Southeast Minnesota Domestic Well Network 2016 Data Report

MDH Minnesota Department *of* Health

DRINKING WATER PROTECTION SECTION

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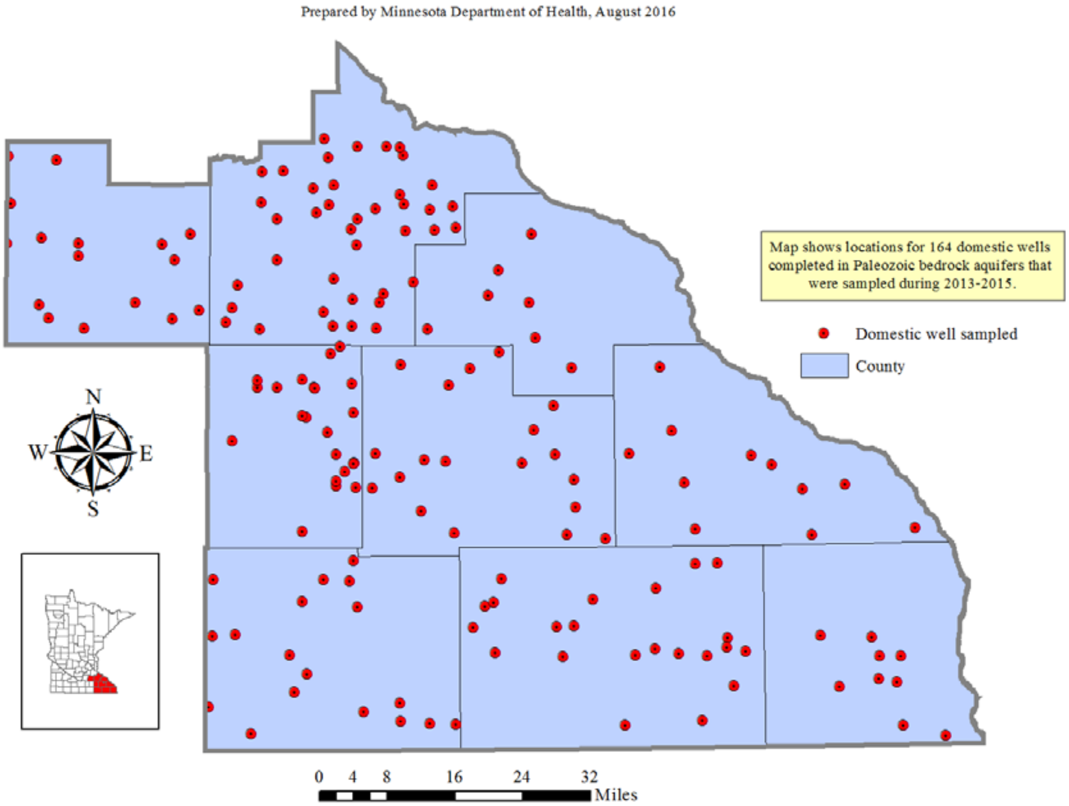
Contents

Introduction

This report presents data and summarizes the latest activities involving ground water sampling and analysis from a subset of wells in the Southeast Minnesota Domestic Well Network (Figure 1). Activities accomplished during the reporting period (August 2013 through June 2015) include the analysis of major ions, trace metals, arsenic, gross alpha and tritium, compared to previous sampling rounds where only nitrate analyses were conducted.

Figure 1. Southeast Minnesota Domestic Well Network Sampling Locations, 2013-2015



The purposes of this report are to:

- Archive project activities since the previous Minnesota Department of Health (MDH) progress report (MDH, 2012a);
- Summarize recently acquired ground water quality data for project bedrock wells; and

- Preserve the domestic well network as “virtual infrastructure” for future groundwater sampling needs.

Existing information valuable to this project has been collected from several sources. Tipping (1994) assessed ground water quality in domestic wells across southeastern Minnesota based on data collected in the 1990s as part of the Minnesota Pollution Control Agency (MPCA) Ground Water Monitoring and Assessment Program (GWMAP); https://www.pca.state.mn.us/water/groundwater-monitoring-and-assessment). Steenberg, et al. (2013) and Runkel, et al. (2013) provide recent insight on factors controlling nitrate occurrence in southeastern Minnesota ground water.

Two previous project reports also provided information:

1. MDH (2009) discussed contributions during the initial project phase comprising network assembly and the first four rounds of sample collection for nitrate analysis; and
2. MDH (2012a) described the methods used to evaluate well construction and geologic data to assess the hydrogeologic sensitivity for wells in the network with only minimal well construction or geologic information.

Project Background

Project origin and history

Domestic well drinking water quality is a concern across southeastern Minnesota, where nitrate loading to the subsurface can be significant and hydrogeologic sensitivity varies between low and very high. Yet the opportunity for technical assistance to domestic well owners concerned about drinking water quality is limited.

In 2007, a consortium of nine southeastern Minnesota counties called the Southeast Minnesota Water Resources Board (SEMNWRB; http://semnwrb.winonastatenews.com/) received a federal 319 grant to establish and monitor a network of domestic drinking water wells for nitrate over time. The grant included funds sufficient for four sampling rounds, and the project featured in-kind contributions from other partners including MPCA, Minnesota Department of Agriculture (MDA), and MDH.

Before sample collection could begin, well network coordinators (county staff) enrolled volunteers (domestic well owners) into the program by collecting detailed information about well location, well construction, and nearby nitrate sources. The resulting Southeast Minnesota Domestic Well Network[1] of over 500 domestic drinking water wells was designed to provide nitrate concentration data to answer the question “what is the quality of water that people are drinking?”

After the first four rounds of sample collection (February 2008 through August 2009), a grant extension funded continued annual nitrate sampling during August of 2010, 2011 and 2012 (rounds 5, 6, and 7). MPCA dedicated Clean Water Funds from the Ambient Groundwater Monitoring Network support additional sample collection and laboratory analysis. This sampling and analysis was performed on a subset of the Southeast Minnesota Domestic Well Network during sampling rounds 8, 9 and 10, completed in June 2015, and is the subject of this report.

Sampling was conducted at wells for which adequate geologic and well construction information was available to allow for a better hydrogeochemical interpretation of water quality results. A total of 206 wells were sampled in the project. Of these, 15 wells were verified

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[1] The original name, the “volunteer nitrate monitoring network”, is modified to reflect the recent expansion of the analyte list discussed in this report.

to be completed in Quaternary aquifers, 168 were verified to be completed in Paleozoic bedrock aquifers, and there was insufficient information to assign an aquifer to the remaining wells. This report only discusses water quality results for the 168 verified Paleozoic bedrock aquifer wells.

Project approach

The initial sampling rounds relied upon a low-cost, non-laboratory nitrate analysis (Hach 4000 spectrophotometer). This nitrate analysis was used during sampling rounds 1 through 7 because: 1) it conserved funds; 2) there is a known strong (greater than 97%) correlation between laboratory and non-laboratory nitrate results; and 3) the sample results were not regulatory, but advice to well owners, who were free to obtain subsequent laboratory analytical samples if desired.

The data presented in this report move away from owner-collected, non-laboratory methods, to professional samplers following standard field procedures to deliver samples to a laboratory for analysis under standard quality assurance requirements.

Project Area Description

The project area (Figure 1) is defined by the nine-county jurisdiction of the SEMNWRB. The geology and hydrogeology of the area is known from over 100 years of study, and is summarized here from published sources.

Paleozoic bedrock geology

The bedrock geology of the nine county area project area is known from geologic mapping and previous studies. Minnesota Geological Survey (MGS) created Part A County Geological Atlases for eight of the nine counties, and other mapping complete the bedrock geologic coverage of the project area. A representative stratigraphic column for southeastern Minnesota is shown in Figure 2.

The sedimentary rocks of southeastern Minnesota consist of a transitional sequence from the Cambrian Mt. Simon and Tunnel City-Wonewoc[2] sandstones to the carbonate rocks of the Devonian Cedar Valley Group. These rocks were deposited within a broad shallow depression during Paleozoic time.

Quaternary geology

The Quaternary history consists of Pleistocene till and outwash deposition in the west, and erosion in the east and southeast. Areas of ground moraine and end moraine are extensive and achieve thicknesses of several hundred feet in some areas. An early remnant clay till sheet covers significant parts of Goodhue, Dodge, and Mower counties, and is variously known as Pierce Formation, Old Gray Till, or Browerville Formation. A younger sand-silt-clay till mixture is present in the westernmost portion of the project area, and is known as the Des Moines Lobe Till.

