Groundwater Atlas of Winona County, Minnesota

Report

County Atlas Series C-34
Part B - Hydrogeology

To accompany these atlas components:
Plate 5, Water Chemistry
Plate 6, Hydrogeologic Cross Sections

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The County Atlas Series

The Minnesota County Atlas Series has been produced since 1982. Recent atlases are produced in two parts: Part A: Geology, and Part B: Groundwater (this atlas). Note that prior to 2019 both were titled the “Geologic Atlas of X County.” The Part B title was changed to “Groundwater Atlas of X County” to distinguish the content.

Part A - Geologic Atlas

The precursor to this atlas is Part A, Geologic Atlas of Winona County, Minnesota (Setterholm, 2014), published by the Minnesota Geological Survey. It contains Plate 1, Data-Base Map (Bauer and Chandler, 2014); Plate 2, Bedrock Geology (Steenberg, 2014a); Plate 3, Surficial Geology (Lusardi and others, 2014); Plate 4, Bedrock Topography and Depth to Bedrock (Steenberg, 2014b).

• More products and information are available online at Minnesota Geological Survey > County Geologic Atlas

Part B - Groundwater Atlas

This portion was published by the Minnesota Department of Natural Resources, who expanded on the geologic information from Part A.

• More products and information are available online at Minnesota Department of Natural Resources, Groundwater Atlas Program.

• Status list of completed atlases: Groundwater Maps and Studies > County Geologic and Groundwater Atlases.

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# Contents

**Executive summary** .................................................................................................................................................................................. 1

**Physical setting and climate** ................................................................................................................................................................. 4

**Geology and physical hydrogeology** ............................................................................................................................................ 5
  - Karst .................................................................................................................................................................................................. 5
  - Surficial aquifers .................................................................................................................................................................................................. 6
  - Bedrock aquifers and aquitards ........................................................................................................................................................................ 9
  - Geologic units ................................................................................................................................................................................................. 10
  - Groundwater flow .................................................................................................................................................................................................. 12

**Water chemistry (Plate 5)** ........................................................................................................................................................................ 19
  - Water sampling ................................................................................................................................................................................................ 19
  - Groundwater recharge .................................................................................................................................................................................... 19
  - Groundwater residence-time indicators .......................................................................................................................................................... 22
  - Inorganic chemistry of groundwater .............................................................................................................................................................. 23

**Pollution sensitivity** ............................................................................................................................................................................. 30
  - Near-surface materials ....................................................................................................................................................................................... 30
  - Bedrock aquifers .................................................................................................................................................................................................. 33

**Hydrogeologic cross sections (Plate 6)** .............................................................................................................................................. 45
  - Groundwater flow direction and recharge .................................................................................................................................................... 45

**Aquifer characteristics and groundwater use** ..................................................................................................................................... 46
  - Aquifer specific capacity and transmissivity ............................................................................................................................................... 46
  - Groundwater level monitoring ........................................................................................................................................................................ 48
  - Groundwater use .................................................................................................................................................................................................. 49

**References** .......................................................................................................................................................................................... 52

**Glossary** .............................................................................................................................................................................................................. 56

**Appendix A** ........................................................................................................................................................................................................ 58
  - Groundwater field sample collection protocols ........................................................................................................................................... 58

**Appendix B** .............................................................................................................................................................................................................. 60
  - Tritium values from precipitation ................................................................................................................................................................. 60
  - Tritium age of historic groundwater samples ................................................................................................................................................ 60
Figures

Figure 1. Winona County, Minnesota ................................................................................................................. 3
Figure 2. Average temperature and precipitation for Winona County, Minnesota ................................................. 4
Figure 3. Sinkhole and stream sink occurrence versus depth to bedrock .............................................................. 5
Figure 4. Area prone to karst feature development and distribution of karst features .............................................. 7
Figure 5. Water-table elevation and sand and gravel wells ...................................................................................... 8
Figure 6. Bedrock stratigraphy, hydrostratigraphy, and distribution of karst features ........................................... 9
Figure 7. Water-table elevation contours of the Shakopee aquifer ........................................................................ 13
Figure 8. Water-table elevation contours of the Oneota aquifer ........................................................................... 14
Figure 9. Water-table elevation and potentiometric surface contours of the Jordan aquifer .................................... 15
Figure 10. Potentiometric surface contours of the Lone Rock aquifer ................................................................. 16
Figure 11. Potentiometric surface contours of the Wonewoc aquifer ................................................................. 17
Figure 12. Potentiometric surface contours of the Mt. Simon aquifer ................................................................. 18
Figure 13. Stable isotope values from water samples collected in Winona County .................................................. 20
Figure 14. Stable isotope characteristics of groundwater samples collected in Winona County ............................ 21
Figure 15. Elevated chloride concentrations from groundwater samples ............................................................... 26
Figure 16. Elevated nitrate concentrations from groundwater samples ................................................................. 27
Figure 17. Continuous nitrate concentrations of the Main Spring at Crystal Springs State Fish Hatchery .................. 28
Figure 18. Piper diagram of groundwater samples collected in Winona County .................................................... 29
Figure 19. Geologic sensitivity ratings for near-surface materials ........................................................................... 31
Figure 20. Pollution sensitivity rating of near-surface materials ........................................................................... 32
Figure 21. Pollution sensitivity ratings for bedrock aquifers .................................................................................. 33
Figure 22. Hydrogeologic cross section illustrating the groundwater system and springs ..................................... 34
Figure 23. Pollution sensitivity of the Cummingsville through St. Peter aquifers .................................................... 38
Figure 24. Pollution sensitivity of the Prairie du Chien aquifer .......................................................................... 39
Figure 25. Pollution sensitivity of the Jordan aquifer ......................................................................................... 40
Figure 26. Pollution sensitivity of the Lone Rock aquifer ..................................................................................... 41
Figure 27. Pollution sensitivity of the Wonewoc aquifer ...................................................................................... 42
Figure 28. Pollution sensitivity of the Mt. Simon aquifer ..................................................................................... 43
Figure 29. Multiple-aquifer wells ....................................................................................................................... 44
Figure 30. Well locations for specific capacity and transmissivity by aquifer ......................................................... 47
Figure 31. Hydrographs of groundwater level monitoring wells near Whitewater State Park ................................... 48
Figure 32. Distribution of groundwater appropriation permits for 2017 by volume reported and use type .................. 50
Figure 33. Distribution of groundwater appropriation permits for 2017 by volume reported and general aquifer classification ........................................................................................................ 51
Tables

Table 1. Transmission rates through unsaturated materials used to assess the pollution sensitivity rating of the near-surface materials ........................................................................................................................................... 31

Table 2. Specific-capacity values of select wells ............................................................................................................................................................................................................ 46

Table 3. Reported 2017 water use from DNR groundwater permit holders .................................................................................................................................................................................. 49

Appendix Table A-1. Groundwater field sample collection and handling details for project samples collected prior to 2016 ........................................................................................................................................................................................................... 58

Appendix Table A-2. Groundwater field sample collection and handling details for project samples collected in 2016 and 2017 ........................................................................................................................................................................................................... 59

Appendix Table B-1. Enriched tritium results from MNgage precipitation station 62 29 22 9 BOULAY P .............................................................................................. 60

Appendix Table B-2. Tritium classification by date of sample collection ........................................................................................................................................................................................................... 60

Plates (accompanying folded inserts)

Plate 5, Water Chemistry
Plate 6, Hydrogeologic Cross Sections

Technical reference

Maps were compiled and generated in a geographic information system. Digital data products are available from the Minnesota Department of Natural Resources, Groundwater Atlas Program at mndnr.gov/groundwatermapping.

Maps were prepared from Minnesota Department of Natural Resources and other publicly available information. Every reasonable effort has been made to ensure the accuracy of the data on which the report and map interpretations were based. However, the Minnesota Department of Natural Resources does not warrant the accuracy, completeness, or any implied uses of these data. Users may wish to verify critical information; sources include both the references here and information on file in the offices of the Minnesota Geological Survey and the Minnesota Department of Natural Resources. Every effort has been made to ensure the interpretations conform to sound geologic and cartographic principles. These maps should not be used to establish legal title, boundaries, or locations of improvements.


Conversion factors

1 inch per hour = $7.056 \times 10^{-6}$ meter per second
1 part per million = 1 milligram per liter
1 part per billion = 1 microgram per liter
1 foot2 per day = 7.48 gallons per day per foot
Groundwater Atlas of Winona County, Minnesota

by John D. Barry

Executive summary

This report and the accompanying plates are Part B of the Winona County atlas. Part B describes the hydrogeology and is produced by the Minnesota Department of Natural Resources (DNR). It builds on the geology described in Part A, which was previously published by the Minnesota Geological Survey (MGS).

The purpose of this atlas is to illustrate groundwater hydrogeologic setting, aquifer distribution, pollution sensitivity, groundwater recharge, and subsurface flow of the aquifers in the county. This information can be used to make land and water management decisions that take into account aquifer sensitivity, water quality, and sustainability.

This report details the methods, results, and interpretations for the county. Plate 5 illustrates the water chemistry; Plate 6 uses hydrogeologic cross sections to show general groundwater flow directions and residence time within the aquifers. This executive summary gives an outline of the detailed sections that follow.

Physical setting and climate (page 4) describes the location of the county, summarizes the average temperature and precipitation, and lays the framework for how these influence groundwater recharge.

Winona County is in southeastern Minnesota with land use that is a mix of agricultural croplands, forest, and small towns. The county lies within three watersheds: the Mississippi River–La Crescent, the Mississippi River–Winona, and the Root River. It has a cool subhumid climate with average temperatures of 70 degrees Fahrenheit (°F) in the summer and 19°F in the winter. Average annual precipitation is approximately 33 inches, making it one of the wetter counties within the statewide range of 20 to 37 inches.

Geology and physical hydrogeology (pages 5–18) describes the aquifers and aquitards and identifies their hydrostratigraphic characteristics and corresponding geologic units from Part A. Groundwater-elevation maps give a broad overview of the direction of groundwater flow in unconfined conditions (water-table elevation) and confined conditions (potentiometric-surface elevation).

The county is underlain by a thick sequence of Paleozoic sedimentary bedrock layers. Bedrock is generally within 50 feet of the land surface and is covered by a veneer of unconsolidated sediment such as loess, sand, and colluvium. Thick layers of unconsolidated sediment generally only exist in valley bottoms, making bedrock aquifers the primary source of drinking water and groundwater discharge to streams.

Much of the county is a karst terrain formed by precipitation and groundwater dissolving the underlying carbonate sedimentary rock. Karst terrains may be characterized on the surface by sinkholes, caves, and springs that provide rapid water movement between land surface and underlying aquifers. Even where surficial evidence of karst features are absent, there can still be connections for rapid water movement between the land surface and aquifers (higher pollution sensitivity).

Groundwater flow directions in the water table are regionally toward the Mississippi River and locally toward streams and creeks. Water-table depth is shallow (0–20 feet) in valley bottoms. Elsewhere it can be very deep and difficult to determine because of the karst setting with unsaturated soils and few shallow wells. In the south-central area near Witoka, soil moisture suggests there is a perched water table. Bedrock aquifers show groundwater flow patterns similar to the water table: regionally toward the Mississippi River and locally toward streams and creeks. Rapid recharge occurs to aquifers above the St. Lawrence aquitard or where aquitards are not present.

Water chemistry (pages 19–29, Plate 5) provides information about the water source, flow path, and travel time of groundwater. These can indicate high pollution sensitivity from the land surface or problems with naturally occurring geologic contaminants.
Human caused (anthropogenic) occurrences of chloride and nitrate-nitrogen (nitrate) are relatively widespread in the water-table aquifer. The water-table aquifer comprises the Prairie du Chien and Jordan aquifers in upland settings and the sand and gravel aquifer in lowland settings. Elevated levels of chloride and nitrate most commonly occur in wells completed in aquifers located above the first regionally competent aquitard, the St. Lawrence aquitard, or in valley bottoms where overlying aquitards are not present. Springs commonly have elevated levels of both chloride and nitrate.

The term nitrate is used in place of the term nitrate-nitrogen throughout this document.

Arsenic and manganese concentrations are generally low within the county. Both are naturally occurring, geologic-sourced contaminants in Minnesota. The Minnesota Department of Health (MDH) recommends water treatment if any arsenic is present.

The pollution sensitivity (pages 30–44) of an aquifer is estimated based on the time it takes water to flow from the land surface through various types and thicknesses of soils and geologic materials. Pollutants are assumed to travel with water at the same rate. The sensitivity is modeled with different methods for the near-surface materials and bedrock aquifers. The model results are evaluated by comparing select chemistry from mapped aquifers. Rapid recharge is associated with high pollution sensitivities.

Near-surface sensitivity ratings can be broadly grouped into two types: 1) Very high sensitivity areas prone to karst feature development that cover the majority of the county and 2) predominately moderate to high sensitivity areas that occur along the Mississippi River valley and in valley bottoms with coarse-grained deposits.

Sensitivity ratings for bedrock aquifers were developed using chemical constituents such as tritium and carbon-14 data for residence time, and select inorganic chemicals such as chloride and nitrate for contamination. Groundwater residence times range from less than 100 to 25,000 years. Anthropogenic chloride and nitrate are relatively widespread in shallow aquifers, especially where wells are completed in aquifers above the St. Lawrence aquitard. Below the St. Lawrence, groundwater shows longer residence times and less contamination. Wells completed in aquifers below the St. Lawrence can provide groundwater unimpacted by human activities if properly installed according to Minnesota well code. Springs commonly have elevated levels of both chloride and nitrate, even if located below the St. Lawrence aquitard.

Hydrogeologic cross sections (page 45, Plate 6) illustrate groundwater flow, residence time, and distribution of chemical indicators. Cross sections help define areas of interest such as locations of important groundwater recharge, discharge, and sensitivity to pollution.

