional Drainage

The lower topographic relief in the outwash plain and ground moraine settings in the eastern part of the study area contributes to generally simpler flow systems than in the collapsed outwash and hummocky moraine settings to the west and south. The ground moraine setting has extensive drumlins and lower permeability sediments that channel water across the surface through numerous streams to the Leaf and Redeye rivers. These major rivers, along with the Long Prairie and Straight rivers, provide discharge outlets for ground water in the outwash plain and ground moraine settings. Ultimately, these waters move east, to the Mississippi River. Ground water in all four settings in the extreme southeast moves to the Eagle and Long Prairie rivers and ultimately to the Mississippi River system.

Ground-water movement in the water-table system in the collapsed outwash and hummocky moraine settings of the western and southern parts of the study area is dominated by local flow systems connected with lakes and wetlands. Many of these lakes occur in closed depressions in the hummocky moraine. A few lakes connect with the Otter Tail or Pomme de Terre rivers that ultimately move water to the Red River of the North and Minnesota River, respectively. In the collapsed outwash setting, many lakes are connected by the Otter Tail or Buffalo rivers or their tributaries.

Influence of Hydrogeologic Setting

Ground-water movement is relatively rapid through the permeable surficial sand and gravel sediments of the outwash plain. In this setting, all of the

Radioactive and Stable Isotopes

Isotopes of a particular element have the same number of protons but different numbers of neutrons. Isotopes are called stable if they are not involved in any natural radioactive decay. Stable isotopes are used to understand water sources or the processes that have affected them. Radioactive isotopes decay at known rates and can be used to measure the length of time water has been removed from the atmosphere.

The important stable isotopes are oxygen (^{16}O and ^{18}O) and hydrogen (^1H and ^2H). The mass differences between ^{16}O and ^{18}O or ^1H and ^2H can cause the concentrations of these isotopes to change (fractionate) during evaporation and precipitation, resulting in different $^{16}\text{O}/^{18}\text{O}$ and $^1\text{H}/^2\text{H}$ ratios in rain, snow, rivers, and lakes. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (δ denotes the relative difference from standard mean ocean water) in precipitation generally plot close to a straight line known as the meteoric water line. The departure of ^{18}O and ^2H values from the meteoric water line can indicate evaporation or mixing of water from different sources.

Tritium (^3H) is a radioactive isotope of hydrogen that is produced naturally by cosmic radiation in the upper atmosphere. Before 1953, naturally occurring levels were around 3 to 5 TU (1 TU = 1 tritium atom per 10^{18} hydrogen atoms). Once created, tritium decays with a half-life of 12.43 years. Atmospheric nuclear weapons testing between 1953 and 1963 released excess tritium into the atmosphere. Atmospheric tritium concentrations peaked between 1962 and 1965. Ground water in Minnesota has been classified into three age categories based on tritium levels (Alexander and Alexander, 1989). Waters with tritium levels of 10 TU or higher are "recent waters" that entered the ground water since 1953. Waters that now contain less than 0.8 TU are classified as "vintage waters" and entered the ground water prior to 1953. Waters with 0.8 to 10 TU are "mixed waters" of the previous two. Recent water that recharged during the 1950's and 1960's may contain significantly more than 10 TU. These waters containing 20 to 100 TU are termed "Cold War era". The advent of modern agriculture, with increasing use of fertilizers and pesticides, also starts in the 1950's, and ^3H is useful for identifying water resources that are vulnerable to contamination from these farming practices.

Carbon-14 (^{14}C) is a radioactive isotope of carbon with a half-life of 5,730 years. It can be used to establish ground-water residence times as old as 35,000 years. It is produced in the earth's upper atmosphere and enters the ground-water system with precipitation. The amount of ^{14}C in the atmosphere remains relatively constant over time; therefore, that amount can be compared with ^{14}C in a ground-water sample to estimate how long the water has been isolated from the atmosphere. Unlike dating a piece of charcoal, the carbon dissolved in water is subject to alteration by physical and chemical processes. Corrections can be made for inorganic sources (carbonate rock), calcite precipitation, and methane production. Physical mixing along flow paths also reduces precision of dates.

water samples from the six wells that are less than 100 feet deep (approximately the maximum thickness of the sand and gravel sediments) had detectable tritium (greater than 0.8 tritium units [TU]) indicating that some or all of the water within the outwash plain deposits has infiltrated during the past 50 years. (For information on tritium and ground-water age, see Radioactive and Stable Isotopes, above.) Four of these samples had recent water (less than 50 years old); the two with mixed water are close to lakes where deeper, older ground water moves upward. Three ground-water samples with vintage water (more than 50 years old) were from deeper wells completed in sand and gravel deposits within the till below the surficial outwash deposits. The water in these three vintage-age samples also had higher concentrations of total dissolved solids¹ (TDS), ranging from 325 milligrams per liter (mg/L) to 595 mg/L TDS, compared with samples from the six shallower wells (190 mg/L to 310 mg/L TDS).

Water samples from wells close to each other in the less permeable sediments of the ground moraine setting showed a decrease in tritium concentrations and an increase in TDS with depth. Vintage water dominated in samples from depths greater than 135 feet. Overall, ground water moves relatively slowly in the ground moraine sediments; however, fractures in the till, root zones, and animal burrows can create preferential flow paths for ground water. These heterogeneities result in a secondary porosity that permits water and contaminants to reach the water table rapidly, bypassing the clay-rich glacial matrix.