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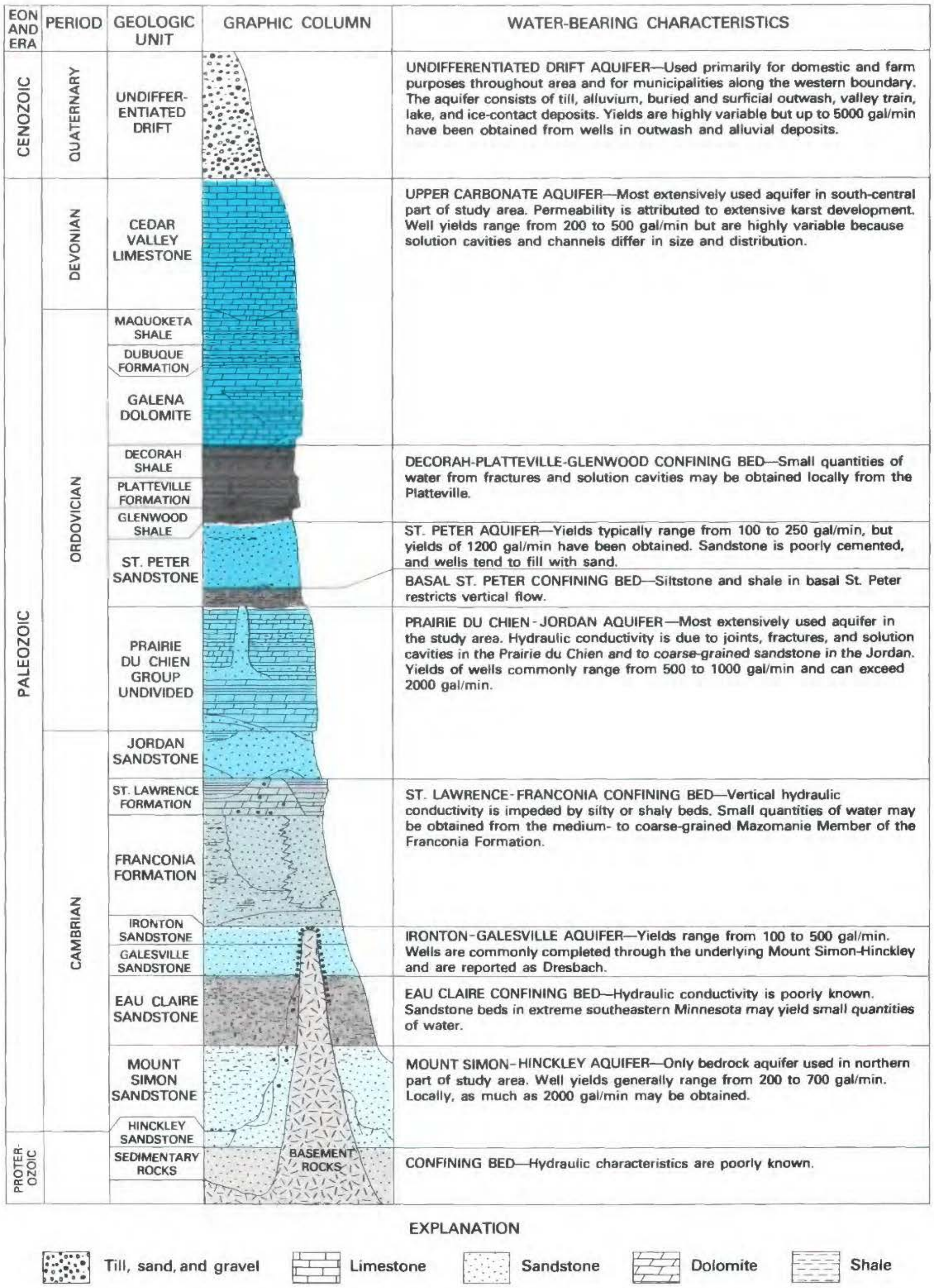
[2] The Tunnel City-Wonewoc was formerly known as the "Franconia-Ironton-Galesville" sandstone as shown in Figure 2 below.

Figure 2. Representative stratigraphic section for southeastern Minnesota (Delin and Woodward, 1984). Hydrogeology



UNDIFFERENTIATED DRIFT AQUIFER—Used primarily for domestic and farm purposes throughout area and for municipalities along the western boundary. The aquifer consists of till, alluvium, buried and surficial outwash, valley train, lake, and ice-contact deposits. Yields are highly variable but up to 5000 gal/min have been obtained from wells in outwash and alluvial deposits.

UPPER CARBONATE AQUIFER—Most extensively used aquifer in south-central part of study area. Permeability is attributed to extensive karst development. Well yields range from 200 to 500 gal/min but are highly variable because solution cavities and channels differ in size and distribution.

DECORAH-PLATTEVILLE-GLENWOOD CONFINING BED—Small quantities of water from fractures and solution cavities may be obtained locally from the Platteville.

ST. PETER AQUIFER—Yields typically range from 100 to 250 gal/min, but yields of 1200 gal/min have been obtained. Sandstone is poorly cemented, and wells tend to fill with sand.

BASAL ST. PETER CONFINING BED—Siltstone and shale in basal St. Peter restricts vertical flow.

PRAIRIE DU CHIEN-JORDAN AQUIFER—Most extensively used aquifer in the study area. Hydraulic conductivity is due to joints, fractures, and solution cavities in the Prairie du Chien and to coarse-grained sandstone in the Jordan. Yields of wells commonly range from 500 to 1000 gal/min and can exceed 2000 gal/min.

ST. LAWRENCE-FRANCONIA CONFINING BED—Vertical hydraulic conductivity is impeded by silty or shaly beds. Small quantities of water may be obtained from the medium- to coarse-grained Mazomanie Member of the Franconia Formation.

IRONTON-GALESVILLE AQUIFER—Yields range from 100 to 500 gal/min. Wells are commonly completed through the underlying Mount Simon-Hinckley and are reported as Dresbach.

EAU CLAIRE CONFINING BED—Hydraulic conductivity is poorly known. Sandstone beds in extreme southeastern Minnesota may yield small quantities of water.

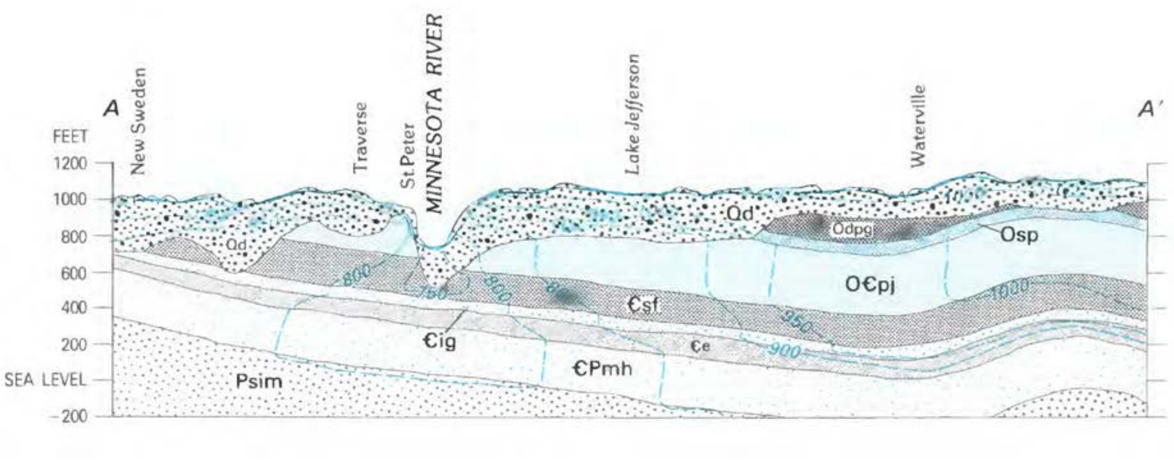
MOUNT SIMON-HINCKLEY AQUIFER—Only bedrock aquifer used in northern part of study area. Well yields generally range from 200 to 700 gal/min. Locally, as much as 2000 gal/min may be obtained.

CONFINING BED—Hydraulic characteristics are poorly known.

Hydrogeology

Within the project area, ground water flows generally eastward within bedrock aquifers toward the Mississippi River. Recharge is generally in the west and ground water discharge is to the east. Ground water flow within the deepest portion of the Paleozoic bedrock aquifer system (Figure 3) achieves depths of 1,000 feet. Carbon-14 analyses show these waters are greater than 35,000 years old (Lively, et al., 1992). Ground water ages for shorter flow paths are recent, as indicated by the common presence of tritium. Fractures are abundant in carbonate aquifers such as the Prairie du Chien and Galena, leading to rapid flow and little filtration of surface contaminants. In such settings, the detection of surface contaminants such as nitrate, pathogens, and agricultural chemicals can demonstrate fast recharge and rapid ground water flow.

Figure 3. Cross section through southern Minnesota



Representative cross section through southern Minnesota (from Delin and Woodward, 1984). Arrows indicate recharge in the west, and discharge east to the Mississippi River. The deepest flow paths are within the basal sandstone layer (Mt. Simon) and carbon.

Bedrock wells sampled for this project were completed in four major bedrock aquifers (see Table 1 below, left column): Devonian Upper Carbonate; Galena; St. Peter-Prairie du Chien-Jordan; and the Tunnel City-Wonewoc. Impermeable rock composed primarily of shale provide confinement between aquifers (right-hand column of Table 1), and some degree of natural protection from contaminants. Hydrogeologic Sensitivity

Hydrogeologic sensitivity is defined as the likelihood that an aquifer will remain isolated from surface contaminants due to intrinsic physical attributes of the geologic setting or geomorphology. A well can be assigned low, moderate, or high hydrogeologic sensitivity according to the presence, partial presence, or absence of overlying low-permeability geologic layers (Table 1) that could provide protection of the aquifer from surface pollutants (Figure 4).

Table 1. Aquifers and Confining Units of the Project Area

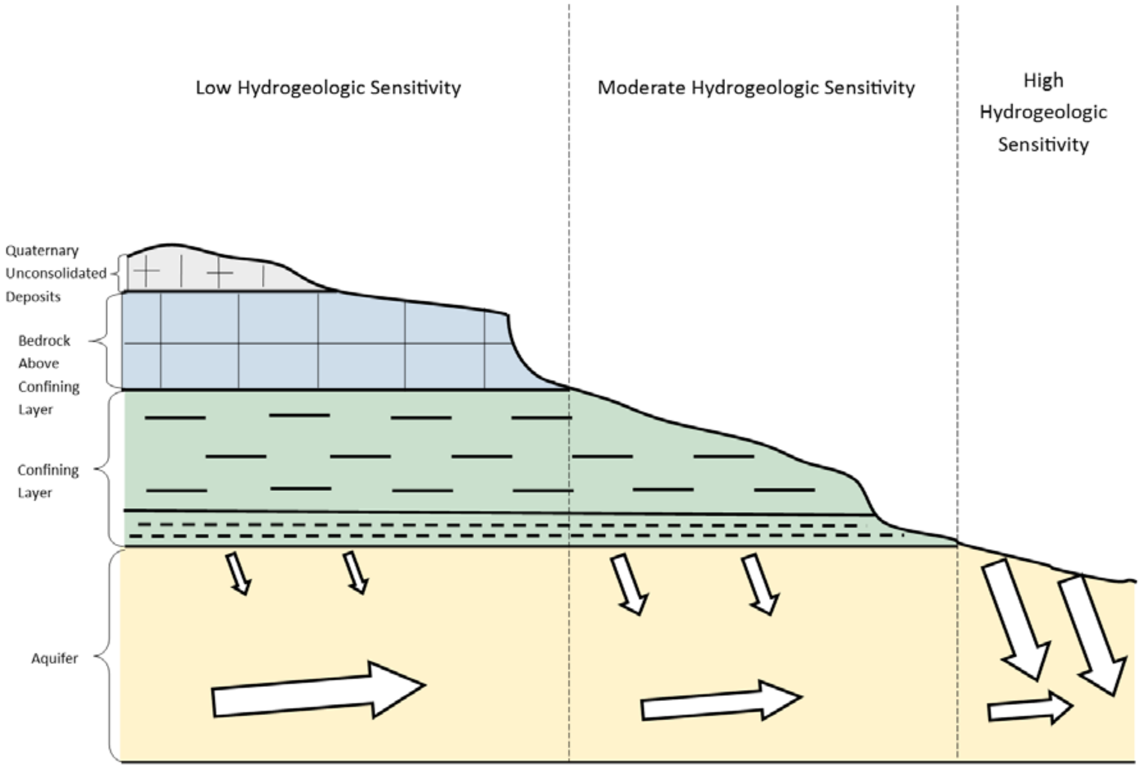
Feature Name (in descending order by depth)	Feature Type
Devonian upper carbonate	Aquifer (coarse clastic and carbonate rocks)
Makoqueta Fm.	Confining Unit (fine clastic rocks)
Galena	Aquifer (coarse clastic and carbonate rocks)
Decorah-Platteville-Glenwood	Confining Unit (fine clastic rocks)
St. Peter-Prairie du Chien-Jordan	Aquifer (coarse clastic and carbonate rocks)
St. Lawrence	Confining Unit (fine clastic rocks)
Tunnel City-Wonewoc	Aquifer (coarse clastic and carbonate rocks)

Figure 4 generalizes low, moderate and high hydrogeologic sensitivity, independent of any particular aquifer system. The figure also suggests relative contributions of water flow for each of the three settings. Groundwater originating from low sensitivity settings would be expected to move along primarily horizontal flow paths, with the water having entered the ground water flow field hundreds or thousands of years ago. Vertical recharge rates are very low, yet may still contribute significant water to the system over large areas. In low sensitivity settings, the likelihood of land use to affect ground water quality is low.