Aquifer characteristics and groundwater use (pages 46–51) summarizes specific capacity tests, aquifer tests, water use records, and groundwater level monitoring data for each aquifer. These data can be used to characterize aquifer recharge in the county and plan for new well installations. The majority of the permitted water use is for municipal and public water supply, which is primarily from the Mt. Simon aquifer. High-volume use is generally centered in the city of Winona, but also near the cities of St. Charles, Lewiston, Altura, and Stockton. The next most common use categories are metal processing and agricultural food processing.
Figure 1. Winona County, Minnesota

Winona County is located in southeastern Minnesota within the surface watershed of the southeast-flowing Mississippi River (1). Additional watersheds are drained by networks of rivers that flow north to the Red River basin (2), east to the Great Lakes basin (3), or southwest to the Missouri River basin (4).
Winona County is located in southeastern Minnesota. The landscape is characterized by broad plateaus intersected with deeply incised valleys. Elevation changes from ridgetops to valleys can surpass 500 feet. The modern landscape was primarily shaped by erosion from river systems.

The county is located on the western edge of the upper Mississippi River valley commonly referred to as the Driftless Area. The term driftless implies the area was never glaciated, however this is not accurate in Winona County. Glacial till of pre-Illinoian age is found in the western portion of the county and scattered glacial material can be found in the east (Part A, Plate 3). Since Winona County was not covered by sediment during recent glaciations, its landscape represents a mature and heavily-eroded ancient surface.

Minnesota is a headwaters state where surface water and groundwater are replenished solely by precipitation. Surface-water flow and groundwater levels fluctuate with wet and dry years. Water levels fluctuate rapidly in rivers and water-table aquifers following precipitation. Water takes longer to travel to deeply buried aquifer systems so the changes are often delayed. Surface water leaves the state by a network of rivers that flow north to the Red River basin, east to the Great Lakes basin, southwest to the Missouri River basin, or southeast to the Mississippi River basin (Figure 1). Groundwater provides baseflow to streams and major river systems.

Surface-water flow in the county is controlled by elevation and landform and drains toward three separate surface watersheds (Figure 1), all of which ultimately flow to the Mississippi River. Surface-water features (lakes and wetlands) are limited because of fracture and conduit networks in the plateaus that prevent water from ponding on the surface. Surface-water features are mostly streams in valleys, many of which are cold-water streams with springs as headwater sources. The Mississippi River forms the entire eastern border of the county and the Whitewater River prominently crosses the northwestern portion. Numerous smaller streams flow in valleys east to the Mississippi or south to the Root River.

Winona County is characterized as a cool subhumid climate with a large temperature differential between summer and winter. Summers have an average temperature of approximately 70 degrees Fahrenheit (NOAA, 2019). The typical growing season is from April to October with an average daily air temperature over 45 degrees Fahrenheit (Figure 2). Evaporation increases dramatically during the growing season through plant uptake and transpiration, reducing the amount of precipitation that ultimately becomes groundwater.

The average winter temperature is 19 degrees Fahrenheit and the ground is frequently covered with snow from December through March. The soil frost depth often ranges from 3 to more than 5 feet for approximately 4 to 5 months of the year, limiting precipitation that can infiltrate and become groundwater. Although diffuse recharge is limited in the winter, focused recharge to sinkholes and stream sinks still may occur.

Average annual precipitation is approximately 33 inches, making it one of the wetter counties within the statewide range of 20 to 37 inches. Historically most annual precipitation (roughly 13 inches) occurs in June, July, and August (DNR, 1981–2010). Only a small fraction of this eventually becomes groundwater because of evaporation, transpiration, and overland runoff to streams. The majority of groundwater recharge occurs in the spring when snowmelt and precipitation infiltrate the land surface prior to the growing season.

Figure 2. Average temperature and precipitation for Winona County, Minnesota
Geology and physical hydrogeology

Bedrock dominates the geology of Winona County. It is generally within 50 feet of the land surface and is covered by a veneer of unconsolidated sediment such as loess, sand, and colluvium (Part A, Plates 3 and 4). Thick layers of saturated unconsolidated sediment generally only exist in valley bottoms, making bedrock aquifers the primary source of drinking water and groundwater discharge to streams.

The St. Charles region of southwestern Winona County contains a high plateau capped by erosion-resistant limestone of the Cummingsville Formation (Part A, Plate 2). Underlying the Cummingsville is the Decorah Shale through the St. Peter Sandstone. This local sequence of rock overlies a prominent regional plateau, the Prairie du Chien Plateau, that is present over the majority of the county. This plateau exists because of the erosion resistant properties of dolostone.

Underlying the Prairie du Chien Group is a sequence of sedimentary layers that are more easily eroded: Jordan Sandstone, St. Lawrence Formation, Lone Rock Formation, Wonewoc Sandstone, and Eau Claire Formation. These units predominately consist of sandstone, siltstone, and shale. These are exposed within the Whitewater River valley and its tributaries and within narrow valleys near the Mississippi River.

Underlying the Eau Claire Formation is the Mt. Simon Sandstone, which is not exposed at the land surface in Winona County. Detailed lithologic descriptions of each of these units are available in Part A, Plate 2.

Karst

Much of Winona County is covered by karst (Figure 4). The term karst is used to describe unique landforms and hydrology formed by precipitation and groundwater dissolving carbonate sedimentary rock. Karst is often characterized on the surface by the presence of sinkholes, caves, and springs, but where these features are absent there can still be rapid connections between the land surface and underlying aquifers. Karst has distinctive hydrology that is dominated by rapid conduit flow. Technically, karst is described as “an integrated mass-transfer system in soluble rocks with a permeability structure dominated by conduits dissolved from the rock and organized to facilitate the circulation of fluid” (Klimchouk and Ford, 2000).

In karst areas, there is a close relationship between the landscape surface and the bedrock below. Connections to enlarged underground pathways allow for rapid transport of water, creating unpredictable groundwater travel times and flow directions. This makes the aquifers particularly vulnerable to human activities and complicates remediation efforts for issues like spills or surface applications of chemicals.

Classification of the karst landscape helps identify the groundwater characteristics beneath it. A companion report identifies these landscapes through analysis of karst feature position, geologic setting, and landscape position: Karst Landscape Units of Houston and Winona Counties (Green and Barry, 2021).

Figure 3. Sinkhole and stream sink occurrence versus depth to bedrock

Over 90 percent of mapped sinkholes and stream sinks occur where there is 50 feet or less of unconsolidated sediment overlying bedrock (Figure 3), which is consistent with other areas of karst in southeastern Minnesota (Alexander and Maki, 1988). Approximately 89 percent of the mapped sinkholes and stream sinks occur where the Prairie du Chien Group is the first bedrock unit below the land surface.

In Winona County, over 90 percent of mapped sinkholes and stream sinks occur where there is 50 feet or less of unconsolidated sediment overlying bedrock (Figure 3), which is consistent with other areas of karst in southeastern Minnesota (Alexander and Maki, 1988). Approximately 89 percent of the mapped sinkholes and stream sinks occur where the Prairie du Chien Group is the first bedrock unit below the land surface.
The erosion-resistant Prairie du Chien Group forms a regional plateau in southeastern Minnesota and contains fracture networks and solution enhanced conduits. It is one of four prominent karst systems described for southeastern Minnesota (Runkel and others, 2003, 2014a). Much of the karstification occurred roughly 460 to 490 million years ago when the tops of the Shakopee Formation and Oneota Dolomite were at the land surface over different periods and were subjected to chemical weathering (Alexander and others, 2013). These weathered formations were subsequently buried by younger rocks and are referred to as paleokarst.

A significant zone of high permeability is found regionally throughout southeastern Minnesota at the contact of the Shakopee and Oneota formations and is a result of karstification of the Oneota Dolomite (Dalgleish and Alexander, 1984; Runkel and others, 2003; Tipping and others, 2006). Sinkhole frequency is greatest near this geological contact (Figure 6).

There have been at least four catastrophic failures of sewage treatment ponds in southeastern Minnesota where this zone of high permeability is close to the land surface, including a large failure in Winona County at the city of Altura (Book and Alexander, 1984; Jannik and others, 1991; Alexander and others, 1993; Runkel and others, 2003; Alexander and others, 2013). Additional collapses of stormwater ponds and water retention structures have occurred where pond bottoms were close to the St. Peter Sandstone and Shakopee Formation contact (E.C. Alexander Jr., University of Minnesota Department of Earth and Environmental Sciences, oral communication).

In incised valleys, rapid flow has been documented through siliciclastic units: sandstone, siltstone, and shale (Green and others, 2008, 2012; Barry and others, 2015). These units are classified as pseudokarst because they mimic the rapid groundwater flow of karst but were formed by processes other than dissolution (Barry and others, 2018). At these locations, surface water in valley streams frequently sinks into the underground and rapidly resurges at springs located farther down the valley.

### Surficial aquifers

The plateaus across much of Winona County are capped by surficial unconsolidated geologic deposits that are generally less than 50 feet thick and are commonly covered by a veneer of loess up to 20 feet thick (Part A, Plate 3). The sediment in these uplands generally is not fully saturated and cannot provide sufficient quantities of water to economically supply a user.

Coarse-grained terrace deposits occur along the modern-day Mississippi River and within the main valley of the Whitewater River and smaller tributaries (Part A, Plate 3). Where saturated, this coarse-grained sediment makes up the surficial sand and gravel aquifer (Figure 5).

The texture of surficial deposits influences the rate and amount of precipitation that infiltrates and eventually becomes groundwater (DNR, 2016a). A detailed explanation of the county’s glacial history and how it relates to present-day surficial geologic deposits is available in Part A, Plate 3 of this atlas.

The water table in the uplands and plateaus is influenced by karst and is best represented by the groundwater elevation contours of the Prairie du Chien and Jordan aquifers. Soil moisture in unconsolidated deposits suggests there is a perched water table in the south-central area of the county near Witoka and in areas south of St. Charles.
Figure 4. Area prone to karst feature development and distribution of karst features

The area prone to karst feature development is shown draped on a hillshade model of county landform. The area delineated as karst prone was created by identifying regions underlain by carbonate bedrock with less than 50 feet of sediment as described in DNR, 2016b. The majority of the county that is prone to karst feature development occurs in upland areas. Sinkholes primarily occur on the plateaus; springs and stream sinks occur within valleys. Sinkholes and stream sink locations are from the Karst Feature Inventory Points (University of Minnesota, 2020). Spring locations are from the Minnesota Spring Inventory (DNR, 2020b).
Figure 5. Water-table elevation and sand and gravel wells

Water-table elevation is poorly defined in the areas delineated as prone to karst feature development. Within the karst area, the water table often exceeds 100 feet deep and is best approximated by the groundwater elevation of the Prairie du Chien and Jordan aquifers. Elsewhere, in valley bottoms and along the Mississippi River, groundwater elevation is estimated from wells completed in the surficial sand aquifer, surface waters, and soil moisture. Wells completed in unconsolidated deposits occur in valley bottoms where deposits are thick.
In general, the bedrock geologic units in Winona County are composed of carbonate (limestone and dolostone), sandstone, or siltstone. The composition, mechanical properties, and degree of karstification ultimately govern whether they behave hydraulically as an aquifer or aquitard.

**Aquifers** are water-bearing permeable rock from which groundwater can be extracted from a well. Many of the aquifers in the county also provide continual cold-water discharge to springs and streams.

**Aquitards** are layers of material with low permeability such as siltstone and shale that impede vertical movement of water. However, some aquitards contain high permeability fractures and bedding plane openings that can yield large quantities of groundwater to springs or wells. For instance, large numbers of springs emerge from the St. Lawrence aquitard (Figure 6).

The depth from the land surface partially controls the ease at which an aquifer or aquitard transmits groundwater. Hydrologists can broadly describe hydrologic behavior using the relative terms of **shallow bedrock conditions** and **deep bedrock conditions**. The boundary between these conditions is not consistent throughout the state. It is estimated to be 50 feet below the bedrock surface in Winona County and most of southeastern Minnesota.

- **Shallow bedrock conditions** (the first 50 feet in the uppermost bedrock units) have a **zone of enhanced permeability** from a combination of interconnected systematic and nonsystematic fractures that developed when the bedrock was exposed and weathered at the land surface. This zone can increase the ability of an aquifer to transmit water but can also degrade its ability to provide protection to underlying aquifers.
- **In deep bedrock conditions** permeability decreases, as there are less interconnected fractures and dissolution networks at deeper depths (Runkel and others, 2006).

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**Figure 6. Bedrock stratigraphy, hydrostratigraphy, and distribution of karst features**

Geologic stratigraphic units (formations or groups) do not always correspond to hydrogeologic units (aquifers and aquitards). The distribution of sinkholes, stream sinks, springs, and seeps is partially controlled by bedrock stratigraphy, hydrostratigraphy, and geologic structure. Karst distribution frequency was determined using modified techniques from Tipping and others, 2001 and Steenberg and others, 2014. Column modified from Part A, Plate 2, Figure 1.
The following section describes the distribution and hydrologic properties of aquifers and aquitards present in the county. The bedrock geologic units are described from the top down to match the stratigraphic column (Figure 6). Much of the hydrologic descriptions come from Runkel and others, 2003.

Mapped karst features are shown in Figures 4 and 6, totalling 426 springs, 1,452 sinkholes, and 36 stream sinks. These numbers represent lower limits of potential karst features because mapping is incomplete and new sinkholes form regularly.

**Cummingsville Formation (aquifer)**

The Cummingsville is a carbonate formation that commonly forms a karst aquifer in southeastern Minnesota. In Winona County it is only present in the southwest near St. Charles. The aquifer is not used for water wells because it is near the land surface and limited in areal extent. Laterally continuous shale beds in the lower Cummingsville can act as an aquitard and focus groundwater to emerge as small springs and seeps. Mapped karst features include 6 springs and 5 sinkholes.