The moderate relief of the collapsed outwash setting and its permeable sand and gravel sediments promote vertical ground-water movement. Measurable tritium was found in all but one ground-water sample from wells to 130 feet deep. Near the north-central boundary of the study area, in a relatively low-relief area of collapsed outwash, a sample from a

¹ Total dissolved solids (TDS) is the sum of dissolved ions in parts per million (ppm). The bicarbonate ions are converted to carbonate by a gravimetric factor of 0.4917 to approximate the residue on evaporation method. This computed value of carbonate is used in the summation of dissolved ions (Hem, 1992).

shallow well (64 feet deep) had vintage water, indicating that there can be pockets of protected water in coarse sediments possibly due to slow, lateral ground-water flow. In the collapsed outwash setting, many lakes are connected by streams and interact with ground water. Ground water can discharge to a lake, or lake water can recharge ground water. This interaction can vary by position on a lake and by seasonal variations in precipitation (see Lakes and Interaction with Ground Water, below).

Short ground-water flow paths connected with surface water typify the shallow ground-water flow in the hummocky moraine setting. High relief, loam to clay loam sediment, and heterogeneities such as buried sand and gravel deposits produce these short flow paths that are not well integrated into the regional ground-water flow system. The short flow paths are indicated by the highly variable water elevations of lakes within small geographic areas. Because the shallow ground-water flow directions in the hummocky moraine represent localized conditions, generalizations about water age and changes of water quality with depth could not be made because water samples from wells were likely from different local flow systems. Collapsed sediment from glacial melting can create interconnected buried sand and gravel deposits. An example of this appears on Plate 3, cross-section C-C', from Clitheral west. Water that enters at the surface can be channeled through these high-permeability flow paths allowing movement of recent water and contaminants to greater depths and to greater lateral distances than would occur in a homogeneous till (see condition 3, Figure 5, on Plate 4).

WATER TYPE AND QUALITY

This section summarizes the water types and water quality in the Otter Tail study area. The summary is based on 88 water samples that were analyzed for major ions. A compilation of the water chemistry data from this study is available from DNR Waters.

Major Ions

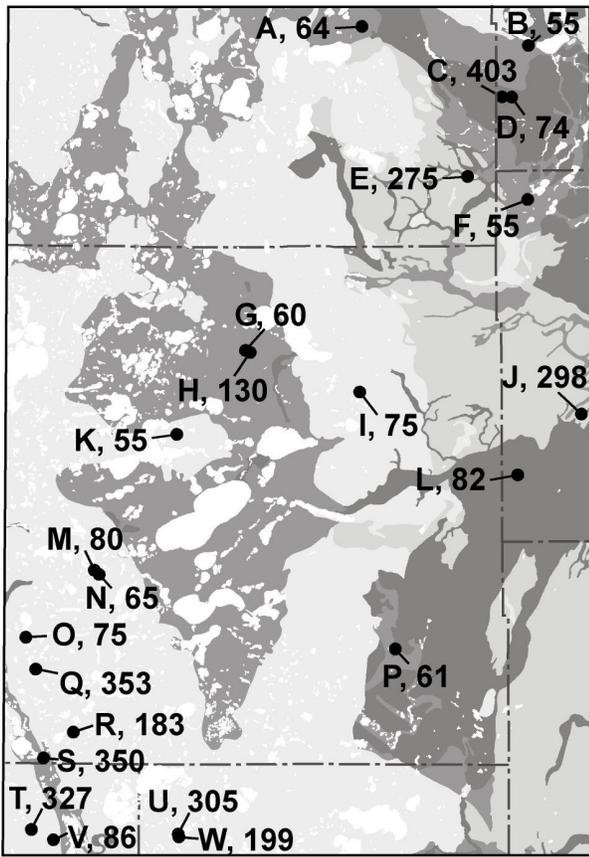
Analysis of the major ions indicates that the waters sampled in this study area resemble the natural waters in most of Minnesota. Calcium (Ca), magnesium (Mg), and bicarbonate (HCO_3) were the predominant ions in most samples of ground water

and all samples of lake water. As precipitation infiltrates through the soil zone, the water interacts with dissolved carbon dioxide gas resulting in relatively high concentrations of bicarbonate. Calcium and magnesium ions are primarily derived from dissolution of minerals in carbonate rocks such as the limestone and dolostone brought to the Otter Tail study area by glaciers.

Due to the predominance of calcium and magnesium ions in the water, most of the water in the study area is hard to very hard. Samples from 72 of 74 wells and all seven of the lakes sampled exceeded 150-mg/L total hardness computed from calcium and magnesium equivalents. This is the concentration at which noticeable scale buildup or staining occurs (Driscoll, 1986).

Sulfate was a major anion in water samples from two wells in the southwest part of the study area resulting in a calcium-magnesium-sulfate (Ca-Mg-SO_4) water type (sites O and V, Figure 1). These wells are from the hummocky moraine setting and are 75 feet and 86 feet deep with sulfate concentrations of 1,000 mg/L and 400 mg/L, respectively (250 mg/L is the U.S. Environmental Protection Agency [EPA] secondary drinking water standard for sulfate). All other water samples had sulfate concentrations less than 200 mg/L. Sulfate can impart an unpleasant odor and taste and can have a laxative effect. Sulfate is mainly produced by oxidation of sulfide (mostly from pyrite) or dissolution of sulfate minerals (such as gypsum) in rock and soil. Detergents in household wastes, wastewater from treatment plants, and agricultural fertilizers can also contribute sulfate to the shallow ground-water system (Safe Drinking Water Committee, 1977).

Sodium and potassium were the major cations in water samples from three deep wells in till resulting in a sodium-potassium-bicarbonate (Na-K-HCO_3) water type (sites C, E, and J, Figure 1). Sodium concentrations exceeded 100 mg/L in each of these "naturally soft" water samples; the hardness of these waters was less than 150 mg/L. Two of these wells, 275 feet and 298 feet deep, are found in the ground moraine setting; the third is 403 feet deep and completed in a buried aquifer in till sediments beneath the outwash plain setting. Sodium and potassium ions in the sediments are released from clay minerals into the ground water when calcium and magnesium ions exchange onto the sediments. Deeper ground water moves very slowly and this ion exchange process has not yet depleted the sodium and potassium from the sediments.



