# Ambient Groundwater Quality Study 1999-2019
## Dakota County, Minnesota

# Private Well Drinking Water Quality in Three Principal Drinking Water Aquifers: Prairie du Chien, Jordan and Unconsolidated Sediments

Environmental Resources Department

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# Acknowledgements

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# Executive Summary

## Introduction

More than 90 percent of Dakota County residents rely on groundwater for their water supply, whether it comes from a public water supplier or from a private drinking water well. Groundwater is the water found in pore spaces and cracks in soil and bedrock at various depths in aquifers below the ground surface. Aquifers store and transmit water. Water is pumped from water wells to homes and businesses for drinking and other uses.

Dakota County residents expect an abundance of clean water for drinking, however, the three principal drinking water aquifers in the county – the unconsolidated sediments, Prairie du Chien and the Jordan Aquifers (in order of depth) – are vulnerable to contamination and have been impacted by contaminants from both human activities and naturally-occurring, geologically sourced chemicals.

The Dakota County Ambient Groundwater Quality Study (Ambient Study or study) began in 1999 to establish a baseline of water quality conditions to which ongoing conditions could be compared over a 20-year period. The term “ambient groundwater” refers to the parts of the water resource that are affected by the general, routine use of chemicals and are not affected by localized pollutants or spills (MPCA, July 2019). The study evaluated groundwater conditions in wells across the County that were selected to represent all three principal drinking water aquifers, in a variety of land-use, soil, and geological settings. The objectives developed were to:

- Determine groundwater quality in private drinking water wells selected to be representative of conditions across the County,
- Determine changes in contaminants of health and environmental concern in drinking water aquifers over time,
- Determine influence of land use, chemical use, geology and water well construction on groundwater quality,
- Develop recommendations to improve drinking water quality,
- Gather information needed to assist with policy decisions.

Sampling a total of 77 private wells multiple times enabled the County to monitor long-term trends in groundwater contamination from human (anthropogenic) sources and activities, such as nitrogen fertilizer and herbicides commonly used on corn crops, and chloride from salt applied to roads for deicing, potassium fertilizer (potash) and water softeners. The well owners consented to the sampling and were provided an explanation of their results. The study also enabled the County to identify where the groundwater contains naturally- occurring contaminants, such as manganese or arsenic, and to monitor the County’s groundwater for industrial chemicals and Contaminants of Emerging Concern, such as per- and polyfluoroalkyl substances (aka PFCs, PFAS, or 3M chemicals), medications, personal care products, household products such as cleaners, and ingredients related to manufacturing.

This report summarizes the data collected from 1999 through 2019 and includes data from other sampling events and studies that occurred in the County, including the Hastings Area Nitrate Study (HANS), the MN Department of Agriculture’s (MDA) Township Testing Program, the Wells and Increased

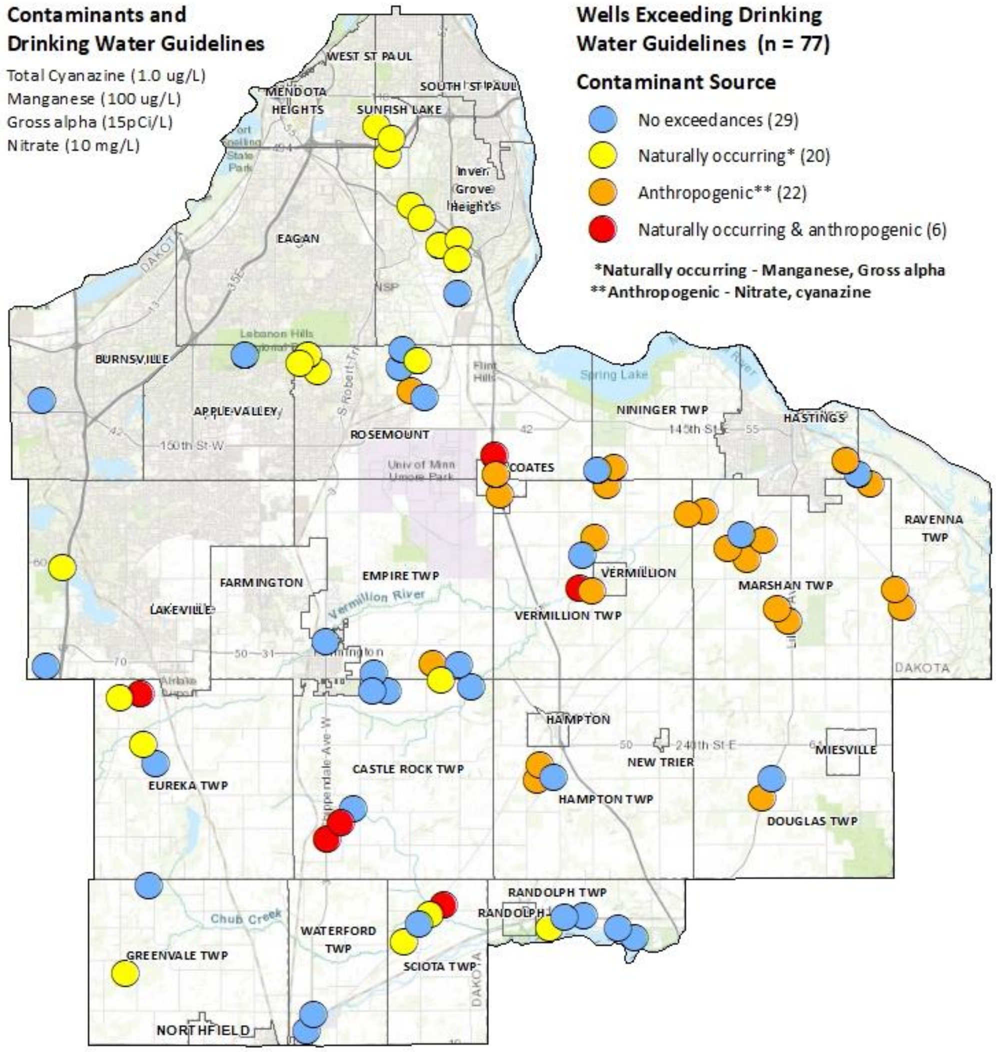
Infant Sensitivity and Exposure Study (WIISE), and the Burnsville, Greenvale and Lakeville Community-Focused Private Well Sampling.

In Minnesota, the Dakota County Ambient Groundwater Quality Study is a unique reference resource. While other studies may provide snapshots of water quality at a single point in time, the Ambient Study provides a chronicle of private drinking water well quality over 20 years. The Dakota County Ambient Study includes one of the most comprehensive sets of data about agricultural herbicides in private wells in the State.

## Key Findings

1. **Contaminant levels exceed health guidelines for both naturally occurring and anthropogenic chemicals in the principal aquifers used for drinking water.** Over the course of the study, sixty-two percent of the sampled wells contained concentrations of at least one chemical contaminant exceeding current Minnesota Department of Health (MDH) drinking water guidelines. Drinking water guidelines do not exist for every contaminant detected. Some wells had multiple chemicals detected that exceed a guideline. Anthropogenic compounds are largely detected in the central and eastern portion of the County where row crop agriculture is the dominant land use. For example, 38 percent of the wells in the study exceed the drinking water guidelines for nitrate as nitrogen (nitrate) or the discontinued herbicide cyanazine. Cyanazine was a weed killer used primarily on corn and soybean crops. The percent of wells that exceed an established drinking water guideline for a chemical are:

| Chemical | Percent of Wells Exceeding Drinking Water Guideline At Least Once between 1999-2019 |
|---|---|
| Manganese | 34 percent of wells sampled exceed the guideline of 0.100 mg/L (milligrams per liter or parts per million) |
| Nitrate | 31 percent exceed the guideline of 10 mg/L |
| Cyanazine breakdown products | 22 percent exceed the guideline of 1 µg/L (micrograms per liter or parts per billion) |
| Gross Alpha | 3 percent exceed the guideline of 15 pCi/L (picocuries per liter) |



Sources: ESRI; Dakota County Environmental Resources

Figure 1. Ambient Study Wells That Exceed Drinking Water Guidelines.

2. **The occurrence and concentrations of anthropogenic contaminants in groundwater reflect land use and the depth of the specific well (Sections 4.1.4, 4.2.3, and 4.3.4).** Nitrate and herbicide levels are higher where row crop agriculture is the dominant land use, whereas chloride levels are highest in urbanized areas where the application of road salt for deicing and water softener use is widespread. Median nitrate and chloride concentrations are higher in shallow wells than in deeper wells. Concentrations of substances related to human activity, e.g., nitrate, chloride, sodium and herbicides, all generally decrease with well depth.

3. **Nitrate is the most commonly detected anthropogenic contaminant exceeding the drinking water guideline (Section 4.1.2).**
    - Maximum nitrate results range from non-detect (less than (<) 0.2 mg/L) to 30.6 mg/L
    - 31 percent of wells have exceeded the drinking water guideline of 10 mg/L at least once
    - 23 percent of wells average (mean) nitrate exceeded 10 mg/L
    - 21 percent of wells median nitrate exceeded 10 mg/L

4. **There are more wells with an upward trend for nitrate than a downward trend. (Section 4.1.3).** Summary of nitrate trends in the 77 study wells:

    - 17 percent of wells have a statistically significant upward trend
    - 4 percent of wells have a statistically significant downward trend
    - 79 percent of wells have stable nitrate levels; 14 percent of wells are stable above 10 mg/L

5. **In the central and eastern portions of Dakota County where row crop agriculture is the dominant land use, average nitrate levels of study wells exceed 10 mg/L and are increasing (Sections 4.1.3).** Wells in eastern, rural Dakota County, in the cities of Coates and Hastings and the townships of Douglas, Hampton, Marshan, Nininger, Ravenna and Vermillion have among the highest levels of nitrate observed in the study. The nitrate result in these wells is, on average, five times higher than the study wells located outside of this area. Seventy percent of these wells exceed the drinking water guideline of 10 mg/L and seventy-seven percent of wells with upward trends for nitrate are located in this area.

6. **The breakdown products of herbicides commonly applied to corn and soybean crops are the most frequently detected pesticides and are found in more than 70 percent of the wells tested (Section 4.2.2). Most herbicides concentrations are below the applicable drinking water guidelines except for the herbicide cyanazine.** The occurrence, concentrations, mobility and persistence of herbicides in groundwater is an important finding of this study. Herbicide compounds were detected in 73 percent of the wells. The herbicides and their breakdown products considered to be “in common detection” by the Minnesota Department of Agriculture (MDA) are the most widely detected — alachlor (73 percent of wells), metolachlor (65 percent of wells), atrazine (64 percent of wells) and acetochlor (56 percent of wells). Cyanazine is not in common detection status.

7. **The production and use of the herbicide cyanazine, common brand name Bladex, was discontinued in 2002; its breakdown products are still detected in 2019, in Ambient Study wells at levels that exceed the drinking water guideline (Section 4.2.7).** Breakdown products of cyanazine, a widely used corn herbicide discontinued in 2002, are found in 65 percent of the wells. Over the period of the study, the total concentration of cyanazine breakdown products exceeded the drinking water guideline of one microgram per liter (µg/L) at least once in 22 percent of the wells. The occurrence and frequency of detection, along with the concentration levels and trends, indicate that cyanazine contamination is moving deeper with time.

8. **Herbicide compound detections generally occur as mixtures with each other and with nitrate, and higher levels of nitrate are accompanied by an increase in the number of herbicide compounds. (Section 4.2.4).** Nitrate concentrations were positively correlated with both the number and concentrations of herbicide breakdown products detected, indicating row crop agriculture as the contaminant source.

   - 86 percent of the wells contained at least one herbicide compound. Fourteen percent had no herbicides.
   - 71 percent of the wells contained two or more herbicide compounds
   - 64 percent of the wells contained five or more herbicide compounds
   - 10 percent of the wells had 20 or more compounds detected at least once over the sampling period.
   - Over the period of the study a median of 15 different herbicide compounds were found in study wells with a median nitrate concentration greater than 3.0 mg/L
   - 54 percent of the wells that exceeded the drinking water guideline for nitrate also exceeded the drinking water guideline for cyanazine

9. **Pesticides are detected in municipal wells in both the 2005-2006 and 2019 sample events (Section 4.2.8).** Total cyanazine was above the 2005 drinking water guideline in one City of Hastings municipal well in 2005. Pesticides were detected in 46 percent (13 of 28 wells) in 2005 and in 62 percent (8 of 13 wells) in 2019. Zero municipal wells exceeded guidelines in 2019.

10. **Manganese, a naturally occurring, geologically sourced contaminant, was detected above the drinking water guideline in 34 percent of the wells (Section 5.1.1).** One-third of the wells exceeded the drinking water guideline of 0.100 mg/L established for infants less than one year of age; 19 percent exceeded the drinking water guideline of 0.300 mg/L established for children older than 12 months and adults. Manganese does not correlate with aquifer, well casing depth or land use.

11. **Arsenic, another naturally occurring, geologically sourced contaminant, was detected in 39 percent of the wells, none over the drinking water guideline (5.1.2).** The maximum arsenic detected was 9.9 µg/L, the drinking water guideline is 10 is µg/L. Arsenic was detected in 31 percent of the study wells; no amount of arsenic is considered safe. Arsenic is positively correlated with manganese and iron.

12. **All three primary drinking water aquifers and well casing depth categories are susceptible to contamination (Section 3.2).** Anthropogenic contamination is found in all the aquifers tested; however, the recently recharged water present in the upper aquifers (unconsolidated sediments and Prairie du Chien) has the highest levels of these contaminants. The unconsolidated sediments and Prairie du Chien aquifers do not show statistical differences for any of the anthropogenic constituents: in these two aquifers, the levels of nitrate, chloride and herbicide breakdown

compounds are similar and suggest that surface contaminants, largely introduced beginning in the 1950s, have migrated to a depth of approximately 330 feet. These contaminants are now at, or approaching, an approximate steady state or equilibrium with ongoing contamination from the surface. The study found that the well casing depth is a better indicator of vulnerability to surface contamination than is the aquifer in which a well is completed.

The Jordan aquifer does show statistically lower concentrations for all the anthropogenic constituents than either the unconsolidated or the Prairie du Chien aquifers because the Jordan is deeper and is below the Prairie du Chien. Where the bottom of the Prairie du Chien is confining, it can protect the Jordan by slowing the migration of contaminants to the Jordan where the water is older except in the few areas where groundwater is upwelling to the surface or the Prairie du Chien is absent. However, even the Jordan aquifer is susceptible to human use of nitrate; 25 percent of the wells in the Jordan and 24 percent in the deep well casing category have nitrate above 3.0 mg/L.

13. **Anthropogenic contaminants of emerging concern (CECs) are widespread at low levels (Section 4.9).** CECs, including per- and polyfluoroalkyl substances (PFAS), were detected in 79 percent of the wells, organic wastewater compounds were detected in 29 percent of the wells and pharmaceuticals were detected in 20 percent of the wells. The detections were below drinking water guidelines, where guidelines are established. Their presence, however, serves as an indicator of the susceptibility of the aquifers to surface contamination from diverse sources and the quick travel time from the surface to the water table. The health effects of consuming water with multiple contaminants are unknown.

**Summary of Anthropogenic Parameters in Ambient Study Wells detected above the laboratory method reporting level:**

- 97 percent contained chloride
- 83 percent contained nitrate
- 79 percent contained PFAS
- 73 percent contained herbicides
- 29 percent contained organic wastewater compounds
- 20 percent contained pharmaceuticals

14. **The age of well water and vertical recharge rates can be estimated using herbicide, nitrate and chloride results over time (Section 4.3.8).** The registration dates of herbicides and the timeframe for the widespread use of synthetic fertilizers and deicing salt are approximately known, which allows for an introduction year to be assigned to these substances. Analyzing data for herbicides, nitrate, sodium and chloride provides a method of estimating vertical recharge rates for the County’s drinking water aquifers. These estimates can help with estimating when changes in land use practices at the surface will result in changes in the groundwater. The water in some of the study wells was a young as 8 years old.

Figure 2 depicts the generalized flow of water and potential contamination from the land surface through the underlying material and aquifers to a well. The depth of a well is an important factor since, in general, deeper water is older and cleaner. When a chemical is applied to the land surface, it infiltrates through the aquifers to greater depths reaching deeper wells over time. The age of the water is the time between when the water infiltrated at the surface and when the water sample was collected from the well.

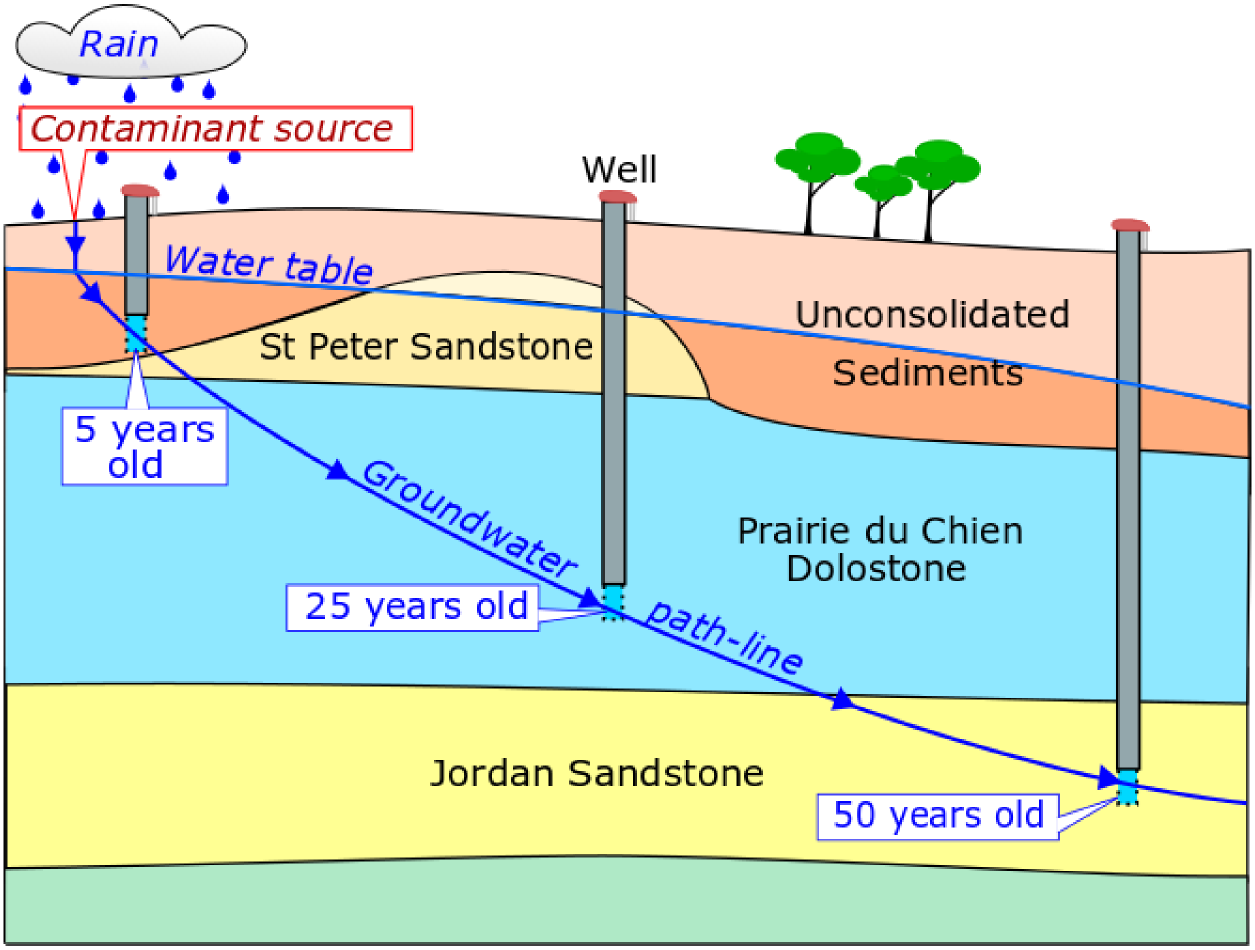


**Figure 2. Geologic Cross-Section and Simplified Contaminant Path to Wells.**

## Conclusions

The Ambient Study found that both anthropogenic and natural, geologically sourced contaminants are widespread in the drinking water aquifers: 62 percent of the wells tested exceed the drinking water guideline for one or more contaminants. Anthropogenic contaminants are persistent and moving deeper into the aquifers over time; with these contaminants, land use and well casing depth are the most important factors. By contrast, naturally occurring, geologically sourced contaminants—in particular, manganese—are widespread but difficult to predict.

Based on the County's groundwater conditions, drilling a deeper well to find "cleaner" water is a poor long-term strategy for a private well owner: anthropogenic contaminants like nitrate, herbicides, or chloride are migrating deeper, so a deeper well will be a temporary fix, and elevated manganese or other naturally-occurring contaminants may be found at any well depth. Better options are to prevent groundwater contamination wherever possible and to use appropriate water treatment where the groundwater is already contaminated.

While land use improvements limiting surface pollution sources may take decades to be fully effective, the sooner they are started, the sooner improvements will be seen. Land use changes implemented today to improve water quality will affect shallow wells first and deeper wells more slowly.

The Ambient Study has proved to be a useful framework to have in place for surveying the County's drinking water aquifers when CECs have been identified. Because of the existing Ambient Study well network, the County was able to conduct widespread sampling for PFAS, organic wastewater components, and pharmaceuticals when these became concerns. Vigilance and awareness are called for as new chemicals are introduced to the environment and new laboratory water testing capabilities make it feasible to detect more contaminants at very low levels.

Whether the contaminants are anthropogenic, naturally occurring, or newly identified, the Ambient Study provides a solid basis for well owner education and outreach, and a baseline of groundwater data for comparison as groundwater conditions change in the future.

## Recommendations

### Assistance and Education

- Increase and improve education and outreach efforts. Develop, implement, and update groundwater contamination maps, develop explanatory factsheets and other information on the County website to help inform private well owners and municipalities.
- To the extent appropriate and possible, collect demographic data to evaluate if water quality problems disproportionately impact specific populations and to address those inequities.
- Develop and implement a sampling schedule that will provide every well owner in the County the opportunity to have their well tested for nitrate, arsenic, manganese, lead and chloride and will also support the Agriculture Chemical Reduction Effort (ACRE) implementation. See the Dakota County Groundwater Plan for a description of the ACRE plan (to be published in fall of 2020).
- Communicate water test results and health risk.
- Ensure information for well owners is available in multiple languages and accessible formats.
- Develop a program promoting the installation and maintenance of household treatment systems (RO) where groundwater contaminants are elevated or exceed drinking water guidance.
- Develop opportunities to work with State and County public health departments to inform local health care providers on the existence and risks associated with elevated nitrate, manganese, arsenic and herbicide concentrations in private water supply wells.
- Support feasibility studies to determine if a rural water supply system or expansion of public water systems are practical.

## Agricultural Chemicals

- Work with MDA to ensure private well sampling schedules support implementation of the Groundwater Protection Rule and Nitrogen Fertilizer Management Plan.
- Partner with MDA to develop a long-term groundwater monitoring network to evaluate effectiveness of the Groundwater Protection Rule, the Nitrogen Fertilizer Management Plan and the Dakota County Agriculture Chemical Reduction Effort.
- Work with MDA and MDH to implement their response to cyanazine breakdown product contamination in Dakota County.

## Contaminants of Emerging Concern

- Work with MPCA to evaluate the source(s) of PFAS in groundwater beginning with an analysis of PFAS near WWTP biosolid application sites in Dakota County.
- When new CECs are identified that could be a risk for County residents, sample private wells to screen the County's drinking water supplies for detections and concentrations of the contaminant.

## Research and Analysis

- Work with state agencies, watershed organizations and others to further research groundwater and surface water interactions.
- Conduct research and analysis to determine the influence of irrigated agriculture on groundwater contaminated with nitrate and pesticides.
- Work with MDA, MDH and the City of Hastings to evaluate the threat to Hastings water supply for non-point agricultural chemicals. Expand sampling within the buried bedrock valley to better understand infiltration and groundwater flow.
- Retain a researcher to conduct an epidemiological analysis that would assess agricultural chemical contamination of drinking water (e.g., complex agricultural chemical mixtures) with health outcomes among Dakota County residents.
- Develop and implement a project to sample private wells for pathogens (viruses, bacteria and protozoan parasites), which MDH detected in 70 percent of non-community and community wells, statewide, as part of their recent pathogen study (MDH Pathogen Project).
- Evaluate impact of land application of sewage sludge and other biosolids on County groundwater quality.
    - Review published literature to identify characteristics of groundwater impacted by land application of sludge and biosolids vs. groundwater not impacted.
    - Identify known locations of sludge, biosolids, and manure applications.
    - With well owner permission, sample potentially impacted and presumably non-impacted wells for pathogens, PFAS, microplastics and organic wastewater compounds.

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# Abbreviations and Definitions

## Abbreviations

| | |
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| < | Less than the laboratory method reporting level |
| ACRE | Agricultural Chemical Reduction Effort |
| AGQS | Ambient Groundwater Quality Study, or Ambient Study |
| AOC | Anthropogenic organic compound |
| ATS | Akritas-Thein-Sen |
| BAC | Biologically active compound |
| Bgs | Below ground surface |
| Cjdn | (Cambrian) Jordan Aquifer |
| CEC | Contaminant of emerging concern |
| County | Dakota County, Minnesota |
| DNR | Minnesota Department of Natural Resources |
| DWS | Drinking Water Standard |
| EPA | Environmental Protection Agency |
| EDP | Endocrine-disrupting potential |
| GAC | Granular activated carbon |
| HRL | Health Risk Limit |
| KCL | Potassium chloride, potash also known as $K_2O$ |
| KW | Kruskal-Wallis statistical method |
| MCL | Maximum Contaminant Level |
| µg/L | Micrograms per liter, equivalent to parts per billion |
| mg/L | Milligrams per liter, equivalent to parts per million |
| MDA | Minnesota Department of Agriculture |
| MDL | Method Detection Limit |
| MDH | Minnesota Department of Health |
| MGS | Minnesota Geological Survey |
| MPCA | Minnesota Pollution Control Agency |
| MRL | Method Reporting Limit |
| MUSA | Metropolitan Urban Service Area |
| MVTL | Minnesota Valley Testing Laboratories |

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|---|---|
| NASS | National Agriculture Statistics Service |
| NWQL | United States Geological Survey, National Water Quality Laboratory (Colorado) |
| OGRL | United States Geological Survey, Organic Geochemistry Research Laboratory (Kansas) |
| Opdc | (Ordovician) Prairie du Chien Aquifer |
| OWWC | Organic wastewater compound |
| p | Probability value |
| PCE | Tetrachloroethene |
| PFCs | Perfluorochemicals |
| PFAS | Per- and Polyfluoroalkyl Substances |
| RO | Reverse osmosis system |
| SDWA | Safe Drinking Water Act |
| SEMWAL | Southeast Minnesota Water Analysis Laboratory |
| SMCL | Secondary Maximum Contaminant Level |
| SOM | Soil organic matter |
| TKN | Total Kjeldahl nitrogen (Sum of ammonia, organic nitrogen, and reduced nitrogen) |
| TOC | Total Organic Carbon |
| Ucs | Unconsolidated sediments aquifer |
| USDA | United State Department of Agriculture |
| USGS | United States Geological Survey |
| USEPA | United States Environmental Protection Agency |
| WWTP | Wastewater treatment plant |

## Definitions

| Term | Definition |
|---|---|
| *Agricultural chemical* | A pesticide, fertilizer, plant amendment, or soil amendment (Minnesota Groundwater Protection Act, Mn. Statute 103H). |
| *Ambient groundwater* | The parts of the water resource that are affected by the general, routine use of chemicals and are not affected by localized pollutants or spills (MPCA). |
| *Anthropogenic* | Environmental change caused or produced by humans. |
| *Aquifer* | A layer of sediment, such as sand or gravel, or a layer of rock, such as sandstone, that stores and transmits water to a well (MDH). |
| *Aquitard* | A layer of sediment such as clay, or a layer of rock such as shale, that restricts the vertical movement of water. Sometimes called a leaky layer. Also see Confining Unit. |
| *Background* | Naturally occurring concentration of a chemical which is: (a) consistently present in the environment and near a site; and (b) attributable to geologic or natural conditions (i.e., too low a concentration to be due to human activity). |
| *Bedrock* | A relatively hard, solid rock that commonly underlies softer rock, sediment, or soil (USGS). |
| *Borehole* | A hole bored or drilled into the earth in which well casing and a pump can be installed to extract water for a water supply well. |
| *Breakdown Product* | A compound produced from the breakdown of the parent chemical, synonymous with degradation product or degradate. |
| *CECs* | Contaminant of emerging concern is commonly sampled for and is not typically regulated. |
| *Clustered Wells (well clusters)* | Specific Ambient Study wells in different aquifers typically located within 1,500 feet horizontally of each other. |
| *Contaminant* | Any physical, chemical, biological, or radiological substance or matter in water. Drinking water may reasonably be expected to contain at least small amounts of some contaminants. Some contaminants may be harmful if consumed at certain levels in drinking water. The presence of contaminants does not necessarily indicate that the water poses a health risk (SDWA). |
| *Confining Unit* | A layer of sediment, such as clay, or a layer of rock, such as shale, that restricts the movement of water and forms the top of an aquifer. |
| *Denitrification* | A microbially-facilitated process where nitrate ($NO_3^-$) is reduced and ultimately produces molecular nitrogen ($N_2$) through a series of intermediate gaseous |

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| | nitrogen oxide products. Denitrifying microbes require a very low oxygen concentration of less than 10 percent, as well as organic C for energy (Wikipedia). |
| *Drinking water guideline* | The advised or recommended concentration when no legally enforceable drinking water guideline exists. This report uses the lowest applicable federal or state health-based guidance. |
| *Drinking water standard* | A legally enforceable concentration established either by the USEPA or the MDH. This report uses the lowest applicable federal or state health-based guideline. See Appendix E.2. for a description of all the guidelines that are applicable in Minnesota. |
| *DWSMA* | Drinking Water Supply Management Area is an area on the land where water leaching down to the groundwater could flow to a public water supply well within 10 years. |
| *Groundwater* | Water that exists underground (beneath the land surface) in saturated zones (where soil is completely saturated with water). The upper surface of the saturated zone is called the water table (USGS). |
| *Grout* | Material used to fill the space between the well casing and the borehole wall to keep surface water and other contaminants from entering the well. Grout is a specific mixture of water and cement, or water and “bentonite” clay, and sometimes other permitted additives such as sand (MDH). |
| *Hardness* | The amount of dissolved calcium and magnesium in the water. “Hard” water is high in these dissolved minerals (USGS). |
| *Infiltration* | The process by which water on the ground surface enters the soil. Some water may remain in the shallow soil layer and some of the water may move (infiltrate) deeper, recharging groundwater aquifers (USGS). |
| *Karst* | Porous limestone with sections that have dissolved over time, riddling the rock with joints and fractures through which water passes quickly. When water comes in contact with limestone, which is predominantly calcium carbonate, it forms carbonic acid, which dissolves and erodes the rock. Karst landscapes feature springs, sinkholes, underground streams, and caves, all of which provide conduits that can quickly transport surface water to the groundwater and water wells. |
| *Kendall Tau* | A ratio of positive minus negative slope pairs to the total possible number of slopes. |
| *Kruskal Wallis Test* | A non-parametric test for differences of medians. |
| *Leach/ Leaching* | The slow movement of liquid, which could carry a contaminant, through the soil or groundwater. |

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| *Loading* | Amount of a substance that is carried from the land surface to the groundwater by leaching. Can be expressed as pounds per acre at the land surface, or as concentration in the leachate or groundwater. |
| *Mean (average)* | Most commonly used measure of central tendency: the average concentration for all samples collected from a well. |
| *Median* | Measure of central tendency: the middle value of all samples when they are ranked from highest to lowest. |
| *MDL* | The Method Detection Limit is the smallest amount of an analyte in a sample that can be reliably determined with a given analytical method. |
| *MRL* | The Method Reporting Limit is the smallest amount of an analyte in a sample that can be reliably reported by a laboratory. |
| *Naturally occurring contaminants* | Contaminants that enter the environment naturally as a mineral from sediment and rocks. As groundwater flows through the ground, metals such as iron and manganese are dissolved and may later be found in high concentrations in water (USGS). |
| *Nitrate* | Nitrate as Nitrogen will be referred to as nitrate. |
| *Non-point source contamination* | A diffuse contamination source that cannot be traced to a single identifiable source, usually covering a large area of land and difficult to control. |
| *Oneota Formation* | The lower formation in the Prairie du Chien group, which acts as a confining layer in most of Dakota County. |
| *Parameter* | A discrete chemical entity that can be assigned a value: commonly a concentration (Wikipedia). |
| *Pesticide* | Chemical used to kill “pests”: unwanted plants (herbicides), insects (insecticides), or fungi (fungicides). Pesticides also include defoliants, desiccants, and plant regulators. |
| *Point-Source contamination* | Contamination from single identifiable sources from which pollutants are discharged, such as a factory, sewage treatment plant, pipe, ditch, or facilities used for the storage, treatment, or disposal of wastes, such as landfills and surface impoundments. |
| *Porosity* | The ratio, expressed as a percentage, of the volume of pores of a substance. Pore spaces are small spaces between soil or rock particles in sand and gravel deposits. |
| *Recharge* | The hydrologic process where water moves downward, from surface water to groundwater (Wikipedia). The recharge rate for a water table aquifer is the rate that water is added to the aquifer from above, normally from rainfall that infiltrates. |

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| *Run-off* | Water that falls on the ground (e.g., rain, snowmelt or other sources) and moves over the landscape before either entering a surface water body or infiltrating into the groundwater (USGS). |
| *SMCL* | Secondary Maximum Contaminant Level is the federal guideline that applies to constituents in drinking water that affect the odor, taste or appearance |
| *Section* | A legal area of land as defined by the Public Land Survey System, approximately one square mile or 640 acres. |
| *Septic system* | Underground treatment structures commonly used in rural areas without centralized sewer systems that treat wastewater from household plumbing. A typical system consists of a septic tank and a drain field, or soil absorption field (EPA). |
| *Toxic endpoint* | The anatomical organ or system at risk of being damaged by a specific contaminant. For example, a chemical may cause cancer, liver damage, kidney damage, neurological or brain damage, reproductive system damage or birth defects, or immune system damage. |
| *Toxic heavy metal* | Any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts (Wikipedia). |
| *Unconsolidated sediments* | Sediments that have not been consolidated into rock. In Dakota County these are sediments deposited by glaciers, streams or lakes. Unconsolidated sediment aquifers occur where glacial processes have deposited concentrations of sand or gravel. Glacial aquifers are often local rather than regional in extent. Glacial till generally refers to glacial deposits high in clay content; till can act as a confining unit. |

# 1. Purpose and Scope

The Dakota County Ambient Groundwater Quality Study (Ambient Study or study) was initiated in 1999. This report summarizes the data collection, analysis, findings and recommendations of the Dakota County Groundwater Protection Unit in the Environmental Resources Department. The subject of this report is the ambient groundwater quality of the three principal aquifers used for drinking water in Dakota County. The initial objective of the study was to determine if the groundwater quality was getting better or worse over time and to collect accurate and detailed analytical data needed to characterize the groundwater quality of private domestic drinking water wells supplied from the Prairie du Chien (Opdc) and Jordan aquifers (Cjdn). Sampling was expanded to evaluate the groundwater quality of the sand and gravel aquifer referred to as the unconsolidated sediments aquifer (Ucs).

**Three Principal Aquifers Used to Supply Drinking Water Wells**

- Ucs—unconsolidated sediments, such as, sand and gravel
- Opdc—(Ordovician) Prairie du Chien Dolostone
- Cjdn— (Cambrian) Jordan Sandstone

The number of wells sampled each year of the study varied somewhat, either because a well was sealed or the well owner decided to no longer participate. Wells were added to the study to replace the discontinued wells where feasible. The dataset for this report consists of 77 wells that have been sampled more than once. All water samples were collected from untreated outdoor faucets from private drinking water wells. The well owners consented to the sampling and were provided with an explanation of their well’s water test results.

The results of the study informed decisions about sampling additional private and municipal wells outside the Ambient Study well network. This Ambient Groundwater Quality Study report summarizes drinking water data collected from 1999 through 2019 and includes data from other sampling events that occurred in Dakota County during this same period. Results of the sampling from 1999–2003 were presented in the Dakota County Ambient Groundwater Quality Study 1999–2003 Report, see www.dakotacounty.us, search *Ambient Groundwater Quality Study*.

## 1.1. Background

Dakota County is the third most populous county in the State of Minnesota with a population of more than 422,000 residents and is expected to increase to 514,050 by 2040. Dakota County is in the Minneapolis-St. Paul Twin City Metropolitan Area (TCMA shaded in Figure 3) comprised of seven metro counties and is bordered by the Minnesota River along the northwest, the Mississippi River along the northeast, and the Cannon River along the southeast.