In moderate sensitivity settings vertical recharge becomes more important as the lateral and vertical integrity of the confining layer decreases due to erosion. Therefore, the likelihood of land use to affect ground water quality in moderate sensitivity settings is somewhat greater than for low sensitivity settings.

In high sensitivity settings, vertical flow becomes most important. Where vertical flow is downward as shown in Figure 4, ground water quality impacts from land use may be likely. In areas that are major groundwater discharge zones (e.g., close to the Mississippi River), the ground water flow direction may be strongly upwards (counter-intuitively changing the vulnerability to low), but this setting did not occur for wells sampled in this project. Figures 5 through 8 show the locations and hydrogeologic sensitivities of the wells sampled within the four aquifer systems.

Figure 4. Schematic diagram showing three bedrock hydrogeologic settings.



Arrows show changing direction and magnitude of lateral ground water flow and recharge with changing bedrock hydrogeologic setting. Where the full thickness of the confining layer (green) is present as indicated by the presence of overlying formations (blue, left side of figure), the bedrock hydrogeologic sensitivity is low. Where the confining layer is present but partly eroded, as shown by the absence of the overlying formations (middle of figure), the bedrock hydrogeologic sensitivity is moderate. Where the confining layer is completely absent and the aquifer subcrops (right side of figure), the bedrock hydrogeologic sensitivity is high.

Figure 5. Sampled Wells and Hydrogeologic Settings Within the Devonian Upper Carbonate Aquifer