Summary Table of Settings and Water Characteristics

	Hummocky Moraine	Collapsed Outwash	Outwash Plain
High TDS (>500 mg/L)	M, N, O, Q, R, T, U, V, W	S	C
NO ₃ – vulnerable	K	G, H	F, P
High Cl/Br (>450 to 1)	I, K	A, G	B, D, L

FIGURE 1. Sites with noted ground-water characteristics. The map and summary table show the relationship between hydrogeologic settings and selected water characteristics. Labels (J, 298) identify well and depth in feet. Shading delineates hydrogeologic settings (Plate 3). Sites E and J are discussed on p.3.

Water Quality

All lake-water samples and 63 of 74 ground-water samples had TDS concentrations less than 500 mg/L. Ten ground-water samples from private wells in the southwest part of the study area had TDS concentrations greater than 500 mg/L (see Figure 1). One of these is a 350-foot-deep well in the collapsed outwash setting; the other nine are in the hummocky moraine setting. A sample from a well in the northeast

also exceeded 500 mg/L TDS but the well is not a water supply well. High TDS (greater than 500 mg/L) can lead to well-screen incrustation. The EPA has set a secondary drinking water standard for TDS at 500 mg/L.

Five ground-water samples had characteristics that meet criteria for nitrate vulnerability (Eh greater than 250 millivolts [mV], dissolved oxygen greater than 1 mg/L, and total iron less than 0.7 mg/L [Mike Trojan, oral commun., 1999]). If there is a local source of nitrate, the water in these wells could become contaminated since denitrification would be limited. In fact, three of these wells had nitrate levels greater than the Health Risk Limit of 10 mg/L established by the Minnesota Department of Health. All three are in the central part of the study area (sites G, H, and K, Figure 1).

Iron and manganese concentrations are above the EPA secondary standards (0.3 mg/L iron, 0.05 mg/L manganese) for most of the ground-water samples (65 of 74 samples exceeded the iron standard and 61 exceeded the manganese standard). High levels of these elements may produce objectionable odor, taste, or staining.

LAKES AND INTERACTION WITH GROUND WATER

Lakes and ground water are different expressions of a single resource. At many locations in the study area, ground water discharges to a lake and lake water recharges ground water, often at the same lake. Stable isotopes of hydrogen and oxygen and water chemistry can be analyzed in samples of ground water and lake water to interpret these interactions.

Deuterium (²H) is an isotope of hydrogen consisting of a proton and a neutron, whereas hydrogen consists of a proton. Deuterium, therefore, has approximately twice the mass of common hydrogen. Similarly, oxygen-18 (¹⁸O) has more mass than the more common oxygen-16 (¹⁶O). Fractionation occurs because of these mass differences. Molecules of water with the more common hydrogen and oxygen are lighter and more readily evaporated, leaving the remaining water more concentrated in the heavier isotopes. Because of this fractionation, lake water typically shows an evaporative signature (a higher concentration of the heavier isotopes than precipitation). Water that infiltrates the ground is not fractionated, so it has a meteoric signature (higher concentration of the lighter, more prevalent isotopes).

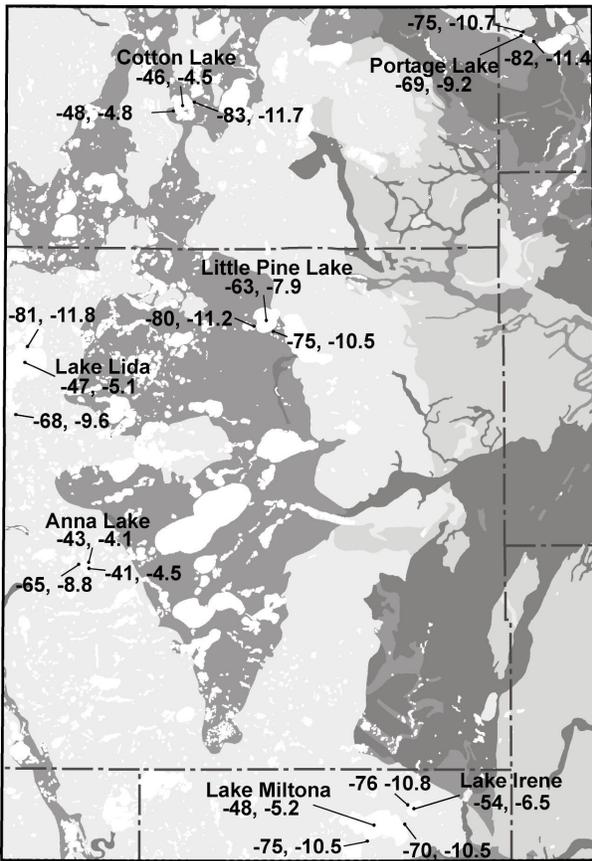


FIGURE 2. Lake and well sites with stable isotope data. The first number is $\delta^2\text{H}$ (per mil) and the second number is $\delta^{18}\text{O}$ (per mil). Shading delineates hydrogeologic settings (see Plate 3).

TABLE 1. Stable isotope data for selected samples from lake and ground-water sources.

[δ , relative difference from standard mean ocean water; per mil, parts per thousand; --, not applicable]

Sample source	Well depth (feet)	Direction from lake	Water elevation (feet)	$\delta^2\text{H}$ (per mil)	$\delta^{18}\text{O}$ (per mil)
Anna (moraine setting)					
Lake	--	--	1317	-44	-4.2
Well	65	South	1317	-41	-4.5
Well	80	West	1312	-65	-8.8
Cotton (outwash setting)					
Lake	--	--	1443	-46	-4.5
Well	70	West	1438	-48	-4.8
Well	77	East	1445	-83	-11.7

Analyses of stable isotopes in water samples from seven lakes were compared with analyses of stable isotopes in water samples from nearby shallow wells. Figure 2 shows the locations of the four lakes (Lida, Anna, Miltona, and Irene) in the hummocky moraine setting and three lakes (Cotton, Portage, and Little Pine) in the outwash settings that were selected for comparison. Figure 3 displays a portion of the North American meteoric data and shows the stable isotope data from these study area sites. TDS concentrations, electrical conductivity, and alkalinity measurements from these seven lakes and electrical conductivity and alkalinity measurements from an additional 32 lakes were studied to make comparisons and generalizations about lakes in hummocky moraine settings and lakes in the outwash settings.