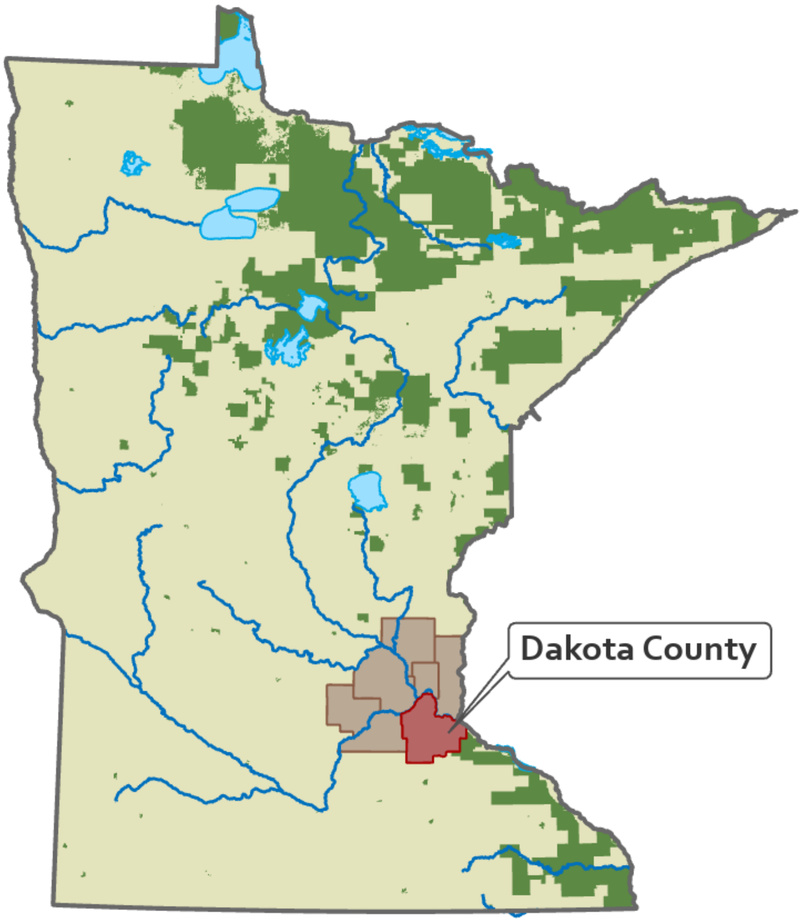


**Figure 3. Dakota County, Minnesota.**

More than 90 percent of Dakota County residents rely on groundwater for their drinking water supply, either from municipal wells (approximately 135 wells) or from privately-owned domestic potable drinking water wells (approximately 8,300), referred to as private wells. Residents in northern Dakota County receive drinking water supplied by St. Paul Regional Water Services, which is treated surface water, augmented with groundwater from Ramsey County.

Groundwater is an integral component of the hydrologic (water) cycle. The cycle begins with precipitation falling to the ground. Rain or snow melt either runs off the land into surface water bodies or infiltrates into the soil. Some water is taken up by plants and transpired back into the air; the rest, called recharge, infiltrates downward to the water table. In general, water moves from higher elevation to lower elevation from where it is recharged to where it discharges to a lake, stream or ocean, and becomes surface water. Surface water can either recharge groundwater or evaporate into the atmosphere where it forms clouds and becomes precipitation to begin the cycle again. Figure 4 shows an illustration of the hydrologic cycle.

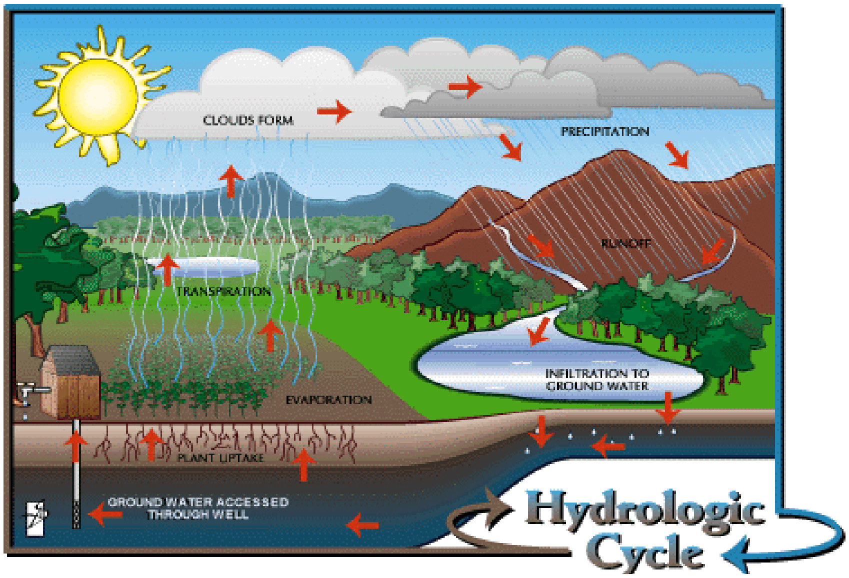


**Figure 4. Hydrologic Cycle.**
**(Source: Ground Water Primer Env. Protection Agency (EPA)**

The most heavily used aquifer for municipal water supply is the Cjdn. Private wells primarily use the Cjdn or Opdc bedrock or wells screened in sand or gravel, the Ucs.

A portion of the County’s available and viable groundwater resources are unsafe for human consumption. The most contaminated groundwater is in the Ucs and Opdc aquifers. Since 1989, well drilling in the Opdc is restricted due to concerns about elevated nitrate throughout much of the southern and southeastern portions of the County. Drillers are prohibited from completing a drinking water well in the Opdc where the depth from the surface to the bedrock is less than 50 feet within a mile of the proposed well’s location, Figure 5 depicts these areas as “Not Permitted.” There are several Ambient Study wells in the Opdc that were drilled prior to 1989 and would not be allowed to be completed in the Opdc aquifer today.

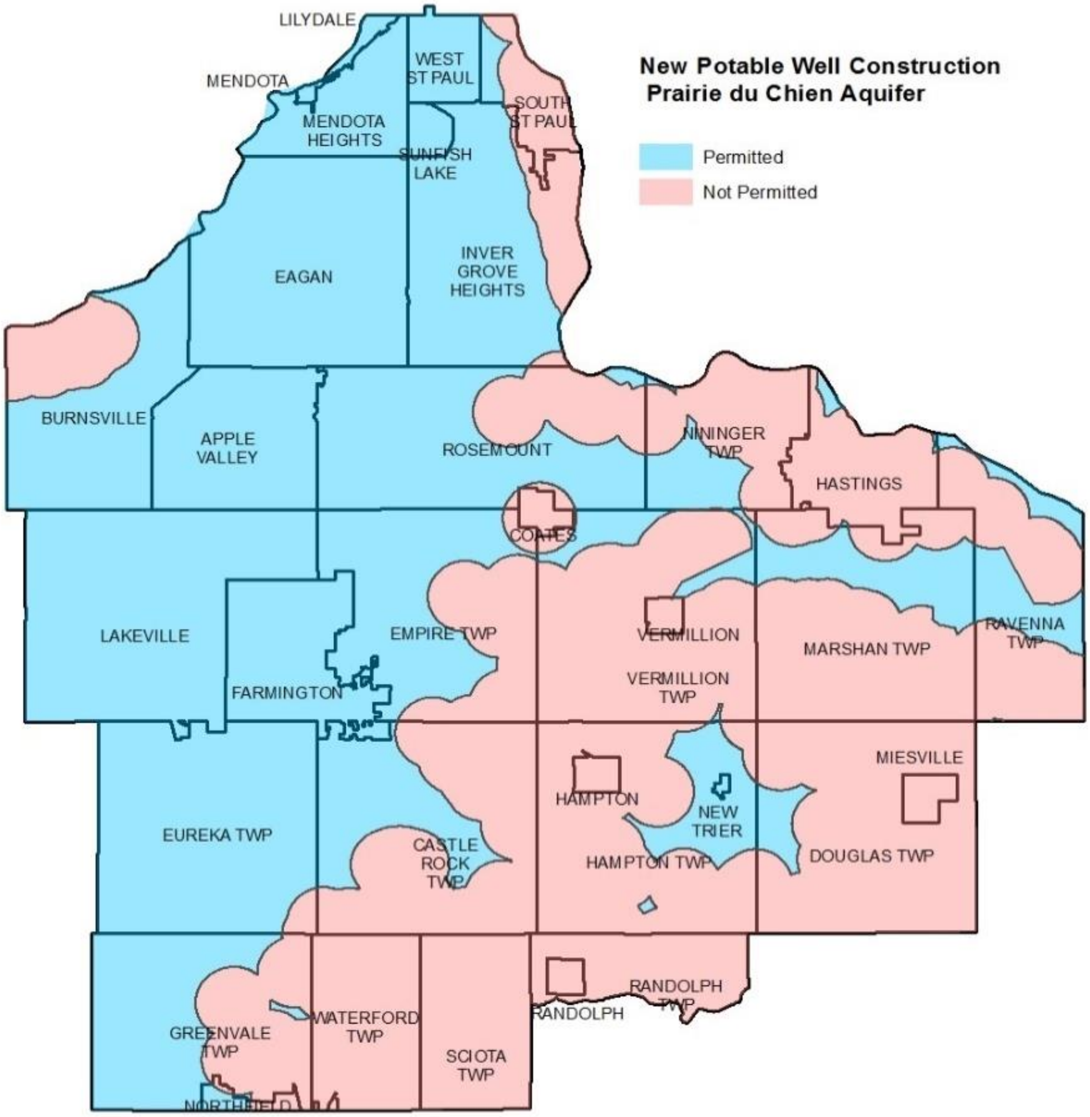


**Figure 5. Permitted and Not Permitted New Well Construction in the Opdc Aquifer.**

Dakota County groundwater use is shown in Figure 6. The water supply is mainly water delivered from cities to residential customers. In the summer months, demand for municipal water can double and even quadruple in some communities in the TCMA for irrigating landscapes and grass (Metropolitan Council 2018).

As the population grows, the demand for groundwater will increase. Groundwater supplies may not be adequate in some areas of the County to meet this demand. It is also unclear what affect the demand will have on surface water features such as trout streams and fens (rare wetlands) that depend on groundwater. Since contaminated water cannot be used for human consumption without treatment, the availability of drinking water may be further decreased unless adequate measures to protect groundwater quality are initiated.

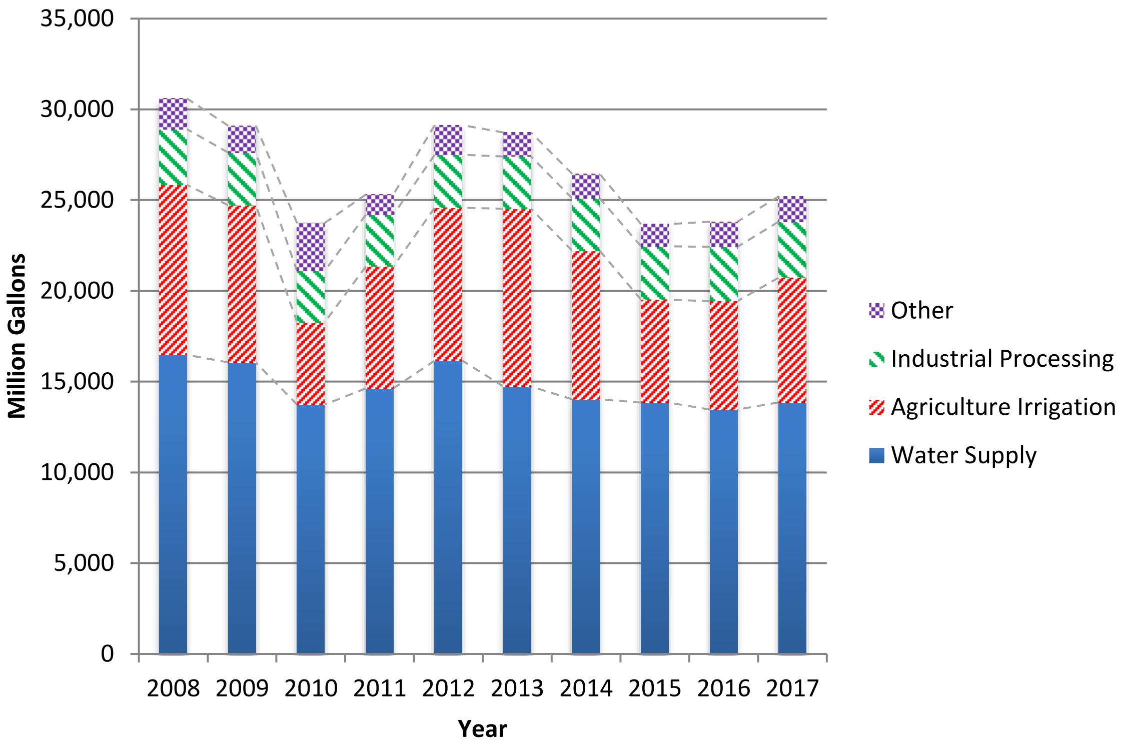
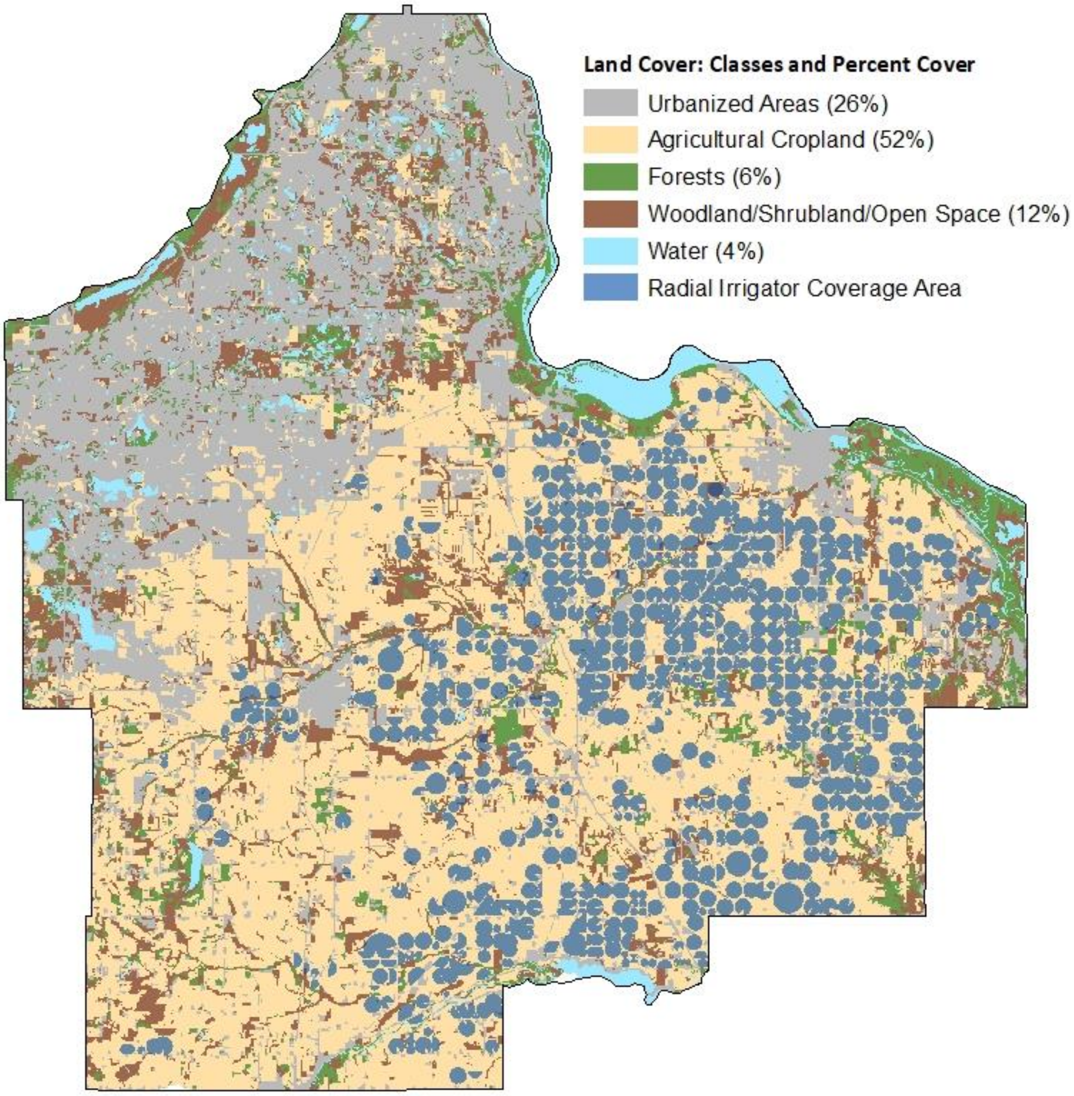


**Figure 6. Dakota County Groundwater Use (MG) per Year by Category. (Source: MN DNR Permitting and Reporting System)**

## 1.2. Land Use

Despite the County’s large population, about half of the land area is rural and is actively cropped. Figure 7 depicts land use; the gray shaded area is the urbanized area served by Metropolitan Urban Service Area (MUSA), where municipal sewer and water are available.

Fifty-two percent of Dakota County’s land area, shown in tan, is agricultural, mostly conventional row crops such as field corn, sweet corn, soybeans, potatoes and peas. Much of the crop land is irrigated; the area irrigated by center pivot irrigators is shown in blue circles in Figure 7. According to Minnesota Department of Natural Resources (MN DNR) records, Dakota County is the second largest user of water for crop irrigation in the state. Older agricultural irrigation wells in Dakota County are constructed with an open interval spanning both the Opdc and Cjdn aquifer formations. This open interval connects the two aquifers, and this is called a multi-aquifer well. When a multi-aquifer well is idle, any pressure difference between the aquifers will produce inter-aquifer flow through the well. Irrigation wells are idle for most of the year. Groundwater flow simulations show that when large multi-aquifer irrigation wells are not pumping, they can passively transmit large volumes of water from the Opdc into the Cjdn with only small differences in pressure. The passively transmitted water creates plumes with high nitrate concentrations that are distributed over the entire thickness of the Cjdn aquifer. That contrasts with normal downward leakage between the aquifers, in which case high nitrate water from the Opdc enters at the top of the Cjdn and moves downward through the Cjdn slowly. Plume migration caused by multi-aquifer wells may explain some of the high nitrate levels observed in very deep wells in Dakota County.



Source: Dakota County Soil and Water Conservation District

**Figure 7. Land Use Classes in Dakota County.**

## 1.3. Climate

Average monthly temperature ranges from around 10°F in January to around 70°F in July. Most rainfall occurs during the months from May to September. Snow usually accumulates and covers much of the ground during the months from December to March. Average annual rainfall in the County ranges between 29 and 32 inches; in 2019, Dakota County received a record 42.99 inches of precipitation. Precipitation is important because any moisture that percolates into the soil will recharge the aquifers. Rain events are more frequent and more intense (MN DNR 2020). Intense rain can lead to less infiltration because the water is rapidly running off into streams where the water is exported out of the County and ultimately out of the State. The amount of estimated average runoff leaving the State was the highest in 2019 since record keeping began in 1901 (USGS Waterwatch 2020).

## 1.4. Geology

### 1.4.1. Shallow (Surficial) Geology

The surface geology of Dakota County (Figure 8) is characterized by the effects of the glaciation that dominated the landscape during the past two million years. The County is covered by variable thicknesses of glacial tills and outwash deposited by ice sheets between 2 million and 10,000 years ago. Collectively these sedimentary deposits are referred to as unconsolidated sediments. The texture and thickness of these glacial deposits influences the location and types of land uses supported and the vulnerability of the groundwater to surface contamination. The rolling hills in the northern and western portions of the County demarcate the location of the glacial moraines, which mark the furthest extent of ice lobes of the most recent glacial advances. Generally, these soils are poorly drained and are not well suited for agriculture; drain tile is used to drain the water from agricultural fields to ditches and surface water.

Outwash plains are located adjacent to most of the moraine areas and were formed when meltwater from the receding glacier deposited and reworked the glacial deposits. These vast areas of level, well-drained soils generally tend to be droughty. However, with large irrigation and fertilizer inputs, these soils, located in the east and southeast portion of the County, can produce optimum yields of high-quality produce. Many of these soils contain significant fractions of gravel or coarse sand; these are of concern where contamination occurs because they transmit water and contaminants quickly. The Minnesota Geological Survey is currently updating the geologic maps for Dakota County as part of the Dakota County Geologic Atlas. This will include refinement of the surficial geology map and mapping the texture and variability of the glacial sediments in cross section to aid on identifying more vulnerable areas.

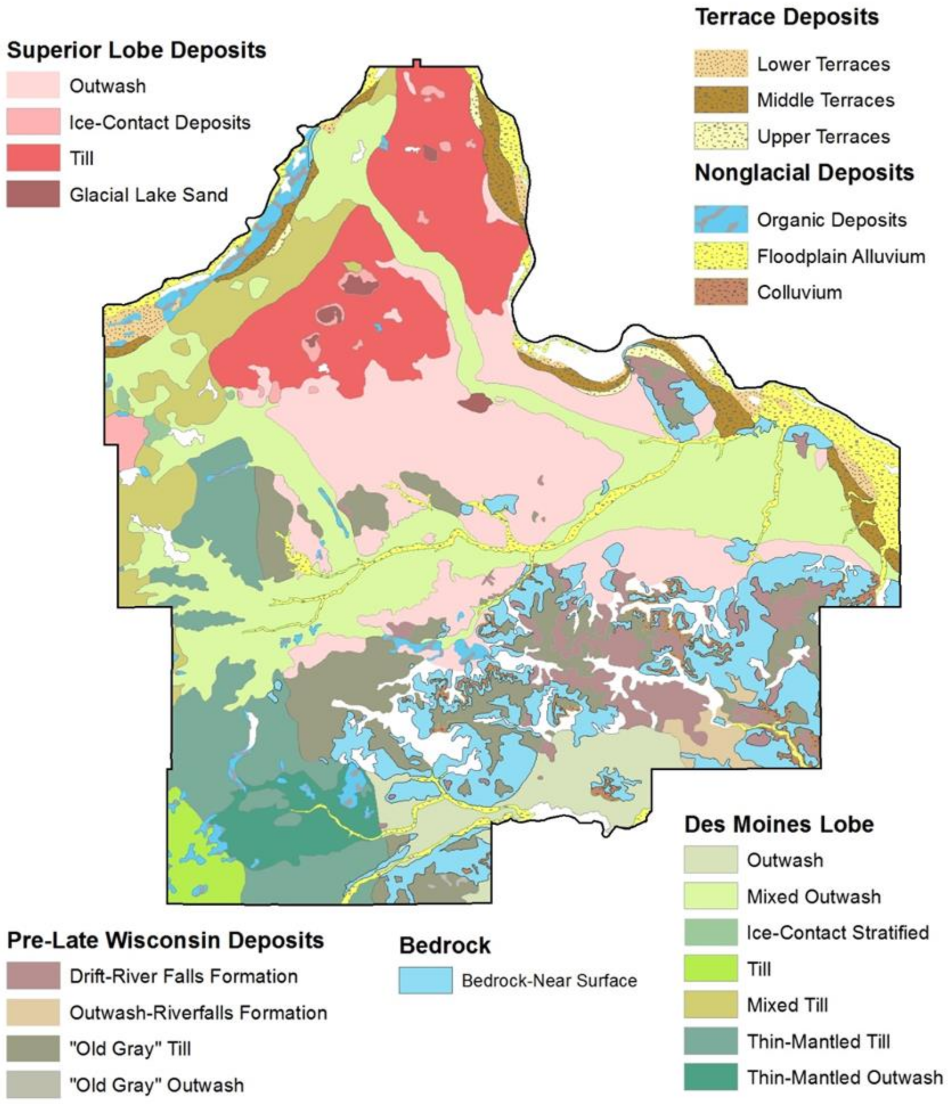


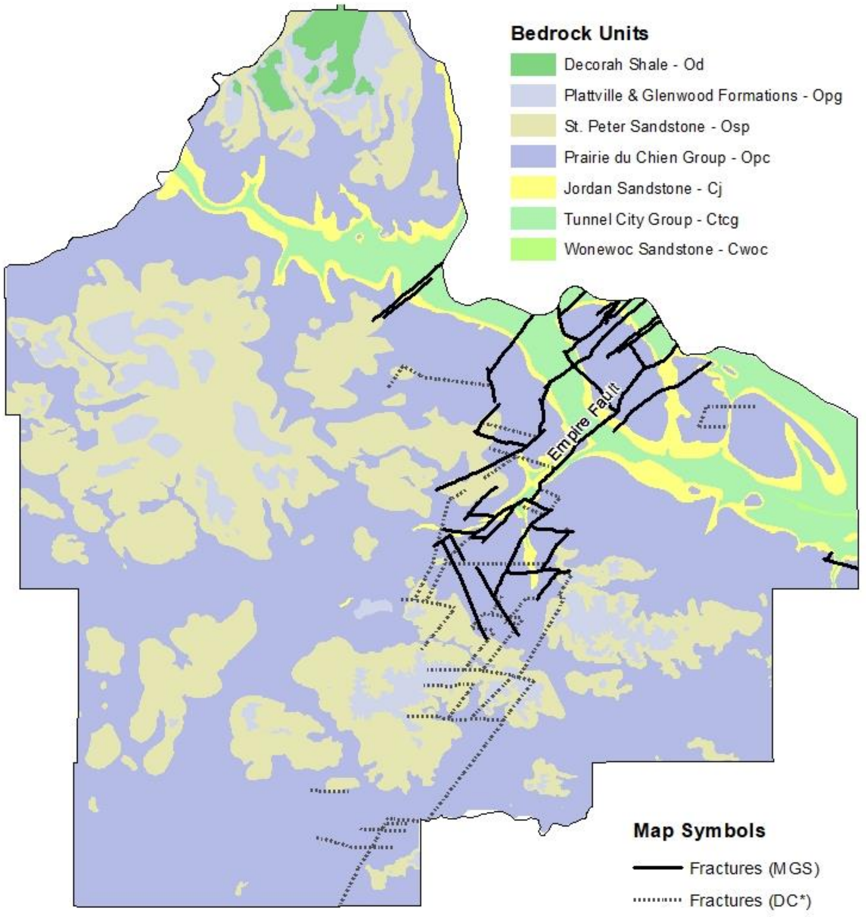
**Figure 8. Quaternary Geology in Dakota County.**
**(Source MN Geological Survey Dakota County Atlas Plate 3)**

### 1.4.2. Geology of the Bedrock Aquifers

The bedrock formations in Dakota County are marine sedimentary rock consisting of dolomite, limestone, sandstone and shales formed when ancient seas covered Minnesota before the glacial period, see Appendix E.3 for detailed geologic column. Although there are six regional bedrock aquifers in Dakota County, the Opdc and Cjdn are the major high-capacity aquifers which serve as the principal water source for about two-thirds of the wells in the County. The Opdc Group is a geologic unit made up of the Shakopee Formation and the Oneota Dolomite. The Shakopee is an aquifer and the Oneota can be a confining unit that separates the upper aquifers from the deeper Cjdn Aquifer. The Opdc ranges in thickness from 130 to 250 feet . The Cjdn formation is poorly cemented, cross-bedded, quartzose sandstone that ranges in thickness from 70 to 125 feet.

Opdc Group underlies most of the County (Figure 9); it is highly fractured and karsted. Karst is porous limestone or dolostone that contains solution channels and sinkholes through which water passes quickly. Karst areas can provide conduits that directly connect surface water to the groundwater and are particularly susceptible to groundwater contamination. A map of the karst areas and a discussion of water quality related to karst can be found in section 4.4.7.iv.

After these formations were laid down, tectonic forces created a series of small folds and faults. Individually, these folds and faults have displacements of about 100 feet for folds and between 50 and 150 feet for faults. The Empire Fault and the Vermillion Anticline (an upward fold) are the two largest structures known in the County. Several other smaller structures exist in the bedrock formations in the eastern part of Dakota County. These structures influence the groundwater flow paths and thus, contaminant migration. Currently an updated bedrock geologic map is being produced for Dakota County by the Minnesota Geological Survey to better refine these structures.



* Fracture locations interpreted from well logs where discontinuities in bedrock elevation occur across neighboring wells

**Figure 9. Bedrock Geology.**
**(Source: MN Geological Survey Dakota County Atlas Plate 2 and Mossler, 2013 and DC- Dakota County)**

Glacial aquifers (Ucs) that are in physical contact with bedrock aquifers are also hydrologically connected; they behave as a single aquifer unit. Where glacial drift aquifers have filled ancient valleys cut deeply into the bedrock, they provide vertical connection between bedrock aquifers that are otherwise separated from each other by bedrock confining layers. In these cases, contaminated water from the Ucs aquifer or from another upper aquifer can enter lower bedrock aquifers. This is a concern in the buried valley in Nininger, Marshan, Ravenna and Vermillion townships. This area has a significant number of high capacity irrigation wells completed in either the Opdc, Cjdn or multi-aquifer with an open hole to both the Opdc and Cjdn aquifers in and near the buried valley, where agriculture chemicals are applied on large-scale row crop agricultural fields. Since 1989, Dakota County regulates well construction and sealing through its MDH Delegated Well Program; the County prohibits the interconnection of the Opdc and Cjdn; they are treated as two distinct aquifers separated by the Oneota Dolomite formation of the Opdc Group.

### 1.4.3. Sensitivity

Land surfaces, soil type and geologic features influence groundwater quality in the County. Coarse-textured sandy soils, shallow depth to bedrock and porous sandstone or karsted limestone or dolostone that contain solution channels, sinkholes and fractures allow water to move quickly vertically and horizontally. Conditions that allow water to move quickly downward from the surface to the water table also allow contamination to move quickly; areas with these conditions are described as “vulnerable” or “sensitive” to pollution. In general, the buried and surficial sand and gravel aquifers, the Ucs, are the most sensitive to surface contamination due to the high rates of recharge and the relatively shallow depths to the water table. The underlying bedrock aquifers are also subject to more rapid infiltration. The Minnesota Geological Survey uses these criteria and others to evaluate the sensitivity of the Opdc and Cjdn aquifers to pollution. This analysis concluded that these bedrock aquifers are either very highly or highly sensitive to contamination across 75 percent of the County (Figure 10).

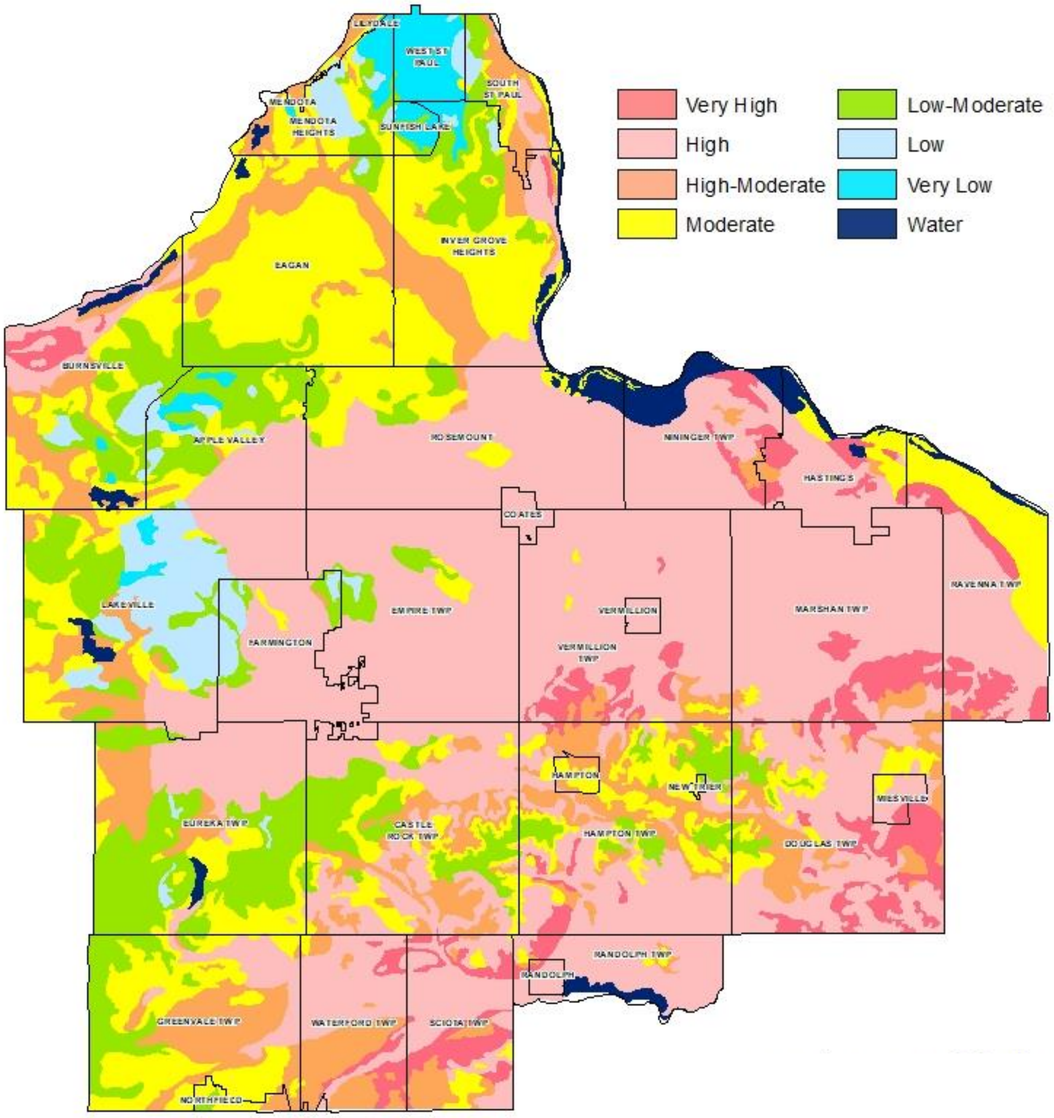


**Figure 10. Pollution Sensitivity of Prairie du Chien and Jordan Aquifers.**
**(Source: MN Geological Survey Dakota County Atlas Plate 7)**

### 1.4.4. Hydrogeologic Setting

Water falls to the ground as rain, infiltrates through the surface and soil, and is transported through an aquifer. Thus, air quality, soil composition and aquifer properties have major impacts on the water yielded by wells. As water enters the aquifer from the soil, it seeps through pore spaces and voids in the geologic material. The water table is the level below which the geologic material is saturated. Below the water table, water moves from high to low head pressure; head pressure is often thought of in terms of elevation. In general, groundwater moves from a recharge area at a higher elevation to a lower elevation.

Groundwater flows from the center of the County toward the Minnesota and Mississippi Rivers to the north and the Cannon River to the South (Figure 11). The Vermillion River bisects the County from southwest to northeast. However, it is a minor tributary to the Mississippi and has less effect on groundwater flow than the other rivers. The rate and direction of flow is controlled by recharge (primarily rainfall), discharge (primarily into these rivers) and by the characteristics of the aquifers. The deeper aquifers receive their water from the shallower aquifers through downward movement, and they give up their water to wells or to shallower aquifers through upward movement. In Dakota County, most downward movement occurs in the central and southeastern regions, while upward movement is typical where the groundwater discharges into the three major river systems: the Mississippi, Minnesota and Cannon Rivers and in lesser rivers.