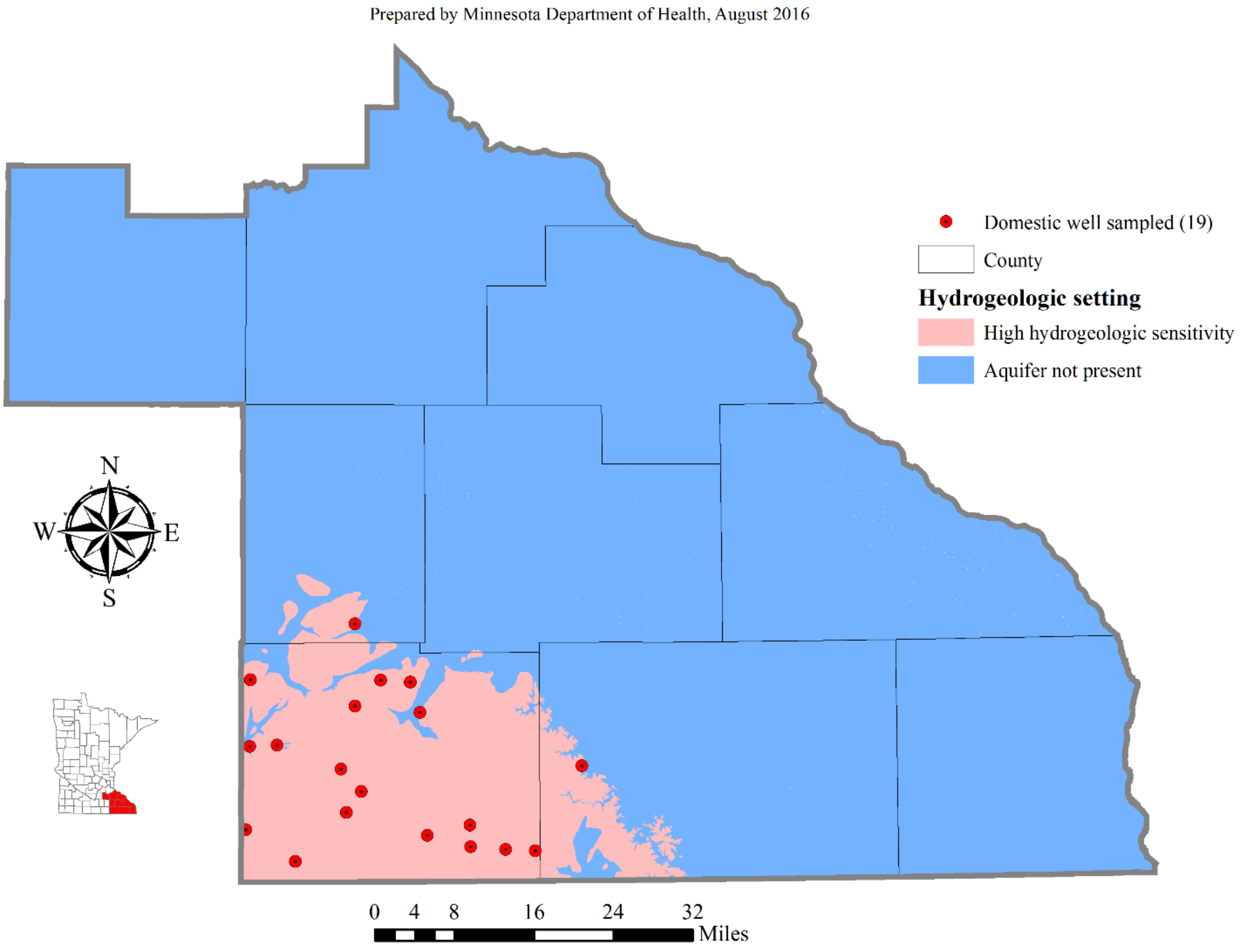


Figure 6. Sampled Wells and Hydrogeologic Settings within the Galena Aquifer

Prepared by Minnesota Department of Health, August 2016

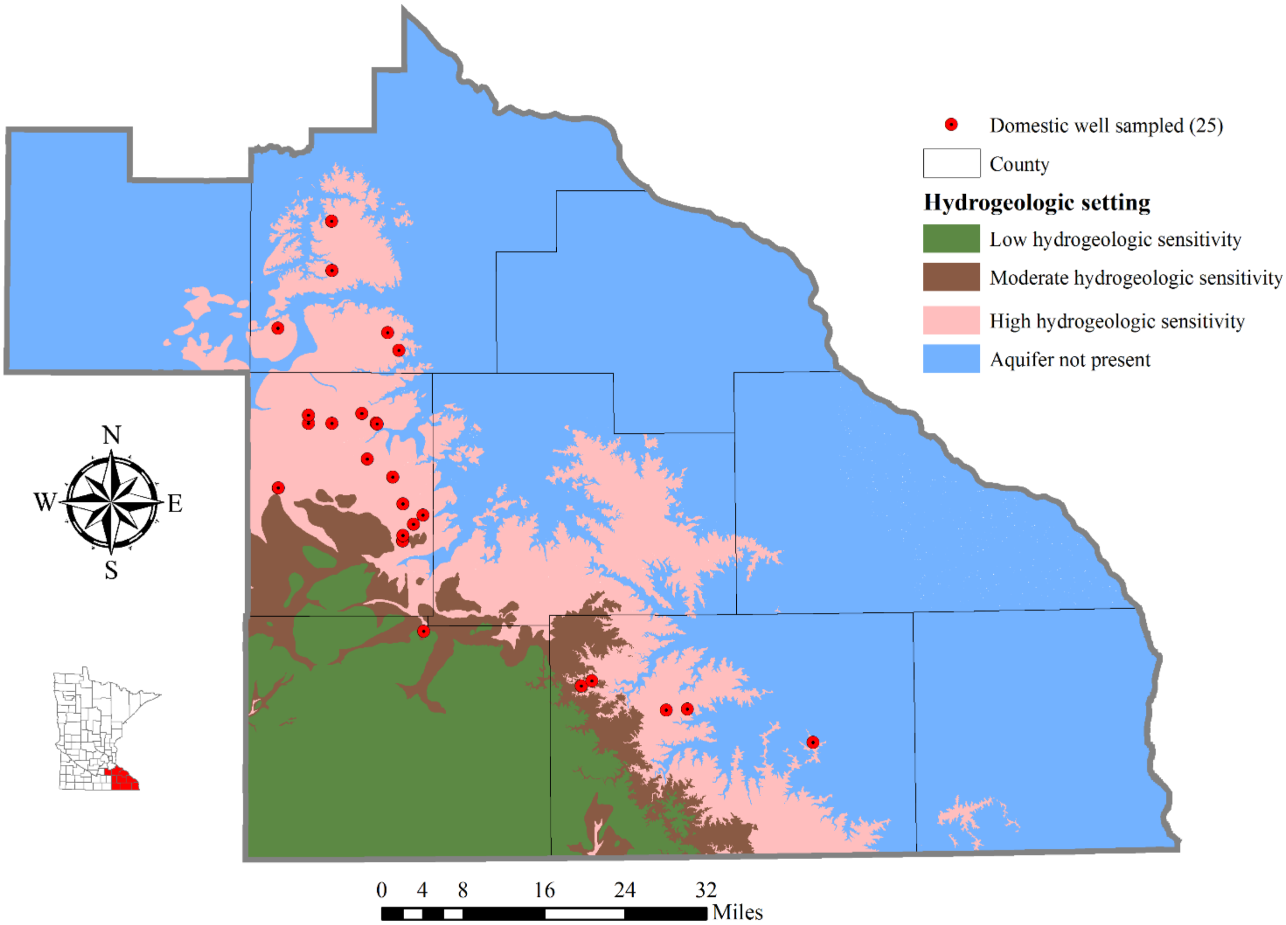
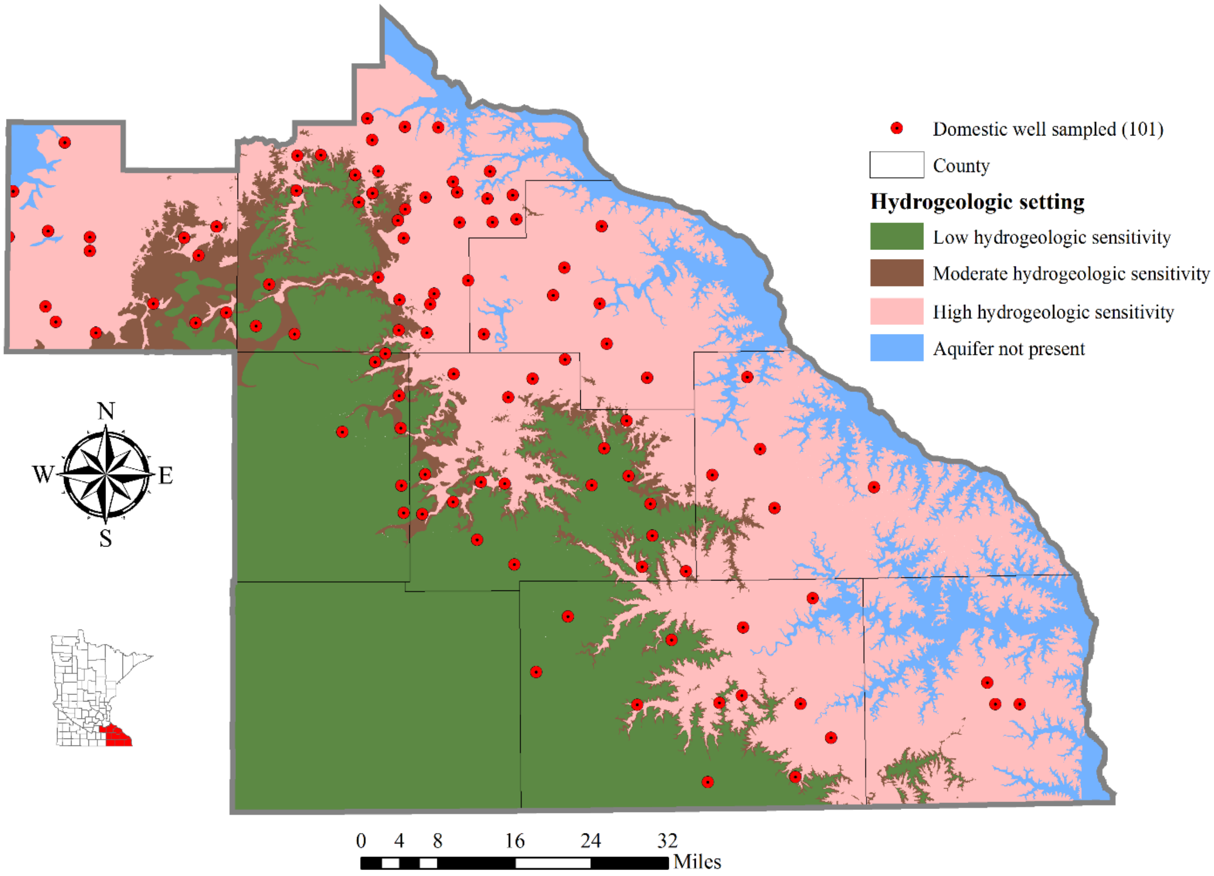
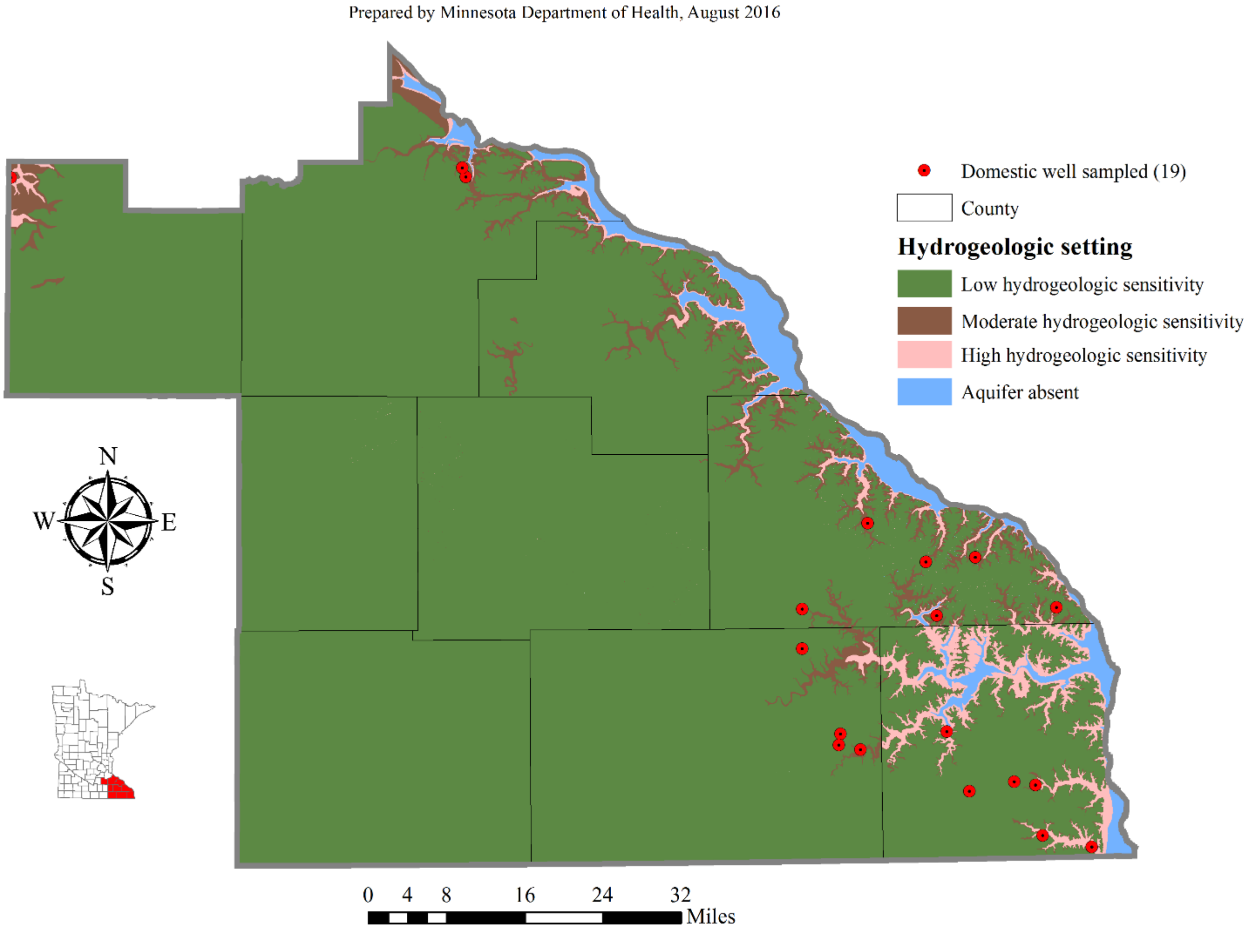


Figure 7. Sampled Wells and Hydrogeologic Settings Within St. Peter-Prairie du Chien-Joredan Aquifer



Prepared by Minnesota Department of Health, August 2016

Figure 8. Sampled Wells and Hydrogeologic Settings Within the Tunnel City-Wonewoc Aquifer



Methods of Investigation

General

The MPCA prepared a Quality Assurance Project Plan (MPCA, 2014). The MDH Public Health Laboratory analyzed the samples.

Network Well Selection and Analytes—Round 8

Two factors (availability of well construction and geologic information, and well owner cooperation) determined the Round 8 (August-September 2013) subset of wells to be sampled. Domestic well owners collected samples from their own wells. The MDH Public Health Laboratory received these samples and analyzed them for chloride, bromide, sulfate, nitrate, nitrite, and ammonia (MDH vulnerability suite; Table 2). Round 8 wells were then assigned hydrogeologic sensitivity based on well construction information and laboratory analytical results, using a weighted approach that considered the factors listed in Table 2 below.

Table 2. Factors Considered in Assigning Hydrogeologic Sensitivity

Data Element	Comment
Well depth	May reflect connection to recharge pathways for surface water
Depth cased	Addresses Sensitive Well Designation in well code
Geologic sensitivity and L-score	Can be used to refine the level of geologic protection
Aquifer code	Identifies aquifers at most risk due to their matrix and secondary porosity
Saturated casing value	May address pumping influence on well construction
Maximum tritium detected	Indicator of recent recharge by surface water
Tritium non-detect	Indicator of geologic protection

Data Element	Comment
Nitrate >= 1 mg/L in past 5 years	Indicator of recent recharge by contaminated surface water
Ammonia detect in past 5 years	Indicator of reducing conditions caused by sewage in some settings
Surface water characteristics	Indicates possible direct connection to surface water

Network Well Selection and Analytes—Rounds 9 and 10

Analyte lists were selected for Round 9 sampling based on the well hydrogeologic sensitivity determined from Round 8 results, as shown in Table 3 below.

- Field measurements (dissolved oxygen, specific conductance, pH, oxidation-reduction potential, and temperature), major ions and trace metals were collected at all wells.
- Gross alpha and arsenic were measured for wells ranked low for hydrogeologic sensitivity. Radium (the main gross alpha emitter) and arsenic are redox-sensitive trace metals mobile under only under low-oxygen conditions.
- Tritium was measured at selected moderate sensitivity wells to provide data to support a confident assessment of well vulnerability to surface contaminants.

Table 3. Analytes and Well Groupings by Hydrogeologic Sensitivity

Analyte	Low	Moderate	High
Field Measurements	X	X	X
Vulnerability Suite	X	X	X
Major ions	X	X	X
Trace metals	X	X	X
Arsenic	X		
Gross alpha	X		

Analyte	Low	Moderate	High
Tritium		X	

Professional samplers collected Round 9 samples during spring 2014, and Round 10 samples during spring 2015 at wells where Round 9 sampling could not occur.