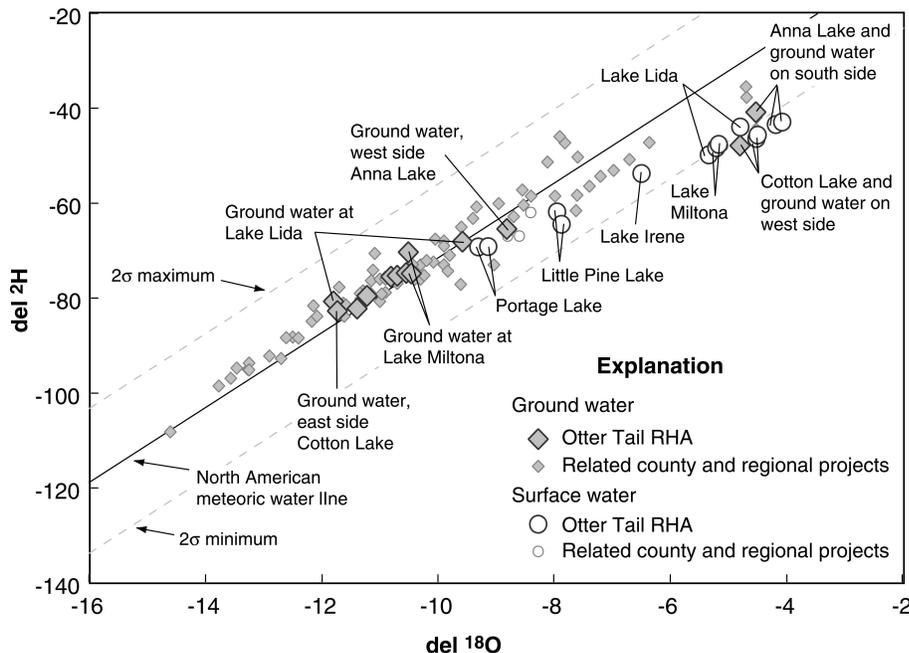


FIGURE 3. Stable isotope data for the study area. Ground-water samples with an evaporative signature similar to the lake water near them are displayed in the upper right. Lake-water samples with shorter residence time or ground-water influence plot closer to the meteoric water line.

Samples from two wells, one (65 feet deep) at a site on the south side of Anna Lake in Otter Tail County and the other (70 feet deep) at a site on the west side of Cotton Lake in Becker County, had stable isotope values showing fractionation from evaporation similar to that seen in surface water. This similarity indicates that lake water recharges ground water at these sites (Table 1). This conclusion about ground water and surface water at the Cotton Lake site was reinforced because the water samples showed similar general chemistry results when strontium, calcium, and magnesium ratios were compared. Conversely, Portage Lake, which receives

ground water, had stable isotope values indicating less fractionation than water samples from other lakes in the study area because water moves quickly through the lake. Water samples from Lake Irene and Little Pine Lake showed some mixing of surface water and ground water.

The direction of lake-water and ground-water flow can vary throughout a lake. For example, although the ground-water samples from Cotton Lake's west side and Anna Lake's south side show strong surface-water influences, the other ground-water sites sampled at these lakes did not (Figure 2 and Table 1). These other sites had stable isotope ratios similar to those of precipitation (nonfractionated) for the study area. The direction of lake- and ground-water exchange could not be determined by stable isotope ratios in samples from lakes and ground-water sites at Lake Milona and Lake Lida.

Most lakes in the hummocky moraine setting are in depressions without inlets or outlets. Water levels in these lakes are controlled by evaporation and precipitation, and residence time is generally longer than in lakes with surface outlets such as most of those in the outwash settings. Consequently, electrical conductivity and alkalinity measurements made in the field were generally higher in the moraine lakes. Ten of 14 samples from moraine lakes had electrical conductivity values greater than 380 microsiemens per centimeter ($\mu\text{S}/\text{cm}$) compared with the samples from outwash lakes where 22 of 24 samples had values less than 380 $\mu\text{S}/\text{cm}$. Alkalinity values were also generally higher in moraine lakes than in outwash lakes (11 of 12 samples with 180 mg/L or more and 18 of 24 samples with 180 mg/L or less, respectively). Water chemistry in the moraine lakes was more variable than in outwash lakes. TDS ranged from 190 mg/L to 300 mg/L in the moraine lakes sampled and from 170 mg/L to 200 mg/L in the outwash lakes sampled.

GROUND-WATER RESIDENCE TIME

Residence time, indicated by isotopic and chemical data, is the time elapsed from when water leaves the atmosphere until it is discharged from the ground-water system. Tritium and carbon-14 (^{14}C) are isotopic indicators of ground-water residence time in aquifers. Seventy-four well-water samples were analyzed for tritium concentrations to determine depths of recent water (less than 50 years old) penetration (see Figure 1 on Plate 3). Water samples from 10 wells were analyzed for carbon isotope concentrations.

Carbon-14 results are modeled to approximate the ages of water older than 100 years (see Radioactive and Stable Isotopes, above, for a description of isotopes). Additionally, analyses of major ions are used to support interpretations of residence time and recharge source.