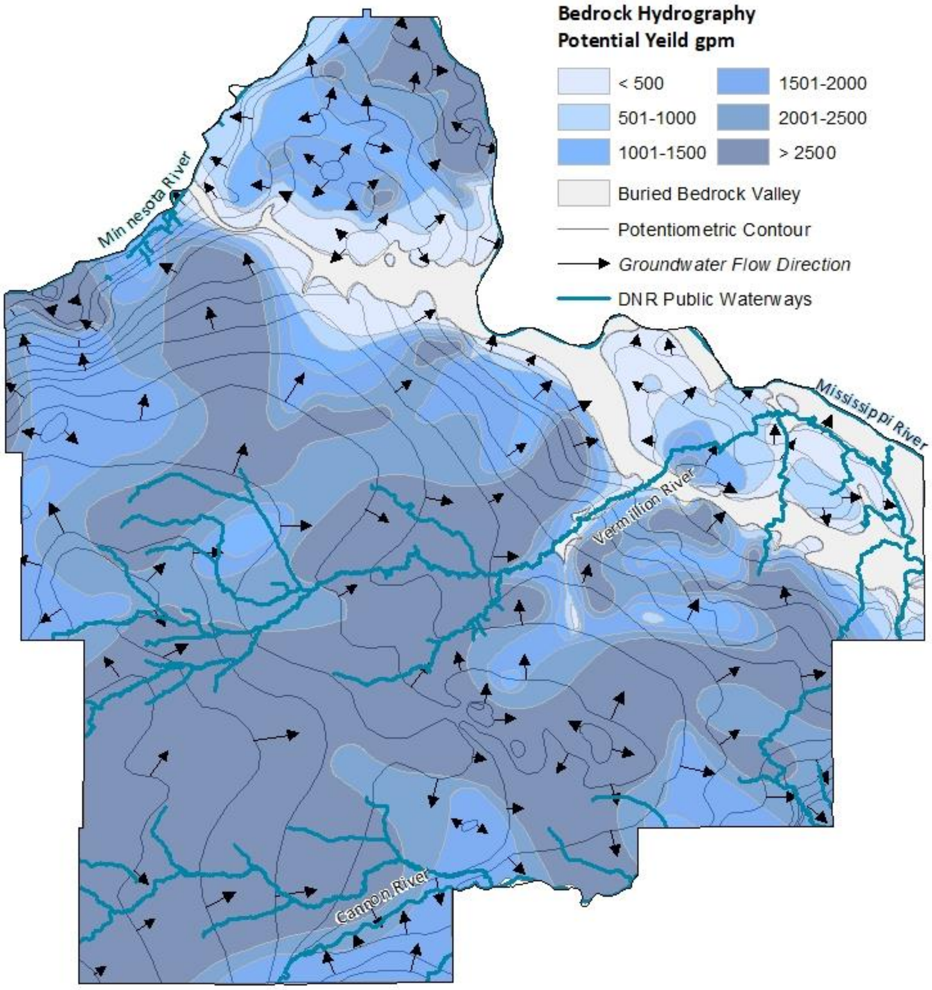
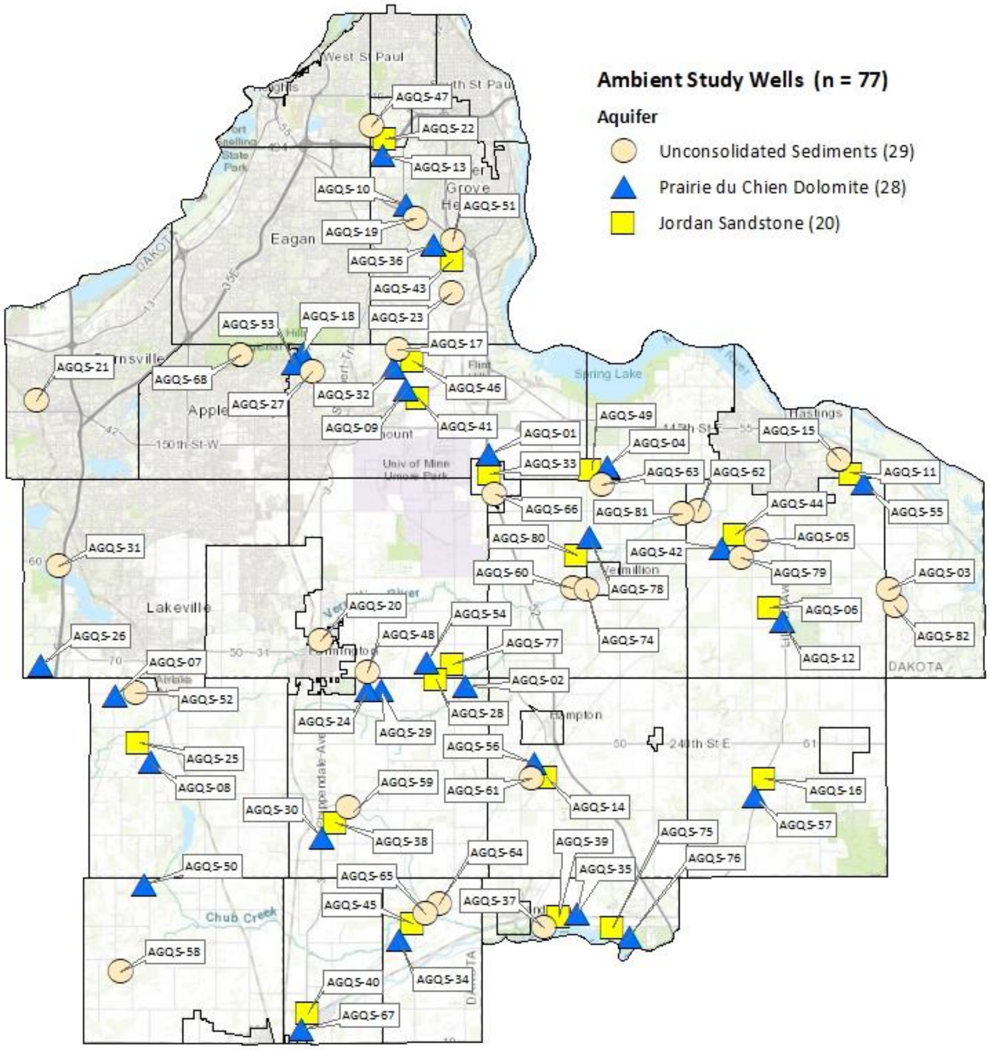


**Figure 11. Opdc-Cjdn Aquifer Groundwater Surface, Flow Directions and Yield. (Source: MN Geological Survey Dakota County Atlas Bedrock Hydrogeology Plate 6)**

# 2. Study Design and Methods

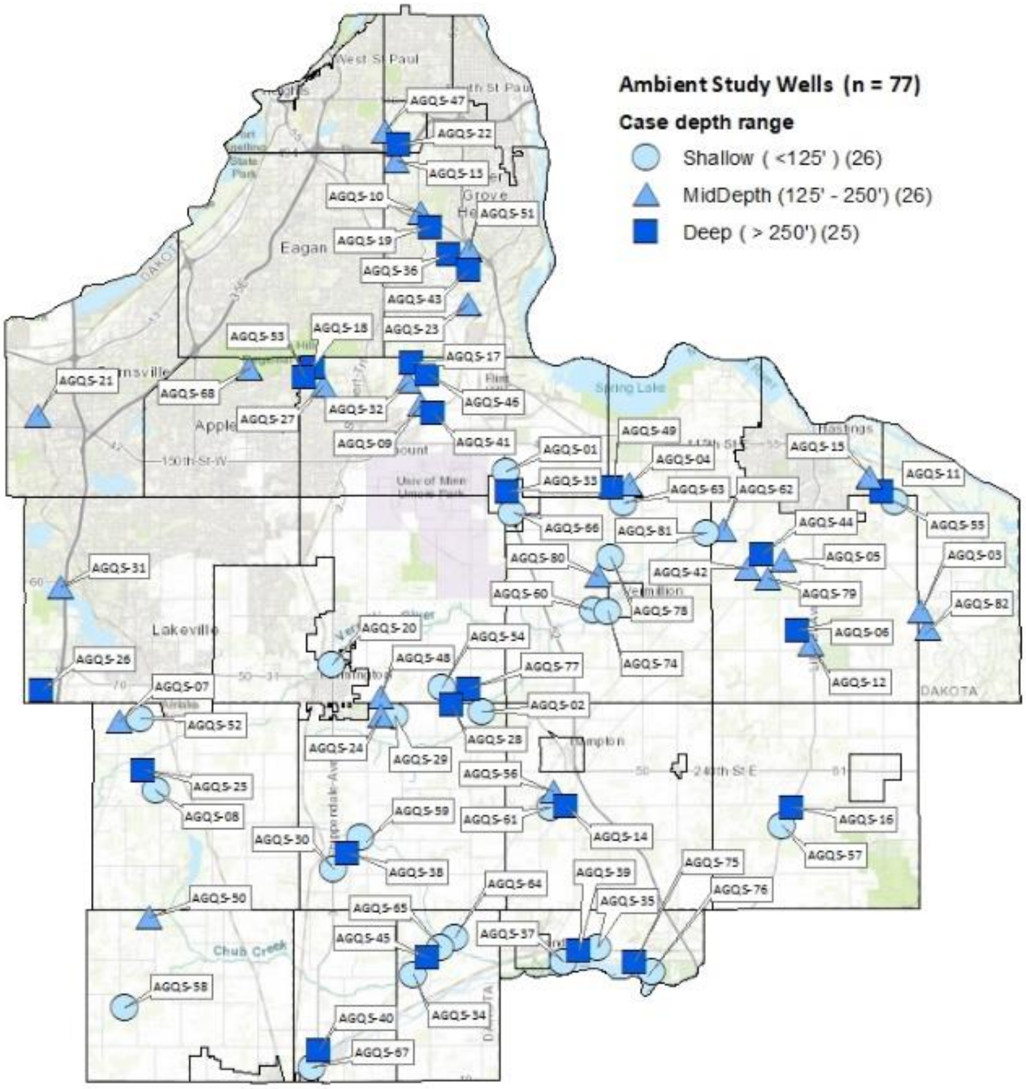
## 2.1. Well Selection Methodology

The Ambient Study wells were selected to be representative of the private drinking water wells in the County. This determination was made through queries of the County’s proprietary Well and Water Supply Management Database, which includes information on well location and construction details. The County has an estimated 8,300 households and businesses that rely on private drinking water wells. An estimated 40 percent of these wells were drilled prior to the passing of the first State well code of regulations regarding water well construction in 1974. These wells are presumed to be shallow and may not be properly grouted. Well contractors were not required by MDH to submit well construction records until 1974. Wells with records, which document how the well was constructed, were preferred. However, several of the study wells do not have a well record; an exception was made to include these wells, based on proximity to another well to create a well cluster for future comparative water quality analysis. Each well is accurately located with sub-meter accuracy based on Global Positioning System (GPS) technology. However, in the maps for this report, the well locations have been moved slightly from the GPS locations for spatial distribution and visual clarity. Select details about the construction of the wells is in Appendix B Table B.1. The 77 Ambient Study wells are labeled with alias, “AGQS” 1 thru 77 and are depicted by aquifer in Figure 12 and by well casing depth in Figure 13. Table B.1. also includes 31 municipal wells, alias “Muni” 1 through 31 that were sampled in either 2005, 2006 and/or 2019.



Source: ESRI; Dakota County Environmental Resources

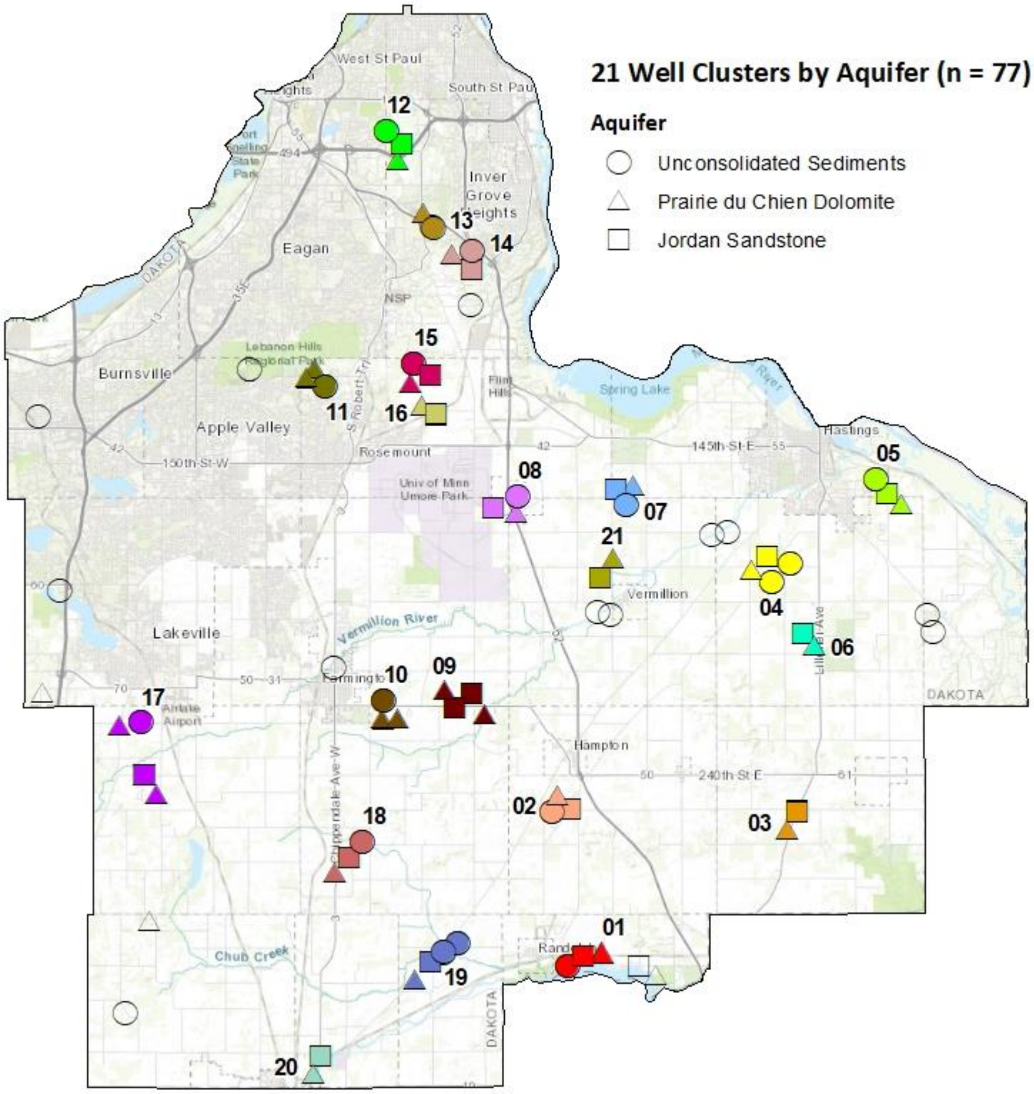
**Figure 12. Location of Ambient Study Wells by Aquifer.**



Source: ESRI; Dakota County Environmental Resources

**Figure 13. Location of Ambient Study Wells by Well Casing Depth.**

A balanced geographical distribution was taken into consideration. Where possible, wells were clustered; in other words, wells were selected that were within 1,500 feet of each other horizontally but completed in different aquifers. In 2004, wells screened in the Ucs were added to the study. The Ucs wells were selected based on proximity to clustered wells already in the study. This created 21 clusters (a total of 60 wells) for comparisons between aquifers. Figure 14 shows the wells and their cluster number, which are also listed in Appendix B Table B.1. The clusters contain either two, three or four wells. One cluster may contain two wells in the same aquifer. Seventeen of the 77 study wells are not in a cluster.



Source: ESRI; Dakota County Environmental Resources

**Figure 14. Location of Well Clusters by Aquifer.**

## 2.2. Well Sampling and Sample Analysis

Since 1999, some of the wells in the study have been sampled as many as 16 times. The sampling parameters are modified somewhat with each sampling event based on budget and emerging concerns. Contaminants of Emerging Concern (CECs) are contaminants that are being detected in ground and surface waters but are not commonly sampled for and are not typically regulated. All the parameters, laboratory methods and method reporting levels are specified in Appendix A.

The following is a summary of the significant modifications since the beginning of the study. In addition to general chemistry, which included nitrate, the following parameters were sampled:

- 2001—The United States Geological Survey (USGS) lab provided a list of triazines and acetamide herbicides commonly applied to corn and soybean crops, including the breakdown products of those herbicides. This list became the routine USGS list of herbicides tested.
- 2003—Analyzed samples from 15 wells for tritium (an isotope of hydrogen) and helium to estimate the age of the groundwater. Results are reported in the 1999–2003 report, see www.dakotacounty.us, search *Ambient Groundwater Quality Study* (p. 46).
- 2005—Sampled 25 municipal water wells for nitrate, nitrite and the routine USGS herbicide list.
- 2005 – 2006 Quarterly testing of five City of Hastings municipal wells for USGS herbicide list, nitrate and general chemistry
- 2008—Analyzed samples for Organic Wastewater Compounds (OWWC) and seven different perfluorochemicals (PFCs). The analysis for organic wastewater compounds included some herbicide parent compounds such as atrazine, alachlor and metolachlor.

Prior to each sampling event, the wells were purged, and stabilization parameters and general chemical parameters were collected. Titrating alkalinity in the field when collecting samples can be time consuming. In 2000, the laboratory showed that the lab alkalinity results were comparable to field alkalinity. (Appendix A Table A.1.). Subsequent alkalinity tests were performed in the lab.

- 2009—Tested samples for the routine USGS herbicide. The County changed from annual to biennial sampling events.
- 2011—Tested samples for an additional list of 51 herbicides in addition to the USGS triazines and acetamide list.
- 2013—Sampled select wells for the routine USGS list of herbicides and added chlorothalonil and three breakdown products. Analyzed the select wells for a list of pharmaceuticals, mainly antibiotics and antibiotic breakdown products.
- 2017—Tested 10 study wells with total cyanazine exceedances over the drinking water guideline and an additional 135 nearby wells for triazine herbicides and their breakdown products.
- 2018—Tested study wells for gross alpha, cyanide and barium. Wells (not completed in the Cjdn aquifer) were tested for seventeen Per- and Polyfluoroalkyl Substances (PFAS).
- 2019—Tested study wells for radium 226 & 228; Cjdn wells were tested for 32 PFAS; 36 study wells tested for 135 pesticides at Weck Laboratories Inc., including two treated water samples collected from refrigerator carbon water filters. MDA collected samples from 27 study wells that were analyzed by Weck for the same 135 pesticides. In addition, MDA collected samples from 72 wells previously sampled in the 2017 Dakota County sample event that exceeded 0.5 µg/L for total cyanazine, 27 in-home water treatment devices; MDH collected samples from 13 municipal wells—all samples were analyzed for the list of 135 pesticides by Weck.

The County obtained permission from the well owners to sample their wells. A letter was sent to each well owner after each sampling event to provide and explain the results. An independent sampling contractor or County staff person collected the samples from an untreated water spigot on the well owner's residence or a water hydrant. The main goal was to sample "aquifer water," not the water distribution system, which includes the pressure tank and pipes or water treatment systems. The wells were purged, and meters or probes were used to determine field parameters: temperature, specific conductivity, pH, oxidation/reduction potential (Eh) and dissolved oxygen. Water samples were collected after the field parameters stabilized. Samples were not filtered. Replicates and blanks were collected per laboratory requirements. Both were analyzed for the same parameters to evaluate the variability in sample collection and the analytical method.

The County used various labs throughout the study. For some parameters, the laboratory method reporting limit (MRL) — the smallest amount of an analyte in a sample that can be reliably determined with a given analytical method — changed over time.

The USGS Organic Geochemistry Research Laboratory (OGRL) reporting level was set at or above the limit of quantitation for each analyte. USGS Laboratory's "less than" reporting level was set at twice the determined long-term method detection level (MDL). Concentrations measured between the method reporting level (MRL) and the long-term MDL are reported as estimated concentrations indicated with an "E." Non-detects were censored to the MRL (Childress, et al. 1999).

At the USGS National Water Quality Laboratory and the USGS OGRL, samples were analyzed with gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS), or liquid chromatography/tandem mass spectrometry (LC/MS/MS).

Concentrations of nitrate and nitrite in water are expressed in this report in units of nitrate as nitrogen and nitrite as nitrogen, respectively.

Statistical significance means that the statistical result is likely not due to chance. The result is a probability value (p), which is the probability of observing a difference in the data if no difference exists.

- >95% significance means ($p < 0.05$) highly significant; less than a 5% probability that this result would occur by chance.
- >90% significance means (p between 0.1 and 0.05, when less than 0.05 it will be reported as >95% significance) that the result is significant; between a 5 to 10% probability that this result would occur by chance.
- <90% significance means ($p > 0.1$) that the result is not significant; a greater than 10% probability this result would occur by chance.

# 3. Results and Data Analysis

## 3.1. Water Quality Data

The water quality data were analyzed using nonparametric statistical tests. (See Appendix A.13. for a description of statistical methods.) The sampling results were compared to aquifer, well depth (total and casing depth), nearby wells (clusters), well construction (grouted or ungrouted), trends and land use (percent in row crop agriculture and percent in irrigated agriculture). **Of these, well casing depth and land use are the best predictors of water quality; in general, the deeper the well and/or the lower the percentage of land in row crop agriculture adjacent to the well, the lower the concentration of anthropogenic chemicals were found in the water.**

Regarding the construction of private wells in Dakota County: aquifer, well depth, and the presence or absence of grout are not independent factors—they are all related to when the well was installed. In general, the more recently a well was installed, the deeper it will be (and hence in a deeper aquifer) and the more likely it is to be grouted. As a result, it can be difficult to evaluate which of these factors has the most influence on the levels of anthropogenic chemicals, such as nitrate, chloride or pesticides, found in well water.

Natural waters, defined as water with a mineral content occurring under natural conditions, vary depending on the geologic characteristics of the aquifer (geologically sourced). In other words, natural waters are aquifers that show no indications of human activity. The typical levels of a parameter that occur naturally are described as “background” levels.

Estimates of background levels of nitrate in the Ucs, Opdc and Cjdn aquifers in Minnesota range from 0.2 mg/L (Olmsted County data, SEMWAL) to 0.595 mg/L (MPCA, 1999). Estimates of background levels of chloride range from 0.3 mg/L (SEMWAL) to 2.6 mg/L (MPCA, 1999). In southeast Minnesota, most detections of nitrate, chloride and sodium at levels above common analytical detection limits indicate contributions from human activities. **In Dakota County, background for nitrate is 0.2 mg/L, chloride less than 3 mg/L and sodium less than 4 mg/L.**

The terms “drinking water guideline” and “guideline” used throughout this report refer to the lowest guideline available from either the EPA or the MDH. All study results are compared to the lowest guideline where a guideline exists. See Appendix E.2. for a description of guidance values and standards, none of which are enforceable regarding private water well quality. Private well owners are responsible for testing and maintaining their private well with the exception of testing that is required at the time of new well construction and property sale.

## 3.2. Water Quality Parameters by Aquifer and Well Casing Depth

Well casing depth by aquifer is summarized in Table 1 and depicted in Figure 12. The average (mean) well casing depth for all study wells in the Ucs and Opdc is 126 feet and 148 feet, respectively, as compared to the average total depth of 319 feet for Cjdn wells. The median well casing depth is 135 feet for both the Ucs and the Opdc.

**Table 1. Well Casing Depth by Aquifer, in feet below ground surface.**

| Aquifer | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| UCS | 29 | 126 | 75 | 10 | 60 | 135 | 176 | 276 |
| OPDC | 28 | 148 | 81 | 12 | 80 | 135 | 204 | 342 |
| CJDN | 20 | 319 | 55 | 245 | 270 | 308 | 353 | 445 |

The study wells were put into categories by the depth of the water well casing with almost equal numbers of wells:

- Shallow—shallower than 125 feet ( n = 26 )
- Middle (Mid)—125 to 250 feet ( n=26 )
- Deep—deeper than 250 feet ( n=25 )

The deep well casing category includes 19 of the 20 Cjdn wells, four Opdc wells and two Ucs wells. The well casing depth by well casing category is summarized in Table 2 and depicted in Figure 13.

**Table 2. Well Casing Depth by Well Casing Category, in feet below ground surface.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26 | 68 | 30 | 10 | 54 | 72 | 100 | 113 |
| Mid 125' to 250' | 26 | 179 | 31 | 130 | 157 | 176 | 204 | 245 |
| Deep >250' | 25 | 312 | 52 | 254 | 267 | 300 | 344 | 445 |

Aquifer may serve as a proxy for well depth, but the variability in elevation, and geologic features such as buried bedrock valleys where deep Ucs wells exist, would argue for using well casing depth as the variable to differentiate the vertical distribution of surface contamination. It is not entirely possible to separate the effects of depth and aquifer with the study dataset, since well depths overlap across aquifers.

The median of all general water quality chemistry parameters was compared to well casing depth and total well depth (Kendall); the statistical differences are summarized in Table 3. The statistical significance results of 90 percent or greater are shaded in lighter blue; the darker blue is significance of greater than 95 percent. White cells indicate no statistical significance above 90 percent. The p-values are provided in Appendix D Table D.1. Parameters by well casing depth overall have more parameters (16) with high statistical significance ($p < 0.05$) than total well depth (13 parameters); therefore, the analyses in the report use well casing depth instead of total well.

**Table 3. Median Statistical Significance of Differences for General Chemical Parameters by Well Casing Depth and Total Well Depth (Kendall).**

| Parameter | Well Casing Depth Statistical Significance | Direction with Well Casing Depth | Total Well Depth Statistical Significance |
|---|---|---|---|
| alkalinity | < 90% | none | < 90% |
| arsenic | < 90% | none | < 90% |
| calcium | > 95% | decreasing | > 95% |
| calcium : magnesium | > 95% | decreasing | > 95% |
| chloride | > 95% | decreasing | > 95% |
| dissolved oxygen | > 95% | decreasing | < 90% |
| Eh | > 95% | decreasing | > 95% |
| fluoride | > 95% | increasing | >90% |
| iron | > 95% | increasing | > 95% |
| magnesium | < 90% | none | < 90% |
| manganese | < 90% | increasing | >90% |
| nitrate | > 95% | decreasing | > 95% |
| pH | > 95% | increasing | > 95% |
| potassium | < 90% | none | < 90% |
| silica | > 95% | decreasing | >90% |
| sodium | > 95% | decreasing | > 95% |
| specific conductance | > 95% | increasing | > 95% |
| sulfate | > 95% | decreasing | > 95% |
| Temperature in Celsius | < 90% | none | < 90% |
| total dissolved solids | > 95% | increasing | > 95% |
| total hardness | < 90% | decreasing | < 90% |
| total Kjeldahl nitrogen | > 95% | decreasing | > 95% |
| total milliequivalents | > 95% | increasing | > 95% |
| total organic carbon | < 90% | none | < 90% |

Dark blue shaded cells indicate 95% or higher statistical significance

Light blue shaded cells indicates 90% to 95% statistical significance

No shading indicates no statistical significance

The median of all general water quality chemistry parameters from the three aquifers and three well casing depth categories were compared (Mann-Whitney) and the statistical differences are summarized in Table 4, the p-values are provided in Appendix D Tables D.2. and D.3. All values are mg/L except pH in standard units, Eh in millivolts, specific conductance in umhos/cm and total milliequivalents in mEq units. Alkalinity and total hardness are in mg/L CaCO3 and calcium:magnesium is a unitless ratio.

### Table 4. Median Statistical Significance of Differences for Chemical Parameters by Aquifer and Well Casing Depth (Mann-Whitney).

| Parameter | Median level by Aquifer | | | Statistical Significance (%) for Aquifer Differences | | | Median level by Well Casing Depth | | | Statistical Significance (%) for Well Casing Differences | | | Parameter Concentration with Depth |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cjdn | Opdc | Ucs | Opdc vs Cjdn | Opdc vs Ucs | Ucs vs Cjdn | Deep >250 ft | Mid 125 -250 ft | Shallow < 125 ft | Mid vs Deep | Mid vs Shallow | Shallow vs Deep | |
| **Anthropogenic - human sourced** | | | | | | | | | | | | | |
| Arsenic | 1.27 | 1.25 | 0.5 | < 90% | > 95% | > 95% | 1.28 | 0.53 | 1.1 | < 90% | < 90% | < 90% | No change |
| Chloride | 3.0 | 12.8 | 15.4 | > 95% | < 90% | > 95% | 3.0 | 13.0 | 18.0 | > 95% | >90% | > 95% | Decreasing |
| Nitrate as N * | 0.2 | 3.8 | 3.0 | > 95% | < 90% | > 95% | 0.2 | 2.5 | 5.8 | > 95% | > 95% | > 95% | Decreasing |
| Sodium | 3.0 | 5.8 | 5.1 | > 95% | < 90% | > 95% | 3.1 | 4.3 | 7.5 | > 95% | > 95% | > 95% | Decreasing |
| **Anthropogenic & Geologically Sourced** | | | | | | | | | | | | | |
| Sulfate | 21.9 | 27.6 | 30.1 | < 90% | < 90% | >90% | 20.7 | 27.8 | 30.1 | < 90% | < 90% | > 95% | Decreasing |
| **Geologically Sourced** | | | | | | | | | | | | | |
| Total Kjeldahl Nitrogen | 0.000 | 0.250 | 0.290 | >90% | < 90% | >90% | 0.000 | 0.250 | 0.400 | >90% | < 90% | > 95% | Decreasing |
| Total Organic Carbon | 1.80 | 2.00 | 2.25 | >90% | < 90% | >90% | 1.17 | 1.00 | 0.90 | < 90% | < 90% | < 90% | No change |
| Iron | 1.11 | 0.27 | 0.16 | < 90% | < 90% | < 90% | 1.35 | 0.22 | 0.11 | < 90% | < 90% | > 95% | Increasing |
| Manganese | 0.400 | 0.013 | 0.020 | < 90% | < 90% | < 90% | 0.040 | 0.005 | 0.018 | < 90% | < 90% | < 90% | No change |
| pH | 7.57 | 7.47 | 7.48 | > 95% | < 90% | > 95% | 7.54 | 7.48 | 7.42 | < 90% | < 90% | > 95% | Increasing |
| Total Hardness | 278 | 300 | 330 | > 95% | < 90% | > 95% | 286 | 301 | 324 | > 95% | < 90% | > 95% | Decreasing |
| Calcium | 66.6 | 73.9 | 80.6 | > 95% | < 90% | > 95% | 68.4 | 75.3 | 80.0 | > 95% | < 90% | > 95% | Decreasing |
| Magnesium | 25.8 | 27.6 | 29.1 | < 90% | < 90% | > 95% | 27.6 | 29.1 | 27.6 | >90% | < 90% | < 90% | No change |
| Calcium:Magnesium | 1.56 | 1.64 | 1.69 | < 90% | < 90% | < 90% | 1.55 | 1.64 | 1.74 | < 90% | < 90% | > 95% | Decreasing |
| Alkalinity | 245 | 251 | 253 | < 90% | < 90% | < 90% | 264 | 253 | 241 | < 90% | < 90% | < 90% | No change |
| Potassium | 1.46 | 1.58 | 1.57 | < 90% | < 90% | < 90% | 1.60 | 1.57 | 1.54 | < 90% | < 90% | < 90% | No change |
| Fluoride | 0.14 | 0.12 | 0.13 | < 90% | < 90% | < 90% | 0.14 | 0.12 | 0.13 | < 90% | < 90% | > 95% | Increasing |
| Silica | 8.2 | 10.0 | 11.9 | > 95% | < 90% | > 95% | 9.0 | 10.0 | 11.4 | < 90% | < 90% | >90% | Decreasing |
| Temperature © | 11.06 | 11.23 | 11.5 | < 90% | < 90% | >90% | 11.2 | 11.3 | 11.1 | < 90% | < 90% | < 90% | No change |
| Dissolved Oxygen | 2.9 | 4.9 | 5.8 | > 95% | < 90% | > 95% | 3.8 | 6.8 | 5.4 | > 95% | < 90% | < 90% | Decreasing |
| Eh | -48 | -34 | -45 | < 90% | < 90% | < 90% | -50 | -48 | -25 | < 90% | > 95% | > 95% | Decreasing |
| Specific Conductance | 518 | 581 | 602 | > 95% | < 90% | > 95% | 519 | 537 | 609 | >90% | >90% | > 95% | Increasing |
| Total Dissolved Solids | 282 | 329 | 367 | > 95% | < 90% | > 95% | 298 | 327 | 358 | > 95% | < 90% | > 95% | Increasing |
| Total Milliequivalents | 11.7 | 12.9 | 13.8 | > 95% | < 90% | > 95% | 11.7 | 12.9 | 13.8 | >90% | < 90% | > 95% | Increasing |

* Quantile test used for better resolution due to large numbers of non-detects (<0.2 mg/L)

Findings:

- Comparison of the water quality data and aquifer found no statistically significant differences, for any parameter except for arsenic, between wells in the Ucs and wells in the Opdc.
- The Cjdn has the lowest median values for anthropogenic parameters, probably due to Cjdn wells mostly being deeper than the other aquifer wells.
- The similarity between the Ucs and Opdc may be due to the shallow nature of both aquifers as compared to the Cjdn, as shown in Table 1.
- The parameters: nitrate, chloride, sodium, Eh and specific conductance are significantly different between the shallow and mid-cased well categories and none that are significantly different when comparing the Ucs and Opdc, except for arsenic. **Casing depth is likely a better variable than aquifer to group and compare the study data.**
- The effects of depth and aquifer are difficult to separate, since well depths overlap across aquifers. The variable, “well casing depth” appears to better represent the “effective” depth of a well for predicting water quality parameters than does aquifer.

## 3.3. Water Quality Parameters by Well Clusters

Well clusters were created to analyze aquifers in a more localized fashion by comparing wells that are close to each other (within 1,500 feet) but completed in different aquifers. Sixty of the 77 study wells were assigned to one of 21 well clusters (Figure 14). The p-values and median differences are summarized in Appendix D Nitrate in Well Clusters (Table D.4) and Chloride in Well Clusters (Table D.5). Well clusters are discussed in more detail in the sections about individual parameters. Since well casing depth, depth to aquifer and aquifer thickness vary considerably across the County, a difference was expected between Ucs and Opdc. However, the cluster analysis found no consistent statistical differences between the two: whether the values were higher, lower or statistically the same; about half the clusters had higher chemicals detected in the Ucs and half were higher in the Opdc.

Figure 15 illustrates how two wells located within proximity to each other may have different groundwater quality. The example in Figure 15 shows the deeper well groundwater source has been impacted by cropland with high-nitrogen and pesticide inputs, whereas the shallower well water is not impacted. In other cases, depending upon groundwater flow, land use and well depths, the reverse could be true and the shallower well may have higher chemicals detected than the deeper well.

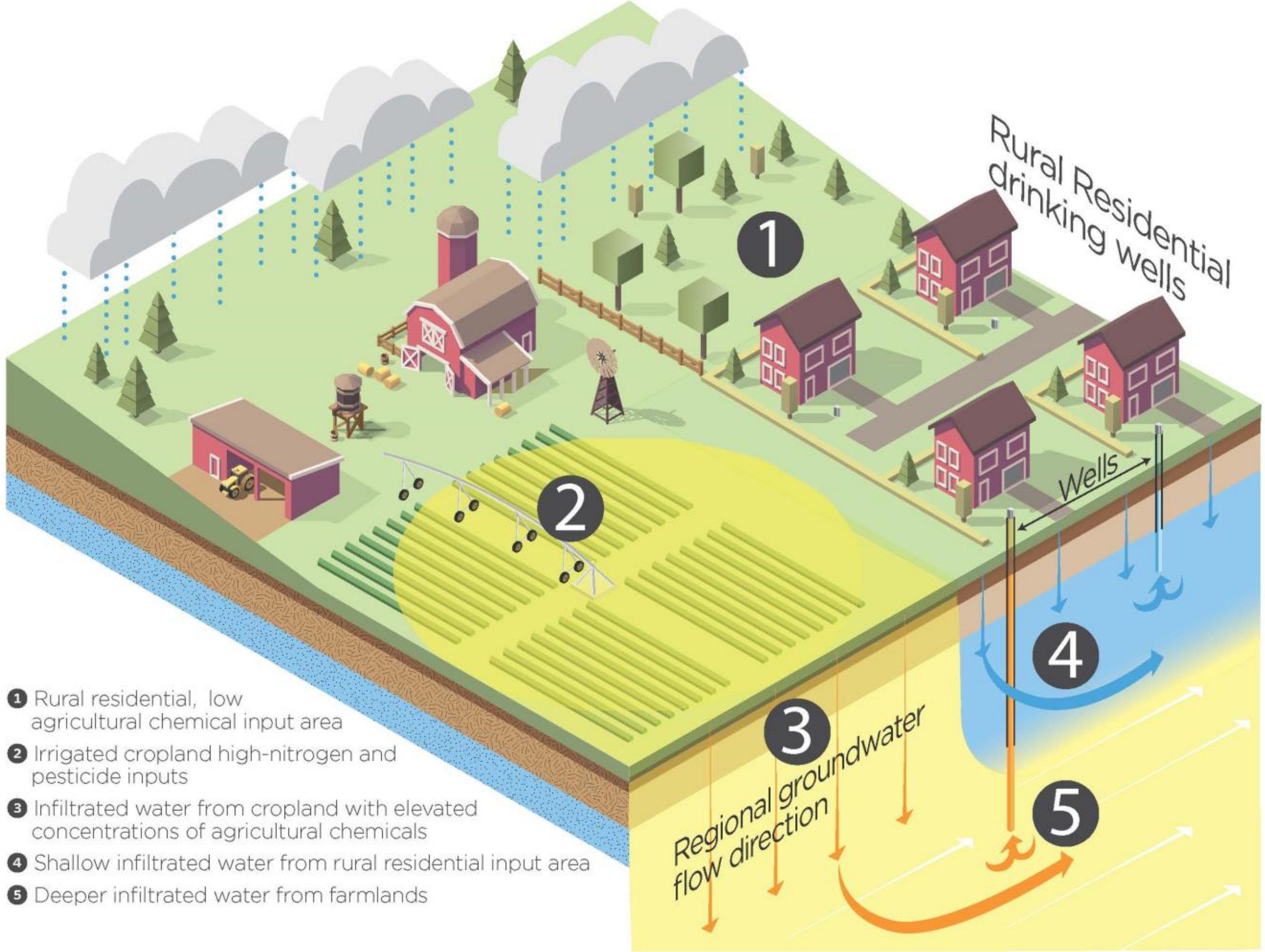


**Figure 15. Well Cluster Example with Different Water Quality**

## 3.4. Water Quality Parameters by Land Use

Groundwater quality in both rural and urban environments is influenced by both natural processes and anthropogenic influences. The thickness and texture of surface soils and land cover varies across the County and affects the rate that groundwater is recharged from the surface. They together with land use also affect the quality of groundwater recharge. Heavy tills in the western and southwestern parts of Dakota County have lower infiltration rates resulting in a greater portion of precipitation being shed directly or indirectly to the Vermillion or Cannon Rivers, and the portion reaching the groundwater potentially taking longer to get there or experiencing more chemical interactions. In contrast, the thin, course soils in the central, eastern and southeastern parts of the County are generally more permeable and water moves rapidly through the soil layer to the underlying aquifer, with fewer chemical interactions.

For substances primarily of anthropogenic origin, loadings on the landscape surface are related to land use. Non-point chemical contamination is an issue in both urban and agricultural land use environments. Anthropogenic (human) sources of chloride, nitrate and herbicides degradates are source pollutants resulting from widespread surface application. These are considered as “area sources”. Chloride, originating from the application of deicing salt (sodium chloride) or water softening recharge brine, is the dominant anthropogenic pollutant associated with urbanized areas, whereas nitrate and herbicide degradates are related to agricultural land use. Chloride also results from potash (potassium chloride) fertilizer use in agriculture, so that chloride is seen in both urban and agricultural settings.

Nitrate is the principal substance used in our analysis to evaluate the relationship between nitrogen loading, as estimated by percent of land in row crop agriculture proximate to a well, and the observed/empirical nitrate levels in groundwater. A key assumption in this analysis is that land use as row crop agriculture has been roughly consistent since about 1960. This year represents the approximate time when large scale inputs of synthetic fertilizers and many herbicides began. The data representing the spatial distribution of cropland in County has been mapped and is maintained by the Dakota County Soil and Water Conservation District following the Minnesota Land Cover Classification System (MLCCS) developed by the Minnesota Department of Natural Resources.

A source area to a well, known as a contributing recharge area, represents the area at the water table that contributes recharge to a pumped well (USGS 2012). Nitrogen loading is the excess nitrogen fertilizer applied on the land surface that is not removed with an agricultural crop, washed away in overland flow, or lost to the atmosphere. There are several methods for estimating the source areas for wells and to estimate nitrogen loadings that depend on the land use.

Using ESRI ArcMap Geographic Information System (GIS) Version 10.7.1, infiltration areas of individual wells were drawn in several ways: circles 100, 500 and 1,000 feet in diameter were drawn around wells, ellipses and wedges in the upgradient direction were drawn from the well and the Public Land Survey (PLS) one-mile section where the well is located. Based on the land use in those areas, the inputs (loading factors) of chloride and nitrate were estimated.

Groundwater models were used, which is described in Appendix H. The groundwater flow model included the depth of the sampled wells and created path lines traced various elevations along the well screen or well open hole to the water table. The groundwater model reported the age of water entering the well along each path line, and separate loading functions estimated the concentrations of chloride or nitrate on each pathline based on the land use and year of recharge. Assuming an even mixing of water inside the well, the average concentration of the simulated pathlines was reported as the estimated concentration in the well in the year sampled. Because the loadings change from year to year, concentrations estimated by this method can change depending on the year sampled.