**Decorah Shale (aquitard)**

The Decorah Shale serves as a regional aquitard across much of southeastern Minnesota but it is only present in Winona County in the southwest near St. Charles. It is primarily composed of shale that restricts the downward flow of water.

Mapped karst features include 6 springs at the top of the Decorah and 7 sinkholes. Seeps areas are common but not all are mapped.

**Platteville and Glenwood formations (aquitards)**

The Platteville and Glenwood are present in southwestern Winona County in the St. Charles area. The Platteville is presented as an aquitard, but layers can connect vertically by secondary porosity from mechanical fractures and karst dissolution.

The Glenwood shale exhibits low hydraulic conductivity in shallow bedrock conditions, creating numerous groundwater seeps that frequently occur near the top of the Glenwood. It generally behaves as an aquitard but is commonly thin with vertical fractures that can connect the overlying Platteville to the underlying St. Peter.

Mapped karst features include 2 springs and 20 sinkholes.

**St. Peter Sandstone (aquifer)**

The St. Peter is primarily composed of coarse sandstone across much of southeastern Minnesota, but extensive fine-grained beds may be found at the base. This aquifer is present in southwestern Winona County near St. Charles and sporadically to the north. Although several characteristics make it a good aquifer, it contains few wells because it is near the land surface and limited in areal extent.

The St. Peter commonly contains voids and fractures in shallow bedrock settings. Voids are relatively common in the Rochester area of neighboring Olmsted County where they have periodically required geo-engineered solutions during building construction.

Mapped karst features include 99 sinkholes. Many of the sinkholes appear at the bottom of slopes or near the contact with the underlying Shakopee Formation of the Prairie du Chien Group.

**Prairie du Chien Group (aquifer/aquitard)**

The Prairie du Chien forms an extensive and prominent plateau across the county. It is composed of two formations, the upper Shakopee Formation and the lower Oneota Dolomite. Although this group is primarily composed of carbonate rock, the lower portions of both formations have coarse sandstone components referred to as the New Richmond Member and the Coon Valley Member, respectively. The New Richmond Member is regionally distributed as a substantially thick sandstone interval with high intergranular permeability.

Both the Shakopee and Oneota are highly fractured under shallow bedrock conditions, allowing for rapid groundwater transport through fractures and voids. Dye-trace investigations in nearby Olmsted County determined a horizontal groundwater velocity of 800 feet per day (Alexander and others, 1991). In nearby Fillmore County, shallow horizontal velocity was as rapid as 6.2 miles per day (Wheeler, 1993). The Prairie du Chien has very low to low vertical permeability, with horizontal permeability as much as 10 times greater.

Rapid vertical migration of water is limited in deep bedrock conditions in the Prairie du Chien, where the lower part of the Oneota behaves as an aquitard. Despite this, sufficient water can be extracted for low-yield uses such as residential wells.

Mapped karst features include 18 springs in the Shakopee and 45 in the Oneota, 718 sinkholes in the Shakopee and 603 in the Oneota, and 4 stream sinks in the Shakopee...
and 4 in the Oneota. Sinkholes prominently occur near the geologic contact between the Shakopee and Oneota (Figure 6).

**Jordan Sandstone (aquifer)**

The Jordan is a regional aquifer across much of southeastern Minnesota. The upper portion is primarily composed of coarse sandstone, making it a productive aquifer. The lower portion is more fine grained, but can yield productive wells because bedding fractures are common. Fractures in shallow bedrock conditions are particularly abundant and can allow surface waters to sink into the aquifer rapidly.

Mapped karst features include 75 springs and 19 stream sinks. Over half of the stream sinks are mapped in the Jordan.

**St. Lawrence Formation (aquitard)**

The St. Lawrence is an important aquitard in southeastern Minnesota. In deep bedrock conditions it is a competent and regionally significant aquitard. It is primarily composed of very fine-grained sandstone and siltstone in its upper part and carbonate rock in its lower. The unit has low vertical permeability, which restricts downward flow.

The Minnesota Well Rules handbook specifically states that “a stratum at least 10 feet in vertical thickness of the St. Lawrence” is a confining layer (MDH, 2011). However, the aquitard loses its protective characteristics under shallow buried conditions or where it is dissected by deeply incised valleys. In these settings water can flow rapidly through the St. Lawrence both vertically and horizontally. Vertical hydraulic conductivity increases with fractures near bedrock valleys (Runkel and others, 2014b, 2018). Dye tracing in St. Lawrence pseudokarst has revealed groundwater velocities of 150–890 feet per day (Green and others, 2008; Barry and others, 2018).

Mapped karst features include 61 springs and 8 stream sinks. Springs commonly form the headwaters of trout streams.

**Tunnel City Group–Lone Rock Formation (aquifer)**

The Lone Rock is an important regional aquifer in southeastern Minnesota. It was formerly known as the *Franconia Formation*, but was renamed to be consistent with nomenclature used in surrounding states (Mossler, 2008). Many well logs and older reports still use the Franconia nomenclature.

The Lone Rock aquifer is primarily composed of very fine-grained sandstone and siltstone in its upper portion with progressively increasing carbonate rock in its lower portion. The lower carbonate portion has a lower vertical hydraulic conductivity (Runkel and others, 2006) that can be highly fractured in shallow bedrock conditions. Dye tracing in Lone Rock pseudokarst has revealed groundwater velocities of tens to hundreds of feet per day (Barry and others, 2015, 2018).

Groundwater freely moves laterally through the upper Lone Rock. It contains the highest number of springs, many of which form the headwaters of trout streams.

Mapped karst features include 160 springs and 1 stream sink.

**Wonewoc Sandstone (aquifer)**

The Wonewoc is a regional aquifer across much of southeastern Minnesota. It is present across all of Winona County and contains the most wells of any aquifer. This sandstone-rich aquifer system was formerly known as the Ironton and Galesville formations. These two formations were combined and renamed to Wonewoc to be consistent with nomenclature used in surrounding states (Mossler, 2008).

Groundwater flow is primarily intragranular, although fracture flow has been documented in both shallow and deep bedrock conditions. Although primarily composed of sandstone, the upper half also contains silt and shale with lower permeability.

Mapped karst features include 48 springs.

**Eau Claire Formation (aquitard)**

The Eau Claire is an important regional aquitard in southeastern Minnesota. It is primarily composed of shale and siltstone that limit vertical flow. In Winona, Houston, and Wabasha counties, it is coarse textured in the upper portion used by wells.

Mapped karst features include 5 springs.

**Mt. Simon Sandstone (aquifer)**

The Mt. Simon is an important regional aquifer in southeastern Minnesota. It can be broadly described in two parts. The upper portion consists of stacked layers of coarse-grained sandstone and fine-grained siltstone that have differing permeability. The lower portion is primarily coarse grained with relatively higher permeability. It is used by nearly 10 percent of wells in the county, primarily in the eastern portions where the depth to the Mt. Simon is not as limiting as elsewhere. The Mt. Simon aquifer is used heavily for municipal and public water supply.

No karst features are mapped because it is not exposed at the land surface.
**Groundwater flow**

Potentiometric surface maps show the direction of groundwater flow. In confined aquifers, hydrostatic pressure greater than atmospheric pressure causes the water level in a tightly cased well to rise above the top of the aquifer. These water-level elevations are measured, mapped, and contoured to create potentiometric surface maps similar to how topographic maps show land-surface elevations.

The potentiometric surface of an aquifer represents the potential energy that is available to move groundwater. As groundwater moves from higher to lower potentiometric elevations, it flows perpendicular to the potentiometric elevation contours. Flow directions are shown on the maps with arrows.

Groundwater flows from recharge areas to discharge locations within a wide continuum of depth, distance, and time. Flow into, through, and out of shallow aquifers can take hours to years to travel distances of up to a mile. Flow in deeper aquifers can take centuries to millennia to travel dozens of miles.

High elevation areas of the potentiometric surface can indicate important recharge areas. River valleys are typical examples of low elevation groundwater discharge areas.

Potentiometric surface maps were created using static water-level data from the County Well Index (CWI), measurements made by DNR staff, and elevation points along the major rivers and streams where groundwater discharge is likely. The CWI records represent groundwater conditions collected under various climatic and seasonal conditions spanning more than 5 decades. This data variability creates some uncertainty in potentiometric surface elevations.

The hydrology of Winona County is heavily influenced by surface topography and by enhanced permeability from karst and pseudokarst. Groundwater elevations of the uppermost aquifers generally follow changes in the surface topography of the central plateau, evident in contour spacing of the potentiometric surface maps.
Figure 7. Water-table elevation contours of the Shakopee aquifer

Due to sparse data, groundwater elevation contours were developed using combined Shakopee, Oneota, and Jordan aquifer wells. In large areas of the county, the Prairie du Chien and Jordan aquifers are unconfined and make up the water-table system. Dashed contours extend outside of the aquifer to indicate generalized groundwater flow direction.
Figure 8. Water-table elevation contours of the Oneota aquifer

Due to sparse data, contours were developed using combined Shakopee, Oneota, and Jordan aquifer well locations. In large areas of the county, the Prairie du Chien and Jordan aquifers are unconfined and make up the water-table system. On a regional scale, the Oneota formation has characteristics of an aquitard, but can supply sufficient water for residential well use.
Figure 9. Water-table elevation and potentiometric surface contours of the Jordan aquifer

Due to sparse data, contours were developed using combined Shakopee, Oneota, and Jordan aquifer well locations. Confined areas of the Jordan are indicated with a stippled pattern, where contours represent the potentiometric surface. Unconfined areas of the aquifer are indicated with no pattern and represent the water-table system.
Figure 10. Potentiometric surface contours of the Lone Rock aquifer

The Lone Rock aquifer is confined over the majority of the county, indicated with a stippled pattern. Unconfined areas are indicated with no pattern.
Figure 11. Potentiometric surface contours of the Wonewoc aquifer

The Wonewoc aquifer is confined over the majority of the county, indicated with a stippled pattern. Unconfined areas are indicated with no pattern. Few wells are completed in the aquifer in the western portions of the county. Dashed lines show areas of the aquifer where potentiometric surface contours are poorly constrained.
Figure 12. Potentiometric surface contours of the Mt. Simon aquifer

The Mt. Simon aquifer is confined over the majority of the county, indicated by a stippled pattern. Unconfined portions exist within the Mississippi River valley where overlying strata have been eroded away, indicated with no pattern. Well data in the central and western portions of the county are limited. Dashed lines indicate areas of the aquifer where elevation contours are poorly constrained. Contours for the western portion are from a regional dataset developed by MDH (J. Blum, MDH, written communication).
Water chemistry (Plate 5)

The types of dissolved elements and compounds in groundwater provide information about recharge areas, groundwater flow paths, and approximately how long the water has been underground (residence time). All groundwater originated as precipitation that infiltrated through soil layers and into pores and crevices of aquifers and aquitards. Water moves in complicated but definable patterns: into aquifers as recharge, through aquifers, and out of aquifers as discharge. Water chemistry is used to provide information such as the following:

- Groundwater recharge from surface water can be identified from the effect of evaporation on the isotopes of hydrogen and oxygen.
- Groundwater residence time is estimated from tritium and carbon-14 isotopes. Tritium is used to identify water that moved into the subsurface since the 1950s. Carbon-14 is used to determine groundwater residence times of decades to millennia.
- The distribution of select chemicals can indicate areas of high pollution sensitivity or where groundwater consumption is a potential concern to human health.

Water sampling

Samples were collected from wells in aquifers most frequently used for domestic water supply and from springs that supply perennial flow to many of the county's trout streams. Wells were selected based on their aquifer characteristics and distribution. Samples were collected according to the protocols outlined in Appendix A. Chemical data from well and spring samples were used along with physical measurements (static water level and aquifer tests) to understand water movement.

An ideal well-sampling network is evenly distributed across the county, includes populated areas, targets surface-water and groundwater interaction, and contains wells constructed to meet MDH standards with construction documentation. The final network sampled for an atlas depends on citizen willingness to participate. Approximately 1000 well owners were contacted for permission to sample; approximately 90 were selected according to county atlas protocol. Approximately 80 percent of the wells sampled by the DNR had adequate construction documentation. The remaining 20 percent lacked robust construction information and were primarily in the Prairie du Chien and Jordan aquifers where newer wells built to modern code are not available.

For this atlas the DNR collected 93 well, 32 spring, and 4 river samples. These data were combined with 11 historic spring samples, 5 historic well samples for carbon-14 residence time investigations, and 65 well samples collected by the MDH. Data from the MDH are from two separate sources: Minnesota Drinking Water Information System, a compliance-monitoring database that emphasizes treated water; and Water Chemistry Database, a nonregulatory investigatory chemistry database.

Groundwater recharge

Chemical changes occur as water moves from precipitation to groundwater. These can help determine whether groundwater was recharged through the land surface, through lakes and open-water wetlands, or a mixture of the two. Stable isotopes of oxygen and hydrogen were used for determining groundwater and surface-water interactions. Oxygen and hydrogen each have two main stable isotopes: $^{16}$O and $^{18}$O, and $^2$H and $^3$H. The different masses cause each to evaporate at a different rate, which results in fractionation, leaving behind different ratios of heavy to light isotopes. This results in unique isotopic signatures for groundwater with different recharge pathways (Kendall and Doctor, 2003).

- Groundwater recharged directly from precipitation has a meteoric isotopic signature. The water infiltrated directly into the ground, leaving the isotopic ratio unchanged.
- Groundwater recharged from lakes or open-water wetlands has an evaporative isotopic signature. This water has been subjected to fractionation where lighter isotopes evaporated into the atmosphere, leaving water enriched in heavier isotopes.

To identify the source of a groundwater sample, oxygen and hydrogen isotopic data are plotted against each other. The x-axis represents the oxygen isotope value ($\delta^{18}$O) and the y-axis represents the hydrogen isotope value ($\delta^2$H). The measured ratio in the sample is divided by the ratio in a standard. The standard used was Vienna Standard Mean Ocean Water (VSMOW).