Tritium

The coarse sediments of the outwash settings permit relatively rapid infiltration of ground water from the surface. Detectable tritium was found in all but one of the 14 samples from wells completed at depths of less than 135 feet in those settings.

In the outwash plain setting, all six of the samples from wells less than 100 feet deep had detectable tritium. Four of nine wells (55 feet to 82 feet deep) sampled had recent water, and samples from two of those wells contained elevated tritium concentrations indicative of water that infiltrated during the Cold War era when atomic weapons testing was at its peak (1950's–1960's). The water from two wells (46 feet and 74 feet deep) had an intermediate concentration of tritium that indicates a mixture of recent and vintage waters. The remaining three wells sampled had vintage water, but the wells are deeper than 135 feet. Ground water within the outwash plain sediments is typically years to a few decades old.

Of 11 wells sampled in the collapsed outwash setting, six wells (less than 135 feet deep) had recent water, including two with high tritium concentrations typical of water recharged during the Cold War era. Two wells (70 feet and 77 feet deep) had mixed water and three wells (64 feet, 135 feet, and 350 feet deep) contained vintage water. The longer residence time in the shallow well (64 feet) indicates slow, lateral ground-water movement in this area. Ground water within the collapsed outwash sediments is typically years to a few decades old.

The sediments in the hummocky and ground moraine settings contain higher proportions of fine silts and clays than those of the outwash settings. These fine sediments retard the movement of ground water, which decreases the rate of ground-water recharge.

In the hummocky moraine setting, half of the sampled wells (22 of 44) had no detectable tritium. The depths of these wells range from 65 feet to 384 feet deep. Tritium concentrations showing mixed water were found in 14 wells (75 feet to 239 feet deep). Eight wells (55 feet to 142 feet deep) had recent water, and three of these wells had water with

high tritium concentrations typical of water recharged during the Cold War era. Although half of the samples from hummocky moraine were vintage water, younger water may be found very deep where sand and gravel deposits provide pathways within the till. With local exceptions, ground-water ages within the buried aquifers in the hummocky moraine setting are decades to centuries or older.

The ground moraine setting is characterized by laterally extensive till that was compacted by over-riding ice. This till can greatly retard the movement of water resulting in long ground-water residence times. Six of 10 water samples from wells that were 135 feet to 298 feet deep had no detectable tritium, and one well (179 feet deep) had a tritium concentration that barely put it in the mixed water category (0.9 TU). There were two more water samples with mixed water from wells 88 feet and 315 feet deep. The latter well is too deep to explain the presence of mixed water geologically, and it is assumed this well could have a construction problem like that shown in condition 4 on Figure 5 of Plate 4. One well (79 feet deep) had recent water that recharged during the Cold War era. In this setting, ground-water ages within the buried aquifers are decades to centuries or older.

Carbon-14

Waters with short residence times in all hydrogeologic settings are readily identifiable by their tritium concentration. To identify residence times exceeding 100 years, 10 wells from three hydrogeologic settings were sampled for carbon-14 age dating. No wells were sampled for carbon-14 in the outwash plain setting because there were few samples with vintage water and it was not expected that any of these waters would be more than a few hundred years old.

Samples of vintage water were collected from two wells in the collapsed outwash setting; one sample had a carbon-14 age of 1,000 years and the other of 4,000 years. Contrary to expectation, the 4,000-year-old water came from a 64-foot-deep well, and the 1,000-year-old water from a 350-foot-deep well. These two samples show that even in the outwash settings, there can be pockets of old water at shallower than expected depths. Most of the ground water sampled in the collapsed outwash sediments, however, was less than 50 years old.

There is no clear relationship between depth and residence time in the hummocky moraine setting.

Ground-water flow can bypass low-permeability, fine-grained sediments by traveling through interconnected sands and gravels (see condition 3 in Figure 5 on Plate 4). To assess ground-water ages in the hummocky moraine setting, six water samples of vintage age were collected for carbon-14 age dating from wells that are 183 feet to 537 feet deep. The modeled ground-water ages ranged from 300 years to 8,000 years.

Most of the samples were vintage water in the ground moraine setting, which indicates slow recharge to buried aquifers. One well that was sampled for carbon-14 had a residence time of about 2,000 years, even though the well is only 142 feet deep.

Hydrogeochemistry and Recharge Sources

The interaction of water with different geologic materials, as it moves through sediments at varying rates, can alter the chemistry of the water. These chemistry changes reveal information about ground-water residence times and recharge sources.

Barium and Strontium. Examples of this chemical change are shown by the concentrations of the naturally occurring trace elements barium (Ba) and strontium (Sr) in ground water (Figure 4). The median concentrations in ground-water samples with recent water were 0.12 mg/L barium and 0.12 mg/L strontium, whereas ground-water samples with vintage water had median concentrations of 0.17 mg/L barium and 0.35 mg/L strontium. Clay minerals in unweathered till provide a source of barium and strontium ions. The clay slows the movement of ground water; consequently, the time that water is in contact with these minerals is longer, allowing barium and strontium ions in the minerals to exchange with ions in the ground water through equilibrium processes. Because of the slow movement of water through the fine-grained till, not enough water has moved through the till to deplete the barium and strontium from the clay minerals.

In the study area, slow ground-water movement commonly occurs in the ground moraine setting where the barium and strontium concentrations were above 0.20 mg/L in all but one of the vintage ground-water samples. The compacted sediments of the ground moraine contain few sand and gravel pathways that could reduce the contact of water with till. These clay minerals also limit the volume of water that passes through the till.

In contrast, the loosely deposited sediments of the outwash plain setting contain much less clay. This

condition allows water to pass through these sediments more quickly than through moraine and limits contact with clay minerals. Over time, enough water moves through these higher permeability sediments to deplete barium and strontium. All of the ground-water samples from wells completed in the outwash plain sediments were recent or mixed water with less than 0.20 mg/L barium and less than 0.10 mg/L strontium.