Using various percent row crop agriculture estimates based on the above GIS buffers and empirical nitrate concentrations in target well water, non-parametric statistical analysis was conducted to test for correlation between the two variables. Regardless of which specific method for calculating/estimating the percent of row crop agriculture, all correlations with nitrate and percent row crop agriculture show statistical significance of 95% or better (Kendall $p < 0.05$). These results did not identify a single “best” way to estimate the infiltration area for a specific well. In general, however, smaller areas showed somewhat better correlations with shallower wells, while larger areas correlated better for deeper wells.

Correlation to land use in a surrounding one-mile section area is among the easiest to apply. The location and density of cultivated row crop agriculture was derived from Minnesota Land Cover Classification System (MLCCS) GIS files produced by the Dakota County Soil and Water Conservation District. The cultivated row cropland data represents cleared and tilled acreage used to produce adapted crops for harvest. This coverage represents a snapshot of the land use occurring at a specific time and only characterizes recent land use. Historical land use and the pollutant loading related to this use is not considered and so the lag time between changes in land use and the changes in water quality are not captured by this approach

# 4. Anthropogenic Parameters

The USGS defines “anthropogenic” as environmental change caused or influenced by humans either directly or indirectly. For example, when agricultural chemicals like nitrogen fertilizer and/or herbicides are applied to fields, excess chemicals can runoff the landscape and impact surface water or leach through the soil and rock to contaminant drinking water aquifers. Many anthropogenic parameters of interest in the Ambient Study have a known year that the chemical was registered for use or was in general use, such as salt for winter road maintenance for deicing.

Over the past 60 years, crop production has increased through a combination of improvements in mechanization, crop hybrids, genetically-engineered glyphosate (Roundup) and dicamba tolerant crops, crop irrigation, and synthetic fertilizers and herbicides. Corn yields increased from 88 bushels per acre in 1988 to 176.4 bushels per acre in 2018 as depicted in Figure 16 (USDA-National Agricultural Statistics Service (NASS) 2019). Soybean yields increased from 27 bushels per acre to 51.7 bushels per acre in the same period, depicted in Figure 17 (USDA-NASS 2019).

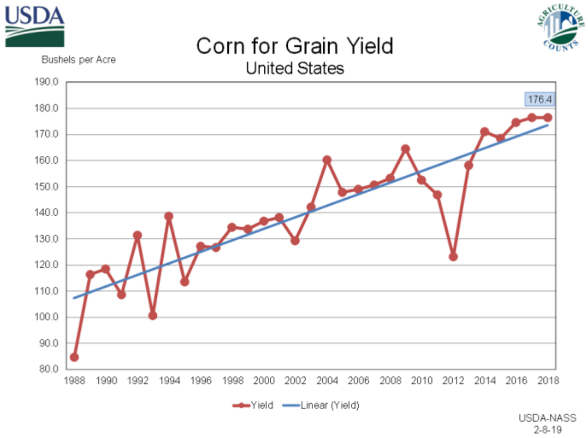


**Figure 16. U.S. Annual Corn Production (Source: USDA NASS)**

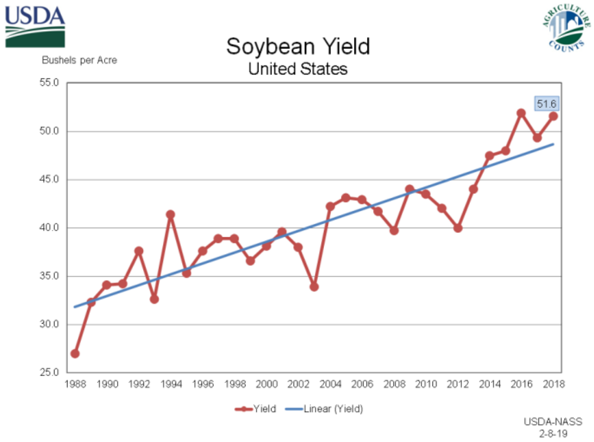


**Figure 17. U.S. annual soybean production (Source: USDA NASS)**

These production trends are reflected in the historical national use data for agrichemicals in Figures 18 and 19. Both the pesticide and fertilizer use graphs show a rapid growth in use throughout the 1960s and 1970s as greater acreage was dedicated to hybrids requiring intensive use of agrichemicals. These national use trends are mirrored in the statewide use data, which show that the total quantity and number of different herbicides applied to croplands has greatly increased in the past 60 years. Currently, there are approximately 700 different pesticide products available for use in Minnesota for corn, soybeans, wheat and hay production (MDA 2016), and their use has become essential. For example, in 1952, only 10 percent of U.S. corn acres planted were treated with herbicides. By 1976, herbicide use had grown to 90 percent of corn acres planted (USDA); during the 2016 crop year, 99 percent of acres planted in corn were treated with herbicides (MDA 2015).

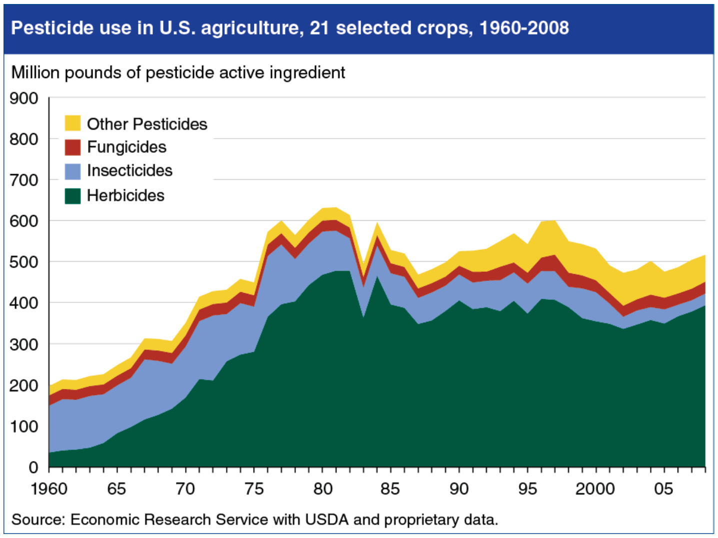


**Figure 18. Pesticide use in U.S. agriculture, 21 selected crops, 1960–2008.**

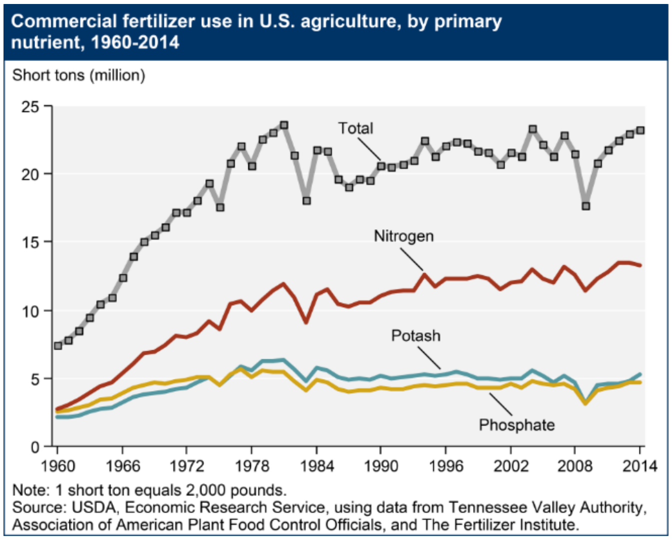


**Figure 19. Commercial Fertilizer Use in U.S. agriculture, by primary nutrient, 1960–2014.**

## 4.1. Nitrate

### 4.1.1. Nitrate Sources and Health Concerns

Nitrate is a concern in the County's groundwater and is one of the most common groundwater contaminants in the U.S. Nitrate — the oxidized form of dissolved nitrogen — is the main source of nitrogen for plants. It occurs naturally in soil and dissipates when the soil is extensively farmed. Synthetic nitrogen fertilizers are applied to replenish the soil, but the nitrate form is highly mobile in soil and can readily leach into groundwater. Numerous factors influence the presence and amount of nitrate found in aquifers related to row crop fertilizer application such as application rates, crop rotation, legumes, irrigation, tillage, soil texture, depth to water, depth to bedrock, drain tile, climate, well construction, and vertical and hydraulic gradient. Additional anthropogenic sources of nitrate can be septic systems, manure, feedlots, land application of municipal wastewater treatment plant biosolids and turf fertilizer. However, where nitrate is elevated in drinking water aquifers and the predominant land use is row crop agriculture, nitrogen fertilizers are the suspected predominant source of nitrate in the drinking water aquifers in Dakota County.

Although a necessary nutrient for plants, high nitrate levels can harm the human respiratory and reproductive system, kidney, spleen and thyroid in children and adults. When consuming drinking water exceeding the guideline of 10 mg/L, nitrate can lead to a health problem called methemoglobinemia or "blue baby syndrome" in infants younger than six months. The condition is characterized by a reduced ability of the infant's blood to deliver oxygen and can lead to death if untreated. In addition, studies (Ward et al., 2018) suggest that the guideline of 10 mg/L may not be protective of health for people of all ages, and it fails to address the chronic, low level exposure of nitrate's effect on health. Nitrate is converted into N-nitroso compounds, such as nitrosamines and nitrosamides, by bacteria in our digestive systems. These substances damage DNA and cause cancers in multiple animal species and different organs, including the stomach, bladder, colon, esophagus and blood (International Agency for Research on Cancer).

Nitrate is only a health risk in drinking or cooking water; there is no risk associated with bathing or washing dishes or clothing. Nitrate has no taste or odor to alert well users to its presence. Nitrate testing is inexpensive and readily available to private well owners through Dakota County's Environmental Resources Department. Nitrate can be removed from drinking water; an MDH Factsheet on home water treatment options is provided in Appendix E.1.

### 4.1.2. Nitrate Results

The 77 Ambient Study wells have been systematically sampled for nitrate since 1999, with some wells sampled every sample event (16 times) and others only a few events (two to five times). The average number of samples per well is ten. All nitrate results by well and year are summarized in Appendix B Table B.16.

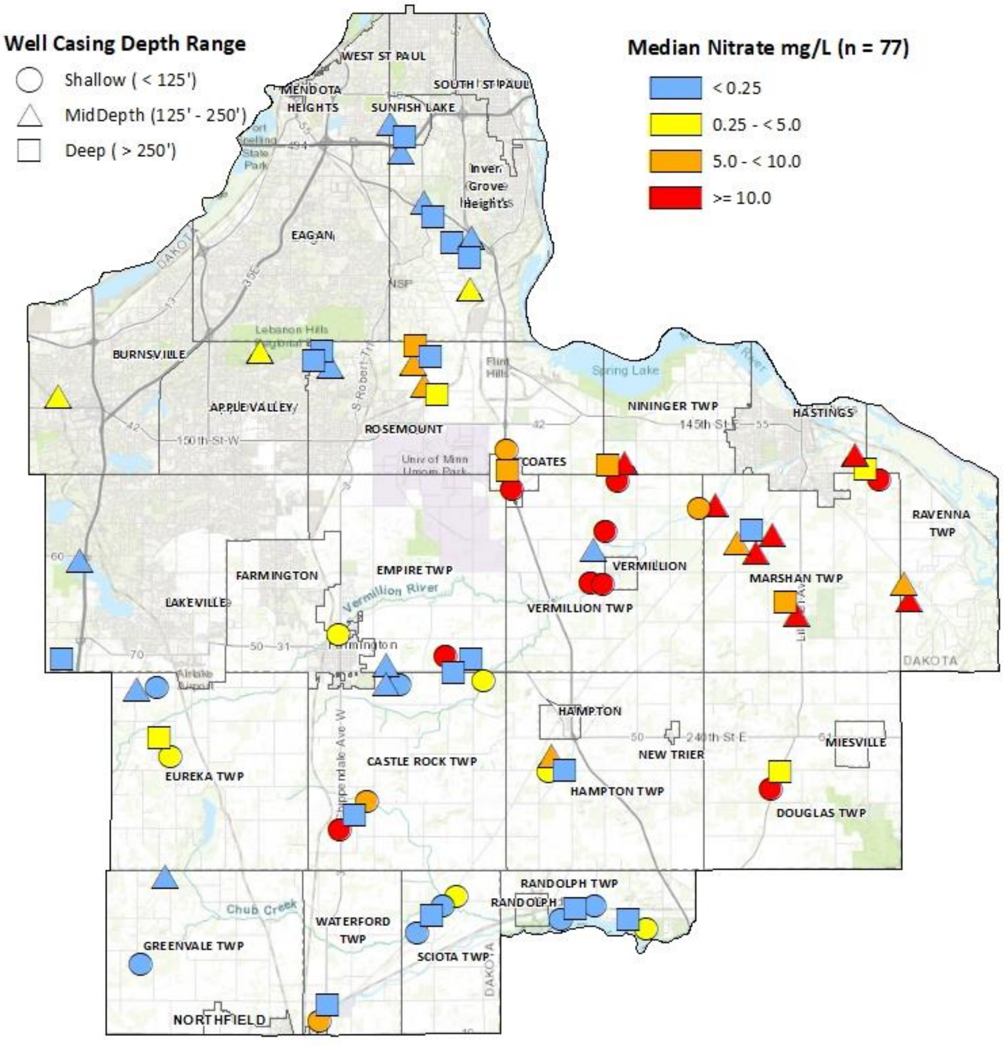
Nitrate findings from 1999 to 2019:

- Nitrate results range from non-detect (less than 0.2 mg/L or < 0.2 mg/L) to 30.6 mg/L
- Nitrate was detected above the MRL at least once in 83 percent of the wells
- 31 percent of wells exceeded the drinking water guideline of 10 mg/L at least once
- 23 percent of wells have average (mean) nitrate that exceeded 10 mg/L
- 21 percent of wells have median nitrate that exceeded 10 mg/L

Comparison of the median nitrate results by well casing depth categories, summarized in Table 5, show that nitrate decreases with depth.

**Table 5. Descriptive Statistics of Median Nitrate Results (mg/L) by Well Casing Depth Category (ft).**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26 | 7.29 | 7.1 | < 0.2 | < 0.2 | 5.7 | 11.9 | 24.9 |
| Mid 125' to 250' | 26 | 7.22 | 8.5 | < 0.2 | < 0.2 | 2.5 | 11.6 | 26.1 |
| Deep >250' | 25 | 1.54 | 2.4 | < 0.2 | < 0.2 | < 0.2 | 2.6 | 8.3 |



Sources: ESRI; Dakota County Environmental Resources

**Figure 20. Median Nitrate by Well Casing Depth.**

### i. Nitrate by aquifer versus well casing depth

Table 6 is excerpted from Table 1 and Appendix D Tables D.2 and D.3. As previously stated, there is no statistical difference between Ucs and Opdc (Mann-Whitney, p = 0.46). Well casing depth, rather than aquifer, appears to be the most significant variable, at least down to the top of the Cjdn.

**Table 6. Statistical Significance of Median Nitrate by Aquifer and Well Casing Depth.**

| **Median level by Aquifer** | | | **p-value for Aquifer Differences** | | |
|---|---|---|---|---|---|
| Cjdn | Opdc | Ucs | Opdc vs Cjdn | Opdc vs Ucs | Usc vs Cjdn |
| < 0.2 | 3.8 | 3.0 | 0.01* | 0.46 | 0.01* |
| **Median level by Well Casing Depth Category** | | | **p-value for Well Casing Depth Differences** | | |
| Deep > 250 ft | Mid 125 ft to 250 ft | <125 ft | Mid vs Deep | Mid vs Shallow | Shallow vs Deep |
| < 0.2 | 2.5 | 5.8 | 0.01* | 0.01* | 0.005 |

*Quantile test used for better resolution due to a large fraction of non-detects.

Shaded Cells > 95% statistical significance

No shading <90% statistical significance

Figure 21 shows the average nitrate results (per well) by well casing depth: the correlation is statistically significant (Kendall, $p < 0.05$) and the line shows that nitrate decreases with well casing depth.

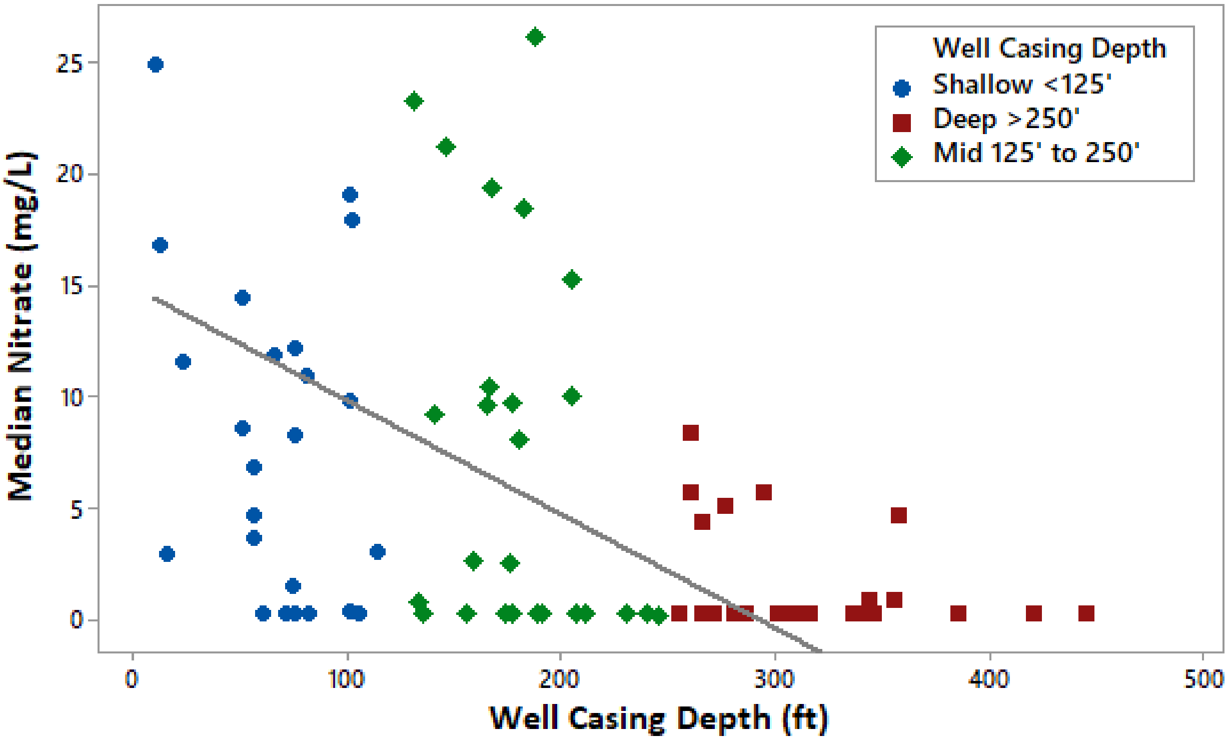


**Figure 21. Correlation of Average Nitrate by Well Casing Depth—Kendall Line.**

From this graph, the infiltration rate can be calculated for *anthropogenic substances* where we have an approximate "start" date for when use and movement from the land surface to groundwater began. A Kendall non-parametric regression line is calculated from the data using all wells collectively and represents a *median line* based on ranks of the data. Where the line intercepts the x-axis at the well casing depth of 310 feet, at zero or non-detect (0.2 mg/L), represents the depth where we no longer see the substance statistically.

Large scale use of nitrogen fertilizer began in Minnesota in about 1960. The intercept depth of 310 feet divided by 49 years (2009–1960) equals 6.3 feet per year infiltration. The year 2009 is used because it is the mid-point of the study years of 1999–2019. This depth divided by the time elapsed from recent sampling to when the substance use began. yields an "average" vertical infiltration rate (feet/year). This rate does reflect two distinct components. First, there is a rapid vertical movement to the water table and, then, a second, much slower, downward vertical movement along with a much larger horizontal movement. The line intercepts the x-axis at 310 feet and is the best statistical representation of the deepest well casing depth where nitrate is zero or non-detect. Three wells with well casing depth deeper than 310 feet have nitrate over 0.02 mg/L. Their higher nitrate than expected may be attributed to excess nitrogen fertilizer application and/or vulnerable soils and geology.

### ii. Nitrate by well clusters

The Ambient Study "well clusters" are explained earlier in the report. Sixty Ambient Study wells are included in 21 well clusters. The nitrate levels in the well clusters were compared and the p-values (Wilcoxon Test) are summarized in Appendix D Table D.4. Fifteen of the 21 clusters had nitrate detections in one or more of the wells; six clusters had no nitrate detected in any well.

When nitrate was examined across all 77 wells in the study, as summarized in Appendix D Table D.2, no difference in nitrate levels was found between Opdc and Ucs wells (Mann-Whitney, $p = 0.46$). However, significant differences were found at the cluster level of analysis.

The findings from Appendix D Table D.4 are summarized below:

- The Ucs vs Opdc wells are all statistically significantly different (Wilcoxon, $p < 0.05$) in all 10 clusters where nitrate is detected.
    - In the 10 clusters that are different the Opdc well has higher nitrate in 6 cluster pairs and the nitrate is higher Ucs in 4 cluster pairs.
- The Ucs vs Cjdn wells are statistically significantly different (Wilcoxon, $p < 0.05$) in 8 of the 10 clusters.
    - In the 8 clusters that are different, the estimated difference in medians is positive/higher in the Ucs in 7 clusters.
- The Opdc vs Cjdn wells are statistically different (Wilcoxon, $p < 0.1$) in 15 of the Opdc-Cjdn 16 pairs of wells where nitrate is detected.
    - In the 15 clusters that are different, the estimated difference in median is positive, the nitrate is higher in the Opdc in 13 clusters.
- There are two clusters with two Opdc wells; both are statistically different (Wilcoxon, $p < 0.05$).
- There are two clusters with two Ucs wells; one is statistically significant (Wilcoxon, $p < 0.05$) and one is not (Wilcoxon, $p > 0.10$).
- In general, the statistical pattern for nitrate is the Opdc>Ucs, Opdc>Cjdn and Ucs>Cjdn.

The differences between paired Ucs and Opdc wells in clusters could be due to examining a smaller sample size or the observed scatter in the data that can be affected by many factors such as the variations in the depth of individual wells, nitrogen fertilizer use, aquifer properties, or ground flow direction.

### 4.1.3. Nitrate Trends

#### i. Trends for nitrate with frequency analysis

In the Ambient Study well data set from 1999 to 2019, not all years had samples for all wells or the same wells in each sampling event. Analysis of the frequency with which nitrate was detected at different levels allows the overall results to be compared from year to year, even though the exact wells used varied somewhat.

The data set was filtered to capture the group of wells that have consistently been tested for nitrate. Figure 22 shows the 15 sample events where 30 or more wells were sampled and the 61 wells that have been sampled at least 10 times.

The nitrate data were divided into four categories:

- Over 10 mg/L, the drinking water guideline
- Between 5 mg/L and 10 mg/L; 5 mg/l is half of the drinking water guideline
- Between 0.2 mg/L and 4.9; 0.2 mg/L is the laboratory minimum reporting level (MRL)
- < 0.2 mg/L, the MRL

Table 7 shows that nitrate has been increasing in Ambient Study wells. From 1999 to 2019, the percentage of wells exceeding the drinking water guideline increased from seven percent to 23 percent. As nitrate levels increase, the wells move from the 5 to <10 mg/L category to the greater than or equal to 10 mg/L category. The percentage of wells with nitrate <0.25 mg/L has decreased; from 53 percent in 1999 to 48 percent by 2019.

*Frequency* is the frequency of detection of an individual contaminant that was computed as the number of samples with a detection of a contaminant, divided by the number of samples in which the contaminant was analyzed and then multiplied by 100.

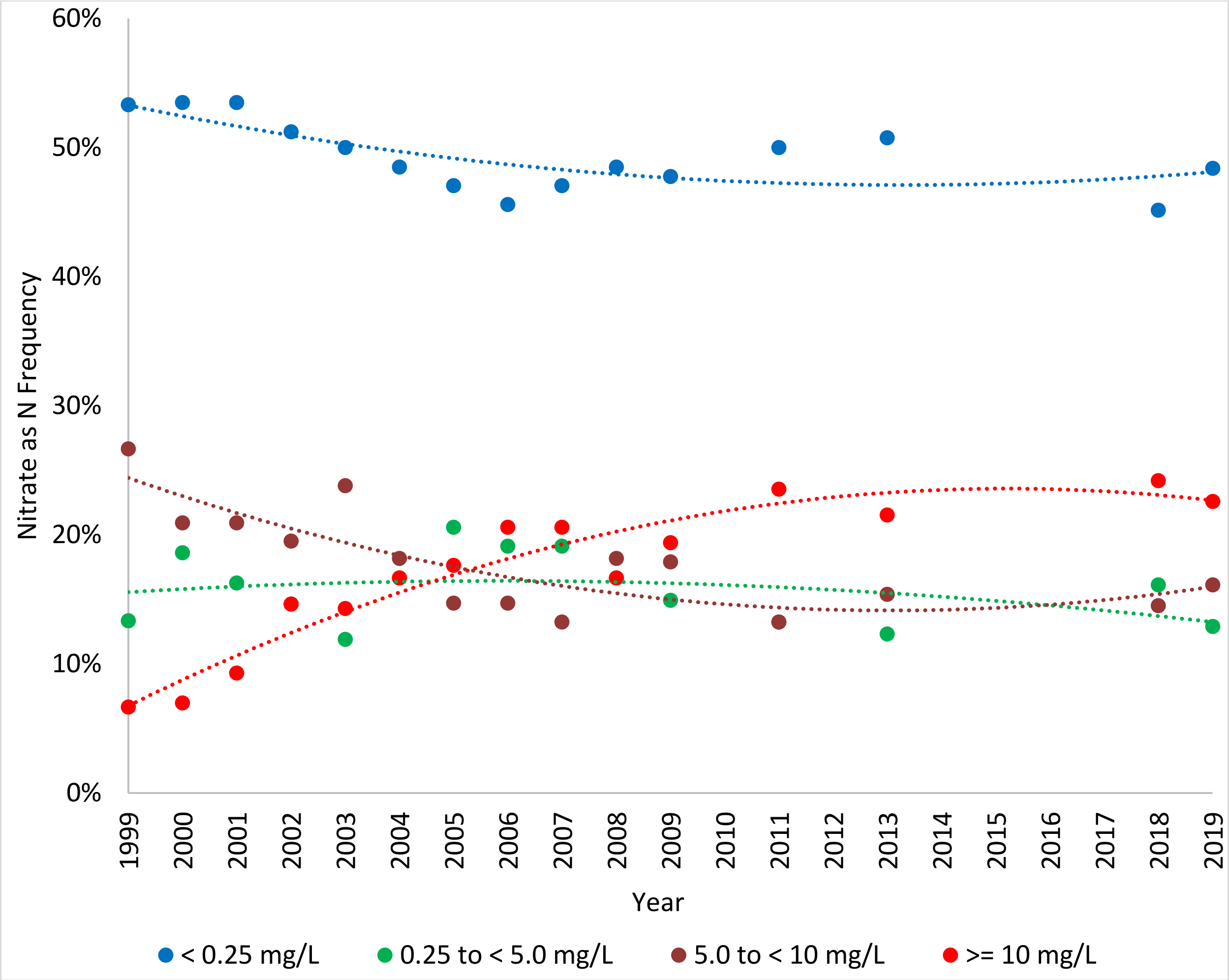


**Figure 22. Nitrate Concentration Frequency by Year.**

**Table 7. Nitrate Frequency by Year and Concentration Category.**

| Nitrate Category | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 | 2006 | 2007 | 2008 | 2009 | 2011 | 2013 | 2018 | 2019 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| < 0.25 mg/L | 53% | 53% | 53% | 51% | 50% | 48% | 47% | 46% | 47% | 48% | 48% | 50% | 51% | 45% | 48% |
| 0.25 to < 5.0 mg/L | 13% | 19% | 16% | 15% | 12% | 17% | 21% | 19% | 19% | 17% | 15% | 13% | 12% | 16% | 13% |
| 5.0 to < 10 mg/L | 27% | 21% | 21% | 20% | 24% | 18% | 15% | 15% | 13% | 18% | 18% | 13% | 15% | 15% | 16% |
| >= 10 mg/L | 7% | 7% | 9% | 15% | 14% | 17% | 18% | 21% | 21% | 17% | 19% | 24% | 22% | 24% | 23% |

### ii. Trends for nitrate and well casing depth

One of the greatest values of the Ambient Study dataset is the multiple years of data, which provide an opportunity to evaluate statistical trends over time. An explanation of statistical methods used to calculate trends is included in Appendix A.13. A minimum of five samples is needed to see a greater than 90 percent statistically significant trend; a well with fewer than five samples is not included in the trend summary. Seven wells were sampled less than five times for nitrate, so valid trend analysis could not be performed.

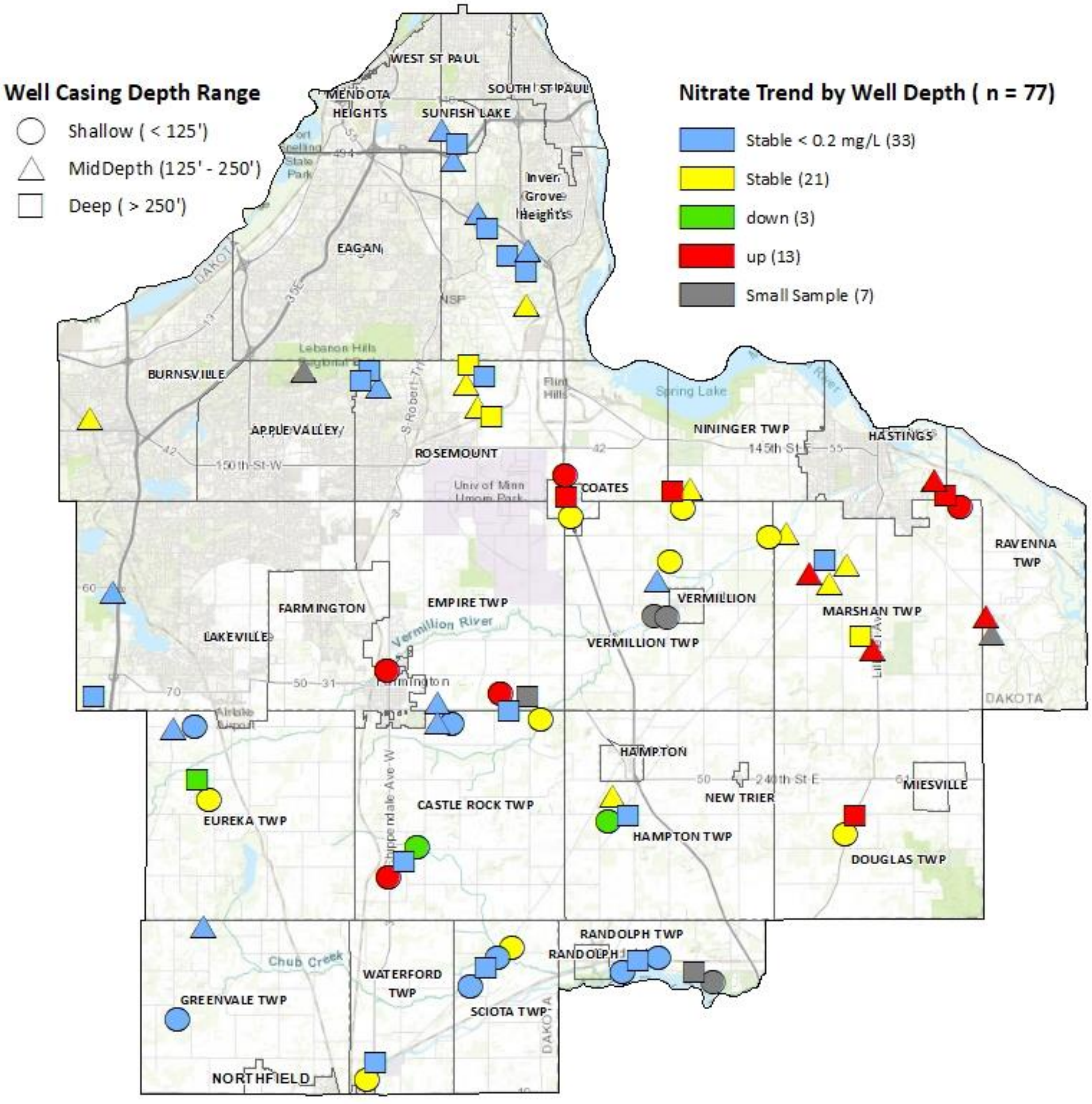
The nitrate trend patterns are listed by well in Appendix B Table B.17. and are summarized by average well casing depth in Table 8. The median nitrate was divided into four categories: <0.2 mg/L, 0.2 mg/L to <5 mg/L, 5 mg/L to <10 mg/L, and greater than 10 mg/L. More wells show an upward trend (13 wells) than a downward (3 wells) trend. Seventy-seven percent (54 wells) that have no trend and are stable for nitrate; the nitrate in the aquifer is in steady-state with the nitrate sources on the surface.

**Table 8. Nitrate Trends by Median Nitrate Concentration and Average Well Casing Depth.**

| Median Nitrate in mg/L | Average Casing Depth in feet | Up Trend # of wells | Down Trend # of wells | No Trend # of wells | Total # of wells |
|---|---|---|---|---|---|
| >=10 | 115 | 5 | 0 | 8 | 13 |
| 5 to <10 | 172 | 5 | 1 | 7 | 13 |
| 0.2 to <5 | 179 | 3 | 2 | 6 | 11 |
| <0.2 | 231 | 0 | 0 | 33 | 33 |
|  | Total | 13 | 3 | 54 | 70 |

The "greater than 10 mg/L" category has 13 wells, of which 5 wells have an upward trend for nitrate and 8 wells have no trend. This category also has the shallowest average well casing depth of 115 feet. As median nitrate decreases, the average well casing depth gets deeper. The three wells with a downward trend are not in the highest or lowest median nitrate category. All 33 wells in the less than 0.2 mg/L category are stable with no trends. These wells are deeper, with an average casing depth of 231 feet, so the nitrate in the aquifer has not penetrated to the depth of the well casing or there is no source of nitrate in the well's infiltration area. Although septic systems are cited as a potential source of nitrate, the study results do not show elevated nitrate to be associated with septic systems. Even though every household in the study has a septic system on the property, 47 percent (33) of the wells have nitrate less than 0.2, indicating those wells have minimal impact from septic systems or fertilizer applied to row crops or turf grass.

The nitrate trends by well are depicted in Figure 23, which shows that wells with an upward trend for nitrate are located in the central and eastern row crop agricultural areas of the County.



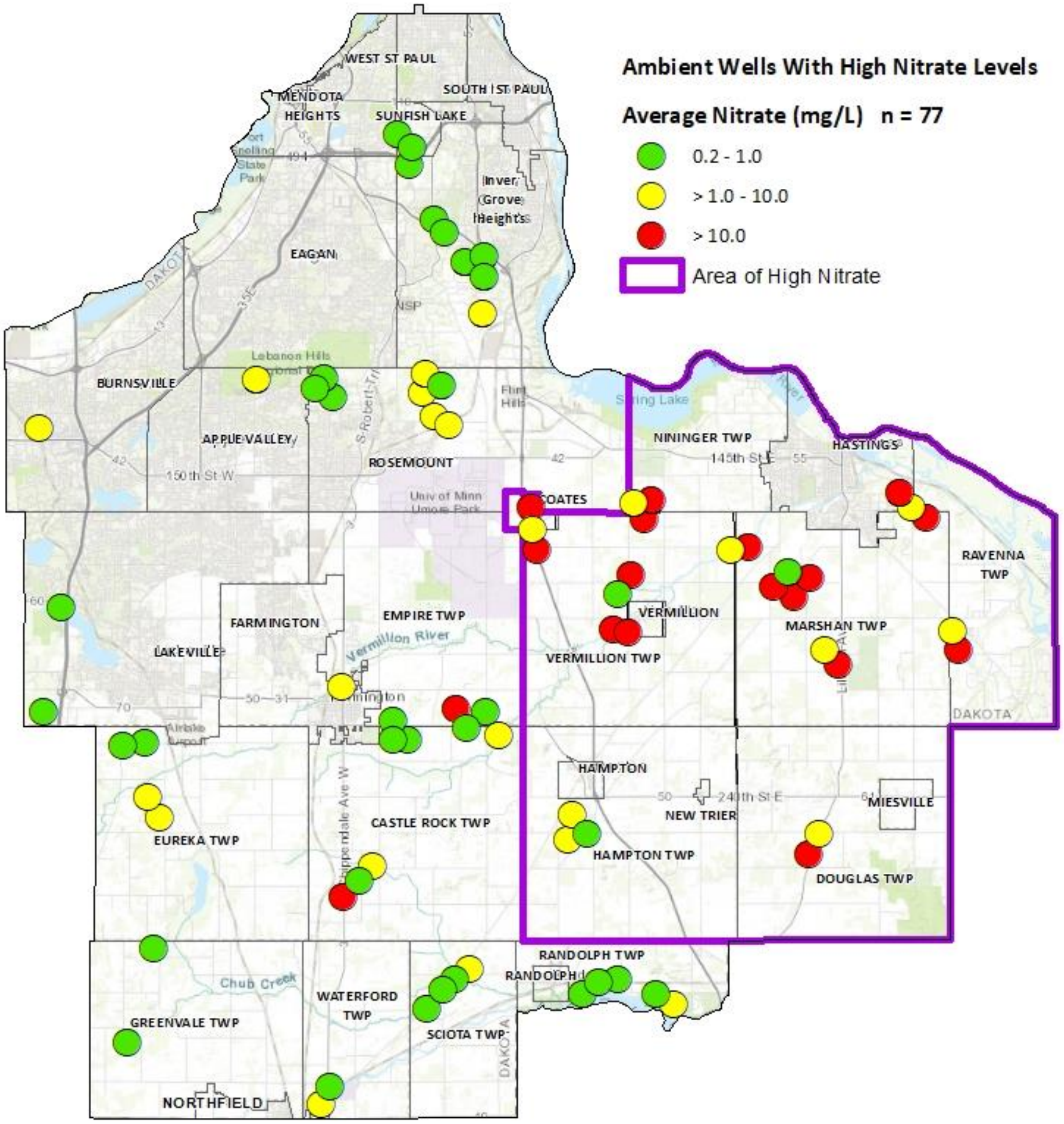
Sources: ESRI; Dakota County Environmental Resources

Figure 23. Nitrate trends by concentration.