Human health criteria

Because the domestic well water samples were analyzed for compounds not previously analyzed, interest in the analytical results was high. To meet the increased interest, Olmsted County prepared letters communicating the analytical results to well owners, including a comparison to available human health criteria. These human health criteria are defined as follows:

- Maximum Contaminant Level (MCL): the highest level of a contaminant that the United States Environmental Protection Agency (USEPA) allows in drinking water. MCLs ensure that drinking water does not pose either a short-term or long-term health risk.
- Health Risk Limit (HRL): defined in rule as “the concentration of a substance or chemical adopted by rule of the commissioner of health that is a potential drinking water contaminant because of a systemic or carcinogenic toxicological result from consumption”. A HRL is the rule-based concentration of a contaminant, or a mixture of contaminants in drinking water that is likely to pose little or no health risk to humans.
- Health Based Value (HBV): the concentration of a contaminant that can be consumed daily with little or no risk to health. HBVs are derived using the same algorithm as HRLs, however they have not been promulgated in rule, have not undergone peer review, and may be based on less data and/or subject to greater uncertainty than HRLs.
- RAA, risk assessment advice: technical guidance concerning exposures and risks to human health. Generally, RAA contains greater uncertainty than HRLs and HBVs because the available information is limited.

The available criteria for analytes included in this project are shown in Table 4. Further information on these human health criteria is available at the following web sites:

- http://www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html
- http://water.epa.gov/drink/contaminants/index.cfm

Table 4. Human Health Criteria for Analytes in This Project

Chemical	MCL	HRL	HBV	RAA
Nitrate	10,000 ug/L	10,000 ug/L	NA	NA
Tritium	NA	NA	NA	NA
Major Ions	NA	NA	NA	NA
Arsenic	10 ug/L	NA	NA	NA
Barium	2,000 ug/L	2,000 ug/L	NA	NA
Boron	NA	NA	NA	1 mg/L
Manganese	NA	100 ug/L	NA	100 ug/L (infant); 300 ug/L (adult)
Zinc	NA	2,000 ug/L	NA	NA
Gross Alpha	15 pCi/L	NA	NA	NA
Vuln. Suite	NA	NA	NA	NA

Summary of Water Quality Results

This section summarizes field and laboratory analytical results from project sampling rounds 8, 9 and 10 (data acquired from MDH Public Health Laboratory on February 8, 2016). The subsections below present laboratory results, and discuss the utility of each analyte in ground water to characterize low, moderate and high sensitivity hydrogeologic settings.

Vulnerability Suite

Laboratory results were reported for a maximum of 168 wells. A “ground water characterization score” (MDH, 2011) was calculated for the analytes collected at each well, and these scores were compared to a strictly geologic assessment of hydrogeologic sensitivity, with very good general agreement.

The chloride-bromide ratio was calculated for 123 samples where both analytes were detected. Tritium is useful for age-dating of ground water, and is typically included in the vulnerability suite. However, the number of samples collected for tritium analysis was restricted due to cost.

Table 5 summarizes the vulnerability suite results. Median concentrations for chloride, sulfate, nitrate, and ammonia are similar to expected background concentrations. Maximum values for chloride (81.80 mg/L), sulfate (94.00 mg/L) and nitrate (24.00 mg/L) indicate that some wells in the data set are likely impacted by surface contaminants. Ammonia, a reduced form of soluble nitrogen, was undetected in most (108) samples, ranging upwards to a maximum value of 3.10 mg/L. The median chloride-bromide ratio is similar to that of rainfall for southeastern Minnesota, suggesting that half of the samples were collected from wells potentially vulnerable to pollutants originating at the land surface (Davis, et. al, 1998; MDH, 2011).

Table 5. Vulnerability Suite Results Summary

Analyte	Units	Count	Det. %	Mean	Min	Max	Q1	Median	Q3
Chloride	mg/L	165	75.2	7.53	(0.50)	81.80	0.56	1.69	9.04
Bromide	mg/L	165	90.9	0.0193	(0.0050)	0.1170	0.0086	0.0141	0.0239
Sulfate	mg/L	163	95.7	21.07	(1.00)	94.00	10.00	17.20	28.00
NO3 + NO2	mg/L	168	44.0	2.02	(0.05)	24.00	(0.05)	(0.05)	1.98
Ammonia	mg/L	165	34.5	0.18	(0.05)	3.10	(0.05)	(0.05)	0.10
[Cl]/[Br]	Ratio	123	--	372	18	4902	95	247	511
Tritium	TU	28	57.1	2.2	(0.8)	5.5	(0.8)	1.3	3.4

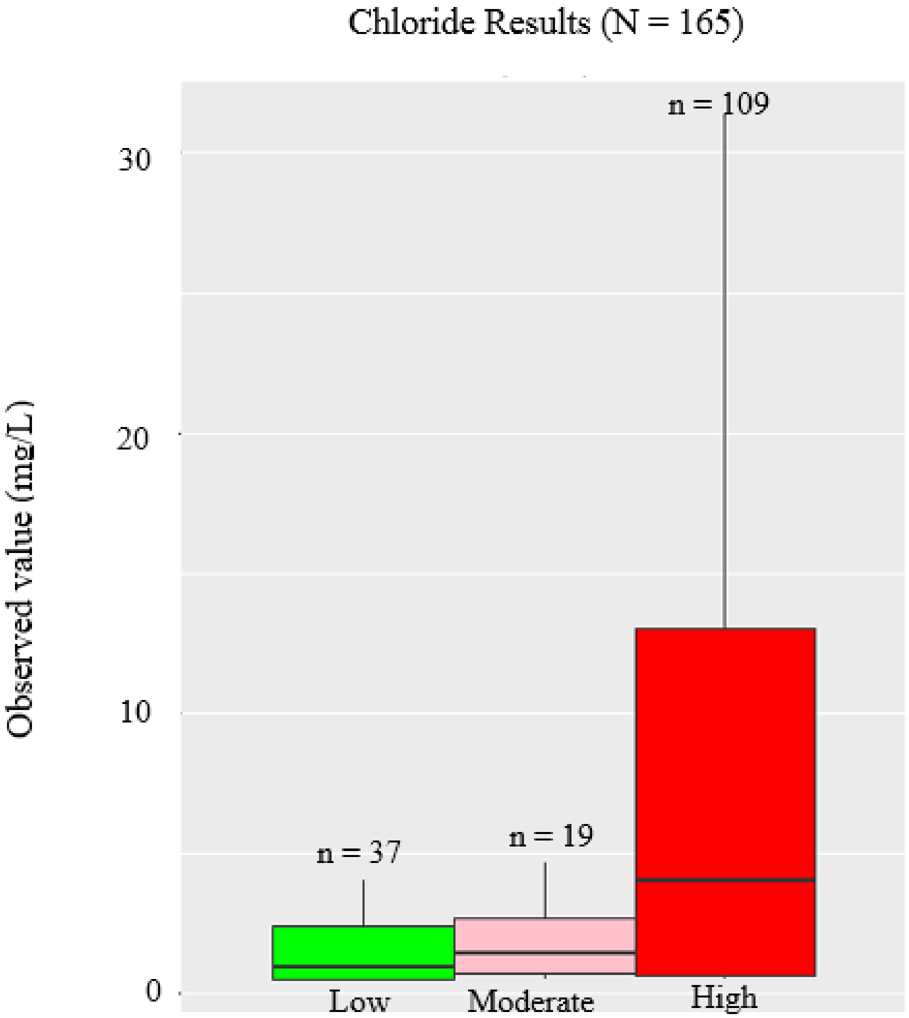
Parentheses indicate not detected. "Q1" and "Q3" indicate first and third quartiles, respectively.

The bullet items below discuss the ability of each analyte to characterize low, moderate and high hydrogeologic settings:

- Chloride. Table 5 and Figure 9 indicate that chloride in the range of up to 5 mg/L cannot characterize the three sensitivity settings. However, chloride greater than 5 mg/L exceeds the range for both low and moderate sensitivity. Therefore, chloride greater than 5 mg/L suggests water collected from a high sensitivity setting.