Definition of delta ($\delta$)

The stable isotope composition of oxygen and hydrogen are reported as $\delta$ values: $\delta (\%o) = (R_s/R) - 1)*1000$.

- $R$ represents the ratio of the heavy to light isotopes $^{18}$O/$^{16}$O or $^2$H/$^1$H.
- $R_s$ represents the ratio of the sample.
- $R$ represents the ratio in VSMOW.

Delta values are reported in units of parts per thousand ($\%o$ or permil) relative to VSMOW.
Recharge results

County results were compared to the *global meteoric water line*, which was developed from precipitation data from around the world (Craig, 1961).

Winona County groundwater samples mostly fall near the intersection of the meteoric water line and the evaporation line. One sample trends along the evaporation line (Figure 13).

- The bulk of the groundwater samples plot above and parallel to the global meteoric water line.
- The partial evaporative signature is a water-table well in the city of Winona near the banks of the Mississippi River (Figure 14). The source of evaporative water to the well is uncertain, but is likely Lake Winona approximately 1.1 miles upgradient of the well.
- The four surface water samples plot parallel to the global meteoric water line, consistent with flowing surface water not subjected to significant fractionation.

![Figure 13. Stable isotope values from water samples collected in Winona County](image)

The **meteoric water line** represents precipitation values from rapid infiltration. The **global meteoric water line** was developed using precipitation samples from around the world and is described by the following equation: \( \delta^{2}H = 8.0 \delta^{18}O + 10.0 \) (Craig, 1961).

The **evaporation line** represents groundwater recharge that came partially from surface-water sources. The evaporation line is from a regression of statewide lake samples in the DNR Groundwater Atlas database and is described by the following equation: \( \delta^{2}H = 5.2 \delta^{18}O - 15.2 \). A single groundwater sample showed evidence of an evaporative signature and is shown as a red diamond.
Figure 14. Stable isotope characteristics of groundwater samples collected in Winona County
Most groundwater samples originated as direct infiltration of precipitation. Well locations symbolized in gray represent meteoric signatures. The red diamond represents a partial evaporative signature.
Groundwater residence time is the approximate time that has elapsed since water infiltrated the land surface to the time it was pumped from a well or discharged to a river or spring. Short residence time generally suggests short travel paths and/or high recharge rates; long residence time suggests long travel paths and/or low recharge rates. The residence time of groundwater was estimated for this atlas using isotopic analysis of the radioactive elements tritium and carbon-14. Groundwater residence time results are shown on Plates 5 (Water chemistry) and 6 (Hydrogeologic cross sections) and Figures 18 (Piper diagram), 20, 23–29 (Pollution sensitivity).

Tritium

Groundwater residence time was interpreted from the concentration of tritium. Although tritium is a naturally occurring isotope of hydrogen, atmospheric concentrations were greatly increased from atmospheric testing of nuclear weapons between 1953 and 1963 (Alexander and Alexander, 1989). Tritium concentrations were used to estimate groundwater residence time using the known half-life of 12.32 years (Lucas and Unterweger, 2000). The concentrations are presented in tritium units (TU) and are referred to as tritium age in the following categories.

- **Recent**: water entered the ground since about 1953 (greater than 8 TU).
- **Mixed**: water is a mixture of recent and vintage (greater than 1 TU to less than 8 TU).
- **Vintage**: water entered the ground before 1953 (less than or equal to 1 TU).

Historical data (sample dates from 1988 to 2017) are used in the residence time interpretations of this report and are classified according to Table B-2 in Appendix B.

Tritium was collected from 124 wells and 35 springs to assist in residence-time interpretations. Of the 159 samples analyzed for tritium, 66 were vintage, 77 were mixed, and 16 were recent. Residence time by aquifer is found in the results section of “Pollution sensitivity, Bedrock aquifers” and on Plate 5, “Water chemistry.”

Carbon-14

Select wells with vintage and mixed tritium-age results were further sampled for carbon-14 ($^{14}$C) to estimate longer residence times. This naturally occurring isotope has a half-life of 5,730 years, and is used to estimate groundwater residence time ranging from less than 50 to greater than 40,000 years.

Carbon-14 sample collection, analysis, and modeling is described in Alexander and Alexander, 2018. When precipitation infiltrates the unsaturated zone it adsorbs carbon dioxide, including carbon-14, from biogenic soil gases forming carbonic acid. This mildly acidic water dissolves calcite and dolomite present in the soil or bedrock. Plant communities present at the time of infiltration determine soil δ$_{13}$C ratios that are used within the model to estimate the groundwater residence time. Approximately half of the dissolved carbon in the groundwater comes from atmospheric carbon in the soil zone during infiltration and half comes from very old bedrock sources where carbon-14 has decayed completely.

Residence times from 23 sampled wells varied from recent (less than 50 years) to 25,000 years. The youngest carbon-14 residence times are in the Prairie du Chien and Jordan aquifers and the oldest are in the Mt. Simon aquifer. Carbon-14 residence time generally increases with depth from land surface. Residence time by aquifer is found in the results section of “Pollution sensitivity, Bedrock aquifers” and on Plate 5, “Water chemistry.”
Inorganic chemistry of groundwater

Water begins dissolving minerals in the soil, sediment, and bedrock as soon as precipitation infiltrates the soil layer. Groundwater chemistry changes as it moves along flow paths.

Groundwater contamination can come from human (anthropogenic) pollution or from dissolution of naturally occurring geologic sources. Elevated concentrations of particular chemicals can indicate short groundwater residence time, high sensitivity, or where groundwater consumption is a potential concern to human health. Anthropogenic sources can be identified by comparing concentrations to naturally occurring background levels.

Water quality evaluations describe contaminants that are potentially harmful (either naturally occurring or anthropogenic) or that affect aesthetics. This atlas uses the following guidelines.

U.S. Environmental Protection Agency
(EPA, 2017 July; EPA, 2017 March)

- **Maximum Contaminant Level (MCL):** legally enforceable federal standards that apply to public water systems, to limit the levels of contaminants in drinking water.
- **Maximum Contaminant Level Goal (MCLG):** nonenforceable health goals set on possible health risks from exposure over the course of a lifetime.
- **Secondary Maximum Contaminant Level (SMCL):** nonenforceable guidelines for contaminants that can cause aesthetic effects or taste and odor problems in drinking water.

Minnesota Department of Health
(MDH, 2012a)

- **Health Risk Limit (HRL):** the concentration of a groundwater contaminant, or a mixture of contaminants, that can be consumed with little or no risk to health and that has been promulgated under rule.
- **Health Based Value (HBV):** derived using the same algorithm as HRLs; however, they have not yet been promulgated as rules.
- **Risk Assessment Advice (RAA):** technical guidance concerning exposures and risks to human health. RAA values contain more uncertainty than HRLs.

Minnesota Department of Natural Resources
Groundwater Atlas Program

- **Anthropogenic:** caused by human activity.
- **Elevated:** values above the indicated levels as detailed in the chemical descriptions that follow.
- **Naturally occurring:** waters contain natural impurities from the rock and soil. Most are harmless, but certain levels in drinking water can be harmful to health.

Chemical descriptions and results

The following chemicals are naturally occurring but some can be elevated by anthropogenic activities. Water quality guidelines and sampled results are presented for inorganic chemistry and include the following.

- The major cations and major anions, reported in units of parts per million (ppm)
- Trace elements such as arsenic and manganese, reported in units of parts per billion (ppb)

Organic chemicals were not studied as they are out of the scope of this project, but can be found in reports from other state agencies (e.g., pesticides and their breakdown products, solvents, degreasers).

Geologically sourced and naturally occurring radionuclides, such as radium and radon, were additionally out of scope for this project, but can be elevated in the Mt. Simon aquifer (Lively and others, 1992). Radium is commonly found in southeastern Minnesota's Paleozoic aquifers. The cities of Winona, Stockton, and Lewiston have had elevated radium levels detected in their municipal wells.

Chloride

**SMCL 250 ppm, elevated ≥5 ppm, anthropogenic: chloride/bromide ratio >300**

Chloride can occur naturally from deep sources such as residual brine or it can come from an anthropogenic source such as road salt, water softener salt, or fertilizer (Davis and others, 1998; Panno and others, 2006). Chloride concentrations above 5 ppm with chlorine/bromide mass ratios above 300 may indicate anthropogenic sources of chloride. The 300 break point was determined using a combination of chloride and nitrate concentrations and tritium and carbon-14 residence time estimates.

**Results (Figure 15)**
- Of the 176 samples analyzed for chloride, 83 were elevated. Elevated samples were collected from 30 springs and 53 wells; none equaled or exceeded the SMCL.

Elevated occurrences were primarily from wells completed in aquifers above the St. Lawrence aquitard or in valley bottoms where overlying aquitards are absent.

- Springs with elevated chloride are common and are primarily located in valley bottoms where overlying aquitards are absent or have diminished protective characteristics.
Nitrate

**MCL and HRL 10 ppm, elevated ≥1 ppm**

Nitrate can occur naturally at low concentrations but elevated concentrations indicate impacts from fertilizer and animal or human waste (MDH, 1998; Wilson, 2012). Concentrations may lessen with time (denitrification) in deep and confined aquifers where there is little oxygen in the groundwater. In Minnesota, groundwater with long residence time typically has little available oxygen and little to no nitrate.

Nitrate concentration is commonly elevated in southeastern Minnesota in the root zone underlying row-crop agriculture. A recent 5-year study collected nitrate concentration from lysimeters in cultivated row crop settings. Results were highly variable and averaged 22.3 ppm with a typical range of 8.0 to 28.0 ppm (Kuehner and others, 2020).

Elevated levels of nitrate may indicate that other surface contaminants have the potential to reach an aquifer. Pesticides are not sampled as part of this study, but frequently co-occur with nitrate. The Minnesota Department of Agriculture (MDA) has found the likelihood of detecting at least one pesticide compound increases as the concentration of nitrate increases (MDA, 2019).

In Winona County, 96 percent (190 of 197) of wells with a nitrate concentration greater than or equal to 3 ppm contained pesticides or pesticide metabolites (B. Schaefer, MDA, written communication, 2020).

A 20-year ambient groundwater quality investigation in a similar geologic setting with similar land use found a median of 15 different herbicide compounds in study wells with a median nitrate concentration greater than 3 ppm (Demuth and Scott, 2020). Elevated levels of nitrate and pesticides have been a concern in Winona County for decades (Wall and others, 1990).

**Results (Figure 16)**

- Of the 187 samples analyzed for nitrate, 85 were elevated. Elevated samples were collected from 36 springs and 49 wells; 12 well samples exceeded the MCL.
- Elevated occurrences were primarily from the Prairie du Chien and Jordan aquifers or in wells completed in valley bottoms where overlying aquitards are absent.
- Springs with elevated nitrate are common and are primarily at the edge of valleys where overlying aquitards have diminished protective characteristics.

These findings are consistent with results from the Township Testing Program (MDA, 2018), which found areas with a high percentage of row crop agriculture and karst vulnerability to be at risk to nitrate contamination. The initial MDA study included volunteers’ wells where specific details about participant wells, such as aquifer, depth, and well construction weren’t always available. The MDA report suggests that many of the wells with insufficient documentation are likely completed in the Prairie du Chien and Jordan aquifers and were likely installed prior to the inception of well code enacted in the 1970s. The MDA initial assessment found nitrate concentrations greater than the MCL in 10 percent or more of the samples collected in the following townships: Elba, Fremont, Hart, Mt. Vernon, Norton, St. Charles, Saratoga, Utica, and Warren. Townships are shown on Plate 5.

The MDA did follow-up tests in these same townships and found nitrate concentrations similar to the initial testing. Following the second round of testing, the MDA removed the results of wells that had insufficient documentation describing the well’s depth, aquifer, or construction details; or wells that could be influenced by point sources of nitrogen. The final well assessment found nitrate concentrations greater than or equal to 5 ppm in over 10 percent of the wells. Freemont and Utica townships had the highest mean nitrate concentration and percentage of wells exceeding the MCL in both the initial and follow-up testing.

Arsenic

**MCL 10 ppb; MCLG 0**

Arsenic is a naturally occurring element that has been linked to negative health effects, including cancer. If arsenic is present the MDH advises domestic well owners to treat drinking water (MDH, 2018a). Current science cannot predict which wells will have high arsenic concentrations, therefore all newly constructed drinking-water wells are analyzed for arsenic (Minnesota Administrative Rules 4725.5650, 2008).

The factors affecting arsenic concentrations in groundwater are not completely understood. There is a strong correlation between arsenic in groundwater and glacial sediment derived from rocks northwest of Minnesota (Erickson and Barnes, 2005a).

Nicholas and others (2017) found that changes in redox conditions are largely responsible for releasing solid phase arsenic into groundwater by one of three mechanisms: desorption, reductive dissolution, or oxidative dissolution and that the aquitard-aquifer interface is very geochemically...
active. Research also indicates that arsenic concentrations are higher in wells that have short-screened sections near the boundary of an aquifer and aquitard (Erickson and Barnes, 2005b).

**Results**

- Of the 138 samples analyzed for arsenic, arsenic was present in 48, 4 of those exceeded 1 ppb, and none exceeded the MCL.

**Manganese**

*HBV 100 ppb; SMCL 50 ppb*

Manganese is a naturally occurring element beneficial to humans at low levels, but at high levels can harm the nervous system (MDH, 2018b). In addition to health effects, concentrations above the SMCL can cause negative secondary effects, such as poor taste, odor, and water discoloration (stained laundry and plumbing fixtures).

Statewide, manganese concentrations were greater than the HBV in drinking-water wells for 57 percent of water-table aquifers and 63 percent of buried sand aquifers (MDH, 2012b). Although there are no clear patterns of manganese distribution across most of Minnesota, the MDH has found that southeastern Minnesota tends to have low levels of manganese (below 50 ppb) and southwestern Minnesota tends to have high levels (some over 1,000 ppb).