Twenty-eight of the Ambient Study wells are in eastern Dakota County, in the cities of Coates and Hastings, and the townships of Douglas, Hampton, Marshan, Nininger, Ravenna and Vermillion (Figure 24) identified as: The Area of High Nitrate. In the study, this area has the wells with the highest average nitrate results and upward trends. The results of the 28 wells are summarized:

- 26 wells have nitrate above 0.2 mg/L and only 2 wells have no nitrate detected above 0.2 mg/L

- 16 wells have average nitrate of 10 mg/L or higher
- 10 wells have statistically significant upward trends
- Only 1 well has a downward trend and average nitrate levels of 0.29 mg/L
- 17 wells have stable nitrate levels; of these, 11 have no trend and 6 have nitrate above 10 mg/L. In these 6 wells, high nitrate levels in the aquifer appear to have reached equilibrium with relatively stable nitrogen inputs on the land surface.



Sources: ESRI; Dakota County Environmental Resources

**Figure 24. The Area of High Nitrate in Drinking Water Wells.**

### 4.1.4. Nitrate and Land Use

The MDA identified 322 feedlots, 94 fertilizer storage locations and 22 spills and investigations in Dakota County in the MDA Final Township Testing Nitrate Report: Dakota County 2013-2015 (MDA 2017). The scope of this study is limited to comparing nitrate levels in the study wells and the percent of land in row crop agriculture. The concentration and distribution of cropland is evaluated as a general indication of where fertilizers would be applied. Loss of nitrogen fertilizer (leaching into groundwater) or over application of fertilizer applied to row crop agriculture specifically irrigated cropland, is identified as a major source of nitrate contamination of groundwater beneath agricultural lands.

To estimate the nitrogen loading area associated with row crop agriculture, Dakota County Environmental Resources personnel developed a simple model involving the calculated percentage of land currently in row crop agriculture for one-mile section (PLS-public land survey) and quarter section. The location and density of cultivated row crop agriculture was derived from MLCCS GIS files produced by the Dakota County Soil and Water Conservation District. The cultivated row cropland data represents cleared and tilled acreage used to produce adapted crops for harvest. This coverage represents a snapshot of the land use occurring at the time of mapping. Land use coverage is regularly updated. Only the areas classified as agricultural were used for analysis to approximate the nitrogen inputs employed in modern row crop agriculture.

Groundwater nitrate results were statistically evaluated against the percentage of land in row crop agriculture in proximate to the wells sampled. This percentage for each well is included in Appendix B Table B.1. The high statistical significance between nitrate and well casing depth (Kendall, $p < 0.05$), nitrate and the percentage of row crop agriculture (Kendall, $p < 0.05$) and nitrate and the percentage of irrigated row crop agriculture (Kendall, $p < 0.05$) in a one-mile section are major factors correlated to nitrate concentration in wells.

Figure 25 compares average nitrate to percent of row crop agriculture. Kendall non-parametric regression line is calculated from the data using all wells collectively and represents a *median line* based on ranks of the data. The line is a prediction that nitrate levels in a well would be about 15 mg/L if row crop agriculture was 100 percent in the section.

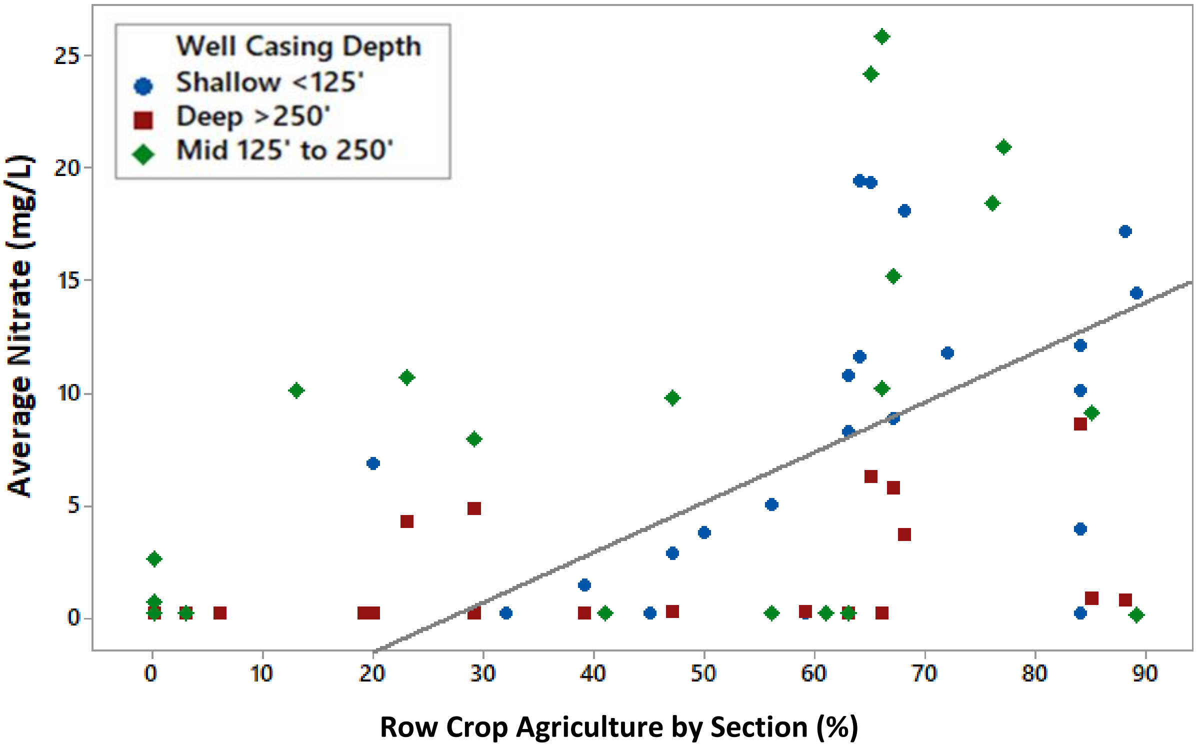


Figure 25. Correlation of Average Nitrate by Percent of Agriculture by Section — Kendall Line.

Table 9 shows the percentage of agriculture by section compared to average nitrate level. The nitrate average, median, and 75th percentile is higher with a higher percentage of agriculture.

Table 9. Descriptive Statistics of Average Nitrate (mg/L) by Row Crop Agriculture by Section (%).

| Agriculture by Section | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| <25% | 25 | 2.4 | 4.7 | 0.2 | 0.2 | 0.2 | 2.6 | 19.4 |
| 25% -50% | 13 | 2.5 | 3.3 | 0.1 | 0.2 | 0.3 | 4.3 | 9.7 |
| 50% -75% | 26 | 7.9 | 8.2 | 0.2 | 0.2 | 6.0 | 12.6 | 25.8 |
| >75% | 13 | 9.0 | 7.4 | 0.1 | 0.8 | 9.1 | 15.8 | 20.9 |

### 4.1.5. MDA Township Testing Program (2013–2015).

In 2013–2015, Dakota County partnered with MDA as the pilot participant in their Township Testing Program. More than 5,000 households were given the opportunity to have their wells tested for nitrate, and nearly 1,400 participated. Overall, 19 percent of the wells tested exceeded the drinking water guideline of 10 mg/L. In eight of the townships tested, more than 10% of the wells were at or over the drinking water guideline of 10 mg/L. In three townships 5% to 9.9% of wells were at or over the guideline and in four townships <5% of wells were at or over the 10 mg/L.

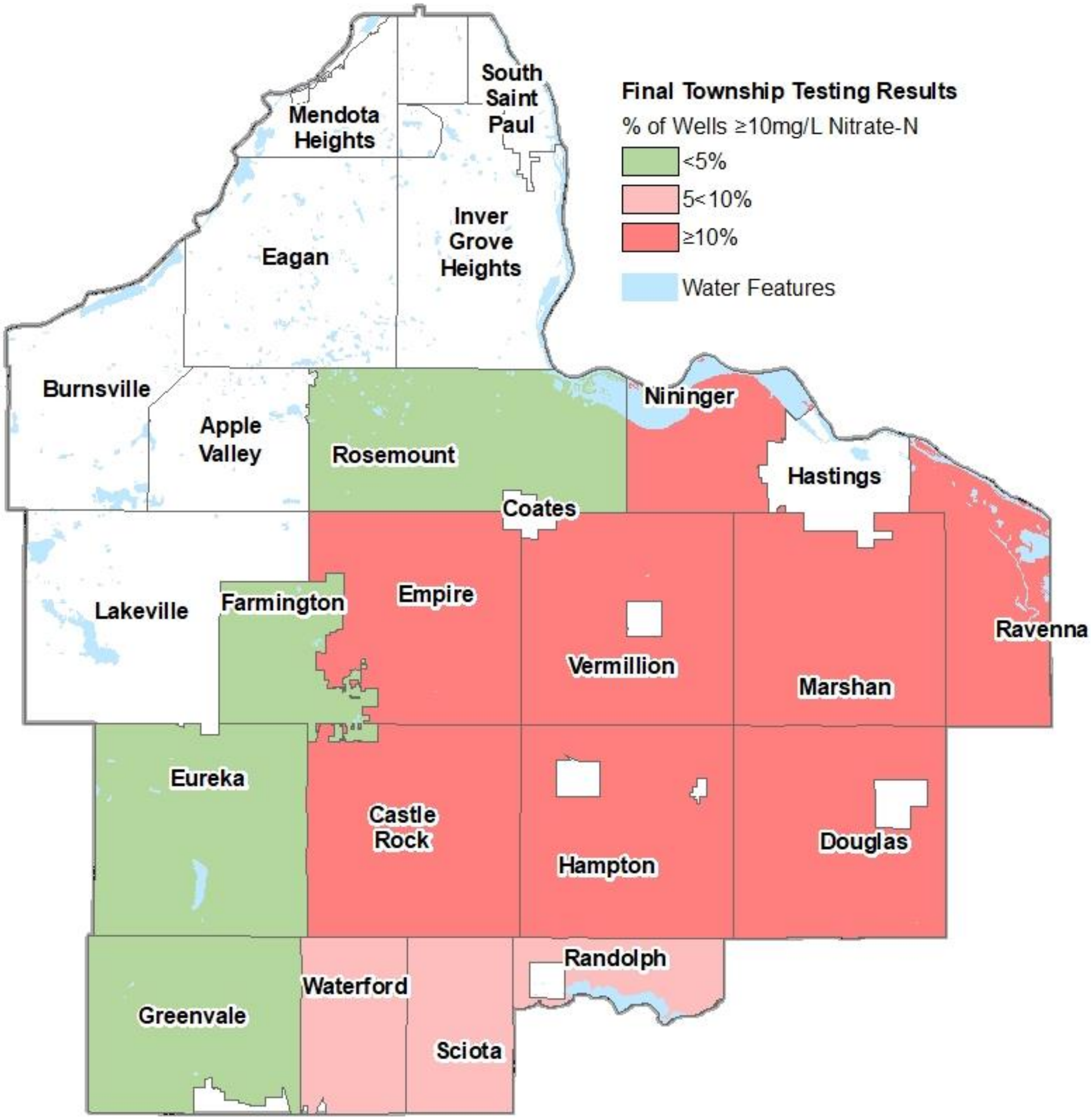


**Figure 26. Results of Township Testing Program 2017.**
**(Source: MDA 2013–2015)**

### 4.1.6. Nitrate in Inver Grove Heights (WIISE STUDY) and Community- Focused Sampling

Often, residential lawn fertilizers, septic systems and golf courses are suspected of contributing to nitrate in the groundwater. These did not turn out to be significant sources of nitrate in three focused sampling projects Dakota County conducted in the communities of Inver Grove Heights, Burnsville and Lakeville.

In 2015–16, because Ambient Study results found elevated levels of manganese in northern areas of the County, MDH and the County conducted a joint study of private wells in Inver Grove Heights, *Wells and Increased Infant Sensitivity and Exposure (WIISE*) (Scher and Demuth, 2017). Inver Grove Heights has approximately 1,500 private wells and septic systems — more than any other city or township in the County. As part of the WIISE Study, 274 Inver Grove Heights private wells were tested for nitrate; 68 percent of the wells had no nitrate above the MRL of 0.05 mg/L and the maximum nitrate detected was 6.1 mg/L.

In 2018, Dakota County began its focused community sampling initiative, in which, in a five-year cycle, all private well owners will be provided a water test kit to collect an untreated water sample from an outside faucet (outside sample) and a second sample from the primary drinking water tap (inside sample) within the residence. The participant completes a form describing the water treatment devices used to treat the inside sample. If the outside sample result exceeds 3.0 mg/L for nitrate, 0.05 µg/L for arsenic, or 0.090 mg/L for manganese, then the inside sample will be tested for that chemical parameter. In addition, every inside sample will be tested for lead and every outside sample for chloride.

Table 10 summarizes the nitrate results from the outside and inside samples from the geographically-focused sampling projects, WIISE and 32 of the 77 Ambient Study participants.

**Table 10. Summary of Nitrate Results (mg/L) Comparing Datasets.**

| Sample Events | Year | # of Samples | # of Samples with Detections (%) | # of Samples above Standard of 10 mg/L | Average | Median | Max |
|---|---|---|---|---|---|---|---|
| Ambient Study outside untreated * | 2018-19 | 32 | 24 (75%) | 13 (54%) | 11 | 11 | 22.3 |
| Ambient Study inside drinking water * | 2018-19 | 24 | 23 (96%) | 7 (30%) | 7.26 | 8.15 | 19.6 |
| Inver Grove Heights outside untreated | 2016 | 274 | 88 (32%) | 0 | 0.61 | <0.05 | 6.1 |
| Inver Grove Heights inside drinking water | 2016 | 32 | 4 (13%) | 0 | 0.19 | <0.05 | 1.14 |
| Burnsville outside untreated | 2018 | 66 | 27 (41%) | 0 | 0.56 | 0.053 | 5.59 |
| Burnsville inside drinking water | 2018 | 6 | 5 (83%) | 0 | 2.56 | 2.68 | 5.37 |
| Greenvale outside untreated | 2019 | 94 | 21 (22%) | 4 (19%) | 4.7 | < 0.05 | 22 |
| Greenvale inside drinking water | 2019 | 8 | 8 (100%) | 4 (50%) | 10.03 | 1.1 | 21 |
| Lakeville outside untreated | 2019 | 100 | 17 | 2 (18%) | 0.52 | < 0.05 | 16.2 |
| Lakeville inside drinking water | 2019 | 3 | 3 | 0 | 4.24 | 0.34 | 7.32 |

*32 of the 77 Ambient Study well owners submitted samples from their inside faucets

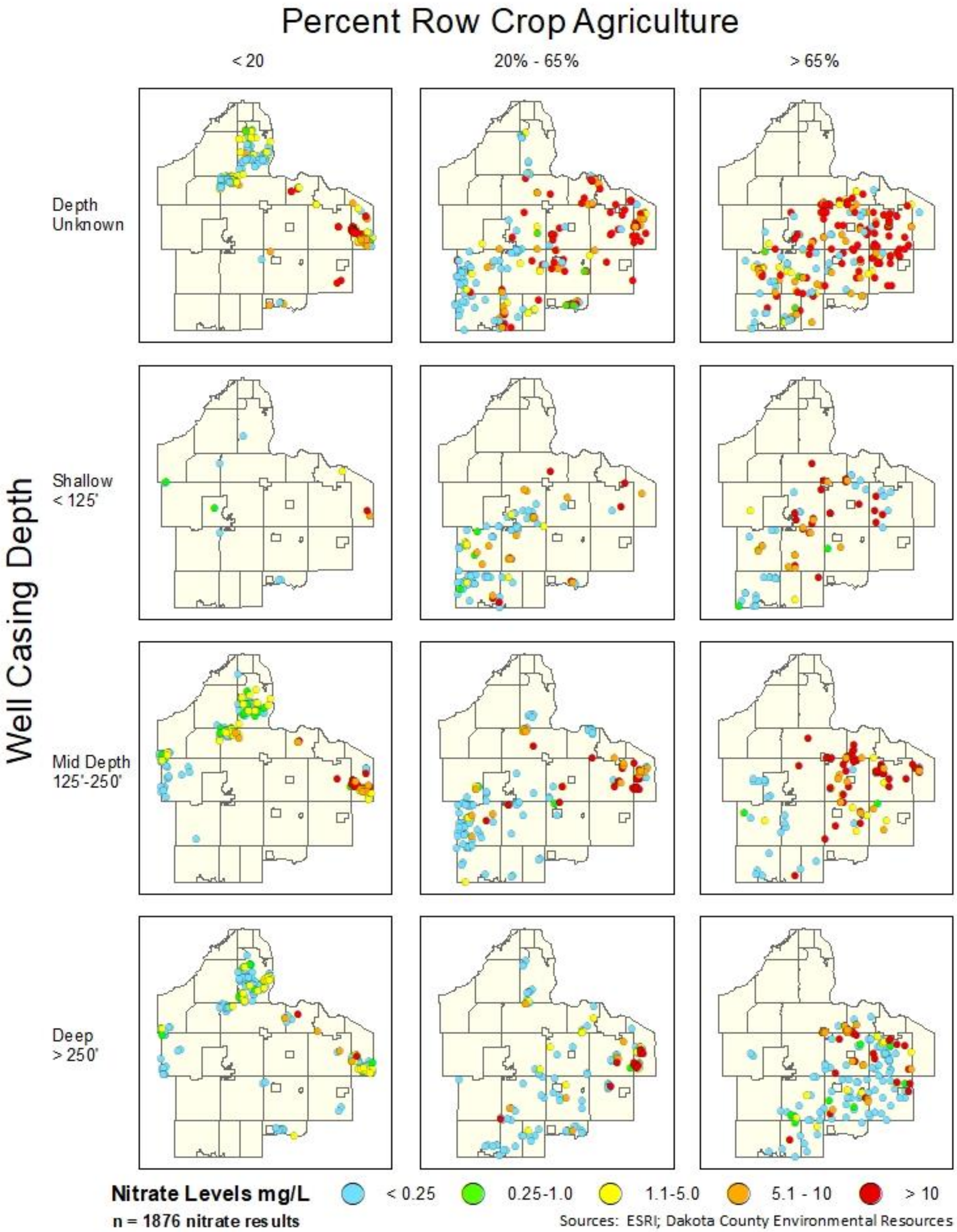
Reverse osmosis systems reduced nitrate levels. Inside water samples with nitrate above the drinking water guideline (10 mg/L) range from a low of 18 percent in Lakeville to a high of 50 percent in the inside Greenvale Twp samples. In every Ambient Study sampling event (as in all Dakota County private well sampling), well owners with elevated nitrate were advised to treat the water with a reverse osmosis system.

Of the 66 private wells tested in Burnsville, 41 percent of the wells had nitrate above the MRL of 0.05 mg/L; the maximum nitrate detected was 5.59 mg/L. The outside median and average nitrate levels are lower in all the different community sampling events than the Ambient Study wells, which had 32 participants. This was expected, because the Ambient Study found nitrate levels to be highly correlated with the percent of nearby land use in row crop agriculture; Inver Grove Heights, Burnsville, and Lakeville have little row crop agriculture. There is a high density of households using wells and septic systems in these rural residential areas, but the nitrate levels were low compared with the row crop agricultural areas of the County.

Greenvale Township is high in row crop agriculture and 22 percent of wells had nitrate detected above the MRL; 19 percent exceed the guideline of 10 mg/L. This is dissimilar from the results of the Ambient Study, where nitrate is detected above the MRL in 75 percent of the wells and 30 percent exceeded 10 mg/L. Greenvale Township generally has lower nitrate, as depicted in Figure 26, than other row crop-intense areas, but nitrate results are higher in the eastern half of the Township. In the western portion of the township, heavy (higher clay content) soils either slow the downward movement of nitrate to the drinking water aquifers, direct water to discharge into surface water bodies or drain tile disrupts the hydrogeologic pattern. In the eastern portion of the township, weathered and dissolved limestone, known as karst, and sand and coarse-grained soils are present. Both karst and coarse-grained soils are very porous, which allows surface pollutants to move quickly to the groundwater.

### 4.1.7. Relationship between Nitrate Concentrations, Well Depth and Percent Agriculture

Figure 27 shows the distribution of 1,876 groundwater nitrate results, obtained from all samples collected between 2000–2019 as part of the Ambient study, MDA Township Testing Program (2013-15), MDH WIISE Study (2016) and Community Testing Program [Burnsville (2018), Greenvale (2019) and Lakeville (2019)]. This spatial presentation of nitrate concentration with well casing depth and with the percentage of land in row crop agriculture shows the influence row crop agriculture plays in the distribution of groundwater nitrate. The variables of well casing depth and percent row crop agriculture have been broken into three range groupings for ease of visualization.



Sources: ESRI; Dakota County Environmental Resources

**Figure 27. Well Casing Depth by Percent of Land in Row Crop Agriculture.**

Figure 27 shows that as the percent of land in row crop agriculture near a well increases, so too does the concentration of nitrate detected in the groundwater, conversely with increased well casing depth, the detected level of nitrate in groundwater is generally lower. In the southwest corner of the County, even at the highest percentage of land in row crop agriculture, the nitrate results are low due, in part, to the heavy soils. By contrast, the presence of coarse soils largely comprised of sand and gravel in the eastern portion of the County allow water to infiltrate quickly to the water table carrying excess nitrate to the groundwater. Ravenna Township, on the east side of the County, has many wells with elevated nitrate in shallow and middle well casing depth categories and areas that are less than 20 percent row crop agriculture.

Note anomalous results where clusters of nitrate levels, in exceedance of drinking water guidelines, occur in areas of low percent row crop agriculture (Ravenna). This occurs in an area of clustered rural residences, located adjacent and immediately downgradient from irrigated row crop agriculture. Sources of nitrate contamination include infiltrate from adjacent agricultural fields and seepage from septic systems. Additional research may be needed to determine the origins and source(s) of the elevated nitrate.

### 4.1.8. Visualizing Nitrate Presence and Movement in Dakota County Aquifers

In addition to the Ambient Study data, Dakota County's Groundwater unit has multiple decades of nitrate sample results from private wells located around the County, collected through its Water Supply Testing Service, the Hastings Area Nitrate Study, nitrate clinics conducted in cooperation with MDA and other sampling activities. The large number of nitrate samples enables a clearer description of the spatial distribution of nitrate throughout the County than is possible with the Ambient Study well data alone. Also, spatial distributions obtained for nitrate can be used to indicate likely spatial distributions for other agricultural chemicals (pesticides) that the study found to be associated with nitrate.

County staff assembled a data set of 10,700 nitrate samples from private wells; more than 8,000 came from wells with known depths. Although the County's data are extensive, they are unevenly distributed in both space and time. A moving window weighted percentile interpolator was selected as a robust and fair way to visualize the actual data. Horizontal slices or vertical cross-section graphics visualize **change through time by displaying time and depth sequences as in Figure 28**. Appendix F provides a detailed explanation of the process.

Percentiles are used because the results do not depend on assumptions about the statistical distribution of the data. The depths shown are depth below the water table rather than depth below land surface. The figures use a color scheme in which hues of blue indicate nitrate concentrations below the drinking water guideline of 10 mg/L (ppm on the legend is equivalent to mg/L), and hues of orange to red indicate nitrate concentrations above the guideline. All hues are faded to white when there are too few samples to create a reliable percentile estimate.

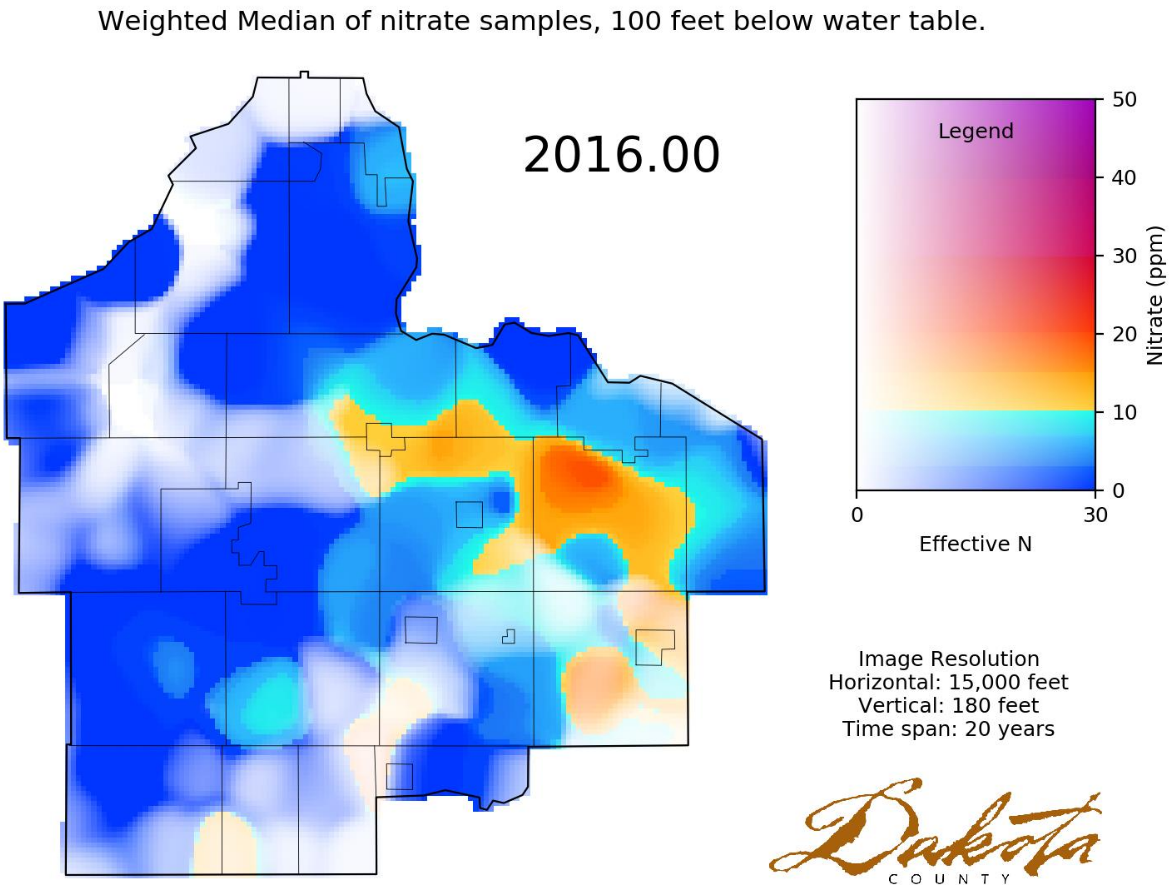


**Figure 28. Plain View of Median Nitrate Concentration in Year 2016, at 100 Feet Below the Water Table.**

In Figure 29, a vertical cross-section line is drawn from west to east, from Burnsville to Hastings. The cross section is drawn at the top and a map showing the location of the cross-section line is drawn in the lower left (the cross-section line in Figure 29 does not represent a groundwater flow path). The map also shows the individual samples used in computing percentiles for the cross-section figure. The samples are shown colored by the concentration in the sample and drawn with sizes proportional to their closeness to the section line in space and their closeness to the time stamp on the image. This figure illustrates how the large area in the west where there are no samples results in a large white area on the cross-section interpolation. Below the map, the 'Image Resolution' describes the distance from the cross-section line within which samples are added to the percentile calculations.

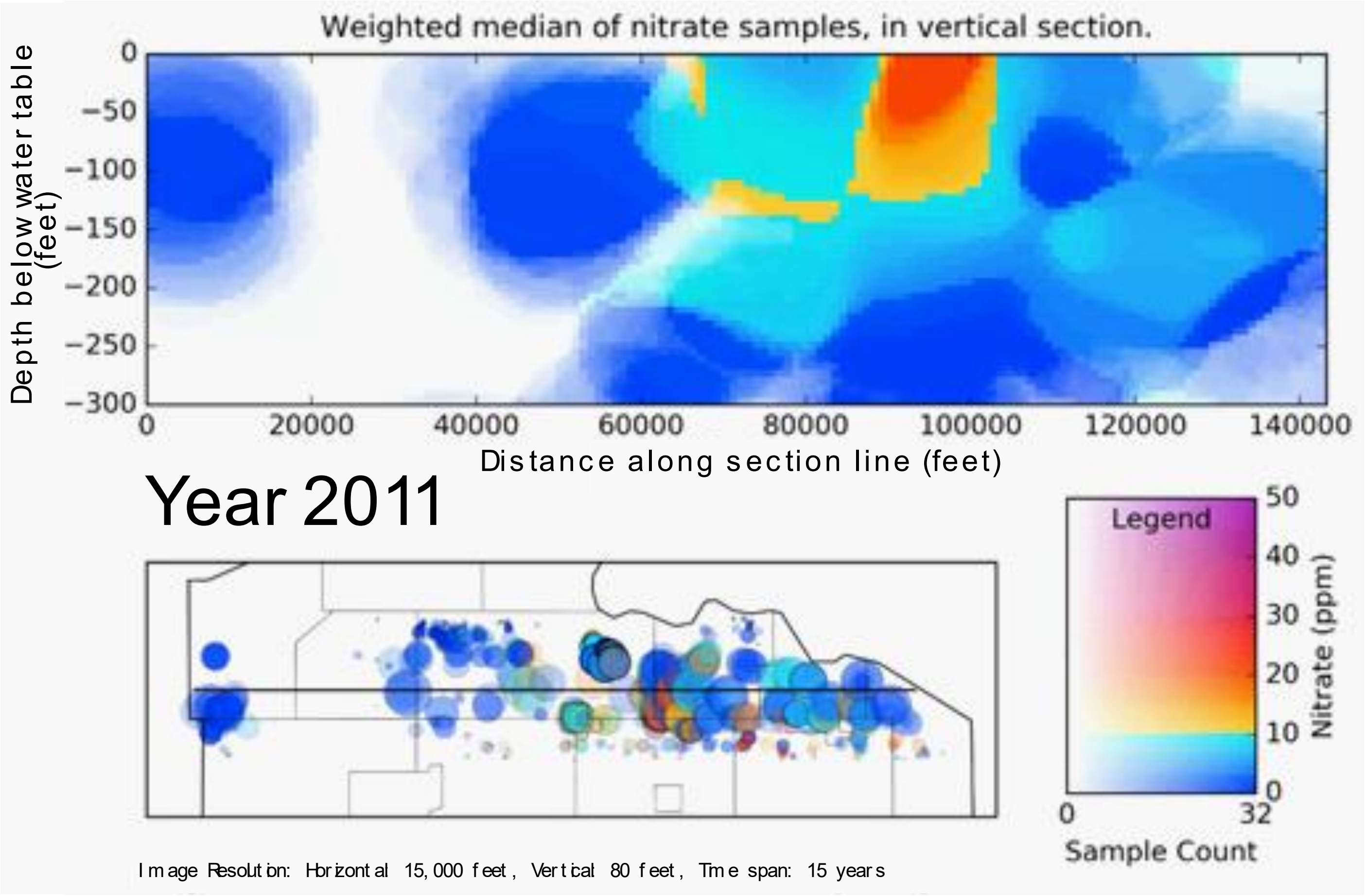


**Figure 29. Vertical Cross-Section of Weighted Median (50th percentile) Along an East-West Line—Frame from Nitrate Time Series Video.**

Percentiles are a flexible way to visualize and think about information. The 50th percentile is the same as the median, half of the data are higher and half of the data are lower. The figures above depict the median. For health and safety concerns, extreme percentiles are often of more interest, for example, the upper 90th percentile or higher.

Figure 30 is grid of figures showing the upper 90th percentile of the nitrate concentration in private well water samples in four different years at three different depths. The meaning of the 90th percentile is that 10 percent of samples had a concentration higher than that color portrayed on the figure, refer to the nitrate concentration legend. Again, the white area represents too few samples in an area to compute a reliable 90th percentile for the year depicted.

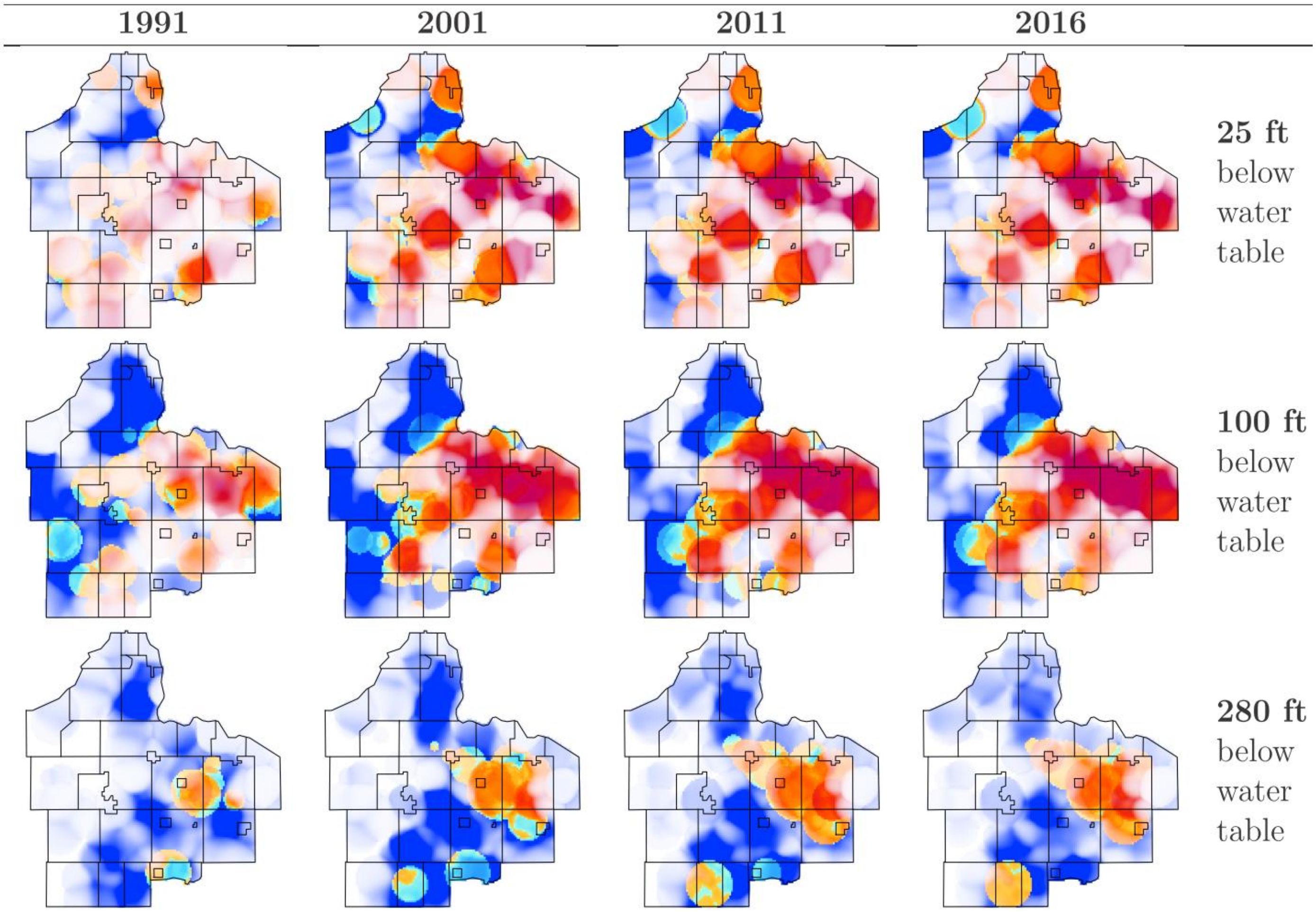
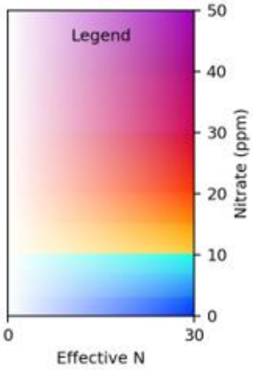


**Figure 30. 90th Percentile Nitrate Concentrations Over Time and Depth.**



These visualizations are consistent with the Ambient Study data and statistical results. The nitrate levels are higher in areas of coarse textured soils and row crop agriculture. Over time, the nitrate is traveling deeper in the aquifers.

Figures at the 50th and 90th percentiles for nitrate are shown in in Appendix F. A time-series video of the nitrate and its progression through time and depth at the 50th and 90th percentiles on the Dakota County website, www.dakotacounty.us, search *nitrate movie.*

## 4.2. Pesticides

### 4.2.1. Pesticide Sources and Health Concerns

Pesticides are a group of chemicals developed, and intentionally added to the environment, to kill or control pest species. Pesticides are classified by the type of pest they control. For example: herbicides control plants, fungicides control fungi or mold and insecticides control insects. In modern agriculture, pesticides are essential to providing higher production yield and quality by reducing crop loss due to insect and disease damage. Once distributed in the environment, however, the toxic effects of pesticides may extend beyond the target organisms degrading surface and groundwater resources and presenting risks to humans, animals and plants in the broader environment. In the Ambient Study, herbicides and herbicide breakdown products are the primary pesticide compounds detected in groundwater.

**Common Detection**

The concept of “common detection” in groundwater is defined in State statutes as *“detection of a pollutant that is not due to misuse or unusual or unique circumstances but is likely to be the result of normal use of a product or a practice.”* The following pesticides are determined by the MDA to be in common detection: acetochlor, alachlor, atrazine, metolachlor and metribuzin.

The predominant crops produced in Dakota County are corn and soybeans (see Figure 31). The large-scale, intensive production of crops practiced in much of Dakota County is accompanied by the use of chemical fertilizers and pesticides. In Minnesota, the herbicide compounds most commonly detected in groundwater are those that currently or historically have been widely applied to corn and soybeans. MDA designates the most widely detected agricultural herbicides as being in “common detection” in Minnesota.

Once applied to plants or soil, pesticides (parent compounds) transform into related compounds referred to as breakdown products or degradates. Generally, breakdown products are more stable and more water soluble than their parent compounds, which influences their movement and persistence in the environment. Over the course of this study, advances in analytical techniques improving the sensitivity of detections resulted in an increased number of detectable herbicide breakdown products. The high occurrence of herbicide detections serves as an indication of the pervasiveness of pesticide sources in the environment and the ease with which these pollutants infiltrate and migrate in groundwater.