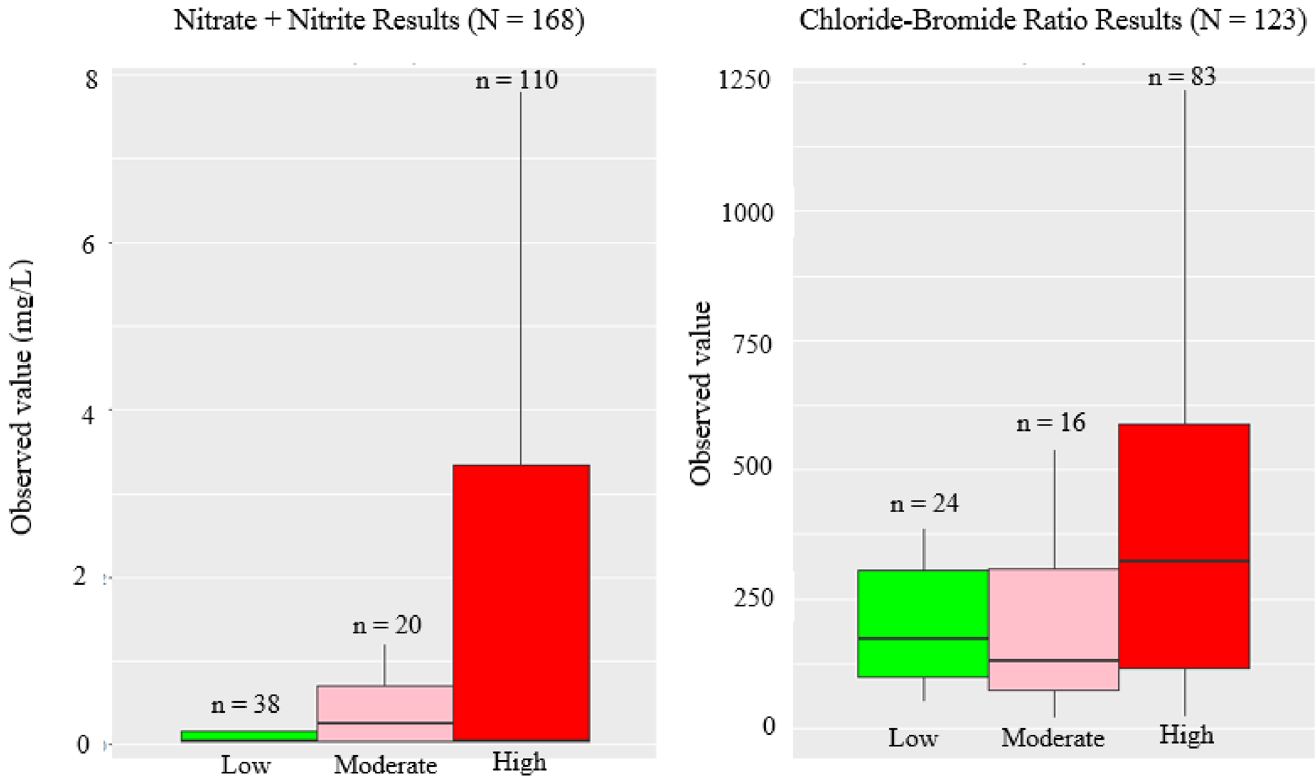
- Bromide. The ranges between the first and third quartiles for all three settings overlap, limiting bromide's ability to characterize hydrogeologic sensitivity.
- Sulfate. The ranges between the first and third quartiles for all three settings overlap, limiting sulfate's ability to characterize hydrogeologic sensitivity.
- Nitrate. Figure 10 indicates that nitrate ranges for the three settings generally overlap, however the range for low sensitivity is very tight. Therefore, nitrate concentrations greater than 0.2 mg/L suggest moderate or high sensitivity. The third quartile and the overall range for highly sensitive waters are well above the overall range for moderate sensitivity, so nitrate concentrations greater than 1.2 mg/L serve as an indicator of water collected from a high sensitivity setting.
- Ammonia. The range of ammonia concentration is less than 0.1 mg/L for waters collected from low or moderate settings. The third quartile ammonia concentration in water collected from high sensitivity settings is 0.1 mg/L and the maximum ammonia concentration was 3.1 mg/L. Ammonia concentrations greater than 0.1 mg/L therefore suggest water collected from a highly sensitive setting.
- Chloride-bromide ratio. Figure 10 indicates that the range of the chloride-bromide ratio for low and moderate settings overlap, with similar median values. However, chloride-bromide ratios are higher for waters collected from highly sensitive settings, as indicated by a larger box and greater overall range than for low or moderate settings. Figure 10 also shows that chloride-bromide ratios greater than 540 indicate water collected from a highly sensitive setting.

Figure 9.Box and whisker plot for chloride.



*On figures 9, 10, 11 and 13, colors indicate water samples collected from wells constructed in geologic materials with low (green), moderate (pink) and high (red) hydrogeologic sensitivity. Box encloses the 25th through 75th percentile (quartile 1 through quartile 3), and lines indicate the greatest extent of data that are not outliers (defined as Q1 - 1.5*IQR or Q3 + 1.5*IQR: data within 1.5 times the Inner Quartile Range (IQR) less than quartile 1, and greater than quartile 3). Outliers are omitted for clarity.*

Figure 10. Box and whisker plots for nitrate (left) and chloride/bromide ratio (right).



See Figure 9 for explanation of box and whisker plots.

Field Measurements

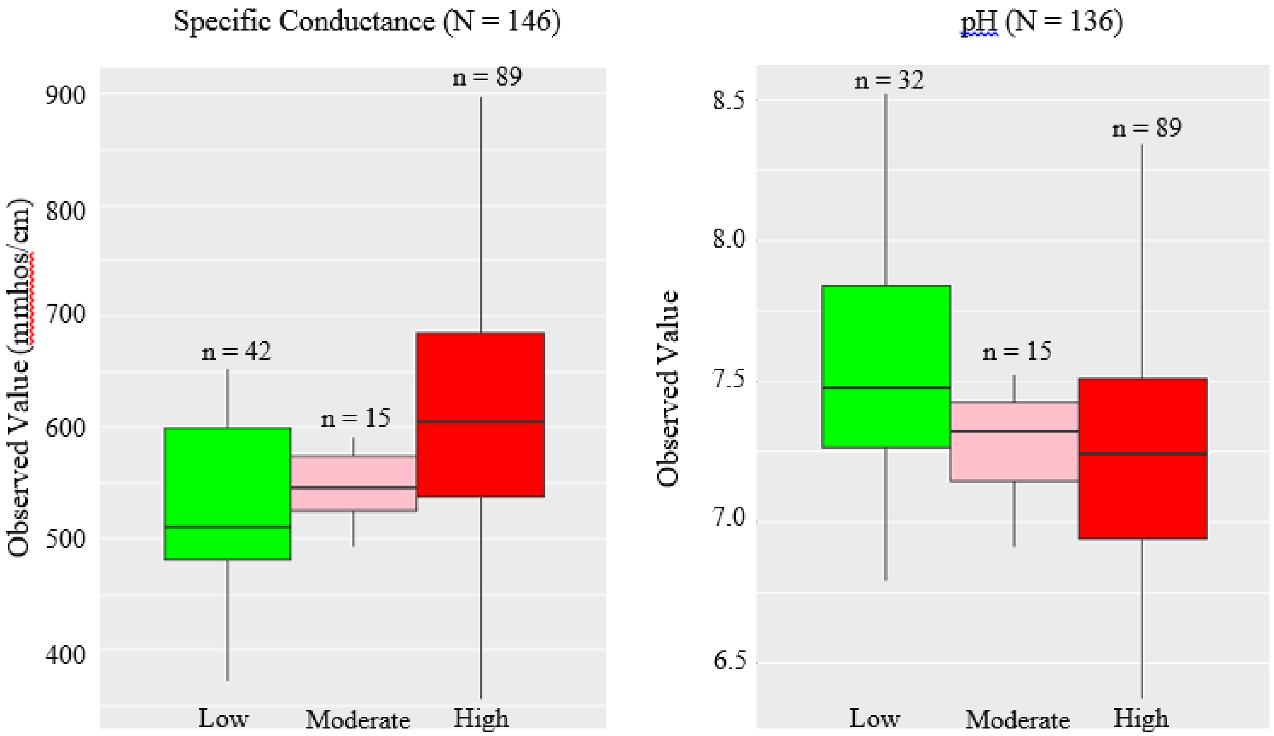
The following field measurements were collected during sampling rounds 9 and 10: specific conductance (SC; micromhos per centimeter, µmhos/cm), pH (unitless), temperature (T; degrees Centigrade), dissolved oxygen (DO; milligrams per liter, mg/L), and oxidation-reduction potential (ORP; millivolts, mV). Table 6 summarizes the descriptive statistics. Field experience shows these measurements may vary in reliability as indicated by precision; for instance, the reported minimum pH measurement is unreasonably low for Minnesota ground water. The most reliable is typically T, followed by SC, pH, and lastly DO and ORP.

Table 6. Field Measurement Results Summary

Analyte	Units	Count	Mean	Min	Max	Q1	Median	Q3
SC	µmhos/cm	146	596.1	300.0	1980.0	511.5	580.5	647.8
pH	None	136	7.33	1.22	9.01	7.03	7.36	7.66
T	deg. C	137	9.17	6.02	12.05	8.91	9.30	9.67
DO	mg/L	146	4.90	0.26	18.07	1.32	2.31	7.63
ORP	mV	111	-12	-241	424	-80	-12	59

Parentheses indicate not detected. “Q1” and “Q3” indicate first and third quartiles, respectively.

Figure 11. Box and whisker plots for specific conductance and pH.



See Figure 9 for explanation of box and whisker plots.

The bullets discuss advantages and limitations of each field analyte in characterizing low, moderate and high hydrogeologic settings.

- Specific conductance. SC measurements greater than 600 µmhos/cm indicate ground water is from a highly sensitive hydrogeologic setting (Figure 11). The low and moderate hydrogeologic sensitivity boxplots overlap and therefore the ability of SC to characterize these two settings is limited.
- pH. Measurements greater than 7.50 indicate water collected from a low sensitivity setting, and pH measurements less than 7.25 suggest water collected from a highly sensitive setting (Figure 11). The range of pH measurements for water collected from moderately sensitive settings generally overlapped with the ranges of pH measurements from low and high sensitivity settings.

- Temperature. First and third quartile temperature measurements for the three hydrogeologic settings were similar. Therefore, the ability of temperature to characterize the three settings is limited.
- Dissolved oxygen. First and third quartile DO measurements for the three hydrogeologic settings were similar. Therefore, the ability of temperature to characterize the three settings is limited.
- Oxidation-reduction potential. First and third quartile ORP measurements for the three hydrogeologic settings were similar. Therefore, the ability of temperature to characterize the three settings is limited.

Major Ions

Four major cations (calcium, magnesium, sodium, potassium) and three major anions (nitrate, chloride, and sulfate), plus alkalinity were measured at a total of 131 wells. Major ions are reported in units of milligrams per liter (mg/L). Ion balances were in the range of 10-15%, which is poor. The cause of the poor ion balance is unknown but may be due to difficult sampling conditions which are common for domestic wells.