In both the hummocky moraine and collapsed outwash settings, the direction and rate of ground-water flow vary because of the settings' high relief and heterogeneities. Where these flow paths are primarily within sand and gravel deposits, barium and strontium should be less than about 0.20 mg/L. However, ground water from wells completed in isolated sand bodies must pass through some clay-rich till. Under these conditions, the concentrations of barium and strontium should be greater than about 0.20 mg/L. As expected, most samples from wells in the collapsed outwash setting had characteristics of water that moved along flow paths dominated by sand and gravel. All of those with recent or mixed water had concentrations of 0.20 mg/L or less barium and less than 0.20 mg/L strontium. In the hummocky moraine setting, few wells are completed in sediments

with uninterrupted flow paths of sand and gravel. In this setting, 27 of 44 samples exceeded 0.20 mg/L strontium (20 vintage water samples and seven mixed water samples). All samples of the recent ground water from the hummocky moraine setting had strontium concentrations of less than 0.20 mg/L. Barium concentrations had the broadest range in hummocky moraine, from 0.01 mg/L to 1.38 mg/L.

Two noteworthy trends are shown on Figure 4. Recent water generally has lower barium and strontium concentrations (less than 0.20 mg/L), and vintage water has decreasing barium concentrations with increasing strontium concentrations. This inverse relationship between barium and strontium is shown in about half of the water samples from wells in the hummocky moraine (Figure 4, vintage water on the right side of plot). A possible explanation is that these waters recharged through wetlands, where organic-rich sediments produce hydrogen sulfide gas (H_2S) (see Figure 5). The hydrogen sulfide gas migrates upward creating zones of high sulfate where barium is removed from the ground water by precipitating as the mineral barite ($BaSO_4$).

Figure 4 also shows that many samples of Cold War era ground water have concentrations of barium and strontium similar to lake water. Water with an elevated tritium concentration (Cold War era) may have entered the ground water from a lake, rather than from infiltration by precipitation from the Cold War era. A lake recharge source for these wells could not be verified because no lake-water samples were analyzed for tritium as a part of this study.

Chloride. The presence of chloride (Cl) from human activities may indicate relatively recent recharge of ground water. Chloride is a component of road salt, agricultural fertilizer, sewage, and water softening salt. Water that contains chloride derived from human activities is generally very depleted in bromide (Br) compared with chloride. For example, sodium chloride salts derived from halite deposits (commonly used in industrial, agricultural, and domestic applications) typically have chloride to bromide ratios greater than 10,000 to 1. Seven of the samples with recent water had chloride to bromide ratios greater than 1,000 to 1, indicating

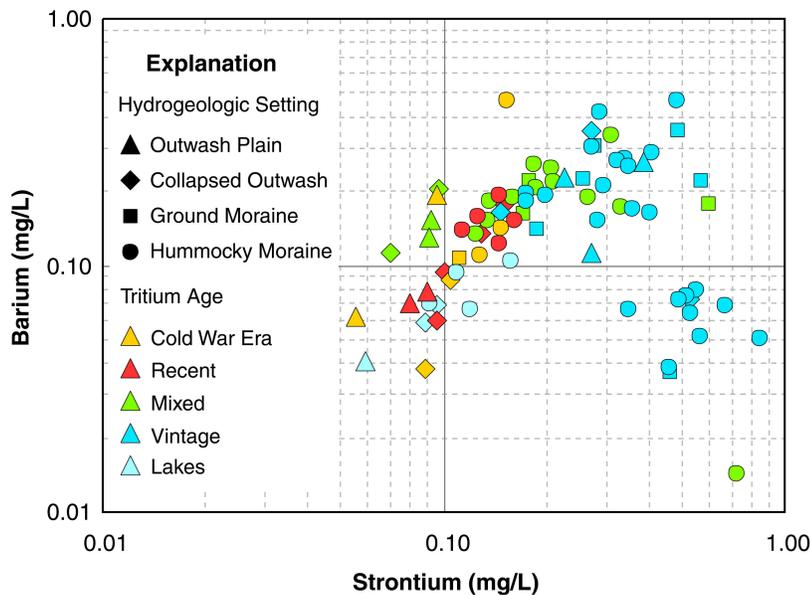


FIGURE 4. Comparison of the cations barium and strontium by tritium age and hydrogeologic setting. Most of the recent water samples shown are from wells in outwash with lower concentrations of barium and strontium. These cations are released into ground water from tills where water movement is slower and the volume of water moving through these sediments is lower. Consequently, the highest concentrations of barium and strontium occur in the vintage water samples (mostly from the moraine settings). The trend for some of these vintage samples to have decreasing barium with increasing strontium is explained in the text.

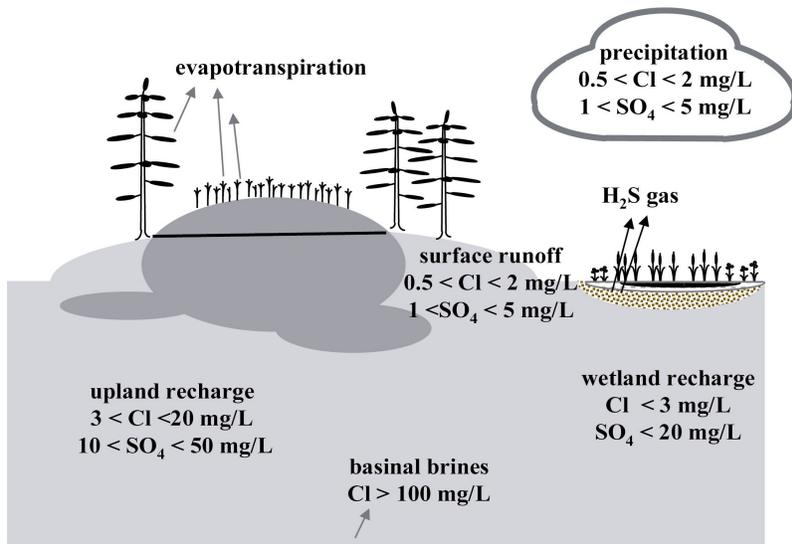


FIGURE 5. Chloride and sulfate in Minnesota waters showing origin of elevated chloride from uplands and low chloride from wetlands.

a human impact (Figure 1). In contrast, rainwater with natural sources of chloride has chloride to bromide ratios near 300 to 1. The two samples with the highest chloride concentrations are both vintage water samples with chloride to bromide ratios of 400 to 1, indicating a natural source of chloride.