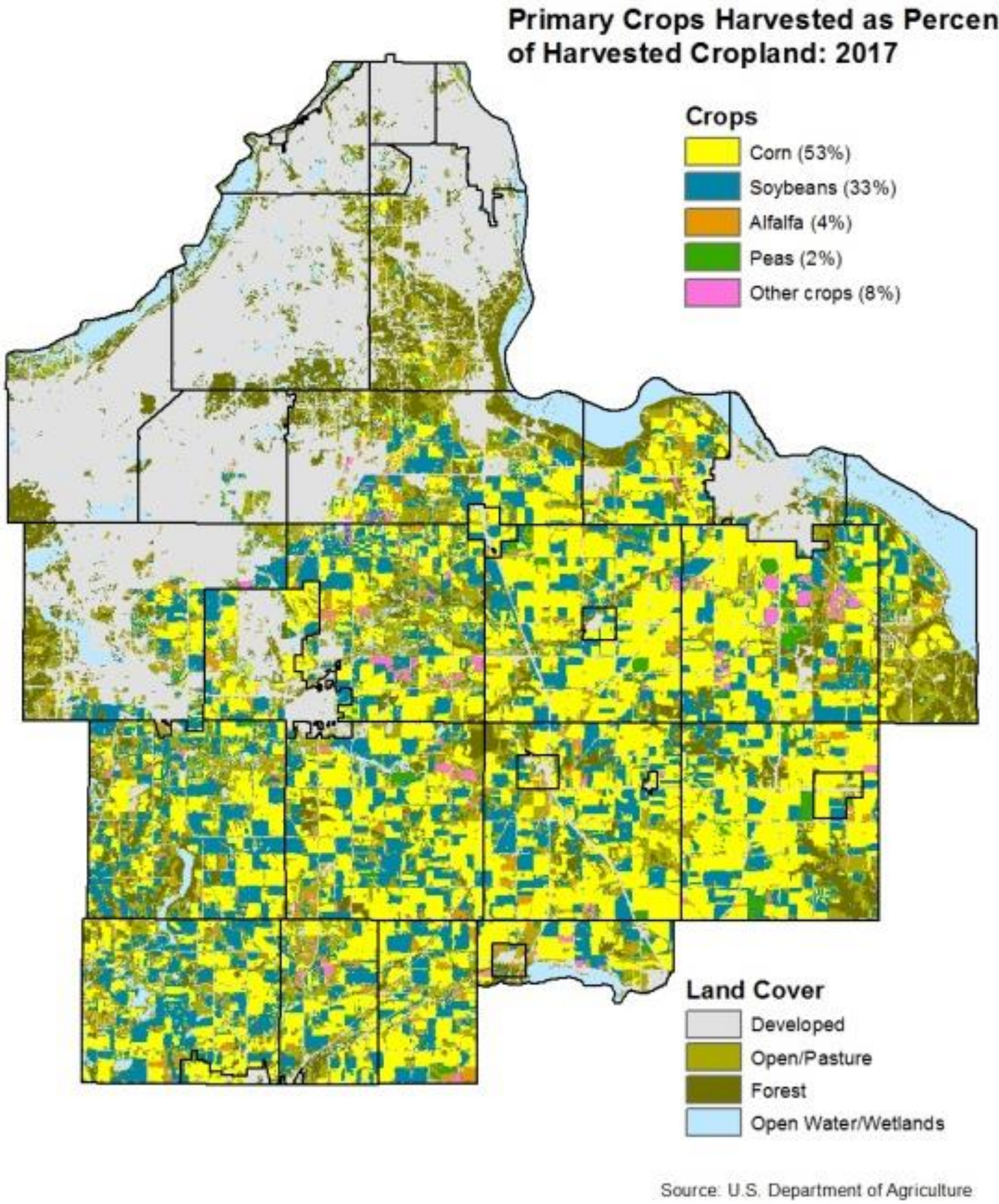


**Figure 31. Primary Crops Harvested as a Percent of Cropland, 2017. (Source USDA, NASS)**

In the study wells, pesticides and pesticide breakdown products are most frequently detected at low levels, often well below drinking water guidelines., (However, individual drinking water guidelines do not exist for every compound detected.) One herbicide, cyanazine, has been detected in Dakota County above the drinking water guideline. In 22 percent of the study wells, the total sum of cyanazine breakdown products (total cyanazine) exceeds drinking water guideline of 1.0 µg/L at least once over the course of the study.

**Degradates of cyanazine**

*Cyanazine specific*
Cyanazine acid CAC)
Cyanazine amide (CAM)
Deethylcyanazine (DEC)
Deethylcyanazine acid (DCAC)
Deethylcyanazine amide (DCAM)

*Two additional cyanazine breakdown products are also breakdown products of atrazine*
Deisopropylatrazine (DIA)
Didealkylatrazine (DDA)

The detection of pesticides in drinking water is a public health concern. Even for the pesticides detected below the health guideline, the long-term exposure to low levels of pesticides, and the overall health impact of contaminant mixtures as was found in this Study is not well understood. Based on the findings of these limited animal studies, drinking water guidelines are established at levels believed to be protective of human health.

The MDH drinking water guidelines for the major herbicides detected are summarized in Table 11. These guidelines apply to a single active ingredient; often the individual breakdown products have not been evaluated for toxicity. (MDH is making progress in providing guidance values for breakdown products.) MDH has established guidance values for some of the most common breakdown products, such as acetochlor ESA, alachlor ESA, and metolachlor ESA. When these chemicals are detected, concentrations are compared to their assigned drinking water guideline to evaluate the risk to human health. For many herbicide breakdown products, such as those of cyanazine, no health risk guidelines have been established. In those cases, based on MDH guidance, the health risk is evaluated by comparing the concentration of the sum of the breakdown products to the drinking water guideline for the parent compound (in this case, total cyanazine). importantly, the overall human-health risks have not been established for mixtures of contaminants, which commonly occur in the environment, and the potential health effects of pesticide mixtures has not been evaluated (USGS Water Quality Benchmarks for Contaminants).

In the Ambient Study, except for well AGQS-23 where the parent alachlor exceeded the drinking water guideline of 0.7 µg/L from 2005 to 2007, total cyanazine is the only herbicide detected above the drinking water guideline. All other pesticides and breakdown products detected were at levels below the drinking water guidelines.

**Table 11. Drinking Water Guidelines for Major Herbicides Detected.**

| Chemical | Common Trade Names | Value Type | Exposure Duration | Value** (µg/L) | Health Endpoint(s) |
|---|---|---|---|---|---|
| Acetochlor<br>*See also* breakdown products:<br>Acetochlor ESA<br>Acetochlor OXA | Harness, Breakfree, Confidence, Surpass, Warrant | $HRL_{18}$ | Chronic | **20** | Liver system; Male reproductive system; Nervous system; Kidney system; Respiratory system |
| Acetochlor ESA (breakdown product of Acetochlor) | | $HRL_{18}$ | Chronic | **300** | Male reproductive system; Thyroid (E*) |
| Acetochlor OXA (breakdown product of Acetochlor) | | $HRL_{18}$ | Chronic | **90** | Thyroid (E) |
| Alachlor<br>*See also* breakdown products<br>Alachlor ESA<br>Alachlor OXA | Lasso, Micro-Tech, Bronco | $HRL_{18}$ | Chronic | **9** | Blood system; Liver system; Kidney system |
| Alachlor ESA (breakdown of Alachlor) | | $RAA_{16}$ | Chronic | **50** | Blood system |
| Alachlor OXA (breakdown product of Alachlor) | | $RAA_{16}$ | Chronic | **50** | Blood system |
| Atrazine | Aatrex, Bicep II Magnum, Brawl II | $HRL_{MCL}$ | Chronic | **3** | Cancer, cardiovascular, eye and muscle degeneration |
| Cyanazine*** | Bladex, Fortrol, Match, Payze | $HRL_{18}$ | Chronic | **1** | Developmental; Female reproductive system; Liver system; Kidney system; Cancer |
| Metolachlor and s-Metolachlor<br>See also breakdown products<br>Metolachlor ESA<br>Metolachlor OXA | Dual Magnum, Cinch, Me-Too-Lachlor II | $HRL_{11}$ | Chronic | **300** | Developmental |
| Metolachlor ESA (breakdown product of Metolachlor) | | $HRL_{11}$ | Chronic | **800** | Liver system |
| Metolachlor OXA (breakdown product of Metolachlor) | | $HRL_{11}$ | Chronic | **800** | None |

*E=Estimated

**https://www.health.state.mn.us/communities/environment/risk/guidance/gw/table.html

***https://www.health.state.mn.us/communities/environment/risk/docs/guidance/gw/cyanazineinfo.pdf

### 4.2.2. Pesticide Results

All pesticide results of interest are summarized by well in Appendix C Tables C.1. through C.68.

#### i. Pesticide results 1999–2001

Analysis of groundwater for herbicides, known as MDA List 1, from 1999–2001 at the Minnesota Valley Testing Laboratories (MVTL) yielded few detections. During the early years of the study, the laboratories employed methods and instruments capable of detecting limited analytes at high detection limits, consisting mostly of herbicide parent compounds. One pesticide, EPTC trade name Eradicane, was detected at very low levels in two of the 30 wells sampled in 1999. In 2000, no herbicides were detected in the sampling of 43 wells. In 2001, Minnesota Valley Testing Laboratory conducted analysis on 42 samples using an expanded parameter list and lower detection limits. The parent compound, atrazine was detected at low levels (0.2–0.3 µg/L) in eight of 42 wells. The breakdown product of atrazine, deethylatrazine, was detected near the detection level of 0.2 µg/L in 12 wells and one well contained the breakdown product deisopropylatrazine at 0.3 µg/L.

#### ii. Pesticide results, USGS National Water Quality Laboratory, 2008

In addition to herbicide analysis (discussed in the next section) by the USGS Organic Geochemistry Research Laboratory (OGRL), the USGS National Water Quality Laboratory (USGS NWQL) analyzed samples in 2008. The USGS NWQL analysis focused on samples from 97 wells, 66 Ambient Study wells and 31 Hastings Area Nitrate Study [HANS] wells, for organic wastewater compounds (OWWC), which is discussed below.

The USGS NWQL analysis included five herbicides, three of which — atrazine, prometon, and metolachlor — are routinely part of the Ambient Study analysis done by USGS OGRL. The USGS NWQL analysis also included pentachlorophenol and metalaxyl. Four of the five herbicides were detected: atrazine, metolachlor, pentachlorophenol and prometon. The results are summarized in Table 12. Metalaxyl was not detected. No detections were higher than the drinking water guidelines. All results were estimated (E) except for the two highest results for atrazine which were 0.22 µg/L and 0.25 µg/L (the method reporting level is 0.20 µg/L).

**Table 12. USGS NWQL Herbicide Results Summarized from Ambient and Hastings Area Nitrate Studies.**

| Compound Name | Possible Use or Source | # of Detects (n=97) in 2008 | Min (ug/L) & MRL | Max (ug/L) | MDH Drinking Water Guideline (µg/L) in 2018 |
|---|---|---|---|---|---|
| Atrazine | Herbicide | 31 | <0.20 | 0.25 | 3 |
| Metolachlor | Herbicide | 8 | <0.20 | E 0.11 | 300 |
| Pentachlorophenol | Herbicide, fungicide, wood preservative | 1 | <0.8 | E 0.1 | 0.3 |
| Prometon | Herbicide (noncrop), applied prior to blacktop | 1 | <0.20 | E 0.4 | 100 |

### iii. Results, 2001–2019

In 2001, Dakota County began a collaboration with the USGS OGRL and the USGS Minnesota Water Science Center and submitted samples from 18 wells to be analyzed for pesticides and pesticide breakdown products. The USGS analytical methods measure parent compounds and their breakdown products at as low concentrations as possible, frequently resulting in detections at concentrations far below established drinking water guidance levels. Samples were submitted to the USGS OGRL in 2001-2017. The USGS OGRL laboratory achieved a lower detection level for an expanded list of herbicides than available from other labs, resulting in higher frequency of detection of herbicide compounds in study wells. The prevalence, distribution, concentrations and number of different herbicides detected in groundwater is an important finding of this study.

In 2019, Dakota County submitted pesticide samples to Weck Laboratories (Weck) after the MDA Laboratory contracted with Weck to develop analytical methods for analysis of cyanazine breakdown products. Prior to 2019, USGS OGRL was the only laboratory capable of analyzing the five cyanazine breakdown products (2019 cyanazine results are further discussed under section 4.2.7.).

### iv. Herbicide results summary

This Ambient Study, and others, have found that breakdown products, not parent compounds, are the most frequently detected pesticide compounds. Appendix A Tables A.7. (USGS) and A.11. (Weck) shows pesticides and pesticide breakdown products analyzed and their reporting limits.

#### ***The breakdown products of herbicides commonly and historically applied to corn and soybean crops are the most frequently detected herbicides***

Herbicide compounds were widely detected in the Ambient Study wells. The breakdown products of herbicides widely used on corn and soybeans — alachlor, metolachlor, acetochlor and atrazine — are the most widely detected but at levels below current established drinking water guidelines. The breakdown products of cyanazine were also widely detected. Cyanazine is not in MDA common detection status.

Herbicide "parent" compounds were observed in 14 percent of the wells from 1999–2019. The two most frequently detected parent compounds were atrazine (47 percent of wells sampled) and metolachlor (16 percent). Herbicide breakdown products, in comparison, were detected in 73 percent of the wells and were 14 of the 15 most frequently detected herbicide compounds (Figure 32). In preparing Figure 32, the data for 10 wells was censored to exclude from the analysis, wells with only one or two pesticide detections at or near the MRL over the course of the study (1999-2019). See Appendix C Table C.67. for a summary of detections by pesticide and by well.

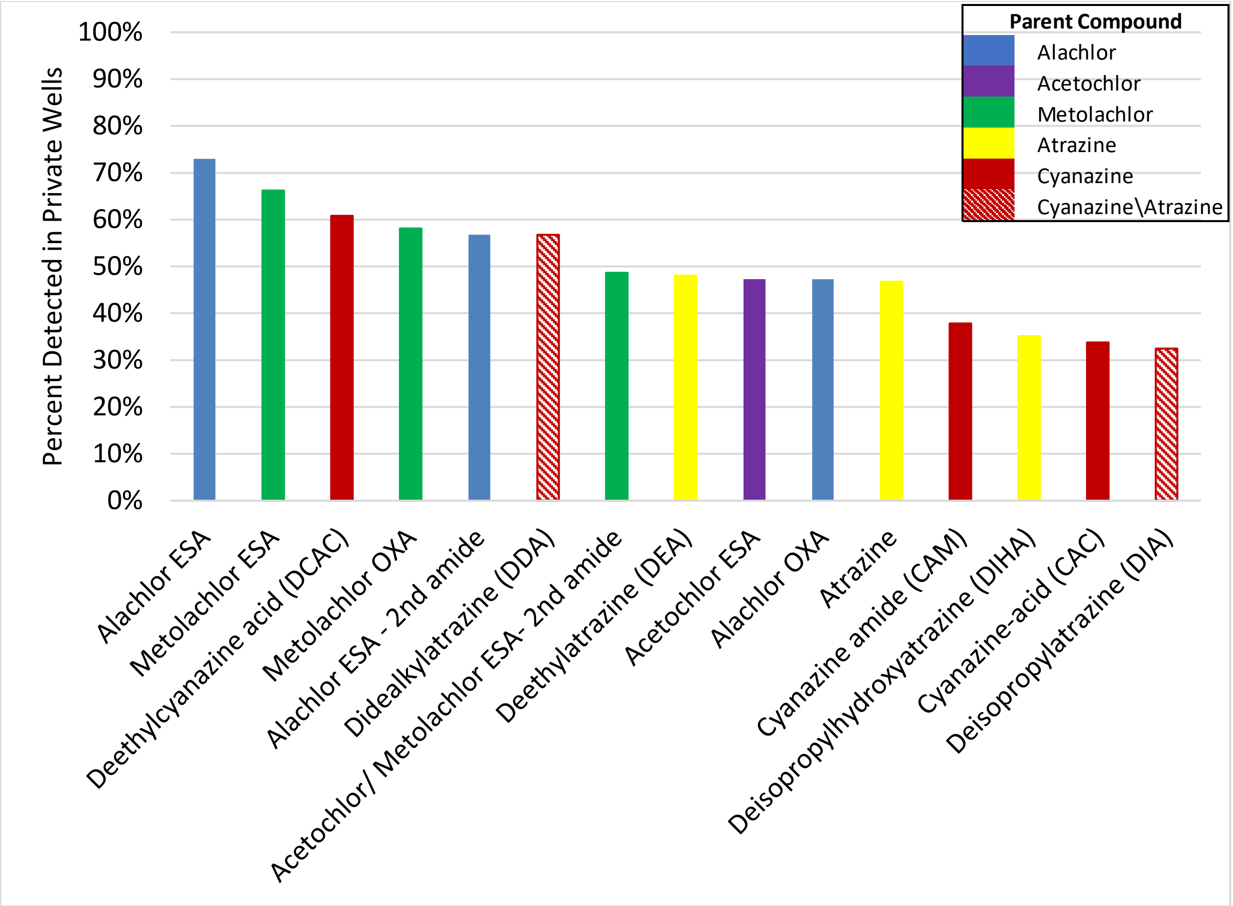


**Figure 32. Frequency of Detection of Herbicide Parent Compounds and Breakdown products.**

Results from the study find that:

- The herbicides associated with corn and soybean production are the most heavily used in the County and were detected most frequently and at the highest concentrations in water samples, particularly where row crop agriculture is the dominant land use.
- Herbicide compounds were detected in 56 of the 77 wells sampled (73 percent).
- The total concentration of cyanazine and its breakdown products exceeded the drinking water guideline of 1.0 µg/L at least once in 22 percent of the study wells sampled from 1999-2019.
- The number of herbicide compounds, the frequency of occurrence of herbicides detected is correlated with nitrate levels and the percent of row crop agriculture adjacent to sampled wells.
- The most commonly detected herbicide compound was alachlor ESA (73 percent) followed by metolachlor ESA (66 percent).
- As many as 25 different pesticide compounds were detected in a single well.
- Based on the frequency of detection, the most commonly detected herbicides were:
  - alachlor and alachlor breakdown products (71 percent of wells);
  - metolachlor and metolachlor breakdown products (65 percent of wells);
  - atrazine and atrazine breakdown products (64 percent of wells);

  - cyanazine breakdown products (64 percent of wells);
  - acetochlor breakdown products (47 percent of wells).
- Of the 15 most frequently detected herbicide compounds in the study, atrazine, introduced in 1957, is the only parent compound.

The cyanazine breakdown products DCAC and CAC were detected at concentrations exceeding the drinking water guideline. All other herbicide parameters were detected at concentrations below their respective drinking water guidelines. Table 13 shows the highest concentration of each compound, the year of the highest detection and the relevant drinking water guideline.

**Table 13. Highest Herbicide Detections Among the 13 Most Frequently Detected Herbicides.**

| Compound | Year of Highest Detection | Highest Detection (µg/L) | Drinking Water Guideline (µg/L) | Highest Detection as a Percentage of the Guideline |
|---|---|---|---|---|
| **Acetamides** | | | | |
| Alachlor ESA | 2002 | 6.14 | 50 | 12.3% |
| Alachlor OXA | 2005 | 1.45 | 50 | 2.9% |
| Metolachlor ESA | 2006 | 7.87 | 800 | 1.0% |
| Metolachlor OXA | 2006 | 3.11 | 800 | 0.4% |
| Alachlor ESA 2nd amide | 2006 | 0.15 | 50 | 0.3% |
| Acetochlor/Metolachlor ESA 2nd amide | 2003 | 0.33 | 800 | 0.04% |
| **Triazines** | | | | |
| Deethylcyanazine acid (DCAC) | 2004 | 5.0 | 1* | 500% |
| Cyanazine acid (CAC) | 2004 | 1.3 | 1* | 130% |
| Cyanazine amide (CAM) | 2005 | 0.43 | 1* | 43% |
| Didealkylatrazine (DDA) | 2013 | 1.1 | 3* | 36.7% |
| Deethylhydroxyatrazine (DEHA) | 2011 | 0.65 | 3* | 21.7% |
| Atrazine | 2006 | 0.6 | 3* | 20.0% |
| Deethylatrazine (DEA) | 2013 | 0.53 | 3* | 17.7% |

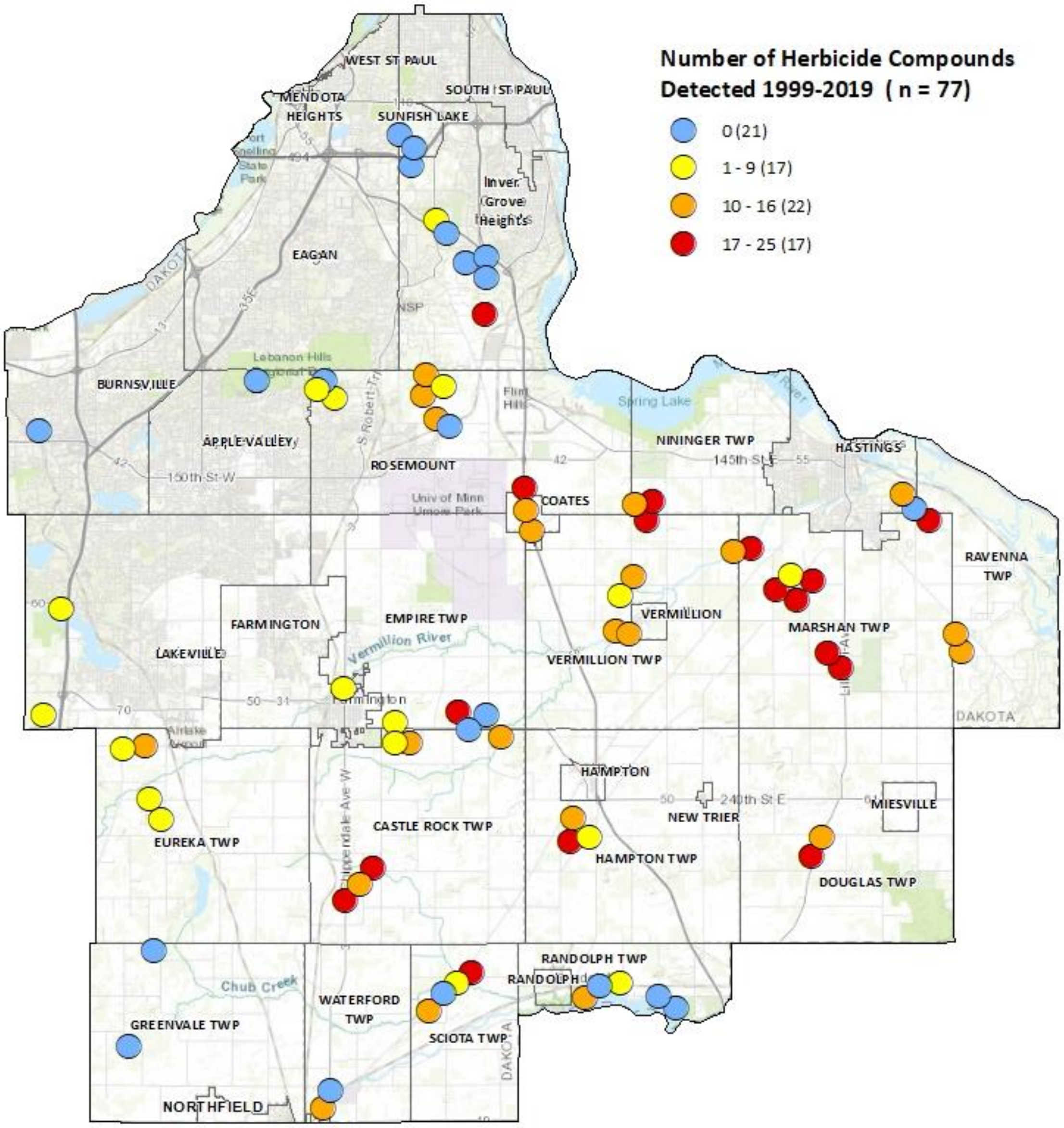
*In the absence of compound-specific toxicological information for pesticide breakdown products, the MDH protectively assumes by default that a pesticide breakdown product has the same toxicological effect as the pesticide parent compound and is as potent.

### v. Co-occurrence of herbicide breakdown products

#### ***Individual herbicide breakdown products were commonly found in mixtures with other herbicide breakdown products***

Herbicides compounds detected in groundwater also frequently co-occurred with other herbicides. The 1999-2019 results (Appendix C Table C.67.) show that the detection of one pesticide compound in a sampled well is most often accompanied by the detection of others. Of the 77 sampled wells, 71 percent contained two or more herbicides compounds while more than half (54 percent) of the wells had nine or more compounds present. In 27 percent of the wells, 15 or more compounds were detected; and in 10 percent of the wells, 20 or more compounds were detected (See Figure 33). Note that, as with nitrate, the wells with the highest number of herbicide compounds detected are largely located in the eastern portion of Dakota County where irrigated row crop agriculture is the dominant land use.

While individually most of these herbicide compounds occurred at concentrations below human health risk guidelines, the potential toxicity and human health risks of these herbicide mixtures has not been studied and is not well understood.



Sources: ESRI; Dakota County Environmental Resources

Figure 33. Wells with Number of Herbicide Compounds Detected.

### vi. Herbicide occurrence by casing depth

Statistical analysis of herbicide concentration by well casing depth was conducted for the 11 most frequently detected herbicide breakdown products. Concentrations for each of the 11 herbicide breakdown products correlates statistically (Kendall, $p < 0.05$), with well casing depth (Table 39). This fits the pattern observed for the anthropogenic compounds nitrate and chloride, where shallow cased wells have the highest detection levels and the deepest wells have the lowest detection levels.

Analysis of alachlor ESA, metolachlor ESA and metolachlor OXA representing the chemical family of acetamides, and deethylcyanazine acid (DCAC), representing the chemical family of triazines, are presented below. These herbicides are the four most frequently detected herbicides over the course of the study.

### ALACHLOR ESA

Figure 34 plots the median alachlor ESA results the most frequently detected herbicide, by well casing depth; the correlation is statistically significant (Kendall, p <0.05), and the line shows that median alachlor ESA concentrations decrease with increasing well casing depth. The line intercepts the x-axis or non-detection (0.2 µg/L) at 291 feet, which is the best statistical representation of the depth that we stop “seeing” alachlor ESA.

This statistical depth is interpreted to represent the year when the use of alachlor in Minnesota (about year 1969) had just begun based on date of registration . Intercept depth of 291 feet divided by 40 years (2009–1969) equals 7.3 feet per year infiltration. The year 2009 is used because it is the mid-point of the study years 1999–2019.

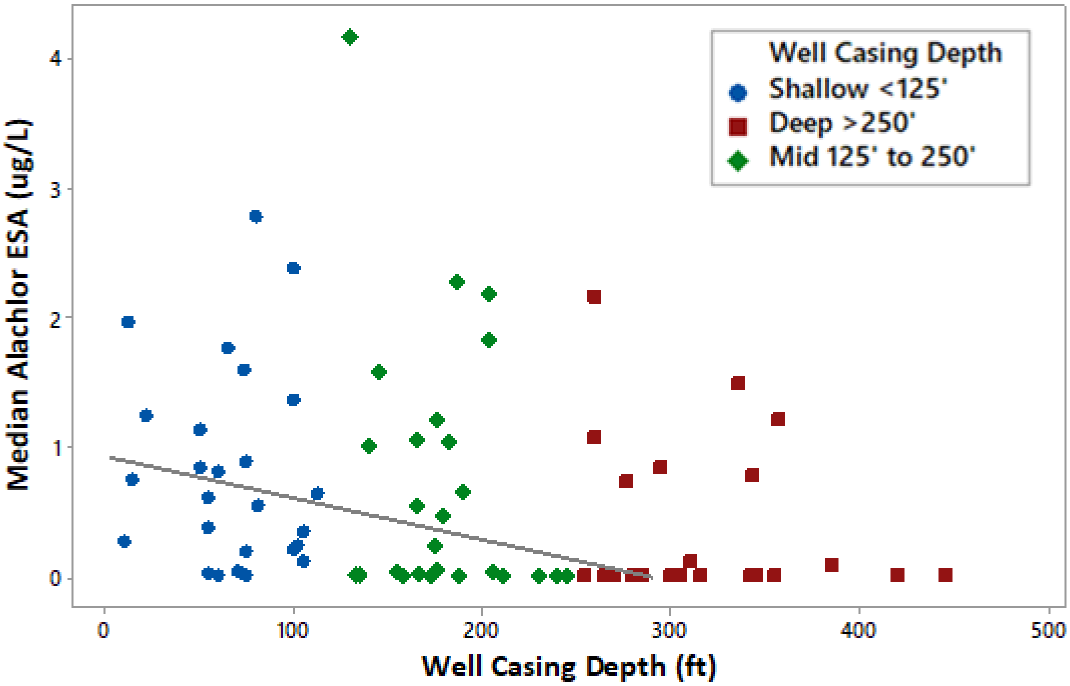


Figure 34. Correlation Alachlor ESA Concentration and Well Casing Depth—Kendall Line.

**Table 14. Median Concentration of Alachlor ESA (µg/L) and Well Casing Depth Ranges.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow < 125' | 26 | 0.82 | 0.77 | 0.02 | 0.21 | 0.63 | 1.27 | 2.79 |
| Mid 125' to 250' | 26 | 0.72 | 1.01 | 0.02 | 0.02 | 0.16 | 1.09 | 4.17 |
| Deep >250' | 25 | 0.36 | 0.59 | 0.02 | 0.02 | 0.02 | 0.77 | 2.17 |

## METOLACHLOR ESA

Figure 35 plots the median metolachlor EXA, the second most frequently detected herbicide, by well casing depth. The correlation is statistically significant (Kendall, p <0.01), and the line show that median metolachlor ESA concentration decreases with increasing well casing depth. The line intercepts the x-axis or non-detection (0.2 µg/L) at 250 feet and is the best statistical representation of the depth that we stop “seeing” metolachlor ESA. This depth is interpreted to represent the year when the use of metolachlor in Minnesota has just begun (about year 1974). Intercept depth of 250 feet divided by 34 years (2009–1974) equals 7.1 feet per year infiltration.

**Table 15. Median Concentration of Metolachlor ESA (µg/L) and Well Casing Depth Ranges.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow < 125' | 26 | 0.95 | 1.46 | 0.02 | 0.03 | 0.32 | 1.41 | 6.77 |
| Mid 125' to 250' | 26 | 0.62 | 0.92 | 0.02 | 0.02 | 0.19 | 0.96 | 3.55 |
| Deep >250' | 25 | 0.10 | 0.23 | 0.02 | 0.02 | 0.02 | 0.05 | 1.05 |

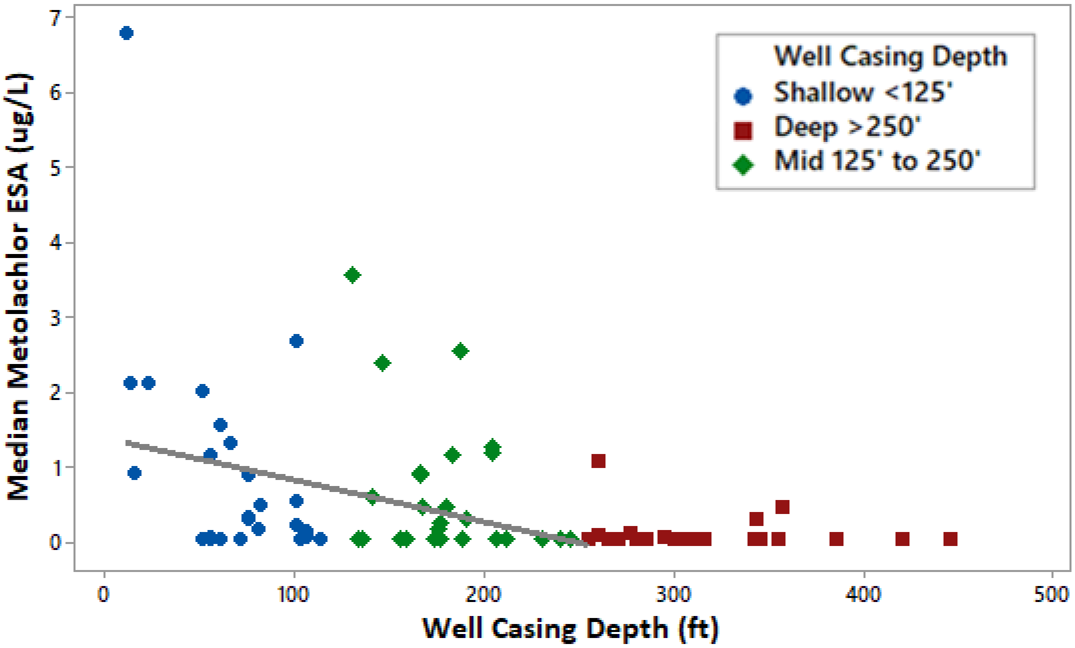


**Figure 35. Correlation Metolachlor ESA Concentration and Well Casing Depth—Kendall Line.**

### DEETHYLCYANAZINE ACID (DCAC)

Figure 36 plots the median DCAC results, the fourth most frequently detected herbicide, by well casing depth; the correlation is statistically significant (Kendall, p <0.01), and the line shows that median DCAC concentration decreases with increasing well casing depth. The line intercepts the x-axis or non-detection (0.2 µg/L) at 244 feet and is the best statistical representation of the depth that we stop "seeing" DCAC. This depth is interpreted to represent the year when the use of cyanazine in Minnesota has just begun (about year 1971). Intercept depth of 244 feet divided by 40 years (2009–1971) equals 6.1 feet per year infiltration.

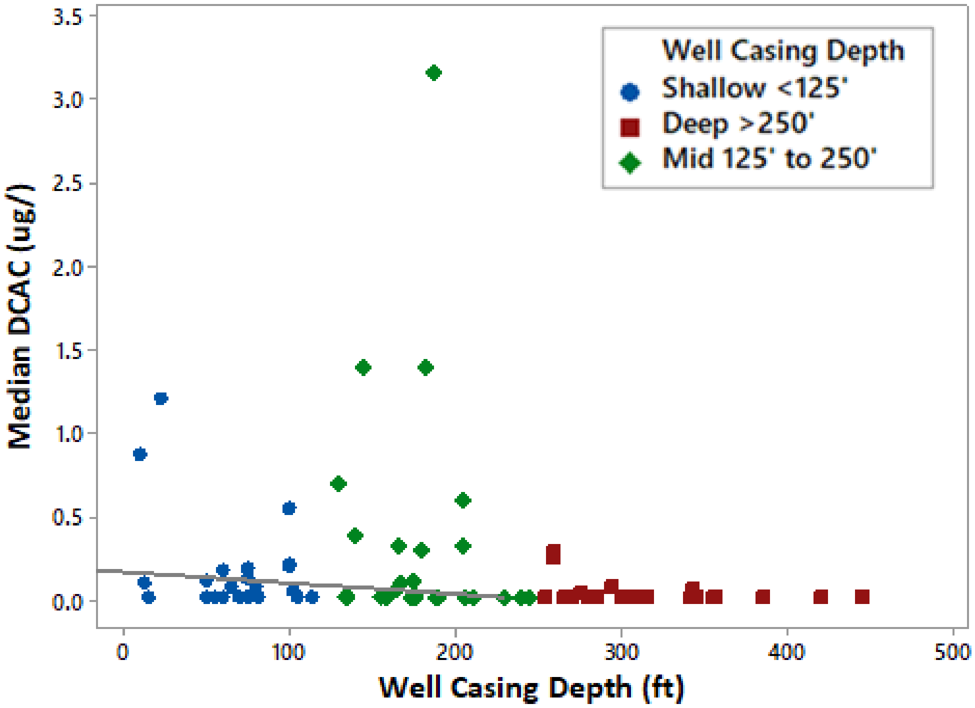


**Figure 36. Correlation Deethylcyanazine acid (DCAC) Concentration and Well Casing Depth—Kendall Line.**

**Table 16. Median Concentration of DCAC (µg/L) and Well Casing Depth Ranges.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow < 125' | 26 | 0.17 | 0.29 | 0.03 | 0.03 | 0.06 | 0.19 | 1.21 |
| Mid 125' to 250' | 26 | 0.36 | 0.69 | 0.03 | 0.03 | 0.03 | 0.35 | 3.15 |
| Deep >250' | 25 | 0.05 | 0.07 | 0.03 | 0.03 | 0.03 | 0.03 | 0.29 |

## METOLACHLOR OXA

Figure 37 plots the median metolachlor OXA, the fourth most frequently detected herbicide, by well casing depth. The correlation is statistically significant (Kendall, p <0.01), and the line show that median metolachlor OXA concentration decreases with increasing well casing depth. The line intercepts the x-axis or non-detection (0.2 µg/L) at 250 feet and is the best statistical representation of the depth that we stop “seeing” metolachlor OXA. This depth is interpreted to represent the year when the use of metolachlor in Minnesota has just begun (about year 1974). Intercept depth of 250 feet divided by 34 years (2009–1974) equals 7.1 feet per year infiltration.