**Results**

- Of the 126 samples analyzed for manganese, 1 was greater than the HBV and 2 were greater than the SMCL.

**Boron**

*RAA 500 ppb*

Boron is a naturally occurring element that has been linked to negative health effects. The MDH developed risk assessment advice (RAA) for boron in drinking water at 500 ppb to protect formula-fed infants (MDH, 2017 October).

**Results**

- Of the 101 samples analyzed for boron, 1 was greater than the RAA and occurred in a well completed in the Mt. Simon aquifer.

**Sulfate**

*SMCL 250 ppm*

Sulfate is largely naturally occurring. Common sources are oxidation of sulfide minerals and the dissolution of gypsum. Minor amounts are introduced from the burning of fossil fuels (Crawford and Lee, 2015). High concentrations in groundwater can negatively affect taste and can act as a laxative.

**Results**

- All samples had sulfate concentrations less than the SMCL.
Figure 15. Elevated chloride concentrations from groundwater samples

Chloride is a common contaminant in Winona County with 83 of 176 groundwater samples exceeding 5 ppm. Naturally elevated chloride is most commonly encountered in wells completed in the Mt. Simon aquifer and was determined using chloride to bromide ratios of less than 300.
Figure 16. Elevated nitrate concentrations from groundwater samples

Nitrate is a common contaminant in Winona County with 85 of 187 groundwater samples exceeding 1 ppm, and 12 exceeding the MCL. Elevated nitrate primarily occurs in wells completed in aquifers located above the St. Lawrence aquitard or in wells in valley bottoms where overlying aquitards are not present. Springs commonly have elevated nitrate.
Nitrate monitoring at Crystal Springs State Fish Hatchery

Understanding nitrate levels in aquifers of varying depths helps to determine their pollution sensitivity. Collecting data from the same location over long periods helps to understand changes in aquifer chemistry or water levels and allows hydrologists to determine trends.

Nitrate concentration has been monitored at the Crystal Springs State Fish Hatchery by the DNR and MDA since 2001. In 2016 intensive continuous monitoring began at the Main Spring, conducted by the DNR and Minnesota Pollution Control Agency (MPCA).

The data were collected at 15-minute intervals using a continuous nitrate probe. Direct water-grab samples were also collected and analyzed for anion chemistry to corroborate the results. Nitrate concentration oscillated between 4 and 5 ppm between fall 2016 and winter 2019 (Figure 17).

The results indicate that fluctuations in nitrate concentrations are related to precipitation and the timing of fertilizer application. Precipitation moves nitrate stored in the soil downward and to the valley edge where it mixes with older water before emerging at the spring.

Fluctuations in nitrate concentration are smaller at this spring because it is deeply seated in the St. Lawrence Formation. Springs emanating from shallowly buried bedrock have rapid increases and decreases in nitrate concentration because of a closer connection to the land surface (Barry and others, 2020).

Long-term monitoring (since 2003) indicates that nitrate is increasing at approximately 1.6 percent per year. (K. Kuehner, MDA, written communication).

Figure 17. Continuous nitrate concentrations of the Main Spring at Crystal Springs State Fish Hatchery (85A0000001)

Nitrate concentration from October 2016 through December 2019 varied between 3.8 and 4.8 parts per million. Nitrate concentration changes in response to precipitation events and localized fertilizer application timing and rates in the watershed. The spring location is shown on Figure 16. The spring’s hydrostratigraphy was determined by the MGS as described in Steenberg and Runkel, 2018.
**Major cations and anions**

Calcium, magnesium, and sodium cations and bicarbonate anions are dissolved out of glacial sediment and bedrock by groundwater. The constituents are derived from limestone and dolomite bedrock and are also common in glacial sediment groundwater aquifers (Hem, 1985). Bicarbonate is also derived from carbon dioxide present in the atmosphere and in soil above the water table.

Sodium is often present in deep aquifers or at mineral interfaces. As groundwater moves through aquifer systems, calcium and magnesium ions are exchanged for sodium ions (Hounslow, 1995). Potassium is naturally released from the weathering of silicate minerals (Hem, 1985). In agricultural areas, fertilization to maintain soil fertility provides an additional source of potassium.

Water is considered hard or soft by the concentrations of calcium, magnesium, and bicarbonate. Hard water contains higher levels of calcium and/or magnesium. Most bedrock aquifers in Winona County produce hard water. Though not required, most residents typically soften their water to improve the taste and smell and to limit the build-up of minerals (scale) on plumbing fixtures, the insides of pipes, and hot water heaters.

The Piper diagram (Figure 18) graphically represents each water sample for the most common ionic constituents in natural waters: calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, and nitrate.

The Piper diagram can reveal information about the following.
- The source of dissolved chemicals as water travels through the aquifers and aquitards
- Water chemistry changes along the groundwater flow path due to ion exchange, precipitation, solution, and mixing of different water types
- Distribution of water types

The Piper diagram has three components: a cation triangle, an anion triangle, and a central diamond. Each sample collected by the DNR is represented by one data point on each. The sample points on each triangle (ternary diagram) reflect the relative percentages of the major cations (lower left triangle) and anions (lower right triangle). These are projected onto the diamond grid. The sample points in the figure are color coded according to tritium age to show chemical relationships.

**Results**

The most common water type in Winona County is calcium+magnesium bicarbonate, which is typical for groundwater from Paleozoic aquifers in southeastern Minnesota.

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**Figure 18. Piper diagram of groundwater samples collected in Winona County**

This diagram compares the relative proportions of cations and anions in groundwater samples. The most common water type is calcium+magnesium bicarbonate, which is typical for southeastern Minnesota.

Groundwater residence time generally increases along the path of the red arrow. Waters that plot along this path evolve from calcium bicarbonate waters to sodium-potassium bicarbonate waters.

Waters within the ellipses of the anion triangle have unique geochemical signatures.
- **Ellipse 1** samples have vintage tritium ages with estimated carbon-14 residence times ranging from 5,500 to 25,000 years and are from the Mt. Simon aquifer.
- **Ellipse 2** samples have mixed tritium ages, anthropogenically elevated chloride and nitrate, and are from all aquifers sampled except the Mt. Simon.
Pollution sensitivity

Pollution sensitivity is defined as the potential for groundwater to be contaminated from land surface activities because of properties of the geologic material. Dissolved contaminants migrate with water through sediment and are typically affected by complex processes such as biological degradation and oxidizing or reducing conditions. The methods used to interpret pollution sensitivity include the following general assumptions:

- Flow paths are vertical and downward from the land surface through the soil and underlying sediment to the saturated zone.
- Contaminants travel at the same rate as water.
- Dissolved contaminants move with water from the surface and are not chemically or physically altered over time.

River valleys can be important groundwater discharge areas where local groundwater movement is characteristicly upward and the actual pollution sensitivity can be less than rated.

Two methods were used to estimate the pollution sensitivity, based on the different properties of the aquifer materials or the thickness of the geologic layers. The central concept for both models is the relative rate of water movement. This is described as infiltration in the unsaturated zone, and recharge in the saturated zone.

The following describes the two methods:

- **Near-surface materials** (unsaturated flow to a depth of 10 feet, the assumed depth of the water table): The primary properties used to estimate sensitivity are texture and distance. This method is used in valleys and along the Mississippi River.

- **Bedrock aquifers**: aquifer chemistry and residence time is combined with depth from the land surface and the presence or absence of karst features and overlying aquitards. These data are used to estimate bedrock pollution sensitivity, in conjunction with the findings of historical investigations that describe the hydrologic properties of Minnesota's Paleozoic bedrock aquifers and aquitards.

### Near-surface materials

The transmission rate varies depending on texture. Coarse-grained materials generally have faster transmission rates than fine-grained materials. The two primary inputs used to estimate transmission rate are the hydrologic soil group and the surficial geologic matrix texture. Attributes of both are used to estimate the time of travel (Table 1) (USDA-NRCS, 2020; Part A, Plate 3).

The time of travel through near-surface sediment varies from hours to approximately a year (Figure 19).

- Areas with a short travel time (hours to a week) are rated high sensitivity.
- Areas with a longer travel time (weeks to a year) are rated low or very low.
- Areas with travel times of more than a year are rated ultra low. There are no ultra low areas in this county.

For further details, see *Methods to estimate near-surface pollution sensitivity* (DNR, 2016c).

Results are depicted in Figure 20.
Table 1. Transmission rates through unsaturated materials used to assess the pollution sensitivity rating of the near-surface materials

<table>
<thead>
<tr>
<th>Hydrologic Soil Group (0–3 feet)</th>
<th>Surficial Geologic Texture (3–10 feet)</th>
<th>Surficial geology map unit (Part A, Plate 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group*</td>
<td>Classification</td>
<td>Transmission rate (in/hr)</td>
</tr>
<tr>
<td>A, A/D</td>
<td>gravel, sandy gravel, silty gravel</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>sand, silty sand</td>
<td>0.71</td>
</tr>
<tr>
<td>B, B/D</td>
<td>silt, loamy sand</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>sandy loam, peat</td>
<td>0.28</td>
</tr>
<tr>
<td>C, C/D</td>
<td>silt loam, loam</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>sandy clay loam</td>
<td>0.035</td>
</tr>
<tr>
<td>D</td>
<td>clay, clay loam, silty clay loam, sandy clay, silty clay</td>
<td>0.015</td>
</tr>
<tr>
<td>--</td>
<td>glacial lake sediment of Lake Agassiz</td>
<td>0.000011</td>
</tr>
</tbody>
</table>

Note that peat is used as an overlay on the map due to variable and typically unknown thicknesses.

*The Natural Resources Conservation Service (NRCS) defines hydrologic soil groups primarily based on texture and the occurrence of low permeability layers (USDA-NRCS, 2009):

Group A: water is freely transmitted. Soils are more than 90 percent sand and gravel.
Group B: soils are less permeable but water transmission is still unimpeded.
Group C: water transmission is somewhat restricted.
Group D: water movement is restricted or very restricted.

**Residuum transmission was rate modified per discussion with MGS.

Figure 19. Geologic sensitivity ratings for near-surface materials
The majority of the county has bedrock near the land surface that is prone to karst feature development and is a unique very high sensitivity area (DNR, 2016b). Elsewhere, the estimated sensitivity predominately ranges from moderate to high in the sandy unconsolidated deposits in valley bottoms and along the Mississippi River. The surficial sand aquifer is used by approximately 8 percent of county wells with known construction information. Samples were collected from 5 wells in unconfined surficial (water table) aquifers and 1 well in a confined sand aquifer; 3 were analyzed for tritium age resulting in 2 mixed and 1 vintage. The vintage sample is likely Mt. Simon water that upwells into the water-table system along the edges of the Mississippi River. Of the 5 samples analyzed for nitrate, 2 were elevated. Of the 4 samples analyzed for chloride, 2 were elevated from anthropogenic sources.

**Figure 20. Pollution sensitivity rating of near-surface materials**

The majority of the county has bedrock near the land surface that is prone to karst feature development and is a unique very high sensitivity area (DNR, 2016b). Elsewhere, the estimated sensitivity predominately ranges from moderate to high in the sandy unconsolidated deposits in valley bottoms and along the Mississippi River. The surficial sand aquifer is used by approximately 8 percent of county wells with known construction information. Samples were collected from 5 wells in unconfined surficial (water table) aquifers and 1 well in a confined sand aquifer; 3 were analyzed for tritium age resulting in 2 mixed and 1 vintage. The vintage sample is likely Mt. Simon water that upwells into the water-table system along the edges of the Mississippi River. Of the 5 samples analyzed for nitrate, 2 were elevated. Of the 4 samples analyzed for chloride, 2 were elevated from anthropogenic sources.
Bedrock aquifers

Methods

The pollution sensitivity ratings for bedrock aquifers are based on estimated vertical travel times defined by the Geologic Sensitivity Workgroup (1991). Travel time varies from hours to thousands of years. Areas with ratings of high or very high have relatively short travel times of less than a few years; areas rated low or very low have estimated travel times of decades or longer (Figure 21).

The ratings are based on estimated vertical travel times inferred from tritium analysis, carbon-14 age dating, the presence or absence of anthropogenic indicators, dye trace investigations (DNR, 2020a), the presence or absence of sinkholes and stream sinks, and the findings from many previous investigations (Tipping, 1994; Tipping and others, 2006; Runkel and others, 2003, 2006, 2014a, 2014b, 2018).

Sensitivity ratings were assigned to delineate areas of the aquifers using Geographic Information System (GIS) analysis of the data listed above.

In the shallow bedrock conditions of valleys, the St. Lawrence transitions from an aquitard to a pseudokarst aquifer (Figure 22). This finding is based on the numerous locations documented in southeastern Minnesota where streams sink into the St. Lawrence aquitard. At several of these locations, water has been documented to travel rapidly to downgradient springs and wells (Green and others, 2008, 2012; Barry and others, 2015, 2018).

Wells located at a distance from incised valleys and in aquifers below the St. Lawrence typically have low nitrate, low anthropogenic chloride, nondetectable tritium, and no detectable dissolved oxygen (Barry and others, 2018).

Pollution sensitivity ratings were compared with the tritium age of groundwater and the presence or absence of other anthropogenic chemical indicators (nitrate and chloride). Higher sensitivity is associated with the following.

- Tritium age is recent or mixed.
- Nitrate is elevated and anthropogenic if concentrations are greater than or equal to 1 ppm.
- Chloride is elevated if concentrations are greater than or equal to 5 ppm. It is anthropogenic if chloride/bromide ratios are greater than 300.

The tritium dataset is a combination of sampling efforts by the DNR and MDH for projects since 1988. Groundwater chemistry was qualitatively compared to the results of the pollution sensitivity modeling.

Tritium detections from aquifers in areas mapped as very low sensitivity should rarely occur, assuming that flow of recent water to the aquifer is vertical and not altered by nearby pumping or compromised well integrity.