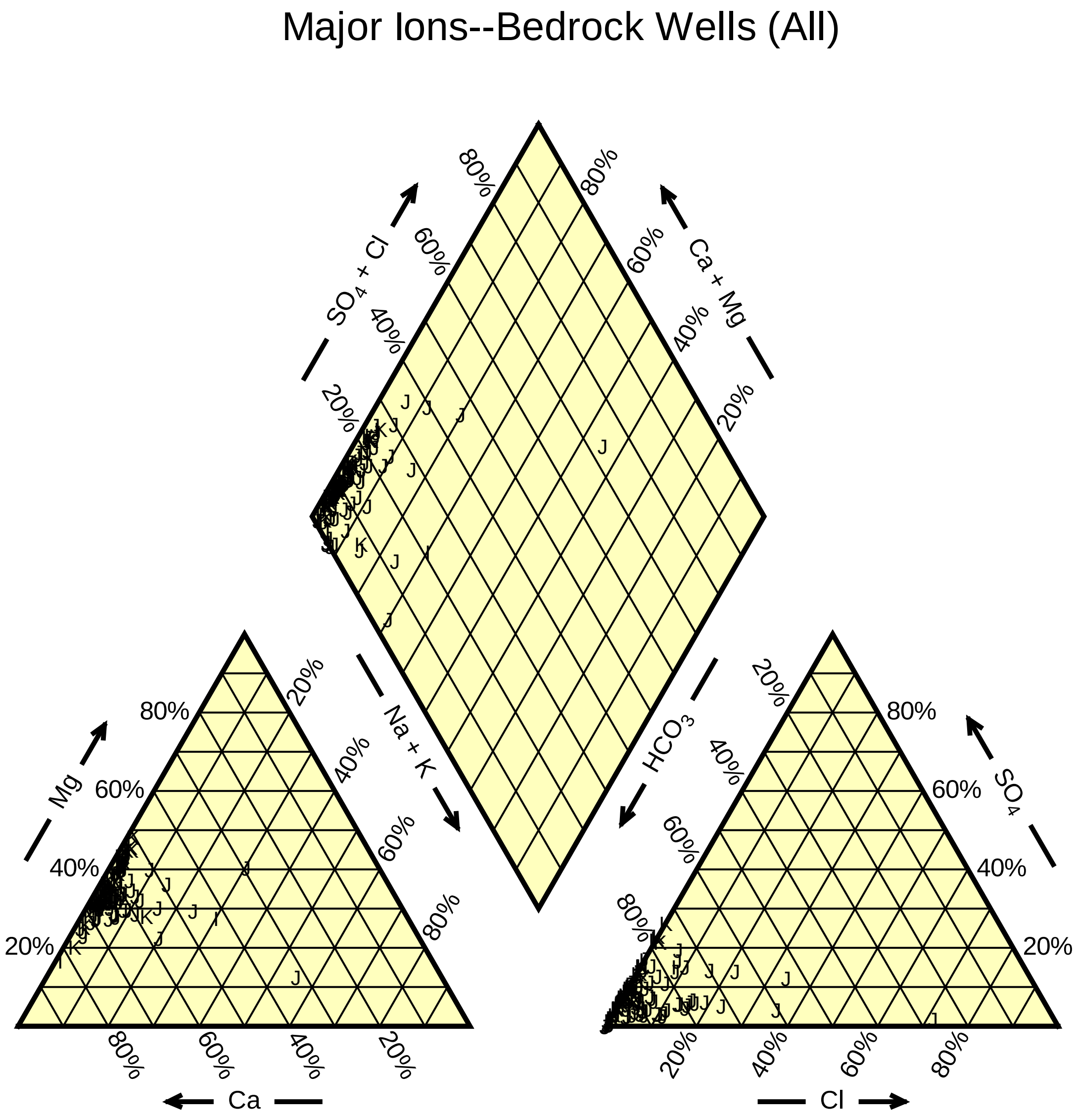
Table 7 summarizes descriptive statistics, indicating that major ion concentrations are similar to those measured in a previous study of southeastern Minnesota domestic well ground water quality (Tipping, 1994). Also consistent with the findings of Tipping (1994), Figure 12 shows that nearly all the wells (129) fall within the calcium-bicarbonate hydrogeochemical class, regardless of aquifer and hydrogeologic setting. Therefore, the ability of major ions to characterize the hydrogeologic setting is limited.

Table 7. Major Ions Results Summary

Analyte (mg/L)	Count	Det. %	Mean	Min	Max	Q1	Median	Q3
Calcium	131	100.0	82.73	39.00	130.00	71.95	82.00	93.00
Magnesium	131	100.0	29.05	13.00	49.90	24.30	28.10	33.90
Sodium	131	100.0	8.96	1.26	235.00	2.69	4.06	7.01
Potassium	131	97.7	1.56	(0.50)	15.40	0.90	1.14	1.65
Alkalinity (total)	131	100.0	276.60	160.00	460.00	240.00	270.00	300.00
NO3 + NO2	130	48.5	2.18	(0.05)	14.00	(0.05)	(0.05)	3.48
Chloride	131	63.4	12.44	(1.00)	443.00	(1.00)	2.47	11.80
Sulfate	131	96.2	21.93	(1.00)	91.30	11.30	18.40	27.15

Parentheses indicate not detected. “Q1” and “Q3” indicate first and third quartiles, respectively.

Figure 12. Piper plot of the major ion results at 131 project wells completed within bedrock aquifers.



Trace metals

Trace metals are typically present in ground water at low concentrations compared to major ions and were reported in units of micrograms per liter (µg/L). Trace metal analytes included arsenic, barium, boron, iron, manganese, strontium, and zinc. Of these, arsenic was the only analyte to be measured using a regulatory compliant method, in a subset of 63 selected wells. Analytical results for the remaining trace metals were generated as part of a non-compliant internal MDH screening method that provides no quality assurance data, but conserves costs. Data from the non-compliant method cannot be used to determine compliance with human health standards.

Arsenic was measured in samples from 63 selected wells. Trace metals were scanned at 131 wells. Detection frequencies for these trace metals ranged between 17.6% (arsenic) and 94.7% (strontium). Table 8 summarizes the descriptive statistics for trace metals.

Arsenic was present above detection limits in samples from nine wells. Of these results above the arsenic detection limit, five were between 1.00 µg/L and 2.00 µg/L, and the four most elevated arsenic concentrations were between 4.99 µg/L and 8.61 µg/L. None of the samples analyzed for arsenic exceeded the HRL of 10 µg/L. All four elevated arsenic samples were collected from wells within Dodge County. The wells were completed within the Galena or Devonian Upper Carbonate Aquifer, within moderately sensitive settings.

Table 8. Trace Metals Results Summary

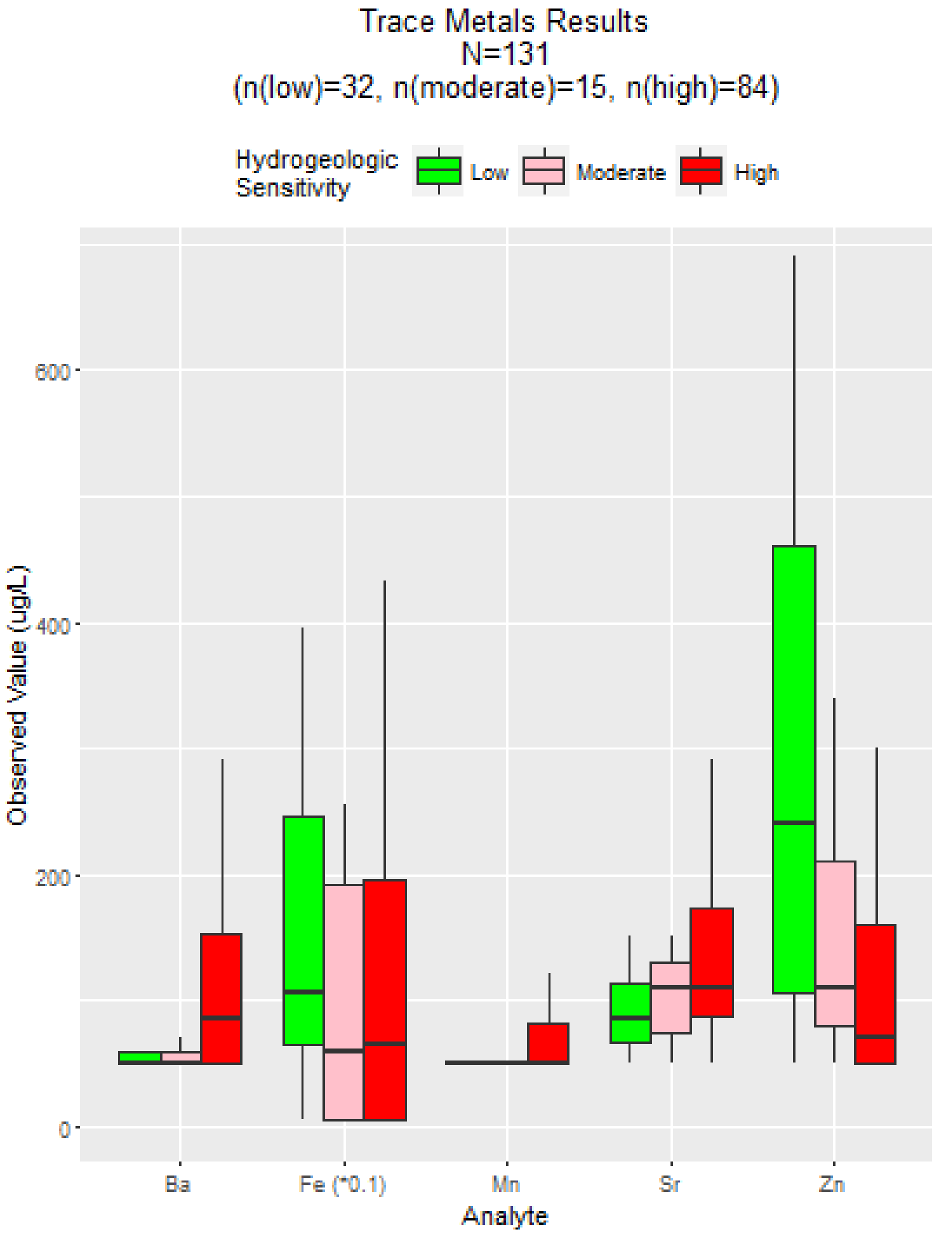
Analyte (µg/L)	Count	Det. %	Mean	Min	Max	Q1	Median	Q3
Arsenic	51	17.6	1.41	(1.00)	8.61	(1.00)	(1.00)	(1.00)
Barium	131	60.3	105.90	(50.00)	900.00	(50.00)	60.00	105.90
Boron	131	18.3	62.52	(50.00)	380.00	(50.00)	(50.00)	(50.00)
Iron	131	73.3	2010.10	(50.00)	46600.00	(50.00)	850.00	2000.50
Manganese	131	32.8	85.19	(50.00)	650.00	(50.00)	(50.00)	70.00
Strontium	131	94.7	141.30	(50.00)	770.00	80.00	110.00	155.00
Zinc	131	68.7	292.70	(50.00)	7310.00	(50.00)	100.00	240.00

Parentheses indicate not detected. "Q1" and "Q3" indicate first and third quartiles, respectively.