A second geochemical indicator of relatively recent recharge of ground water is evidence of ammonia fertilizers in ground water. Anhydrous ammonia, a commonly applied fertilizer, is a very strong cation exchanger. Both anhydrous ammonia and ammonia from animal manure displace cations held naturally on clay minerals in the soil. Calcium and magnesium are the dominant cations on the clay minerals but are held less strongly than strontium. Fertilizer also provides a source of chloride ions, which do not interact with the clay minerals. Therefore, comparing the chloride concentration to the molar ratio of strontium to calcium plus magnesium (Figure 6) can help separate natural processes from human activities. Recent ground water, as expected, shows proportionally low strontium to calcium plus magnesium ratios and often contains elevated chlorides. In contrast, vintage water contains a higher proportion of strontium to calcium plus magnesium.

Recharge Sources. Identifying the source of older waters is important for protecting future ground-water supplies. Geochemical evidence can separate these older waters into aquifers that received either wetland or upland recharge. Minnesota rainwater typically contains about 0.5 mg/L to 2 mg/L chloride, and in wetlands, the evaporative concentration of chloride from rainwater is relatively small. Consequently, ground water recharged from wetlands will typically contain less than 3 mg/L chloride. Fifty-one of 75 ground-water samples from wells throughout the study area had a wetland recharge signature and 25 of these had vintage water (Figure 6). The depths of these wells ranged from 46 feet to 537 feet deep. In upland soils, on the other hand, evapotranspiration can remove most of the available water, producing chloride concentrations of up to 20 mg/L.

Eight ground-water samples from wells ranging in depth from 65 feet to 403 feet deep had an upland recharge signature, and all but one of these had vintage water.

Wetlands represent the largest sources of ground-water recharge for this study area (Figure 6). Until the settlement of Minnesota in the 1860's, about

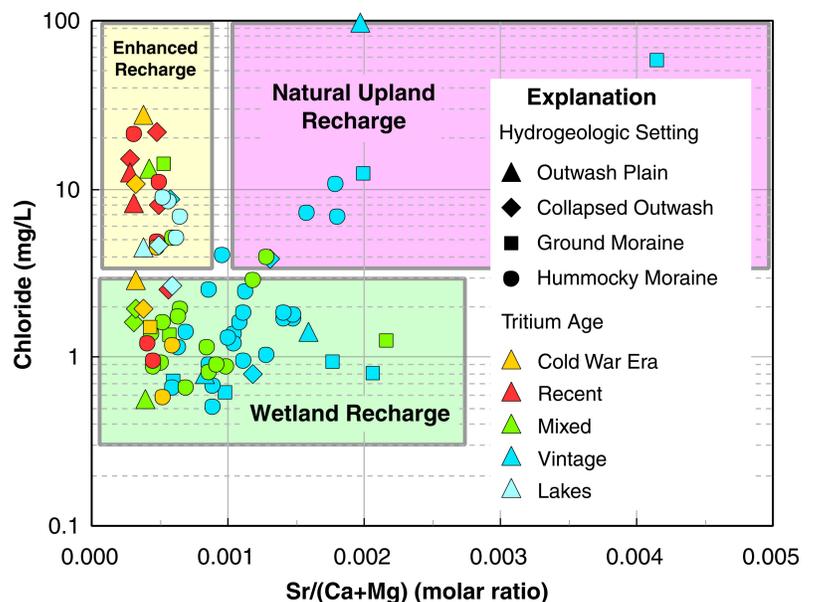


FIGURE 6. Recharge environment based on comparison of chloride concentration to the molar ratio of strontium (Sr) to calcium (Ca) plus magnesium (Mg).

18.6 million of its 53.6 million acres were wetlands. Today only half of that wetland acreage remains (Minnesota Board of Water and Soil Resources, [n.d.]). Continued preservation of wetlands will help ensure recharge for future water supplies.

Attention can be focused on areas most susceptible to contamination from human activities, such as in recharge areas and geologic settings that produce deeper ground-water flow. In such areas, ground-water pumping for municipalities, industry, and agriculture can reduce residence times and draw modern contaminants deeper more quickly than they would reach under undisturbed conditions. Additionally, efforts to look for specific contaminants, like agricultural pesticides or human pathogens, can focus on ground waters with rapid recharge rates in areas of intensive land use.

SENSITIVITY MAP PREPARATION

Geologic sensitivity to pollution can be evaluated by relating it to the travel time of water to a target of interest. Shorter travel times may indicate higher sensitivity to pollution. Longer travel times may represent an increased level of geologic protection for an aquifer. The map on Plate 4 is an interpretation of the geologic sensitivity to pollution of a defined target zone in the Otter Tail study area. These sensitivity and travel-time relationships are shown in Figure 1 on Plate 4. The method for determining this geologic sensitivity is described below.