The following section describes and illustrates the results of the bedrock aquifers in stratigraphic order (Figure 6). It includes the extent, depth, thickness, use, mapped karst features, pollution sensitivity, residence time, and chemistry.

Groundwater system

Groundwater collected from wells and springs in aquifers located stratigraphically above the St. Lawrence aquitard typically show anthropogenic influences: elevated nitrate and chloride and tritium ages of less than 70 years. Groundwater from these aquifers also frequently has measurable dissolved oxygen. Oxygenated groundwater likely reflects aeration within conduit networks that allow for rapid vertical recharge from the land surface to deeper aquifers.

Wells and springs located within or near incised valleys generally have elevated nitrate, chloride, tritium, and/or detectable dissolved oxygen. Here the St. Lawrence aquitard is typically thinner, compromised by fractures, or absent.
Springs are highly susceptible to human impact and contamination, especially those that emanate above the St. Lawrence aquitard. Springs in valleys are a mixture of younger local impacted water and older regional groundwater. Tritium-age color is based on chemical results from spring and well samples collected from aquifers ranging from the Shakopee to the Wonewoc. Aquitard units are represented with brown hues.

Springs
- Of the 43 samples collected, 35 were analyzed for tritium age with the following results: 12 recent and 23 mixed.
- Of the 43 samples analyzed for nitrate, 36 were elevated.
- Of the 43 samples analyzed for chloride, 30 were elevated from anthropogenic sources.

Wells
- Of the 49 samples analyzed for nitrate with recent or mixed tritium age, 35 were elevated.
Results

Cummingsville through St. Peter aquifers (Figure 23)

- **Extent**: Present in the southwest and includes intervening aquitard units.
- **Depth**: 0–300 feet.
- **Thickness**: The Cummingsville ranges from 0–75 feet; the St. Peter from 0–80 feet.
- **Use**: Less than 0.1 percent of county wells with known construction information. Because these aquifers are near the land surface they are sensitive to pollution and are not generally used for potable water supply.
- **Mapped karst features**: 131 sinkholes.
- **Pollution sensitivity**: Very high, due to proximity to land surface, mapped karst features, and the presence of anthropogenic influences in groundwater chemistry.
- **Residence time**: One sample collected from a St. Peter aquifer well southeast of St. Charles had mixed tritium age.
- **Anthropogenic chemistry**: The same well had elevated nitrate and chloride.

Prairie du Chien aquifer (Figure 24)

- **Extent**: Present over most of the county as the first bedrock unit beneath land surface.
- **Depth**: 0–580 feet. Its greatest depths occur in the southwestern area of the county, where it is deeply buried under overlying bedrock.
- **Thickness**: 0–300 feet.
- **Use**: Less than 4 percent of county wells with known construction information. The aquifer is made up of two geologic formations with different hydrologic properties: the Shakopee and the Oneota. The Shakopee is more productive than the Oneota, which has properties of an aquitard on a regional scale. It is saturated over large portions of the county, except in the narrow ridges of the eastern and southern portions where it may be substantially dewatered.
- **Mapped karst features**: 1,321 sinkholes and 8 stream sinks.
- **Pollution sensitivity**: Very high, due to its proximity to land surface over much of the county, karst features, and the presence of anthropogenic influences on groundwater chemistry. New Prairie du Chien wells are prohibited in Winona County except in small geographic areas in northern Saratoga and southern St. Charles townships.
- **Residence time**: Samples were collected from 5 springs and 10 wells from the Shakopee and Oneota combined; 10 were analyzed for tritium age with the following results: 2 recent, 7 mixed, and 1 vintage. The vintage sample had a carbon-14 residence time of 2,500 years and was from a well in the southwestern portion of the county. Although documentation for the well is incomplete, the well's total depth terminates within the Oneota Formation which can behave more as an aquitard than an aquifer. In this location, the vintage tritium age and carbon-14 residence time suggests the Oneota has limited hydraulic connection to the overlying Shakopee.
- **Anthropogenic chemistry**: Of the 12 samples analyzed for nitrate, 10 were elevated. Of the 12 samples analyzed for chloride, 11 were elevated from anthropogenic sources.

Jordan aquifer (Figure 25)

- **Extent**: Present over most of the county.
- **Depth**: 0–675 feet. The greatest depths occur in the southwestern area of the county, where it is deeply buried under overlying bedrock.
- **Thickness**: 0–100 feet. The aquifer is fully saturated in the western portions of the county, generally where it is confined. However, in the narrow ridges of the eastern and southern portions it may be substantially dewatered.
- **Use**: Approximately 11 percent of county wells with known construction information.
- **Mapped karst features**: 19 stream sinks, commonly occurring in valleys where overlying units have eroded away.
- **Pollution sensitivity**: Complex, ranging from moderate to very high. Wells cased near the top of the Jordan can extract water that is geochemically different than wells cased near the bottom.

Moderate sensitivity occurs where there is complete thickness of the Oneota and at least 30 feet of the Shakopee Formation overlying the Jordan. This condition generally occurs where the Jordan is confined, an area covering the southwestern portion of the county extending east through St. Charles, Utica, and north of Lewiston. The area mapped as moderate exhibits a wide range of residence time and connectivity to overlying aquifers, with some well samples showing vintage tritium age and carbon-14 residence times that are several thousand years old and others showing recent tritium age and elevated nitrate and chloride.

High sensitivity occurs where the overlying Prairie du Chien is thinner than the criteria set for moderate sensitivity. This includes large portions where the Oneota is the first bedrock unit. An example of the Jordan
aquifers elevated sensitivity is evident from time-series sampling of a municipal well in the city of Utica, where water samples show increasing nitrate concentration over time (R. Tipping, MDH, written communication).

Very high sensitivity occurs where the Jordan aquifer has no overlying bedrock units. In this setting, surface water can disappear into stream sinks and travel rapidly to springs farther down the valley.

- **Residence time**: Samples were collected from 4 springs and 36 wells. Of these 40, 33 were analyzed for tritium age with the following results: 5 recent, 17 mixed, and 11 vintage. Vintage samples had carbon-14 residence times ranging between recent and 4,500 years.

- **Anthropogenic chemistry**: Of the 33 samples analyzed for nitrate, 24 were elevated and 7 were above the MCL. Of the 33 samples analyzed for chloride, 21 were elevated from anthropogenic sources.

**Lone Rock aquifer (Figure 26)**

- **Extent**: Present over most of the county.
- **Depth**: 0–900 feet. Its greatest depths occur in the southwestern area of the county, where it is deeply buried under overlying bedrock.
- **Thickness**: 0–150 feet. The aquifer is fully saturated and confined everywhere except in valleys where the overlying St. Lawrence aquitard is thin or absent.
- **Use**: Approximately 12 percent of wells with known construction information. It provides water to 38 percent of mapped springs, which provide baseflow to coldwater trout streams.
- **Mapped karst features**: 1 stream sink in the southeastern portion of the county near the border.
- **Pollution sensitivity**: Very low over the majority of the county, increasing to high and very high near valley edges where the St. Lawrence aquitard is thin or absent. Very low sensitivity occurs where the Lone Rock is buried deeply and underlies the St. Lawrence aquitard. High sensitivity occurs where the St. Lawrence aquitard is the only bedrock unit above the Lone Rock.
- **Residence time**: Samples were collected from 27 springs and 34 wells. Of these 61, 51 were analyzed for tritium age with the following results: 9 recent, 18 mixed, and 24 vintage. Vintage samples had carbon-14 residence times ranging between 3,000 and 6,000 years.

**Wonewoc aquifer (Figure 27)**

- **Extent**: Present over most of the county.
- **Depth**: 0–1,020 feet. The greatest depths occur in the southwestern area of the county, where it is deeply buried under overlying bedrock.
- **Thickness**: 0–115 feet. The aquifer is fully saturated and confined everywhere except in valleys where the overlying Lone Rock aquifer is thin or absent.
- **Use**: Approximately 21 percent of wells with known construction information. It provides water to 11 percent of mapped springs.
- **Pollution sensitivity**: Very low for most of the aquifer because of its position below the St. Lawrence aquitard and its distance from the land surface. Moderate sensitivity occurs where the Lone Rock aquifer is the only bedrock unit above the Wonowoc. High sensitivity occurs where the Wonowoc aquifer has no overlying bedrock units.
- **Residence time**: Samples were collected from 1 spring and 30 wells. Of the 31 total samples, 27 were analyzed for tritium age with the following results: 13 mixed, and 14 vintage. Vintage samples had carbon-14 residence times ranging between 3,500 and 6,000 years.
- **Anthropogenic chemistry**: Of the 30 samples analyzed for nitrate, 8 were elevated. Of the 28 samples analyzed for chloride, 4 were elevated from anthropogenic sources. Almost all samples with mixed tritium or elevated nitrate or chloride occurred in valleys where the Wonowoc aquifer is less protected from pollution because of thin or absent overlying aquitards, with only one exception.

**Mt. Simon aquifer (Figure 28)**

- **Extent**: Present throughout the entire county.
- **Depth**: Generally ranges between 70 feet along the Mississippi River to greater than 1,300 feet in the west. The greatest depths occur in the southwest, where it is deeply buried under overlying bedrock.
- **Thickness**: 300–350 feet. It is fully saturated and confined everywhere except in valleys where the overlying Eau Claire aquitard is thin or absent.
• **Use:** approximately 6 percent of wells with known construction information.

• **Mapped karst features:** No springs are mapped, however, along the Mississippi River the aquifer provides continuous discharge that serves as baseflow and artesian pressure can create flowing well conditions.

• **Pollution sensitivity:** Very low over the majority of the county and moderate in valleys and along the Mississippi River where the overlying Eau Claire aquitard is absent.

• **Residence time:** All 28 samples were from wells, 18 were analyzed for tritium age with the following results: 5 mixed and 13 vintage. Carbon-14 residence time from 8 of the vintage samples ranged between 5,500 and 25,000 years.

• **Anthropogenic chemistry:** Of the 24 samples analyzed for nitrate, none were elevated. Of the 20 samples analyzed for chloride, 2 were elevated from anthropogenic sources; 9 others were naturally elevated by ancient brine. Elevated natural chloride in the Mt. Simon is common in Winona County and elsewhere in Minnesota.

**Multiple-aquifer wells (Figure 29)**

Multiple-aquifer wells intersect more than one aquifer. Minnesota well code no longer allows well screens or open holes to span multiple aquifers because they can become conduits for contamination.

• **Residence time:** Of the 15 samples collected, 10 were analyzed for tritium age with the following results: 9 mixed and 1 vintage. One mixed tritium-age well intersects both the Wonewoc and Mt. Simon aquifers and has an estimated carbon-14 residence time of 1,000 years.

• **Anthropogenic chemistry:** Of the 12 samples analyzed for nitrate, 7 were elevated, 5 of these occurred above the St. Lawrence aquitard, and 2 occurred in combined Lone Rock–Wonewoc wells in valleys. Of the 10 samples analyzed for chloride, 7 were elevated from anthropogenic sources.
Figure 23. Pollution sensitivity of the Cummingsville through St. Peter aquifers
Sensitivity of each aquifer is very high, due to proximity to land surface, mapped karst features, and the presence of anthropogenic influences on groundwater chemistry.
Figure 24. Pollution sensitivity of the Prairie du Chien aquifer

Sensitivity is very high due to proximity to land surface over much of the county, mapped karst features, and the presence of anthropogenic influences on groundwater chemistry.
Figure 25. Pollution sensitivity of the Jordan aquifer

Sensitivity varies. Moderate sensitivity occurs where there is the entire thickness of the overlying Oneota Dolomite and at least 30 feet of the Shakopee Formation. High sensitivity is found in areas where the overlying Prairie du Chien is thinner than the criteria set for moderate sensitivity. Very high sensitivity occurs in valleys where the Jordan is the first unit below ground surface. In this setting, surface water can disappear into stream sinks and travel rapidly to springs farther down the valley.
Figure 26. Pollution sensitivity of the Lone Rock aquifer

Sensitivity is very low over the majority of the county but increases to high and very high near valley edges where the St. Lawrence aquitard is thin or absent. High sensitivity is delineated where the St. Lawrence aquitard is the only bedrock unit above the Lone Rock. Very high sensitivity is delineated where there are no overlying bedrock units.
Figure 27. Pollution sensitivity of the Wonewoc aquifer

Sensitivity is very low for most of the aquifer because of its position below the St. Lawrence aquitard and its distance from the land surface. In valleys, the sensitivity increases to moderate where it solely underlies the Lone Rock aquifer. Sensitivity increases to high in valleys where it is the first bedrock unit below land surface.
Figure 28. Pollution sensitivity of the Mt. Simon aquifer
Sensitivity is very low over the majority of the county and moderate in valleys and along the Mississippi River where the overlying Eau Claire aquitard is absent.
Figure 29. Multiple-aquifer wells

Multiple-aquifer wells intersect more than one aquifer. Minnesota well code no longer allows well screens or open holes to span multiple aquifers because they can become conduits for contamination.
The hydrogeologic cross sections shown on Plate 6 illustrate the horizontal and vertical extent of aquifers and aquitards, general groundwater flow direction, residence time, and chemistry.

The cross sections were constructed in GIS using a combination of well data from CWI and sections of Part A: Bedrock Geology (Plate 2), Surficial Geology (Plate 3), and Bedrock Topography (Plate 4). Well information was projected onto the trace of the cross section from distances no greater than 3.8 kilometers.

### Groundwater flow direction and recharge

Groundwater moves from higher to lower potential energy. The direction of groundwater movement is interpreted from the *equipotential contours* constructed from measured water levels in wells. Equipotential contours show areas where the pressure head of groundwater is the same. Groundwater flow is perpendicular to these lines in the direction of decreasing pressure. These contours can be used to identify groundwater flow direction, recharge zones, and discharge zones.