The remaining trace metal results are illustrated in Figure 13, and summarized below:

- Barium. Concentrations greater than 80 µg/L indicate water collected from a highly sensitive setting. The barium concentrations ranges for low and moderate hydrogeologic sensitivity overlap.
- Boron. The low detection frequency reflects the fact that it is not common to groundwater of southeastern Minnesota.
- Iron. The first and third quartiles are similar and concentration ranges overlap significantly for iron analyses of waters collected from low, moderate and high hydrogeologic sensitivity settings.
- Manganese. The detection frequency for manganese was low (32.8%) and concentrations were low, consistent with MDH (2012b). Consequently, manganese concentration ranges overlap significantly for waters collected from low, moderate and high hydrogeologic sensitivity settings.
- Strontium. In Figure 13, strontium concentrations greater than 150 µg/L indicate water collected from highly sensitive hydrogeologic settings. The first and third quartiles are similar and concentration ranges overlap significantly for waters collected from low and moderate hydrogeologic sensitivity settings.
- Zinc. The zinc concentration ranges overlap significantly for waters collected from moderate and high sensitivity settings. However, zinc concentrations greater than 200 µg/L indicate water collected from low hydrogeologic sensitivity settings.

Figure 13. Box and whisker plots of analytical results for barium, iron, manganese, strontium and zinc.



Note that iron is plotted as a factor of 0.1. See Figure 9 for explanation of box and whisker plots.

Gross Alpha

Radioactive isotopes such as radium-226 (^{226}Ra) and radium-228 (^{228}Ra) occur naturally at elevated levels in ground water within the Jordan and Mt. Simon (Paleozoic bedrock) aquifers in southeastern Minnesota (Lively, et al., 1992; MDH, 2010). Gross alpha is a screening tool for radioactivity that is sensitive to alpha particle emissions from ^{226}Ra. This project measured gross alpha emissions in a subset of 46 wells during sampling Round 9, and Table 9 summarizes the descriptive statistics.

Because the drinking water standard (MCL) of 15 picocuries per liter (pCi/L) was exceeded in 5 wells, thirty-three of the Round 9 wells were re-sampled. Following current knowledge about radium distribution in southeastern Minnesota aquifers (MDH, 2010), most wells selected for re-sampling were completed in parts of the St. Peter, Prairie du Chien or Jordan aquifers, and located in the western half of the project area in locations where these aquifers are covered by a complete confining layer (Decorah-Platteville-Glenwood).

Table 9. Gross Alpha Results Summary

Analyte	Count	Det.%	Mean	Min	Max	Q1	Median	Q3
Gross alpha (pCi/L)	46	52.2	11.66	(3.00)	200.00	(3.00)	3.50	5.98

Parentheses indicate not detected. "Q1" and "Q3" indicate first and third quartiles, respectively.

In each case, the re-sampled gross alpha results were lower than the initial results. Only two of the initially elevated re-sampled wells changed with respect to the MCL, and both met the gross alpha MCL in the second sample. In one well, initial gross alpha result was anomalously high (200 pCi/L). A time-series test carried out in June 2015 to develop an exposure management strategy produced equivocal results because the initial elevated gross alpha radiation could not be reproduced.

Summary of Analytes as Tools to Characterize Hydrogeologic Sensitivity

The findings of this report do support the concept of constructing a hydrogeochemical framework for hydrogeologic sensitivity. This project collected water samples to be analyzed for twenty-five field and laboratory parameters, however only a subset of these parameters was helpful in defining hydrogeologic sensitivity.

Table 10: Summary Table of Chemical Signature by Hydrogeologic Setting

Group	Low	Moderate	High
Field	pH > 7.50		pH < 7.25
			SC > 600 umhos/cm
Vulnerability Suite		0.2 mg/L < [NO3] < 1.2 mg/L	[NO3] > 1.2 mg/L
			[Cl] > 5 mg/L
			[NH3] > 0.1 mg/L
			[Cl]/[Br] > 540
Trace Metals			[Ba] > 80 ug/L
			[Sr] > 150 ug/L
	[Zn] > 200 ug/L		

Table 10 lists the nine most helpful analytes, and the ranges across which these analytes may serve as useful indicators of the hydrogeologic setting from which a water sample was collected:

- Low hydrogeologic sensitivity settings (pH and zinc);
- Moderate hydrogeologic sensitivity settings (nitrate);

- High hydrogeologic sensitivity settings (pH, specific conductance, nitrate, chloride, ammonia, chloride-bromide ratio, barium, and strontium).

Summary and Conclusions

This report concludes a series of reports documenting ground water quality monitoring accomplished through the use of the Southeast Minnesota Domestic Well Network. The first report in the series (MDH, 2009) discussed:

- Methods used to assemble the sampling network;
- Data receipt and storage for sampling Rounds 1-3;
- Maps showing network well locations, the distribution of various well construction and geologic features of network wells, and distribution of nitrate results for sampling Rounds 1, 2, and 3.

The second report of the series (MDH, 2012a) discussed:

- Methods of assessing aquifer of completion and nearby potential sources of nitrate contamination for wells enrolled into the network;
- Field definitions for the nitrate monitoring database;
- Assessment of nitrate results from sampling Rounds 1-6.

This report describes a significant expansion of the analyte list to provide hydrogeochemical context on the available nitrate database. The additional analyte groups include field measurements, vulnerability suite, major ions, trace metals, and gross alpha radiation. The data support an assessment of the returned ground water quality from the standpoint of hydrogeologic sensitivity. The most useful analytes were:

- Low hydrogeologic sensitivity (pH and zinc);
- Moderate hydrogeologic sensitivity (nitrate); and
- High hydrogeologic sensitivity (pH, specific conductance, nitrate, chloride, ammonia, chloride-bromide ratio, barium, strontium).

The assembly of the Southeast Minnesota Domestic Well Network has provided a means to collect ground water quality data that is important to county staff and the well owners whose wells are enrolled in the network. Hydrogeochemical results from domestic wells throughout the region have provided valuable information in identifying aquifer hydrogeologic sensitivity. We have further found the network to be useful for sample collection not only for nitrate, but for other anthropogenic or natural contaminants of future concern to domestic well owners (e.g., manganese, radio-nuclides, agricultural chemicals, road salt, etc.). The continued existence of the network depends upon its continued use, and will require the well owners to be kept engaged, reminded that their participation is important and useful in ways that we are still discovering.

The short term continuation of the network seems assured because the nine counties of the Southeast Minnesota Water Resources Board will continue routine monitoring of network wells for nitrate (in coordination with the Minnesota Department of Agriculture, as part of the long range monitoring goals). Other potential uses of the domestic well network include:

- Assessment of characteristic water chemistry signatures by hydrogeologic setting, where geologic and well construction data are unavailable. In these situations, sampling and comparing to a distinctive signature, for which Table 9 above may be a prototype, may be easier than logging the well;
- Predicting source water quality for new domestic wells;
- Using differences from known ambient hydrogeochemistry to identify failing or damaged wells;
- Support ground water chemistry studies involving contaminant loading to ground and surface waters (e.g., MDA township testing for nitrate, watershed studies, etc.);
- Studies of naturally-occurring contaminants such as arsenic or radium;
- “Edge” studies, for example the Decorah, St. Lawrence, or Des Moines Lobe till edge.

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References

Davis, Stanley N., Whittemore, Donald O., and Fabryka-Martin, June, (1998), *Uses of chloride/bromide ratios in studies of potable water,* Ground Water Journal, vol.36, no.2, March-April 1998, pp. 338-350.

Delin, G.N., and Woodward, D.G., 1984, *Hydrogeologic setting and potentiometric surfaces of regional aquifers in the Hollandale Embayment, southeastern Minnesota, 1970-80*: U.S. Geological Survey Water-Supply Paper 2219, p. 56.

Lively, Richard S., Jameson, Roy, Alexander, E.C., Jr., and Morey, G.B., (1992), *Radium in the Mt. Simon-Hinckley Aquifer, east-central and southeastern Minnesota*, Minnesota Geological Survey Information Circular 36, University of Minnesota, St. Paul, Minnesota.

MDH, 2009, *Minnesota Department of Health Contribution to Final Report—Southeast Minnesota Voluntary Nitrate Monitoring Network*, 22 pp., http://www.health.state.mn.us/divs/eh/water/swp/nitrate/reports/mdhcontrfinal.pdf

MDH, 2010, Distribution of Radium in Minnesota Drinking Water Aquifers, December 21, 2010, 13 pp., http://www.health.state.mn.us/divs/eh/water/swp/radium/2010_radium.pdf.

MDH, 2011, *Assessment monitoring pilot study*, Minnesota Department of Health, December 2011, 58 pp.

MDH, 2012a, *Volunteer nitrate monitoring network: methods and results*, Source Water Protection Unit, April 2012, 21 pp., http://www.health.state.mn.us/divs/eh/water/swp/nitrate/reports/methodsresults.pdf

MDH, 2012b, Initial assessment of manganese in Minnesota groundwater, MDH memorandum to the Manganese Group dated September 5, 2012, 15 pp., http://www.health.state.mn.us/divs/eh/water/swp/manganese/iamemo.pdf

MPCA, Ground Water Monitoring and Assessment Program (GWMAP) website, https://www.pca.state.mn.us/water/groundwater-monitoring-and-assessment.

MPCA, 2014, Southeast Minnesota domestic well monitoring network CWP Project (Quality Assurance Project Plan, QAPP), https://www.pca.state.mn.us/water/groundwater.

Mossler, John H., (2008). RI-65 Paleozoic stratigraphic nomenclature for Minnesota, Minnesota Geological Survey. Retrieved from the University of Minnesota Digital Conservancy, http://purl.umn.edu/58940.

Runkel, Anthony C., Tipping, Robert G., Alexander, E. Calvin, Jr., Green, Jeffrey A., Mossler, John H., and Alexander, Scott C, 2003, *Hydrogeologic of the Paleozoic Bedrock in Southeastern Minnesota*, Minnesota Geological Survey Report of Investigations 61, University of Minnesota, Saint Paul, MN, 105 pp.

Runkel, Anthony C., Steenberg, Julia R., Tipping, Robert G., and Retzler, Andrew J., 2013, *Geologic controls on groundwater and surface water flow in southeastern Minnesota and its impact on nitrate concentrations in streams*, Minnesota Geological Survey, downloaded from www.mngs.umn.edu/ on November 25, 2013.

Steenberg, Julia R., Tipping, Robert G., and Runkel, Anthony C., 2013, Geologic controls on groundwater and surface water flow in southeastern Minnesota and its impact on nitrate concentrations in streams: local project area report, Minnesota Geological Survey, downloaded from www.mngs.umn.edu/ on November 25, 2013.

Tipping, Robert G., 1994, *Southeastern Minnesota regional ground water monitoring study, a report to the Southeast Minnesota Water Resources Board*, Minnesota Geological Survey Open-File Report 94-1, April 29, 1994, St. Paul, Minnesota.