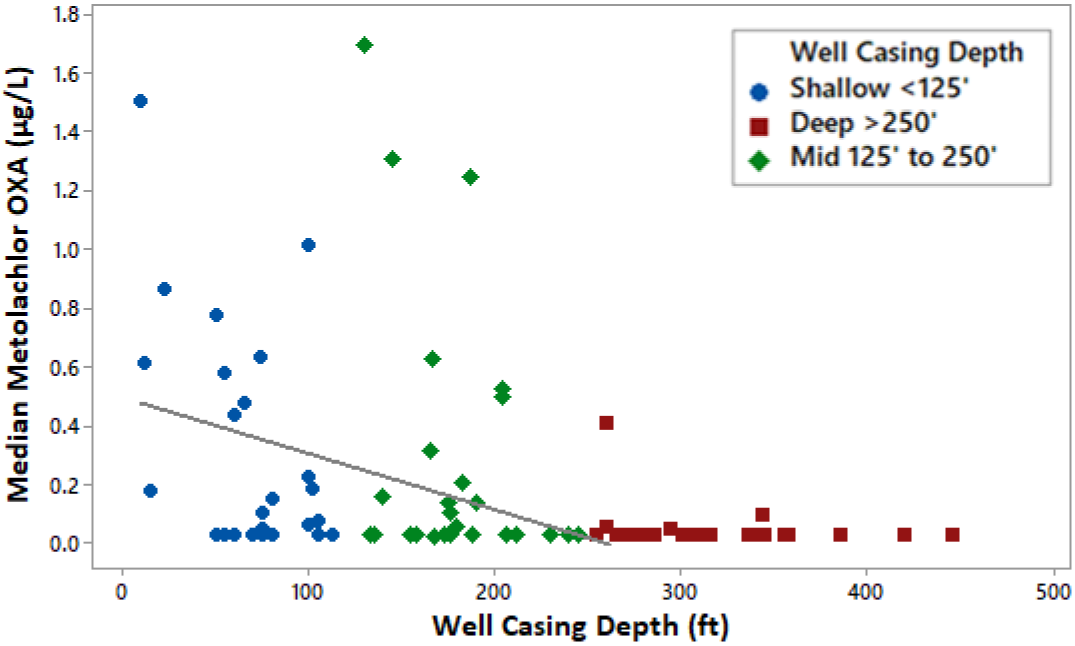


**Figure 37. Correlation Metolachlor OXA Concentration and Well Casing Depth—Kendall Line.**

**Table 17. Median Concentration of Metolachlor OXA (µg/L) and Well Casing Depth Ranges.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow < 125' | 26 | 0.31 | 0.39 | 0.02 | 0.02 | 0.12 | 0.58 | 1.50 |
| Mid 125' to 250' | 26 | 0.28 | 0.46 | 0.02 | 0.02 | 0.04 | 0.36 | 1.69 |
| Deep >250' | 25 | 0.04 | 0.08 | 0.02 | 0.02 | 0.02 | 0.02 | 0.41 |

## SUMMARY OF HERBICIDE DETECTIONS AND CASING DEPTH

Like the anthropogenic compounds nitrate and chloride, the detection of herbicide compounds is inversely correlated with depth, with the highest frequency of detection in the shallow and middle well casing category wells (which are presumed to have the most rapid recharge rates and the most direct connection with the land surface). Table 18 shows the median number of herbicide compounds identified per well and the average and median nitrate concentrations per well, for the three depth ranges.

Table 18. Number of Herbicide Compounds Per Well by Depth Category Compared to Nitrate Results (n=77).

| Casing Category | # of Wells | Median # of Unique Compounds | Avg Nitrate (mg/L) | Median Nitrate (mg/L) | 75th Percentile Nitrate (mg/L) | Maximum Nitrate (mg/L) |
|---|---|---|---|---|---|---|
| Shallow < 125’ | 26 | 12 | 7.29 | 5.7 | 11.9 | 24.9 |
| Mid-depth 125’ to 250’ | 26 | 9.5 | 7.22 | 2.5 | 11.6 | 26.1 |
| Deep > 250’ | 25 | 0 | 1.54 | < 0.2 | 2.6 | 8.3 |

### 4.2.3. Herbicides and Land Use

The statistical relationship between land use and the average concentration of herbicide breakdown products detected in wells across the landscape was examined. Analyzing the density and distribution of cropland provides a general indication of where fertilizers and pesticides would be applied. Agricultural chemicals applied to row crop agriculture is identified as a major source of nitrate and pesticide contamination of groundwater resources beneath agricultural lands.

All the herbicide breakdown products correlate with percent agriculture. Groundwater alachlor ESA and DCAC results, representing herbicide classes of acetamides and triazines respectively, are presented. These select herbicide breakdown products were statistically evaluated against the percentage of land in row crop agriculture proximate to the wells sampled. Both herbicide breakdown products correlated with well depth (Kendall, $p < 0.05$) and the percentage of row crop agriculture (Kendall, $p < 0.05$) per one-mile section (PLS-public land survey) row crop. See Table 19.

Table 19. Correlation Between the 15 Most Frequently detected Herbicides Compared to Percent of Land in Row Crops (1999-2019).

| Parameter | % Significance |
|---|---|
| Alachlor ESA | > 95% |
| Metolachlor ESA | > 95% |
| Deethylcyanazine acid (DCAC) | > 95% |
| Metolachlor OXA | > 95% |
| Alachlor ESA - 2nd amide | > 95% |
| Didealkylatrazine (DDA) | > 95% |
| Acetochlor/ Metolachlor ESA- 2nd amide | > 95% |
| Deethylatrazine (DEA) | > 95% |
| Acetochlor ESA | > 95% |
| Alachlor OXA | > 95% |
| Atrazine | > 95% |
| Cyanazine amide (CAM) | > 95% |
| Deisopropylhydroxyatrazine (DIHA) | > 95% |
| Cyanazine-acid (CAC) | > 95% |
| Deisopropylatrazine (DIA) | > 95% |

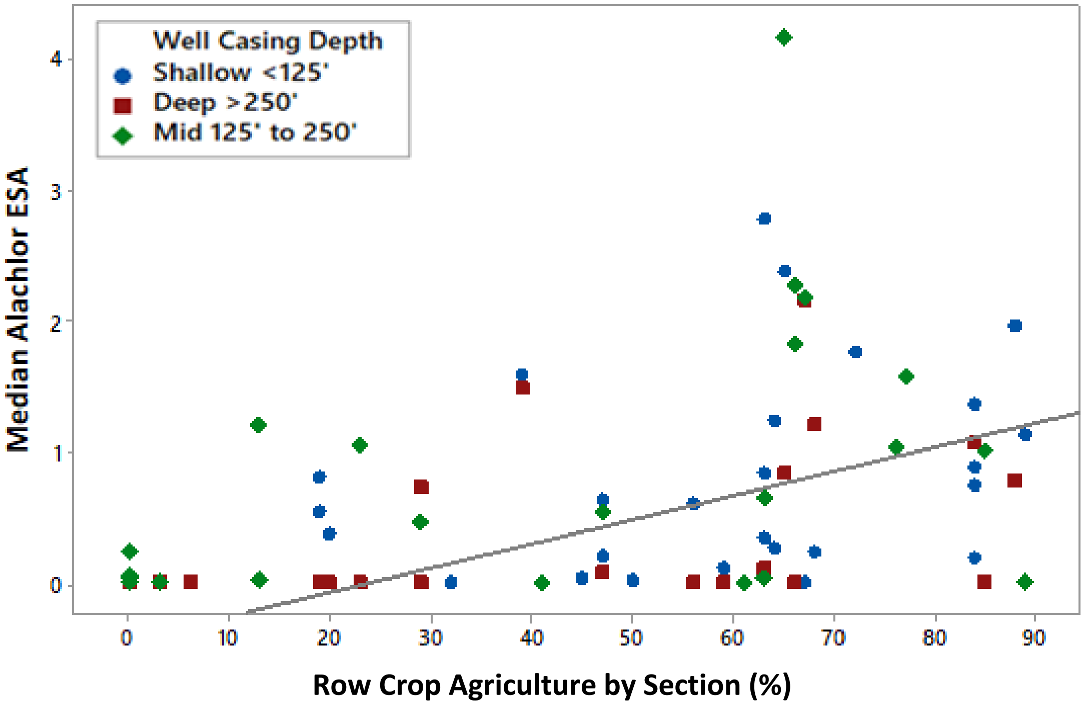


Figure 38. Correlation Alachlor ESA Concentration and Row Crop Agriculture (%)—Kendall Line.

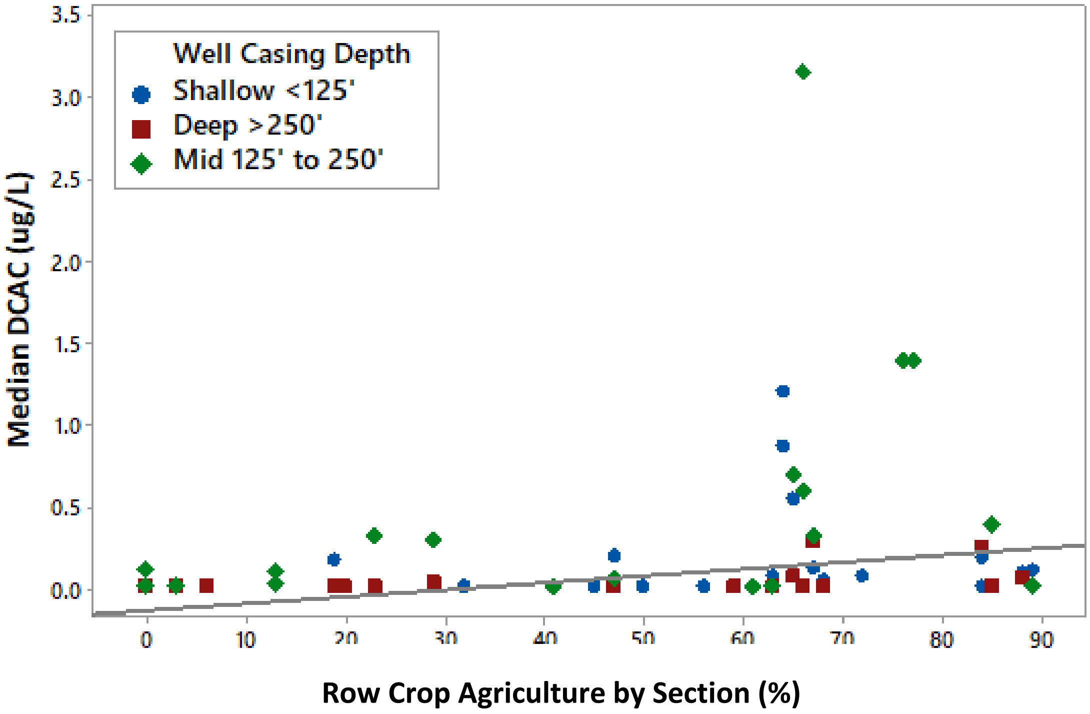


Figure 39. Correlation DCAC Concentration and Row Crop Agriculture—Kendall Line.

### 4.2.4. Co-occurrence of Herbicides and Nitrate

***Greater concentrations of nitrate are generally accompanied by an increase in the number of herbicide compounds, the frequency of occurrence and concentrations of herbicides detected.***

As stated previously, the number and concentration of herbicide compounds and nitrate in groundwater varies greatly based on land use and geologic sensitivity. The data also show that agricultural chemicals (nitrate and herbicide breakdown products) are also highly correlated with each other. The relationship between these variables is shown in Figures 40 and 41; Figure 40 depicts average number of pesticide detections with average nitrate concentration, while Figure 41 depicts pesticide detection frequency with average nitrate concentration.

Nitrate concentrations were positively correlated (Kendall, $p < 0.05$) with the number of herbicide breakdown products detected, indicating a common activity as the pollution source. Herbicide compounds were detected in 92 percent of the wells with nitrate levels above 1.0 mg/L. The number of pesticide compounds detected increases with increasing nitrate concentration range.

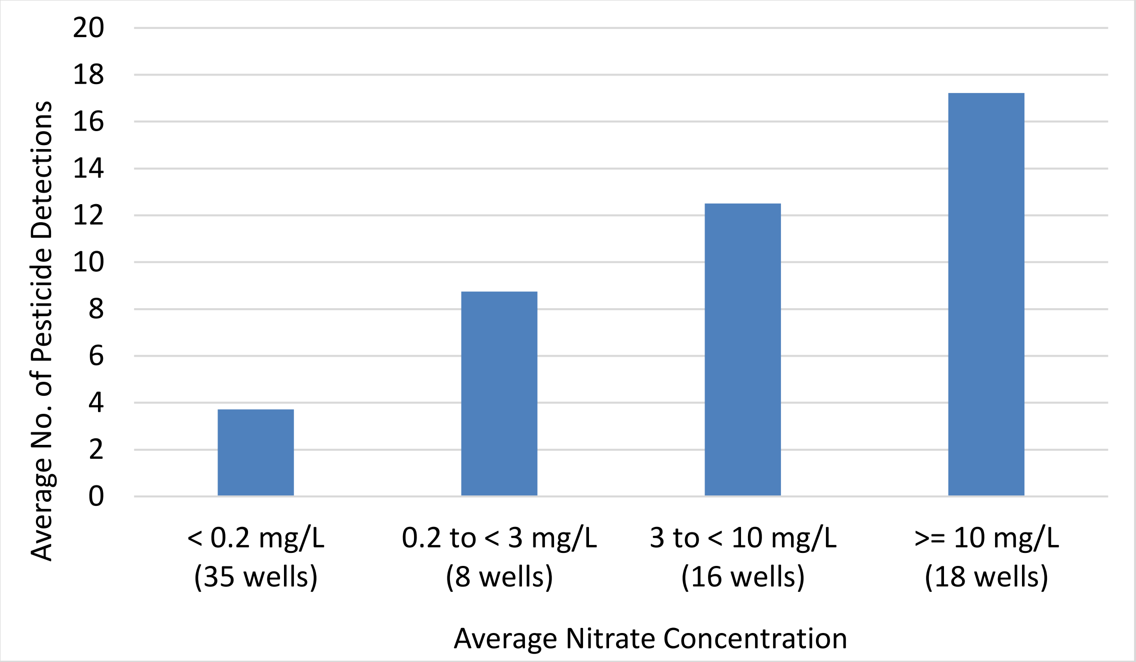


**Figure 40. Average Nitrate Concentration and the Average Number of Pesticide Compounds Detected per Well. 77 Wells Sampled 1999-2019**

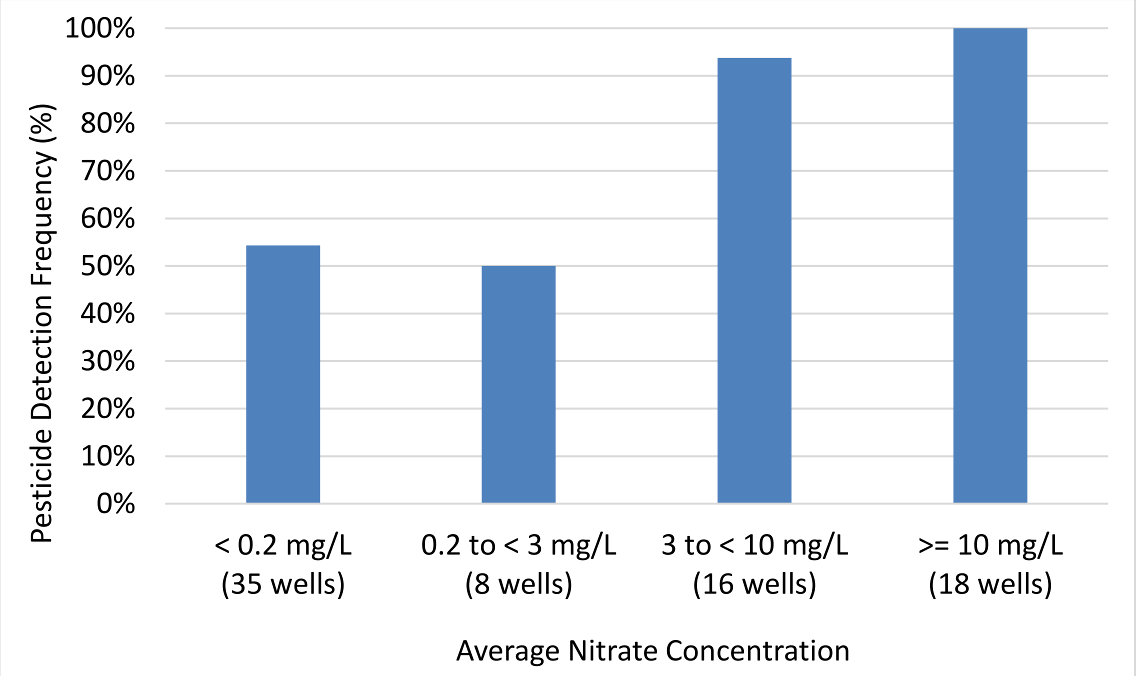


**Figure 41. Average Nitrate Concentration and the Pesticide Frequency of Detection- 77 Wells Sampled 1999-2019**

Table 20 summarizes median nitrate correlated with 12 individual herbicide breakdown products (Kendall, $p < 0.05$).

**Table 20. Correlation Between 12 Select Herbicides & Breakdown Products and Median Nitrate.**

| Parameter | % Significance for median level of herbicides vs. median levels of nitrate (Kendall) |
|---|---|
| Didealkylatrazine (DDA) | > 95% |
| Deethylatrazine (DEA) | > 95% |
| Deisopropylhydroxyatrazine (DIHA) | > 95% |
| Atrazine (Aatrex) | > 95% |
| Deisopropylatrazine (DIA) | > 95% |
| Cyanazine amide (CAM) | > 95% |
| Deethylcyanazine acid (DCAC) | > 95% |
| Cyanazine acid (CAC) | > 95% |
| Dimethenamid ESA * | >95% |
| Acetochlor ESA | > 95% |
| Metolachlor ESA | > 95% |
| Alachlor ESA | > 95% |

The presence of nitrate greater than 3.0 mg/L generally indicates contamination (Madison and Brunett, 1985) , and a more recent nationwide study found that concentrations over 1 mg/L nitrate indicate human activity (Dubrovsky et al. 2010). In the 34 Ambient Study wells (44 percent) with an average nitrate concentration greater than 3.0 mg/L:

- Six or more herbicide breakdown products were detected in 97 percent of the impacted wells;
- Ten or more herbicide parent or breakdown products were detected in 91 percent; and
- Fifteen or more herbicide parent or breakdown products were detected in 53 percent.

Twenty-four of 77 study wells (31% that exceeded the drinking water guideline for nitrate at least once during the study period (1999-2019), 13 of 24 (54%) also exceeded the drinking water guideline of 1.0 ug/L for total cyanazine at least once.

Figure 42 shows the statistical relationship between the concentration of nitrate and the number of unique herbicide compounds in a well (Kendall, $p < 0.05$). This analysis clearly shows a statistical relationship between nitrate and the detection and number of unique herbicide compounds, but its usefulness of using nitrate results alone in predicting pesticide concentrations has not been established.

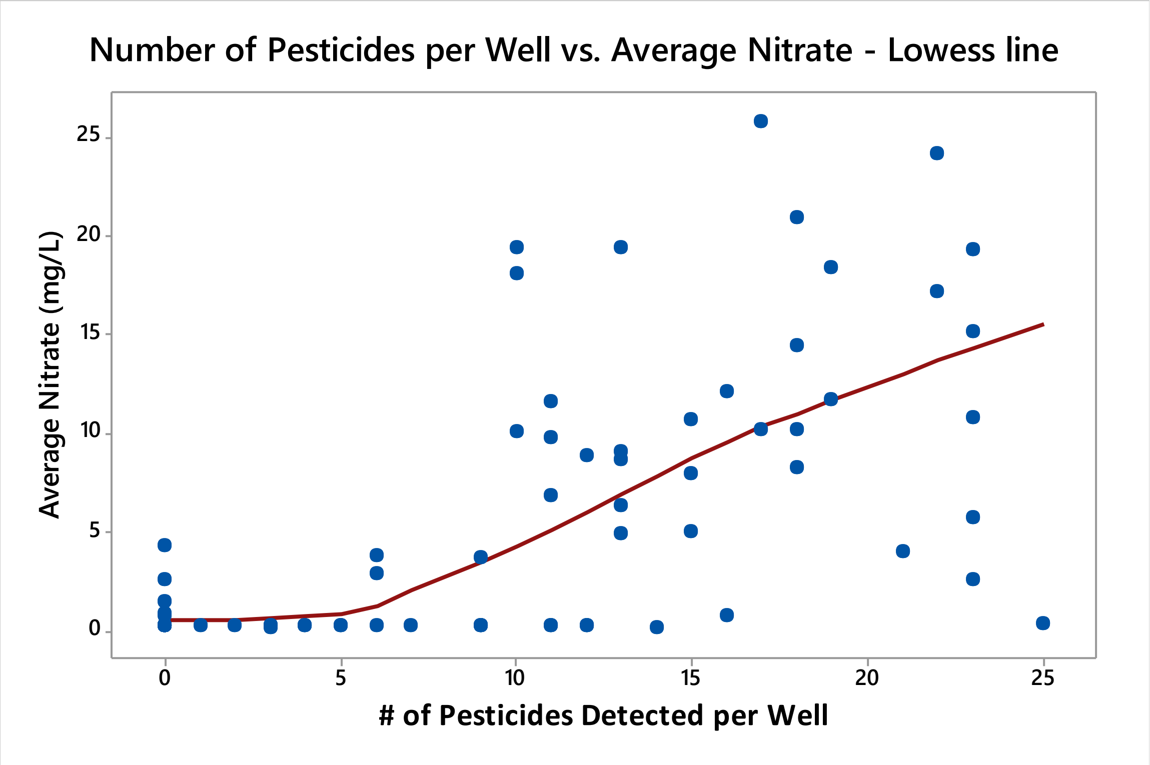
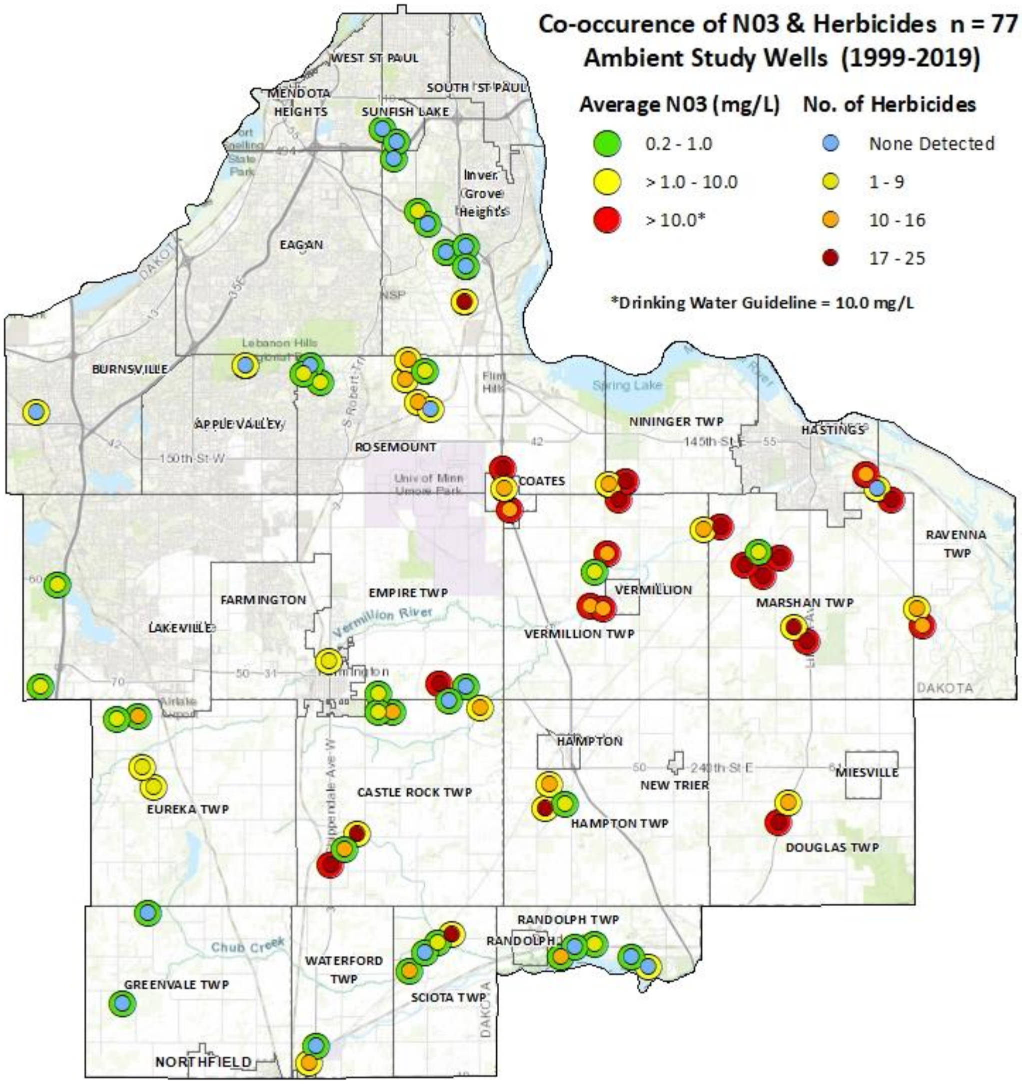


**Figure 42. The Correlation Between Average Nitrate Concentration and the Number of Pesticides Detected. Ambient Study Wells (1999-2019).**



Sources: ESRI; Dakota County Environmental Resources

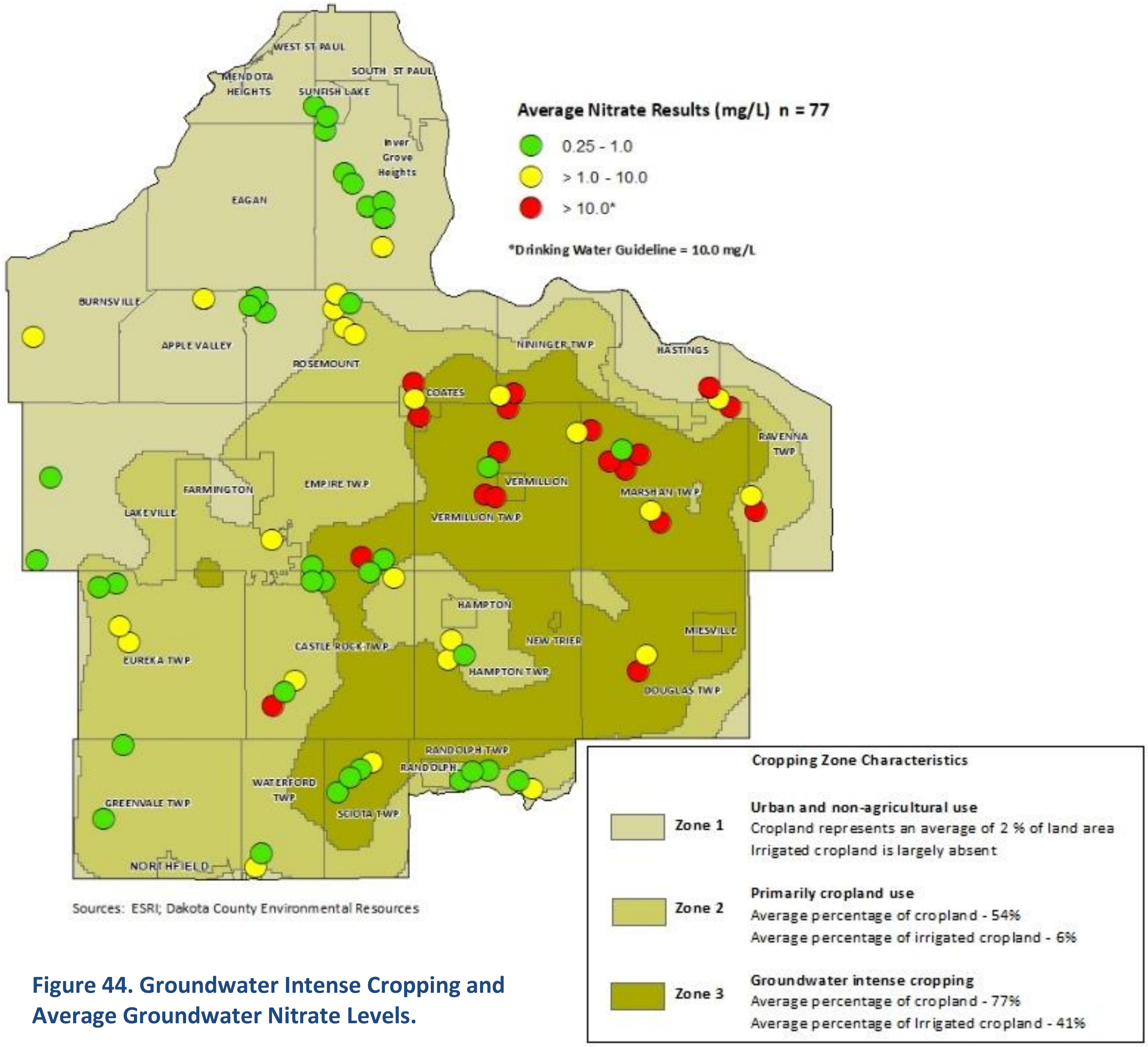
**Figure 43. Co-Occurrence of Nitrate and Number of Herbicide Compounds per Well.**

The spatial distribution of nitrate and unique herbicide compounds detected shows that the high concentrations of nitrate and the greater number of herbicides detected in a well are most common in the eastern portion of the County where groundwater intensive cropping is practiced.

### 4.2.5. Groundwater Intensive Cropping Model — Nitrate, Herbicides and Land Use: Model Development

In this section, the spatial distribution of cropland and irrigated cropland was used to calculate a relative measure of the groundwater intensity of cropping practices. To calculate a relative measure of groundwater intensive cropping across the county, the percentage of acreage in crop production and percentage of irrigated cropland for each quarter-section of land was interpreted from aerial photographs. An additive factor was assigned to the irrigated cropland acreage to account for the increased yield (productivity) and rate of nitrogen application typical of irrigated crop production (MDA 1999). Thus, irrigated cropland has a total weighting of two. This serves to represent and differentiate the expected increase in input associated with groundwater-intensive cropping but is not and should not be used for mass-balance estimates. The sum of cultivated and irrigated acreage values was then assigned to the centroid calculated for each quarter-section. This value represents the groundwater cropping intensity index. These values were smoothed using a mathematical process referred to as kernel density. The percentage of irrigated lands is added to represent the excess infiltration presumed to be associated with irrigation. Figure 44, the Groundwater Intense Cropping Map is not intended to estimate nitrate or herbicide concentrations for a specific well, instead, it is intended to convey the susceptibility of a geographic area to groundwater contamination from row crop agriculture, especially irrigated cropping. Three categories of row crop land use are defined as:

- Zone 1 Urban and non-agricultural: row crops average 2 percent of the land area; irrigation of row crops is mostly absent.
- Zone 2 Primarily crop land: row crops average 54 percent of the land area; on average, 6 percent of the land area is irrigated.
- Zone 3, Groundwater-intensive crop land: row crops average 77 percent or more of the land area; on average, 41 percent of the land area is irrigated.



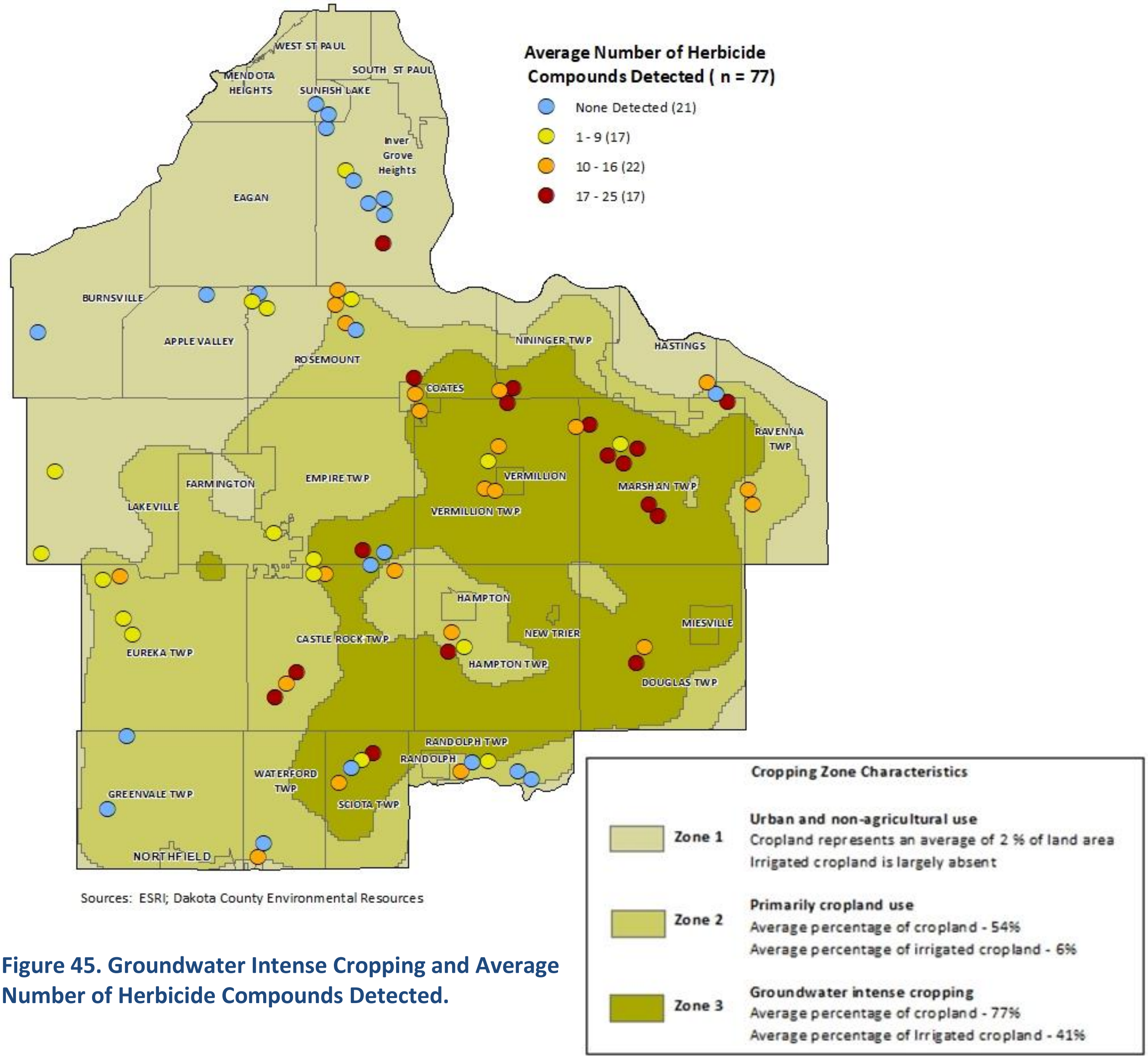
Sources: ESRI; Dakota County Environmental Resources

**Figure 44. Groundwater Intense Cropping and Average Groundwater Nitrate Levels.**

**Table 21. Descriptive Statistics of Average Nitrate (mg/L) by Cropping Zone.**

| Cropping Zone | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| 1 | 19 | 1.7 | 3.0 | 0.2 | 0.2 | 0.2 | 2.5 | 10.7 |
| 2 | 33 | 3.8 | 5.1 | 0.1 | 0.2 | 0.3 | 7.6 | 19.4 |
| 3 | 25 | 10.3 | 8.4 | 0.1 | 0.5 | 10.1 | 18.2 | 25.8 |

The next analysis consisted of evaluating the number of unique herbicide detections in wells by cropping zone.



Sources: ESRI; Dakota County Environmental Resources

**Figure 45. Groundwater Intense Cropping and Average Number of Herbicide Compounds Detected.**

**Table 22. Number of Herbicide Compounds Detected per Well, by Cropping Zone.**

| Cropping Zone | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| 1 | 19 | 4 | 7 | 0 | 0 | 0 | 6 | 23 |
| 2 | 33 | 8 | 7 | 0 | 0 | 9 | 13 | 25 |
| 3 | 25 | 14 | 7 | 0 | 10 | 16 | 19 | 23 |

Statistical analysis (Mann-Whitney) shows statistically significant differences at >90 percent for nitrate between zone 1 and zone 2. All other comparisons between zones were >95 percent for both nitrate and the number of herbicide compounds detected. This analysis allows us to infer a relationship between the concentration of nitrate, the number of herbicides detected in wells and the land area used for crops, especially groundwater intensive cropping zones.

**Table 23. Groundwater Intensive Cropping Zones: Nitrate & Herbicide Counts.**

| Cropping Zone Comparison | Zone 1 to Zone 2 | Zone 1 to Zone 3 | Zone 2 to Zone 3 |
|---|---|---|---|
| **Parameter** | **% Significance** | **% Significance** | **% Significance** |
| Nitrate | > 90% | > 95% | > 95% |
| Herbicide Compound Count | > 95% | > 95% | > 95% |

### 4.2.6. Herbicide Trends

The Ambient Study includes many detections of the breakdown products of two herbicides that are no longer in use, cyanazine and alachlor. Cyanazine, an herbicide introduced in the early 1970s for application to corn crops, was discontinued in 2002. The sum of the breakdown products indicates that total cyanazine in drinking water wells are still being detected in Dakota County groundwater at levels above the drinking water guideline (1.0 µg/L). Concentration for the cyanazine breakdown product, DCAC, is generally stable which suggests that the cyanazine breakdown products are persistent. The continued presence of DCAC in the wells with mostly stable trends is discussed below.

Alachlor, an herbicide used to control weeds in field corn and soybeans, has not been registered for use since 2016. Figure 46 (USGS: Estimated Annual Agricultural Pesticide Use) shows the dramatic decline in the use of alachlor beginning in the early 1990's. The breakdown product, alachlor ESA, is the most commonly detected herbicide compound in the study, but it is also the herbicide breakdown product with the largest number of wells with a downward trend (18). Alachlor use dropped considerably with the widespread use of glyphosate. Figure 47 shows the increased use of glyphosate beginning in the early 1990s. During this time other acetamide herbicides (metoloachlor-S, acetochlor) were introduced up until its registration ended in 2016.