Precipitation is the source of recharge to unconsolidated deposits, which then provide recharge to deeper aquifers. Recharge to aquifers above the Jordan is heavily influenced by karst which has high infiltration rates. However, recharge may be limited where less permeable loess overlies bedrock.

- Recharge to the surficial aquifers ranges from 1.2 to 15.2 inches per year (Smith and Westenbroek, 2015).
- Recharge to bedrock aquifers is generally less than 1 percent of average precipitation, or roughly 0.33 inches per year (Delin and Falteisek, 2007).
- Recharge rates can be influenced by high-volume pumping, which may steepen groundwater gradients locally, increase recharge, and affect groundwater quality (Tipping, 2012).
- The Mississippi River is the major groundwater discharge feature for the surficial sand and bedrock aquifers.
- Groundwater discharge provides baseflow to numerous springs and trout streams.

Detailed descriptions are found on Plate 6.
Aquifer characteristics and groundwater use

Aquifer specific capacity and transmissivity

Specific capacity and transmissivity describe how easily water moves through an aquifer. Larger values indicate more productive aquifers.

**Specific capacity** is the pumping rate per unit depth of drawdown. It is typically expressed in gallons per minute per foot (gpm/ft) and is determined from short-term pumping or well-development tests performed after a well is drilled.

To ensure that the specific-capacity values reflect actual pumping (not air lifting), the pumping-test data were obtained from CWI for wells with the following criteria:

- The casing diameter was at least 6 inches.
- The well was pumped for at least 4 hours.
- The pumping-water level was inside the well casing, at least 2 feet above the well screen or open hole.

Specific-capacity values of 27 wells in Winona County met these conditions: 1 in the water-table aquifer, 2 in buried artesian aquifers (confined sand and gravel), and 24 in bedrock aquifers. The highest mean specific capacity of 13.7 gpm/ft was calculated for a bedrock well completed with an open hole across the Eau Claire aquitard and Mt. Simon aquifer (Table 2 and Figure 30).

**Transmissivity** is an aquifer’s capacity to transmit water. It provides a more accurate representation of aquifer properties than specific capacity because it is from longer-term and larger-scale aquifer tests. It is determined by multiplying the thickness of the aquifer by the hydraulic conductivity of the aquifer material (the rate groundwater flows through a unit cross section).

### Table 2. Specific-capacity values of select wells

<table>
<thead>
<tr>
<th>Aquifer</th>
<th>Casing diam. (in.)</th>
<th>Mean (gpm/ft)</th>
<th>Min (gpm/ft)</th>
<th>Max (gpm/ft)</th>
<th>No. of wells</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unconsolidated aquifers</strong></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Water table</td>
<td>8</td>
<td>12.5</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Buried artesian</td>
<td>6</td>
<td>4</td>
<td>0.5</td>
<td>7.5</td>
<td>2</td>
</tr>
<tr>
<td><strong>Bedrock aquifers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prairie du Chien</td>
<td>6</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Jordan–Wonewoc</td>
<td>20</td>
<td>4.8</td>
<td>-</td>
<td>-</td>
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</tr>
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<td>Lone Rock</td>
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<td>Lone Rock–Wonewoc</td>
<td>6</td>
<td>5.8</td>
<td>-</td>
<td>-</td>
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<td>Wonewoc</td>
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<td>Wonewoc–Eau Claire</td>
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<td>-</td>
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</tr>
<tr>
<td>Eau Claire–Mt. Simon</td>
<td>20–24</td>
<td>13.7</td>
<td>12.7</td>
<td>14.6</td>
<td>2</td>
</tr>
<tr>
<td>Mt. Simon</td>
<td>10–24</td>
<td>10.8</td>
<td>3.3</td>
<td>17.9</td>
<td>12</td>
</tr>
</tbody>
</table>

Specific capacity data adapted from the CWI
Dash means no data
A number of consulting firms and state agencies have completed aquifer tests in Winona County, but the documentation is insufficient to include in this report. Transmissivity values are shown for nine aquifer tests: 1 water-table aquifer and 8 bedrock aquifers. The water-table aquifer ranged from 18,700 ft²/day to 62,200 ft²/day. Tests from the Wonewoc aquifer ranged from 66 ft²/day to 4,540 ft²/day. Tests completed in the Mt. Simon aquifer ranged from 2,040 ft²/day to 54,900 ft²/day, including a well completed in the combined Eau Claire–Mt. Simon. The upper range for bedrock represents wells that intersect intra-aquifer fracture networks.

Figure 30. Well locations for specific capacity and transmissivity by aquifer

A number of consulting firms and state agencies have completed aquifer tests in Winona County, but the documentation is insufficient to include in this report. Transmissivity values are shown for nine aquifer tests: 1 water-table aquifer and 8 bedrock aquifers. The water-table aquifer ranged from 18,700 ft²/day to 62,200 ft²/day.

Tests from the Wonewoc aquifer ranged from 66 ft²/day to 4,540 ft²/day. Tests completed in the Mt. Simon aquifer ranged from 2,040 ft²/day to 54,900 ft²/day, including a well completed in the combined Eau Claire–Mt. Simon. The upper range for bedrock represents wells that intersect intra-aquifer fracture networks.
The DNR maintains a statewide groundwater level monitoring program for assessing groundwater resources, determining long-term trends, interpreting impacts of pumping and climate, planning for water conservation, evaluating water conflicts, and managing water resources (DNR, 2020c).

Well nests consist of closely spaced wells that are constructed in different aquifers. Long periods of record from multiple aquifers are useful for determining trends and provide insight into how aquifers respond to recharge events, climatic conditions, and pumping stresses.

Figure 31 shows the groundwater elevation hydrographs of two monitoring wells from a well nest located in the Whitewater Wildlife Management Area (WMA). Groundwater elevation is compared to daily precipitation and monthly precipitation collected at National Weather Service Reporting Station 210146 in Altura, Minnesota.

- Well 814902 is constructed to a depth of 305 feet in the Jordan aquifer and shows annual groundwater elevation increases in response to snowmelt and precipitation followed by declines over the winter months.
- Well 814903 is constructed to a depth of 500 feet in the Lone Rock aquifer and shows responses similar to well 814902.

Groundwater elevation differences between the Jordan and Lone Rock aquifers at this location show the hydraulic gradient is generally upward from the Lone Rock aquifer to the Jordan, except in the springtime when recharge to the Jordan is greater than to the underlying Lone Rock. These data show that the St. Lawrence aquitard acts a confining layer in this area of the county, which is consistent with well chemistry and the pollution sensitivity models of the Jordan and Lone Rock.

Groundwater elevation difference across the St. Lawrence can be much greater than at the Whitewater WMA nest. A pair of wells approximately 5 miles northwest of this WMA had an elevation difference between the Jordan and Lone Rock of approximately 27 feet. The protective nature of this aquitard is illustrated by large head differences across the St. Lawrence coupled with different groundwater chemistry above and below the layer (Runkel and others, 2018).

Figure 31. Hydrographs of groundwater level monitoring wells near Whitewater State Park
Groundwater use

A water appropriation permit is required from the DNR for groundwater users withdrawing more than 10,000 gallons of water per day or 1 million gallons per year. This provides the DNR with the ability to assess which aquifers are being used and for what purpose. Permits require annual water-use reporting. This information is recorded using the Minnesota Permitting and Reporting System (MPARS), which helps the DNR track the volume, source aquifer, and type of water use.

Reported water use of high-volume users for 2017 is categorized in Table 3 and in Figures 32 and 33 by type of water use and aquifer type (DNR, 2018). The highest permitted groundwater use (66 percent) is for municipal and public water supply, with the majority extracted from the Mt. Simon aquifer. In general, high-volume use is centered in the city of Winona, but also near the cities of St. Charles, Lewiston, Altura, and Stockton. The second largest use (14 percent) is for metal processing, with the majority of this water coming from the Mt. Simon aquifer, and with additional from the Lone Rock and Wonewoc aquifers (multiple aquifer well). The third largest use (7 percent) is for agriculture and food processing, which primarily uses the Mt. Simon aquifer. These three water uses collectively made up approximately 87 percent of the permitted water used in 2017.

There are no reporting requirements for well owners that use less than 10,000 gallons per day or 1 million gallons per year, but the CWI maintains data for well use type and aquifer type for these wells. This report included approximately 3,500 wells in the analysis. Of the wells with identified use codes, the majority are for domestic use (70 percent). Of the wells with identified aquifers, most are completed in the Wonewoc (73 percent), followed by the Lone Rock (12 percent), and finally the Jordan (11 percent).

Permitted water use varies annually due to factors such as annual precipitation and economic conditions. Municipal water supply had the largest use difference over the 5-year period from 2013–2017.

Table 3. Reported 2017 water use from DNR groundwater permit holders

<table>
<thead>
<tr>
<th>Aquifer</th>
<th>No. of wells</th>
<th>Water supply</th>
<th>Industrial</th>
<th>Noncrop irrigation</th>
<th>Special use</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Municipal/public water supply</td>
<td>Commercial/Institutional/Private water supply</td>
<td>Metal processing</td>
<td>Agriculture/food processing</td>
</tr>
<tr>
<td>Quaternary aquifers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water table</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bedrock aquifers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jordan, Jordan–St. Lawrence</td>
<td>9</td>
<td>22.7</td>
<td>0.9</td>
<td>5.5</td>
<td>4.8</td>
</tr>
<tr>
<td>Lone Rock</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lone Rock–Eau Claire, Lone Rock–Wonewoc</td>
<td>9</td>
<td>2.3</td>
<td>3.9</td>
<td>33.6</td>
<td>39.9</td>
</tr>
<tr>
<td>Wonewoc, Wonewoc–Eau Claire</td>
<td>8</td>
<td>9.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eau Claire–Mt. Simon, Mt. Simon</td>
<td>27</td>
<td>1,104.5</td>
<td>1.4</td>
<td>251.7</td>
<td>131.5</td>
</tr>
<tr>
<td>Jordan–Wonewoc, Wonewoc–Mt. Simon</td>
<td>3</td>
<td>74.2</td>
<td>13.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (mgy)</td>
<td>--</td>
<td>1,213.0</td>
<td>15.0</td>
<td>255.6</td>
<td>132.4</td>
</tr>
<tr>
<td>Total (percent)</td>
<td>--</td>
<td>65.8</td>
<td>0.8</td>
<td>13.9</td>
<td>7.2</td>
</tr>
<tr>
<td>Highest annual use from 2013 to 2017 (mgy)</td>
<td>--</td>
<td>1,373.8</td>
<td>22.7</td>
<td>284.2</td>
<td>354.6</td>
</tr>
</tbody>
</table>

Data from MPARS; mgy, million gallons per year; dash marks (--) indicate no use in those categories; percentages may not equal 100 due to rounding.
Figure 32. Distribution of groundwater appropriation permits for 2017 by volume reported and use type

Municipal and public water supply accounts for the largest permitted groundwater use.
Figure 33. Distribution of groundwater appropriation permits for 2017 by volume reported and general aquifer classification

The majority of permitted water used in the county is from bedrock aquifers.
References


DNR, 2016a, Methods for estimating water-table elevation and depth to water table: Minnesota Department of Natural Resources, Groundwater Atlas Program, GW-04.

DNR, 2016b, Minnesota regions prone to surface karst feature development: Minnesota Department of Natural Resources, Groundwater Atlas Program, GW-01.

DNR, 2016c, Methods to estimate near-surface pollution sensitivity: Minnesota Department of Natural Resources, Groundwater Atlas Program, GW-03.
MDH, 2012a, Human health-based water guidance table: Minnesota Department of Health website under Environmental Health.


MDH, 2017 October, Boron and drinking water: Minnesota Department of Health, Human Health-Based Water Guidance Table website.

MDH, 2018a, Arsenic in well water: Minnesota Department of Health, document ID# 52971.

MDH, 2018b, Manganese in drinking water: Minnesota Department of Health, Health Risk Assessment Unit Information Sheet.


### Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>anion</td>
<td>a negatively charged ion in which the total number of electrons is greater than the total number of protons, resulting in a net negative electrical charge.</td>
</tr>
<tr>
<td>anthropogenic</td>
<td>relating to or resulting from the influence of humans on nature.</td>
</tr>
<tr>
<td>aquifer</td>
<td>an underground layer of water-bearing permeable rock or unconsolidated materials (sand and gravel) from which groundwater can be extracted using a water well.</td>
</tr>
<tr>
<td>aquitard (or confining layers)</td>
<td>layers made up of materials with low permeability, such as clay and shale, which prevent rapid or significant movement of water.</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>a chemical element that is sometimes dissolved in groundwater and is toxic to humans. Natural arsenic contamination of groundwater affects millions of people across the world, including over 100,000 people served by domestic wells in Minnesota.</td>
</tr>
<tr>
<td>bedrock</td>
<td>the consolidated rock underlying unconsolidated surface materials such as soil or glacial sediment.</td>
</tr>
<tr>
<td>buried aquifer</td>
<td>a body of porous and permeable sediment or bedrock which is separated from the land surface by low permeability layer(s).</td>
</tr>
<tr>
<td>carbon-14 (14C)</td>
<td>a radioactive isotope of carbon that has a half-life of 5,730 years. It is used to identify groundwater that entered the ground from less than 50 to greater than 40,000 years before present.</td>
</tr>
<tr>
<td>cation</td>
<td>a positively charged ion in which the number of electrons is less than the number of protons, resulting in a net positive electrical charge.</td>
</tr>
<tr>
<td>County Well Index (CWI)</td>
<td>a database developed and maintained by the Minnesota Geological Survey and the Minnesota Department of Health containing basic information for wells drilled in Minnesota. Information includes location, depth, static water level, construction, and geological information. The database and other features are available through the Minnesota Well Index online mapping application.</td>
</tr>
<tr>
<td>dolostone, or dolomite rock</td>
<td>a sedimentary carbonate rock that contains a high percentage of the mineral dolomite. Most dolostone formed as a magnesium replacement of limestone or lime mud prior to lithification. It is resistant to erosion and can either contain bedded layers or be unbedded. It is less soluble than limestone, but it can still develop solution features over time.</td>
</tr>
<tr>
<td>formation</td>
<td>a fundamental unit of lithostratigraphy. A formation consists of a number of rock strata that have a comparable lithology, facies, or other similar properties.</td>
</tr>
<tr>
<td>fractionation</td>
<td>a separation process in which a mixture (solid, liquid, solute, suspension, or isotope) is divided based on the difference of a specific property of the components. Stable isotopes are fractionated by mass.</td>
</tr>
<tr>
<td>groundwater</td>
<td>water that collects beneath the surface of the earth, filling the porous spaces below the water table in soil, sediment, and rocks.</td>
</tr>
<tr>
<td>half-life</td>
<td>the time required for one half of a given mass of a radioactive element to decay.</td>
</tr>
<tr>
<td>hydrogeology</td>
<td>the study of subsurface water, including its physical and chemical properties, geologic environment, role in geologic processes, natural movement, recovery, contamination, and use.</td>
</tr>
<tr>
<td>hydraulic</td>
<td>relating to water movement.</td>
</tr>
<tr>
<td>hydraulic conductivity</td>
<td>the rate at which groundwater flows through a unit cross section of an aquifer.</td>
</tr>
<tr>
<td>infiltration</td>
<td>the movement of water from the land surface into the subsurface under unsaturated conditions.</td>
</tr>
<tr>
<td>isotope</td>
<td>variants of a particular chemical element. All isotopes of an element share the same number of protons but a different number of neutrons.</td>
</tr>
<tr>
<td>meteoric</td>
<td>relating to or derived from the earth's atmosphere.</td>
</tr>
<tr>
<td>nitrate (NO3, nitrate-nitrogen, nitrate-N)</td>
<td>a common form of nitrogen (N), the water-soluble anion NO3-. Elevated nitrate in water samples is a useful indicator of groundwater pollution by human activities. Humans are subject to nitrate toxicity, with infants especially vulnerable to methemoglobinemia, also known as blue baby syndrome. Nitrogen is an important nutrient, a major component of fertilizers, and a significant component of animal and human waste.</td>
</tr>
<tr>
<td>Paleozoic</td>
<td>an era of geologic time from approximately 542–251 million years ago.</td>
</tr>
<tr>
<td>potentiometric surface</td>
<td>a surface representing the total head of groundwater in an aquifer, defined by the levels to which water will rise in tightly cased wells.</td>
</tr>
<tr>
<td>Quaternary</td>
<td>geologic time period that began 2.588 million years ago and continues to today. The Quaternary Period comprises the Pleistocene and Holocene epochs.</td>
</tr>
</tbody>
</table>
radioactive—a property of an element that spontaneously decays or changes to a different element through the emission of radioactive particles.

recharge—the process by which water enters the groundwater system.

residence-time indicators—chemical and/or isotope used to interpret groundwater residence time.

specific capacity—the discharge of a well divided by the drawdown in the well.

stable isotope—chemical isotopes that are not radioactive.

static water level—the level of water in a well that is not affected by pumping.

stratigraphy—a branch of geology that studies rock layers and layering (stratification). It is primarily used in the study of sedimentary and layered volcanic rocks.

till—unsorted glacial sediment deposited directly by ice. It is derived from the erosion and entrainment of rock and sediment.

transmissivity—an aquifer’s capacity to transmit water, determined by multiplying the hydraulic conductivity of the aquifer material by the thickness of the aquifer.

tritium (³H)—a radioactive isotope of hydrogen that has a half-life of 12.32 years. The nucleus of tritium contains one proton and two neutrons. It is used to identify groundwater that entered the ground since the 1950s.

tritium unit (TU)—one tritium unit represents the presence of one tritium atom for every \(10^{18}\) hydrogen atoms.

unconfined—an aquifer that has direct contact with the atmosphere through an unsaturated layer.

water table—the surface between the unsaturated and saturated zone where the water pressure equals the atmospheric pressure.

watershed—the area of land that drains into a specific downstream location.

well nest—two or more wells in close proximity completed in different aquifers.
Appendix A

Groundwater field sample collection protocols

Groundwater samples were collected from an outside faucet or hydrant. The wells were purged prior to sampling to remove stagnant water from the well bore and plumbing system. Samples were collected after the following field parameters had stabilized: temperature, dissolved oxygen, conductivity, oxidation reduction potential, and pH. Each was filtered and preserved according to protocols listed below and submitted to laboratories for analysis.

Project samples collected prior to 2016 were analyzed by DNR staff; the University of Minnesota, Department of Earth and Environmental Sciences Laboratory (UMN); or the University of Waterloo Environmental Isotope Laboratory (Waterloo). The well owners received a copy of the results including some background reference information regarding their meaning.

Appendix Table A-1. Groundwater field sample collection and handling details for project samples collected prior to 2016

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Enriched tritium</th>
<th>$^{18}$O and $^2$H (Deuterium)</th>
<th>Cations</th>
<th>Anions</th>
<th>Trace constituents</th>
<th>Alkalinity</th>
<th>$^{14}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab</td>
<td>Waterloo</td>
<td>Waterloo</td>
<td>UMN</td>
<td>UMN</td>
<td>UMN</td>
<td>DNR</td>
<td>UMN</td>
</tr>
<tr>
<td>Sample container</td>
<td>500 ml HDPE</td>
<td>60 ml HDPE</td>
<td>15 ml Fisherbrand BLUE cap</td>
<td>50 ml Argos BLACK bottle***</td>
<td>15 ml Sarstedt RED cap</td>
<td>500 ml plastic</td>
<td>30 gallon barrel</td>
</tr>
<tr>
<td>Head space</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Rinse</td>
<td>no</td>
<td>no</td>
<td>yes*</td>
<td>yes*</td>
<td>yes*</td>
<td>yes**</td>
<td>no</td>
</tr>
<tr>
<td>Filter</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Preservative</td>
<td>no</td>
<td>no</td>
<td>1 drop 6N HCl</td>
<td>no</td>
<td>5 drops 15N HNO$_3$</td>
<td>no</td>
<td>NH$_4$OH added to adjust pH</td>
</tr>
<tr>
<td>Refrigeration</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes, if not analyzed onsite</td>
<td>no</td>
</tr>
<tr>
<td>Shelf life</td>
<td>long</td>
<td>long</td>
<td>2–3 weeks</td>
<td>2–3 weeks</td>
<td>2–3 weeks</td>
<td>24–48 hours</td>
<td>years</td>
</tr>
<tr>
<td>Field Duplicate</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Field blank</td>
<td>none</td>
<td>none</td>
<td>1 for every 20****</td>
<td>1 for every 20****</td>
<td>1 for every 20****</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Storage duplicate</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

*Sample bottle was rinsed three times with sample water prior to collecting the sample (filtered water if sample was filtered). Rinsing process was filling the bottle with sample water and then pouring the contents out over the cap.

**Rinsed the bottle three times with sample water prior to collecting the sample. Bottle and cap were submerged and sealed to ensure no remnant bubbles.

*** 50 ml anion bottle was filled, unless filtering was very difficult. All bottles were filled to at least 1/3 full.

****Deionized (DI) water was used for field blanks. DI water was poured into the back of filtering syringes when the plunger was removed. Bottles were filled by forcing water through filter.
Project samples collected in 2016 and 2017 were analyzed by DNR staff; the Minnesota Department of Agriculture (MDA); the Minnesota Department of Health (MDH); the University of Minnesota, Department of Earth and Environmental Sciences Laboratory (UMN); or the University of Waterloo Environmental Isotope Laboratory (Waterloo).

Appendix Table A-2. Groundwater field sample collection and handling details for project samples collected in 2016 and 2017

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Enriched tritium</th>
<th>$^{18}$O and $^2$H (Deuterium)</th>
<th>Nitrate/Nitrite &amp; Total Phosphorus</th>
<th>F, Cl, SO$_4^-$</th>
<th>Metals</th>
<th>Bromide</th>
<th>Alkalinity</th>
<th>$^{14}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab</td>
<td>Waterloo</td>
<td>Waterloo</td>
<td>MDA</td>
<td>MDA</td>
<td>MDA</td>
<td>MDH</td>
<td>DNR</td>
<td>UMN</td>
</tr>
<tr>
<td>Sample container</td>
<td>500 ml HDPE</td>
<td>60 ml HDPE</td>
<td>250 ml plastic</td>
<td>250 ml plastic</td>
<td>250 ml plastic</td>
<td>125 ml plastic</td>
<td>500 ml plastic</td>
<td>30 gallon barrel</td>
</tr>
<tr>
<td>Head space</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>Rinse</td>
<td>no</td>
<td>no</td>
<td>yes*</td>
<td>yes*</td>
<td>yes*</td>
<td>yes**</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>Filter (micron)</td>
<td>no</td>
<td>no</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>no</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>Preservative</td>
<td>no</td>
<td>no</td>
<td>5 ml 10 percent H$_2$SO$_4$ (yellow cap)</td>
<td>no</td>
<td>2.5 ml 20 percent HNO$_3$ (red cap)</td>
<td>no</td>
<td>no</td>
<td>NH$_4$OH to pH 8.5</td>
</tr>
<tr>
<td>Refrigeration</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes, if not analyzed onsite</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>Holding Time</td>
<td>long</td>
<td>long</td>
<td>28 days</td>
<td>28 days</td>
<td>6 months</td>
<td>28 days</td>
<td>24–48 hours</td>
<td>years</td>
</tr>
<tr>
<td>Field duplicate</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>1 for every 20 samples</td>
<td>none</td>
</tr>
<tr>
<td>Field blank</td>
<td>none</td>
<td>none</td>
<td>1 for every 20***</td>
<td>1 for every 20***</td>
<td>1 for every 20***</td>
<td>1 for every 20***</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Storage duplicate</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td></td>
</tr>
</tbody>
</table>

*Rinse the bottle three times with sample water prior to collecting the sample (FILTERED if sample is filtered). Rinsing process was filling the bottle with sample water and then pouring the contents out over the cap.

**Rinsed the bottle three times with sample water prior to collecting the sample. Bottle and cap were submerged and sealed to ensure no remnant bubbles.

***Use DI water from designated lowboy for blanks. Attach lowboy to the inline filter with a 3/8” tube and purge 1 L of water to rinse tubing and filter. Rinse and fill bottles through filter with the procedures outlined above.
Appendix B

Tritium values from precipitation

Samples were analyzed for enriched tritium by the University of Waterloo Environmental Isotope Laboratory for determination of tritium values. Precipitation composites were collected at a Minnesota DNR MNgage climatology monitoring station in Maplewood (Twin Cities metropolitan area). Samples were composited over the course of 30-day periods between spring and fall over the years 2012 through 2017.

For additional tritium information, contact the DNR Groundwater Atlas Program.

For additional weather station information, contact the MNgage program.

Appendix Table B-1. Enriched tritium results from MNgage precipitation station 62 29 22 9 BOULAY P

<table>
<thead>
<tr>
<th>Sample date range</th>
<th>Tritium (TU)</th>
<th>Analytical error</th>
<th>Sample type</th>
</tr>
</thead>
<tbody>
<tr>
<td>05/21/2012–06/20/2012</td>
<td>8.7</td>
<td>0.7</td>
<td>Precipitation composite</td>
</tr>
<tr>
<td>09/30/2012–10/30/2012</td>
<td>6.7</td>
<td>0.7</td>
<td>Precipitation composite</td>
</tr>
<tr>
<td>05/09/2014–06/09/2014</td>
<td>7.0</td>
<td>0.7</td>
<td>Precipitation composite</td>
</tr>
<tr>
<td>10/01/2014–10/31/2014</td>
<td>6.7</td>
<td>0.7</td>
<td>Precipitation composite</td>
</tr>
<tr>
<td>05/01/2015–05/31/2015</td>
<td>5.3</td>
<td>0.6</td>
<td>Precipitation composite</td>
</tr>
<tr>
<td>08/17/2016–09/16/2016</td>
<td>8.3</td>
<td>0.8</td>
<td>Precipitation composite</td>
</tr>
<tr>
<td>04/01/2017–04/30/2017</td>
<td>8.1</td>
<td>0.7</td>
<td>Precipitation composite</td>
</tr>
<tr>
<td>09/06/2017–10/06/2017</td>
<td>6.5</td>
<td>0.6</td>
<td>Precipitation composite</td>
</tr>
</tbody>
</table>

Tritium age of historic groundwater samples

The Part B atlas series uses tritium data to assess the residence time of groundwater, which is then used to evaluate atlas pollution sensitivity models and recharge conditions. Where current data is insufficient, historical data is used from collaborating partners.

Residence time is classified for the time the sample was collected. Historic tritium unit (TU) values change over time because of tritium’s relatively short half-life of 12.32 years (Lucas and Unterweger, 2000). Historic values were converted to coincide with the time of sample collection for this atlas as shown in Table B-2.

The Cold War era classification is a special case and implies that groundwater sampled for an atlas infiltrated into the ground in the 1960s. This classification is only assigned to samples collected contemporaneously with an atlas. No samples collected for the Winona project had a Cold War era classification.

Appendix Table B-2. Tritium classification by date of sample collection

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold War era</td>
<td>&gt;15 TU</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Recent</td>
<td>≥8 to 15 TU</td>
<td>≥8 TU</td>
<td>≥10 TU</td>
</tr>
<tr>
<td>Mixed</td>
<td>&gt;1 to &lt;8 TU</td>
<td>&gt;1 and &lt;8 TU</td>
<td>&gt;1 and &lt;10 TU</td>
</tr>
<tr>
<td>Vintage</td>
<td>≤1 TU</td>
<td>≤1 TU</td>
<td>≤1 TU</td>
</tr>
</tbody>
</table>
500 Lafayette Road
St. Paul, MN 55155-4025
888-646-6367 or 651-296-6157
mndnr.gov

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