Four main hydrogeologic and geologic factors were identified that influence vertical travel time of water: hydrogeologic setting, surficial sediment, unsaturated thickness, and target zone lithology. Two factors are based on spatial data from Plate 3 and from Plate 1 of Part A (hydrogeologic setting and surficial sediment, respectively), and two are based on point data from field measurements and well logs (unsaturated thickness and target zone lithology). Each factor was subdivided into categories. The factors and their associated categories (in parentheses) are hydrogeologic setting (outwash plain, collapsed outwash, hummocky moraine, ground moraine), surficial sediment (sand and gravel, sandy loam, loam, loam to clay loam), unsaturated thickness (0 to 20 feet, 21 to 50 feet, greater than 50 feet), and target zone lithology (no clay, some clay, all clay). A value representing the vertical time of travel for water to reach a depth of 20 to 50 feet (the target zone) was assigned to each of the categories.

The study area was divided into 83 map poly-

gons to apply the factors to an assessment of geologic sensitivity. The boundaries of a polygon enclose a geographic area with a single hydrogeologic setting and surficial sediment, and an overall similarity in unsaturated thickness and target zone lithology.

Spatial Data

Vertical ground-water travel time to the target zone was approximated for each category within a spatial factor based on hydraulic conductivity values from literature (Stephenson and others, 1988, and Soil Survey staff, 1998). These hydraulic conductivity values represent vertical flow rates through saturated porous sediment. Some or all of the sediment above the target zone is unsaturated throughout most of this study area. Except for flow through fractures and other pathways, ground-water flow through unsaturated sediments is slower than flow through saturated sediments. Applying the faster saturated flow rates to unsaturated sediment may result in a shorter than realistic travel time. However, this effect is diminished by the unsaturated thickness category, which assigns longer travel times to thicker unsaturated sediment.

Each category within the setting and sediment factors was given a value on a scale of 1 to 5 corresponding to the range of travel time (Figure 1 on Plate 4) for water to enter the target zone: 1 = hours to months, 2 = weeks to years, 3 = years to decades, 4 = decades to a few centuries, and 5 = decades to several centuries. The categories within the settings factor and their associated travel time value in parentheses are outwash plain (1), collapsed outwash (2), hummocky moraine (3), and ground moraine (4). The categories within the sediment factor and their associated travel time values are sand and gravel (1.5), sandy loam (2.5), loam (4), and loam to clay loam (4.5).

Point Data

The point data were assigned a numerical value for each category. The unsaturated thickness factor was divided into the following categories: 0 to 20 feet (some to all of the sediment above the target zone is unsaturated) = 1, 21 feet to 50 feet (the unsaturated sediment continues into the target zone) = 2, and greater than 50 feet (the sediment is unsaturated to below the target zone) = 3. A representative value for each map polygon was calculated based on the percentage of data points within each of these

categories. This representative value was adjusted to a scale of 1 to 5 to correspond to the spatial data scale. The target zone lithology factor accounts for the possibility that sediments within the target zone are different from those mapped at the surface, a difference that would affect vertical time of travel. This factor was divided into three categories: no clay = 1, some clay = 2, and all clay = 3. Again, a representative value for each map polygon was calculated and adjusted to a scale of 1 to 5.

Sensitivity Rating

The sum of the numerical values for the four factors was averaged for each map polygon, and an initial sensitivity rating was assigned based on that average as follows: 1 to 1.7 = very high, 1.8 to 2.5 = high, 2.6 to 3.4 = moderate, 3.5 to 4.2 = low, and 4.3 to 5 = very low. The matrix in Figure 3 on Plate 4 shows the results of this process. Sensitivity ratings of map polygons that lacked point data were compared with similar neighboring map polygons to determine their geologic sensitivity rating. If the average value for a map polygon fell close to a boundary between two ratings, the value for that map polygon was re-examined using qualifying information.

Qualifying information was used to validate or adjust the initial sensitivity rating for each map polygon based on the physical and chemical environments. The following are examples of features of the physical environment. Many isolated lakes or wetlands in low-lying areas of a map polygon suggest sluggish ground-water movement. Well-developed stream networks (dendritic streams) suggest a preference for precipitation to run off rather than infiltrate. Either of these conditions could result in a lower sensitivity rating. The chemical environment was also examined to validate or adjust sensitivity ratings. The presence of tritium in ground-water samples or evidence of enhanced recharge, for example, ruled out the possibility of a low sensitivity rating.

Examples of the Process

The following two examples illustrate the process described above. The factors and time of travel values (in parentheses) for a map polygon in the area of Sebeka were the following: ground moraine (4), sandy loam (2.5), unsaturated thickness (averaged 2.0 on a scale of 1 to 3; adjusted to 3 on a scale of 1 to 5), and target zone lithology (averaged

2.5 on a scale of 1 to 3; adjusted to 4 on a scale of 1 to 5). These values were summed: $4 + 2.5 + 3 + 4 = 13.5$ and then averaged: $13.5 \div 4 = 3.4$. This value corresponded to an initial sensitivity rating of moderate but was close to the value for a low rating. Qualifying information was considered to validate or adjust the rating of the map polygon. This is an area of well-developed stream drainage, which suggests that water moves out of this area rather than infiltrating deeply. Additionally, there was no detectable tritium from water samples in this map polygon; therefore, the final rating for this map polygon was adjusted to low.

Another example is a map polygon that runs from Wadena to the east. Its categories with time of travel values in parentheses were the following: outwash plain (1), sand and gravel (1.5), unsaturated thickness (averaged 2.2 on a scale of 1 to 3; adjusted to 3 on a scale of 1 to 5), and target zone lithology (averaged 1.4 on a scale of 1 to 3; adjusted to 2 on a scale of 1 to 5). These values were summed: $1 + 1.5 + 3 + 2 = 7.5$ and then averaged: $7.5 \div 4 = 1.9$, yielding an initial sensitivity rating of high. The final sensitivity rating was adjusted to very high because field-measured data (depth to water) showed the unsaturated thickness was thinner than when historical data (from the County Well Index) were included in the analysis. Additionally, the flat terrain in coarse sediments means that precipitation can infiltrate readily.

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