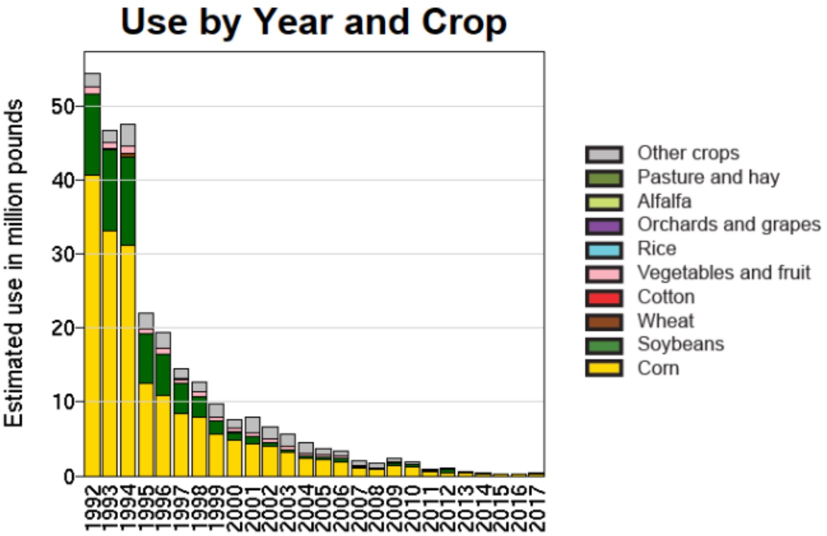


Figure 46. Alachlor Use, 1992-2017. (USGS)

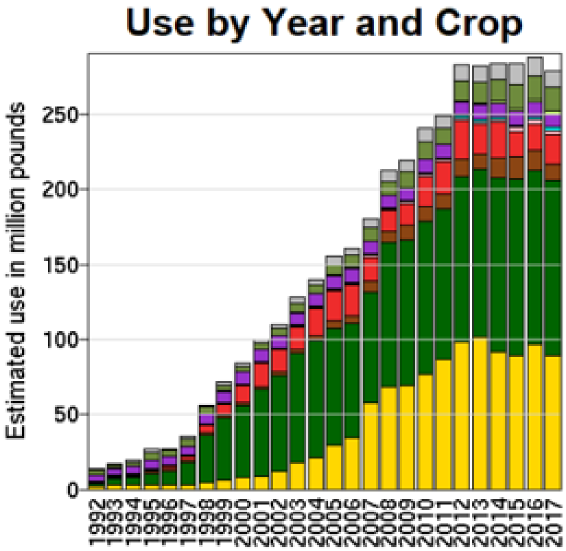


Figure 47. Glyphosate Use, 1992-2017. (USGS)

The introduction of glyphosate-resistant, "Roundup Ready," crops radically changed the use of other herbicides on Minnesota crops. Glyphosate-resistant soybeans were available for commercial planting in 1996 and corn was available for commercial planting in 1998. The rise in glyphosate use was accompanied by a sharp decline in the use of other herbicides on corn and soybeans. However, by the year 2000, the first glyphosate resistant weeds were detected in Delaware (VanGessel, 2001) and in 2006, the first glyphosate-resistant weed in Minnesota (giant ragweed) was identified (Weedscience.org). As a result, non-glyphosate herbicides are rebounding in use (MDA, 2019). The Ambient Study wells were never tested for glyphosate based on recommendations from the USGS (Personal communication Tim Cowdry-USGS) , confirmed by MDA (MDA, 2019), that it is detected in surface water, not groundwater.

The sharp reduction in alachlor use is anticipated to be reflected in a reduction of the concentration of alachlor and alachlor breakdown products found in drinking water wells in agricultural areas. The 2019 sampling is the first sampling event that includes alachlor and its breakdown products since alachlor was removed from the market in 2016. It is expected that the concentration in the shallower wells would be reduced first and the statistically calculated trends would be in a downward direction. To evaluate this hypothesis, the descriptive statistics for the same 38 wells that were analyzed for Alachlor ESA in both 2013 and 2019 are summarized in Table 24. Alachlor ESA was selected to be representative of changes in the application of alachlor because it is the most detected alachlor degradates in the study. This simple comparison shows that the median and average 2019 results were lower in all three depth categories.

**Table 24. Comparison of Alachlor ESA Results in µg/L by Well Casing Depth Category Before and After 2016.**

| 2013 Descriptive Statistics for Alachlor ESA | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
| Shallow <125' | 20 | 0.79 | 0.55 | 0.16 | 0.28 | 0.65 | 1.28 | 1.90 |
| Mid 125' to 250' | 12 | 0.93 | 1.02 | 0.02 | 0.07 | 0.84 | 1.48 | 3.50 |
| Deep >250' | 6 | 0.96 | 0.35 | 0.58 | 0.60 | 0.98 | 1.30 | 1.30 |

| 2019 Descriptive Statistics for Alachlor ESA | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
| Shallow <125' | 20 | 0.37 | 0.53 | 0.04 | 0.06 | 0.17 | 0.56 | 2.30 |
| Mid 125' to 250' | 12 | 0.44 | 0.57 | 0.04 | 0.05 | 0.19 | 0.68 | 2.00 |
| Deep >250' | 6 | 0.57 | 0.68 | 0.04 | 0.07 | 0.31 | 1.13 | 1.80 |

The trends tell a similar story. One of the greatest values of the Ambient Study dataset is the multiple years of data, which provide an opportunity to evaluate statistical trends over time. An explanation of statistical methods used to calculate trends is included in Appendix A.13. A minimum of five samples is needed to see a greater than 90 percent statistically significant trend; a well with fewer than five samples is not included in the trend summary. Statistical trend analysis was performed on the same 62 wells for alachlor ESA concentrations from 2001 to 2013 and 2001 to 2019 and are summarized in Table 25. More wells have a downward trend in alachlor ESA concentrations in 2019 (17 wells) compared to 2013 (12 wells), especially in the shallow well casing category, 9 wells in 2019 versus 5 in 2013. Six wells that were stable (no trend) in 2013 had a downward trend in 2019. One well that had an upward trend in 2013, had a stable trend in 2019. An increase in the number of wells with a downward trend is expected to continue given the discontinued use of alachlor.

**Table 25. Comparison of Alachlor ESA Results in µg/L Trends by Well Casing Depth Category before and after 2016.**

| Category | 2001-2013 Trend Direction | | | | | | 2001-2019 Trend Direction | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Down | Stable | Up | <MRL | SS | Total | Down | Stable | Up | <MRL | SS | Total |
| Shallow < 125' | 6 | 12 | 2 | 0 | 2 | 22 | 9 | 10 | 1 | 0 | 2 | 22 |
| Mid 125' to 250' | 3 | 9 | 0 | 5 | 3 | 20 | 6 | 6 | 0 | 5 | 3 | 20 |
| Deep >250' | 3 | 3 | 2 | 12 | 0 | 20 | 2 | 5 | 1 | 12 | 0 | 20 |
| Total | 12 | 24 | 4 | 17 | 5 | 62 | 17 | 21 | 2 | 17 | 5 | 62 |

Table 26 summarizes the statistical individual well trend patterns for the four most detected herbicide breakdown products based on 77 Ambient wells 1999 through 2019 for alachlor ESA. Three wells were sampled less than five times for metolachlor ESA, DCAC and metolachlor OXA so valid trend analysis could only be performed on 74 wells for those parameters. Note that there are different lab detection limits for different breakdown products over the duration of the Study; data was censored at the most common laboratory MRL. The majority of the

Individual wells are stable for an herbicide breakdown product or are consistently less than the MRL but some wells do show statistical up, down or a peaked pattern where the concentration of alachlor ESA was increasing during the course of the study and is not decreasing. The trend pattern for each well can be found on Appendix C Tables C.15, C.29, C.38 and C.39.

The trend patterns summarized in Table 26 indicated some patterns that are consistent with when specific herbicides were approved for use and with the depth of the well. Depth is directly related to water age. For example, there are 2 wells with an upward trend and 18 with a down trend and one peaked (up then down) alachlor ESA. Forty-one of the 49 wells with trends are in a well cluster, Appendix Table C.68. summarizes the wells with a trend grouped by well and well cluster. Seventeen of the 19 wells that are either down or peaked are in the shallow or mid well casing depth category. The two wells with an upward trend for alachlor ESA are in the mid and deep well casing category. This result is consistent with the age of water in these wells and with the dramatically decreasing use of alachlor after 1992.

Cyanazine use was discontinued in 2002, DCAC the most common cyanazine breakdown product, has six wells with an upward trend three of which are in the deep well casing category, 2 in the shallow and one in the mid depth, while the three wells with downward trend; two are in the mid and one in the shallow well casing category. In every well cluster where there are multiple wells with a trend for both alachlor ESA and DCAC, the alachlor ESA trend is downward and the DCAC trend is upward, even in the same well, Alias-56. This could be due to herbicide usage and/or persistence of triazine herbicides in the environment.

When metolachlor ESA and metolachlor OXA have a trend in either the same well or the same cluster, the trend is always in the same direction.

**Table 26. Trends for the Four Most Frequently Detected Herbicide Breakdown Products by Number of Wells**

| Trend Pattern | Alachlor ESA | Metolachlor ESA | DCAC | Metolachlor OXA |
|---|---|---|---|---|
| Up | 2 | 3 | 6 | 3 |
| Down | 18 | 5 | 3 | 8 |
| Peaked | 1 | 0 | 0 | 0 |
| < 5 sample events | 12 | 9 | 8 | 9 |
| Stable -No Trend | 23 | 29 | 19 | 21 |
| <MRL | 21 | 28 | 38 | 33 |
| Total # of wells | 77 | 74 | 74 | 74 |
| Censored (ug/L) | 0.02 | 0.02 | 0.025 | 0.02 |

Acetamides

Triazines

### 4.2.7. Cyanazine

***Breakdown products of the herbicide cyanazine are persistent and readily move with the infiltrating water.***

#### i. Cyanazine Sources, Health Concerns and Drinking Water Treatment

Cyanazine was first introduced to the market in 1971 for the control of broadleaf weeds and grasses in agricultural corps, primarily corn. During 1991-1997, use of five herbicides (acetochlor, alachlor, atrazine , cyanazine and metolachlor) on corn and soybeans accounted , on average, for about 70% of the annual herbicide use on field crops in the Mississippi River Basin (Clark, Goolsby 1999) For several decades after its registration, cyanazine was among the most widely used herbicide on corn in the United States. Data regarding the use of cyanazine in Minnesota was unavailable for review, however it is believed to have been widely applied to corn in Minnesota and in Dakota County. The manufacturers discontinued production of it in 1999; the USEPA canceled its product registration and prohibited its sale or use after September 2002, due to concerns about its risks to human health. As shown in Table 11, the MDH drinking water guideline for chronic exposure to cyanazine is 1.0 µg/L; the breakdown products do not have individual guidelines. The health risk studies conducted as part of the product's registration showed that cyanazine produced teratogenic (causing birth defects) effects (USEPA 1985, MDH 2018). Cyanazine is listed as a possible human carcinogen (cancer causing) (USEPA 2018).

Analytical methods (liquid chromatography/mass spectrometry) developed in the late 1990s, allowed for the investigation of cyanazine degradates in water resources. Over the course of the study, the USGS laboratory (2001-2017), and in 2019 Weck Laboratory , which analyzes water samples for pesticides using a direct aqueous injection LC- MS/MS method used to analyze the study samples, achieved lower reporting and detection levels on most parameters and increased the number of herbicides and herbicide breakdown products analyzed (Appendix A Table A.11). This allowed Dakota County to assess drinking water for the presence of low-levels of cyanazine and its breakdown products. During the Ambient Study, total cyanazine (the sum of cyanazine breakdown products as advised by MDH) is the only herbicide found to exceed the drinking water guideline in more than one well.

Cyanazine has a high potential to contaminate groundwater. In soil, the parent compound readily degrades to breakdown products, but the breakdown products of cyanazine are observed to be more persistent and stable than the parent compound and highly mobile in groundwater. The parent Cyanazine was not detected in any of the private wells in the study but was detected in a City of Hastings municipal well in 2006. Cyanazine shares breakdown products (DIA, DDA), with other triazines herbicides, especially atrazine, which somewhat complicates the evaluation of cyanazine detections, fate and transport.

No specific household water treatment systems are known to be independently certified to reduce or remove cyanazine breakdown products from drinking water. As mentioned in section 4.2.9, in 2019, MDA conducted a limited, observational field study of the effectiveness of home water treatment systems at removing pesticides. Household reverse osmosis (RO) systems performed well at reducing the total concentration of pesticides and the number of detectible pesticides. Specific to cyanazine breakdown products, the RO system results showed 100 percent removal of: cyanazine amide (n=9), cyanazine acid (n=12) and deethylcyanazine acid (n=21) (MDA 2019).

### ii. Cyanazine results

Breakdown products of cyanazine are found in 64 percent of the Ambient Study wells. In 22 percent of study wells, total cyanazine exceeded the drinking water guideline established at 1.0 µg/L. DCAC, the breakdown product of cyanazine is the third most frequently detected herbicide compounds in the Ambient Study (Figure 32).

When evaluating the frequency of detection of individual cyanazine breakdown products by depth, the proportion of the cyanazine degradates shows a distribution where the detection frequency generally decreases with increasing well depth (Table 27). Using well depth as an indicator of the age of the water, more recently infiltrated water is found in shallow wells with the age of water increasing with increasing well casing depth. This observation holds true for all the cyanazine breakdown products except for DCAM, which shows a higher frequency of detection in the mid-depth wells. With the discontinued use of cyanazine in 2002, we would expect these proportions of detections to decline in the shallow wells and increase in the deeper wells as the cyanazine moves deeper. The data indicates that this is the case. However, cyanazine breakdown products appear persistent.

**Table 24. Detection and Distribution of Cyanazine Breakdown Products by Well Casing Depth (1999-2019)**

| Analyte (Common Name) | Samples Analyzed | Number of Detections | Percent Detected (%) | Proportion Shallow (< 125’) | Proportion Mid-Depth (125’-250’) | Proportion Deep (>250’) | Maximum Detection (µg/L) |
|---|---|---|---|---|---|---|---|
| Cyanazine (Bladex) | 490 | 0 | 0.0% | 0.0% | 0.0% | 0.0% | ND |
| Deisopropylatrazine* (DIA) | 660 | 87 | 13.2% | 59.7% | 28.7% | 11.5% | 0.42 |
| Didealkylatrazine * (DDA) | 461 | 204 | 44.3% | 47.5% | 33.3% | 19.1% | 1.1 |
| Cyanazine amide (CAM) | 562 | 124 | 22.1% | 83.9% | 35.6% | 16.9% | 0.43 |
| Cyanazine acid (CAC) | 461 | 93 | 20.2% | 43.0% | 39.8% | 17.2% | 1.3 |
| Deethylcyanazine (DEC) | 461 | 0 | 0.0% | 0.0% | 0.0% | 0.0% | ND |
| Deethylcyanazine acid (DCAC) | 461 | 202 | 43.8% | 44.6% | 37.6% | 17.8% | 4.6 |
| Deethylcyanazine amide (DCAM) | 461 | 8 | 1.7% | 37.5% | 62.5% | 0.0% | 0.05 |

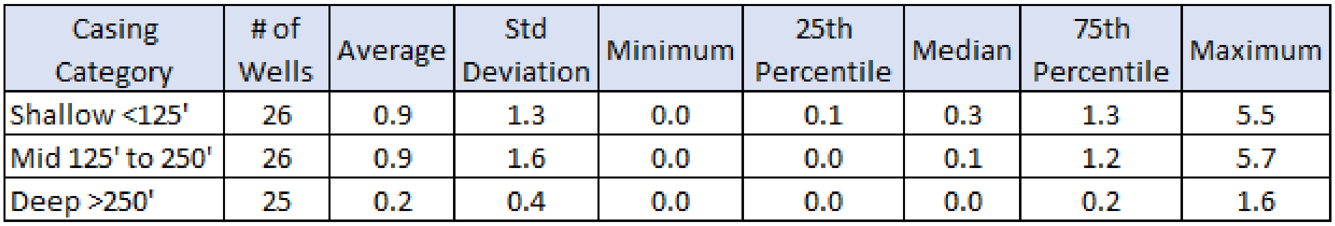
*Breakdown products are common to both atrazine and cyanazine

ND = not-detected over the MRL

Data represents analysis from several laboratories, employing different analytical methods and with differing reporting limits.

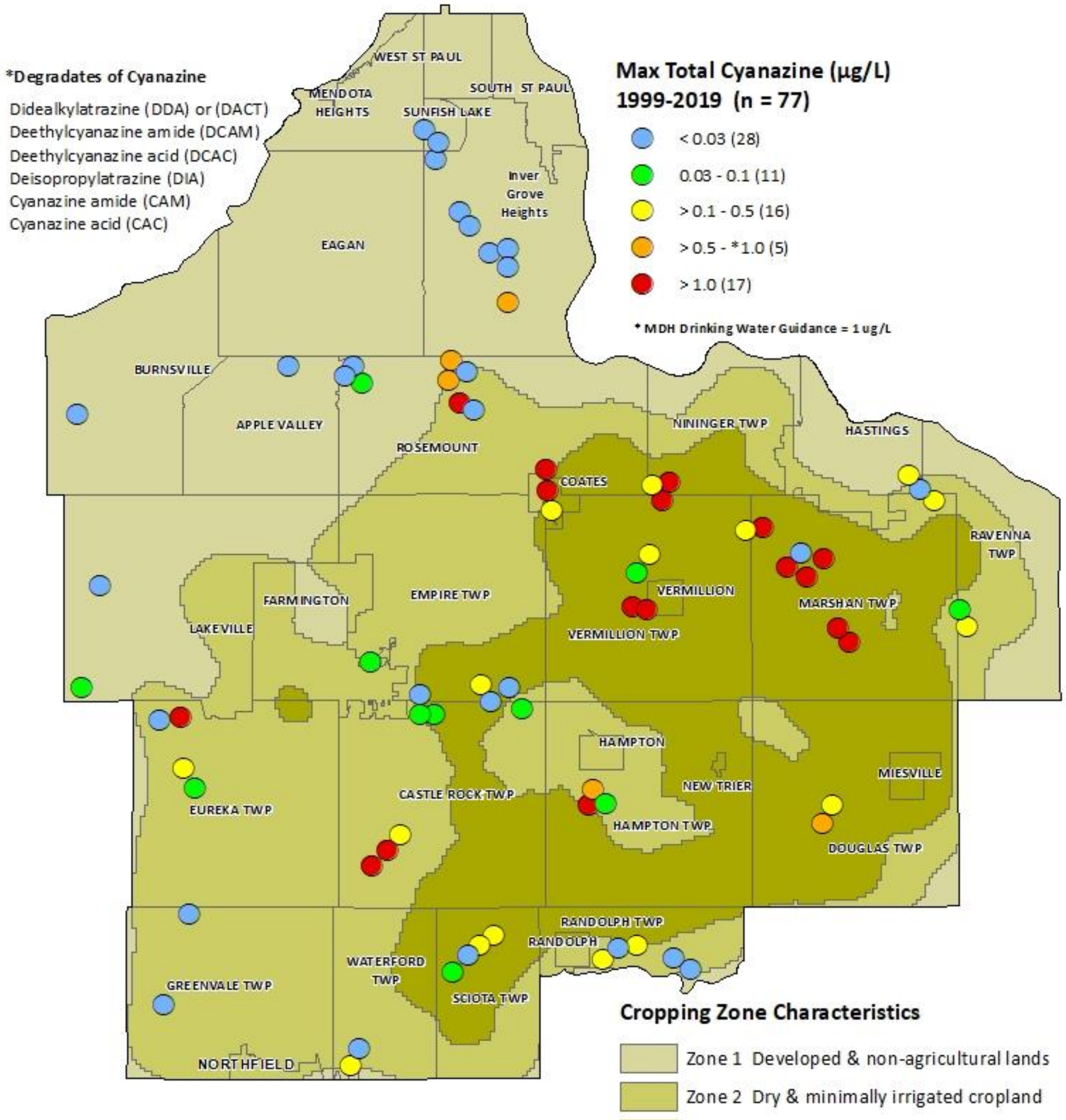
Total cyanazine is still detected at concentrations exceeding the drinking water guideline more than 18 years after cancellation of its registration. In general, the wells with the highest total cyanazine are in the shallow and middle well casing category characterized as having the most rapid recharge rates. Most of the study wells are in the shallow and middle well casing depth categories and are also in the Ucs and the Opdc. However, cyanazine breakdown products are found at levels exceeding the drinking water guideline in all three aquifers and casing categories.

**Table 25. Maximum Total Cyanazine in µg/L by Well Casing Depth Category (1999-2019).**



| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26 | 0.9 | 1.3 | 0.0 | 0.1 | 0.3 | 1.3 | 5.5 |
| Mid 125' to 250' | 26 | 0.9 | 1.6 | 0.0 | 0.0 | 0.1 | 1.2 | 5.7 |
| Deep >250' | 25 | 0.2 | 0.4 | 0.0 | 0.0 | 0.0 | 0.2 | 1.6 |

Figure 48 shows the wells with maximum values for the sum of cyanazine breakdown products occur in the most row crop intensive area.



Sources: Dakota County Environmental Resources

Figure 48. Maximum Concentration of Total Cyanazine Breakdown Products.

### iii. Cyanazine frequency 2005-2019.

The frequency of contaminant detection was also examined. In the Ambient Study well data set from 1999-2019, not all years had samples for all wells or the same wells in each sampling event. Analysis of the frequency with which the sum of cyanazine breakdown products was detected at different levels allows the overall results to be compared from year to year, even though the exact wells varied somewhat.

The sum of cyanazine breakdown products were divided into four categories:

- Over 1.0 µg/L, the drinking water guidance guideline
- Greater than 0.5 µg/L to 1.0 µg/L (0.5 µg/L is half of the drinking water guideline)

- Between 0.1 µg/L and less than 0.5 µg/L
- < 0.1 µg/L, the MRL

Figure 49 shows the concentration trend lines for total cyanazine results for the 62 wells, summarized in Table 29, that have had more than five samples since 2005; in years where over 50 wells were sampled. Only the results of cyanazine specific degradates (CAC, CAM, DEC, DCAC and DCAM) were used in the calculation to minimize skewing by the breakdown products DIA and DDA that are common to other triazine herbicides and cyanazine.

Trendlines were calculated using a trendline tool available in Microsoft Excel (Microsoft Excel for Office 365). Generally, the results suggest that the proportion of the wells in the lowest concentration category have been stable over the sampling period from 2005-2019, while the proportion of the wells in the highest concentration ranges (0.5 to < 1.0 µg/L and >= 1.0 µg/L) has increased. Wells in the concentration range 0.1 to < 0.5 µg/L. initially showed an upward trend, peaked in 2011, and have since declined. However, it must be noted that statistical trend analysis for this data set has not yet been completed and this analysis is preliminary thus conclusions regarding trends from visualizing the graph may not be accurate.

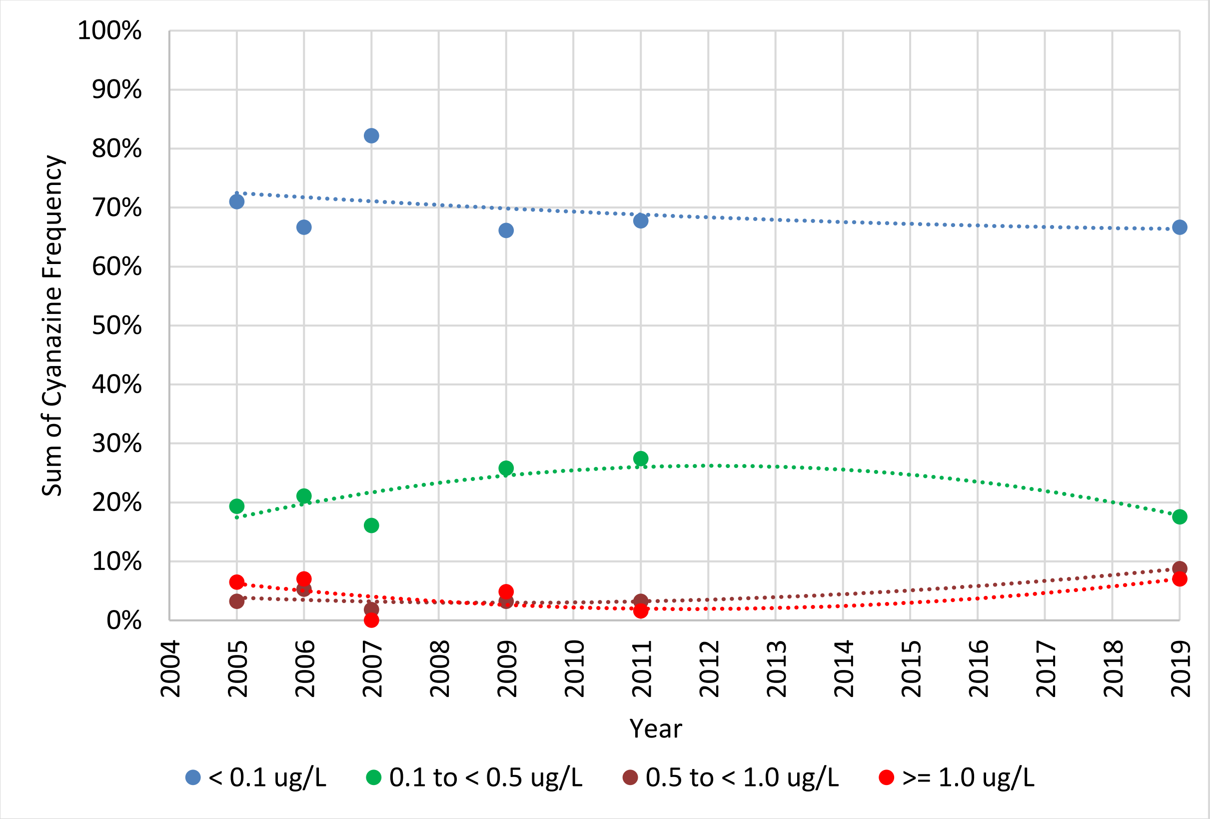


Figure 49. Total Cyanazine Concentration Frequency by Year - without DIA and DDA (2005-2019).

**Table 26. Total Cyanazine Frequency by Year and Concentration Category - without DIA and DDA (2005-2019).**

| Cyanazine Category | 2005 | 2006 | 2007 | 2009 | 2011 | 2019 |
|---|---|---|---|---|---|---|
| < 0.1 µg/L | 71% | 67% | 82% | 66% | 68% | 67% |
| 0.1 to <0.5 µg/L | 19% | 21% | 16% | 26% | 27% | 18% |
| 0.5 to <1.0 µg/L | 3% | 5% | 2% | 3% | 3% | 9% |
| >= 1.0 µg/L | 6% | 7% | 0% | 5% | 2% | 7% |

To further understand the movement and distribution of total cyanazine results, concentration trends were calculated by well casing depth to evaluate patterns (Figure 50). The data was parsed into well casing depth categories and evaluated by concentration ranges. Generally, the data shows mixed results. The proportion of wells in the lowest category (< 0.1 µg/L) has remained very consistent across the years and at various depth ranges. This may be a refection that 38 percent of the wells are in areas where agriculture in not a dominant land use and thus the use of agricultural chemicals is low. Surprisingly, the proportion of wells in the highest category are increasing in both the shallow and deepest depth ranges. With the discontinued use of cyanazine in 2002, one would expect that the cyanazine degradates would be infiltrating deeper, beyond the screened interval of the shallowest wells. Again, we must caution that the statistical analysis for these data have not been completed and these visual interpretations are preliminary.

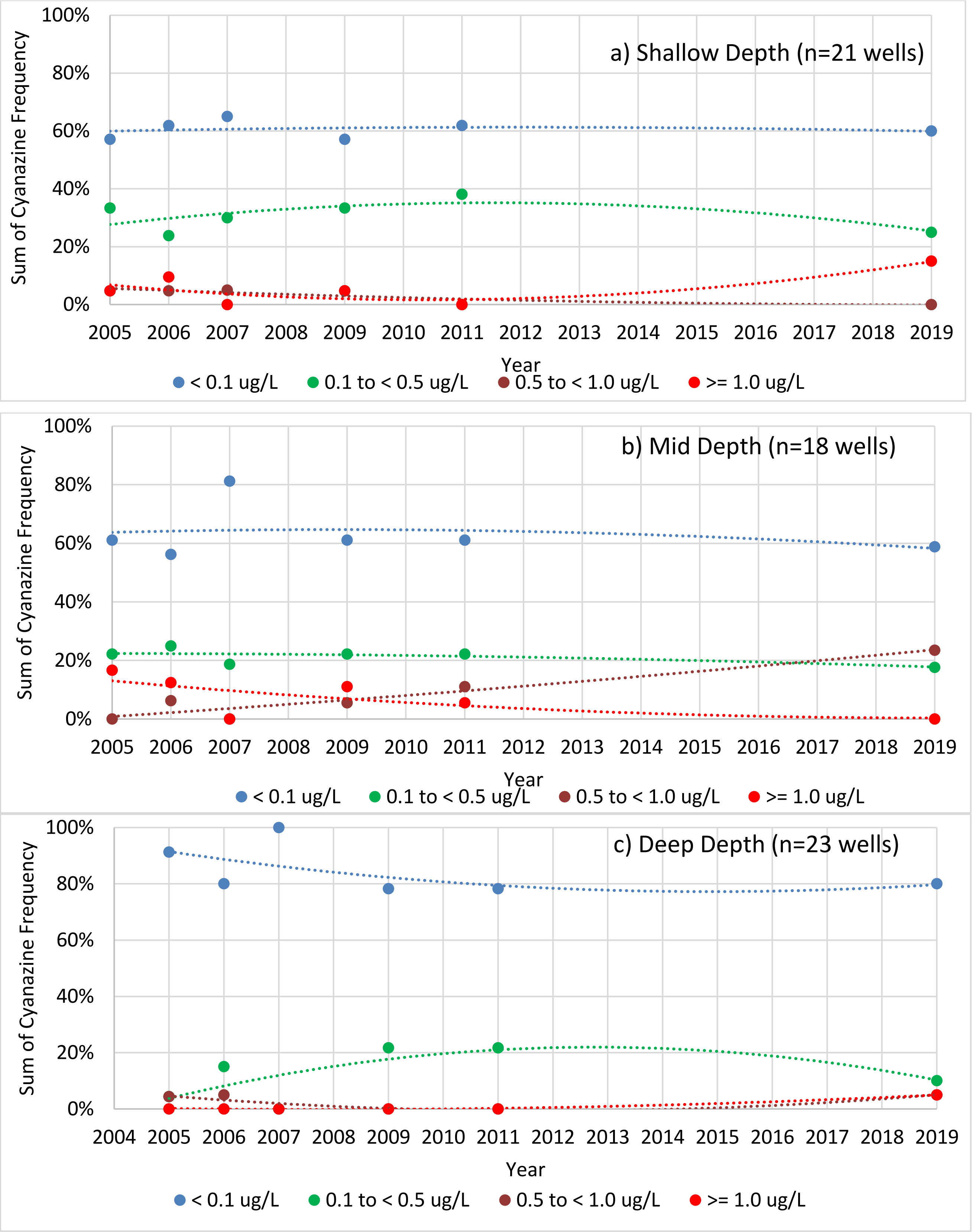


**Figure** 50. Total Cyanazine Frequency-Deep- by Year and Concentration Category and Depth Range - without DIA and DDA (2005-2019).

### iv. Expanded cyanazine sampling, 2017

To further evaluate the presence of cyanazine breakdown products in private wells in Dakota County, in 2017, an expanded group of wells was tested for cyanazine breakdown products. The County identified private wells within a half-mile radius of ten Ambient Study wells where cyanazine greater than 1 µg/L had previously been detected, then invited the well owners to have their wells tested. A total of 136 private well owners agreed to participate along with the ten Ambient Study well owners with known cyanazine exceedances, for a total of 146 wells. Untreated well water was collected and analyzed for nitrate, triazine herbicides (including cyanazine and atrazine), triazine breakdown products, chloride, manganese and arsenic. Herbicide samples were sent to the USGS OGRL laboratory for analysis.

Results from this sampling event were analyzed independent of the Ambient Study wells. Ninety-one wells (62 percent) had detections of cyanazine breakdown products, of which 12 (8 percent) exceeded 1 µg/L, whereas 50 Ambient Study wells (65 percent) had detections, of which 17 wells (22 percent) exceeded 1 µg/L at least once. Breakdown products of atrazine were detected in 83 wells (57 percent). Eighty-five wells (58 percent) had nitrate detected and 41 wells (28 percent) had nitrate above 10 mg/L, compared to nitrate detected in 64 wells (83 percent) of Ambient Study wells with 24 wells (31 percent) exceeding 10 mg/L at least once.

Herbicide breakdown products and nitrate concentrations inversely correlated with well casing depth (Kendall, $p < 0.05$) and positively correlated with the percentage of row crop agriculture (Kendall, $p < 0.05$) in a one-mile section (PLS-public land survey). Although wells different from the Ambient Study were sampled, the regression analysis and calculated infiltration rates for the herbicides, nitrate and chloride were consistent to those observed in the study wells.

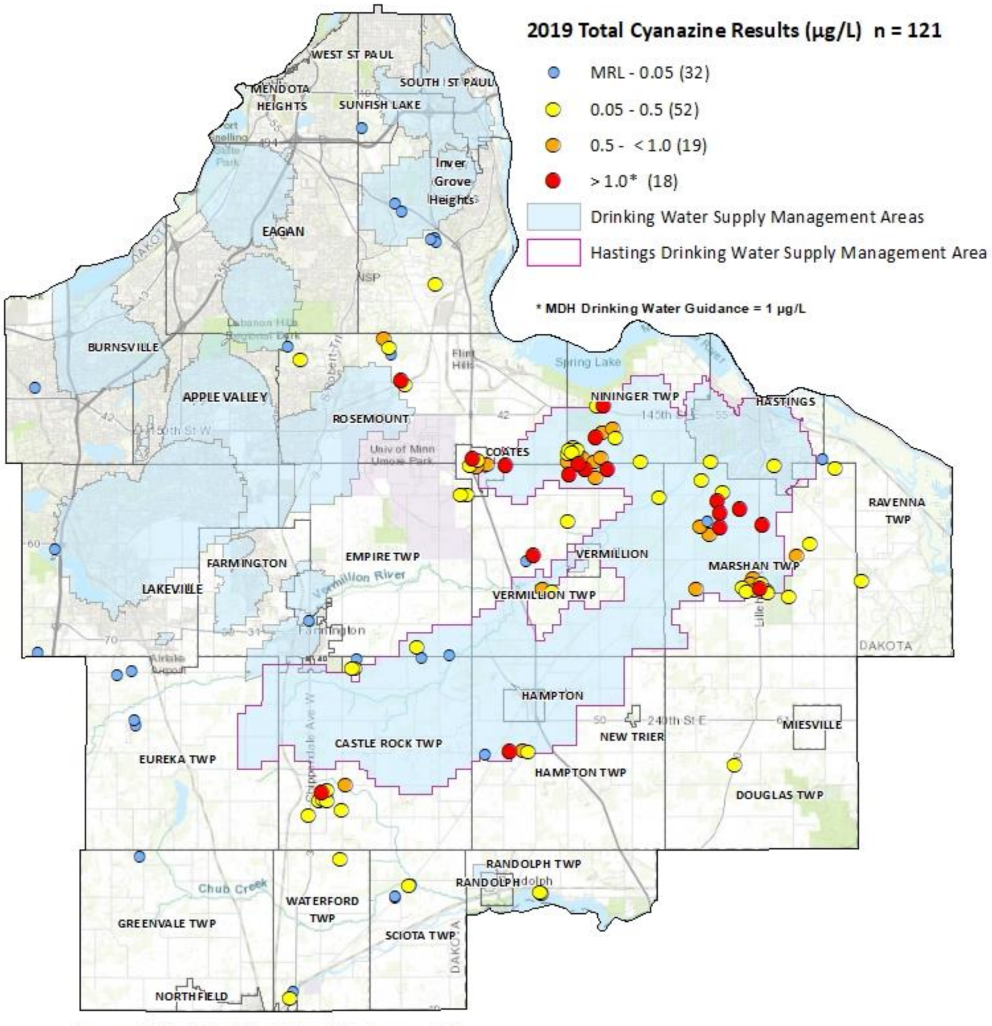
The MDH performed a cumulative health risk assessment on the nitrate, herbicide, manganese and arsenic results. Seventy of the 146 well owners were informed that their water quality indicates one or more of the following health concerns: blood (60 wells), nervous system and developmental affects (14 wells), non-organ specific – may affect the endocrine system (12 wells). One well had high levels of cyanazine degradates and manganese that indicate concern for nervous system, development, and the non-organ-specific effects, as well as shorter duration developmental, liver, kidney, and female reproductive effects. (MDH 12-21-18).

### v. Cyanazine sampling, 2019

In response to the detection of cyanazine breakdown products in the expanded 2017 sample event, the MDA conducted confirmation sampling of the previous USGS OGRL results from the study by offering a pesticide test to 150 well owners where previous total cyanazine was 0.5 µg/L or higher. Of these, MDA sampled 84 wells, which included 25 Ambient Study wells, for nitrate and pesticides. Forty-six split samples were analyzed by Weck Laboratories, Inc. and the MDA lab. Split samples were also sent to the USGS OGRL but were unable to be analyzed due to lab equipment failure. MDA previously utilized the Weck Lab for pesticides analysis and requested that both Weck and the MDA lab add cyanazine degradates to their analytical list. Dakota County sampled the remaining 37 Ambient Study wells using Weck Lab for the analysis of the same list of pesticides. See Appendix A Table A.11 for the list of pesticides and analytical method information. The two labs use different methods and MDH found that the Weck lab results were consistently higher than the MDA lab for DCAC and DDA. Weck made improvements to their method and three wells were resampled and split samples were analyzed at both the MDA and Weck labs.  The results were lower, two of the three analyzed by Weck exceeded the cyanazine guideline and one of the three analyzed by MDA exceeded. Figure 51 depicts the 2019 sampling for cyanazine.

The results of all 121 wells are summarized:

- 15 percent (18 wells) exceeded the drinking water guideline of 1.0 µg/L for cyanazine. A significant number of wells 14 of 18 wells (78%) exceeding the drinking water guideline are within the Hastings Drinking Water Supply Management Area (Figure 51).
- 31 percent (37 wells) exceeded the guidance value of 10.0 mg/L for nitrate.
- 32 percent (12 wells) exceeding the guideline for nitrate (10 mg/L) also exceeded the cyanazine guideline (1.0 µg/L)



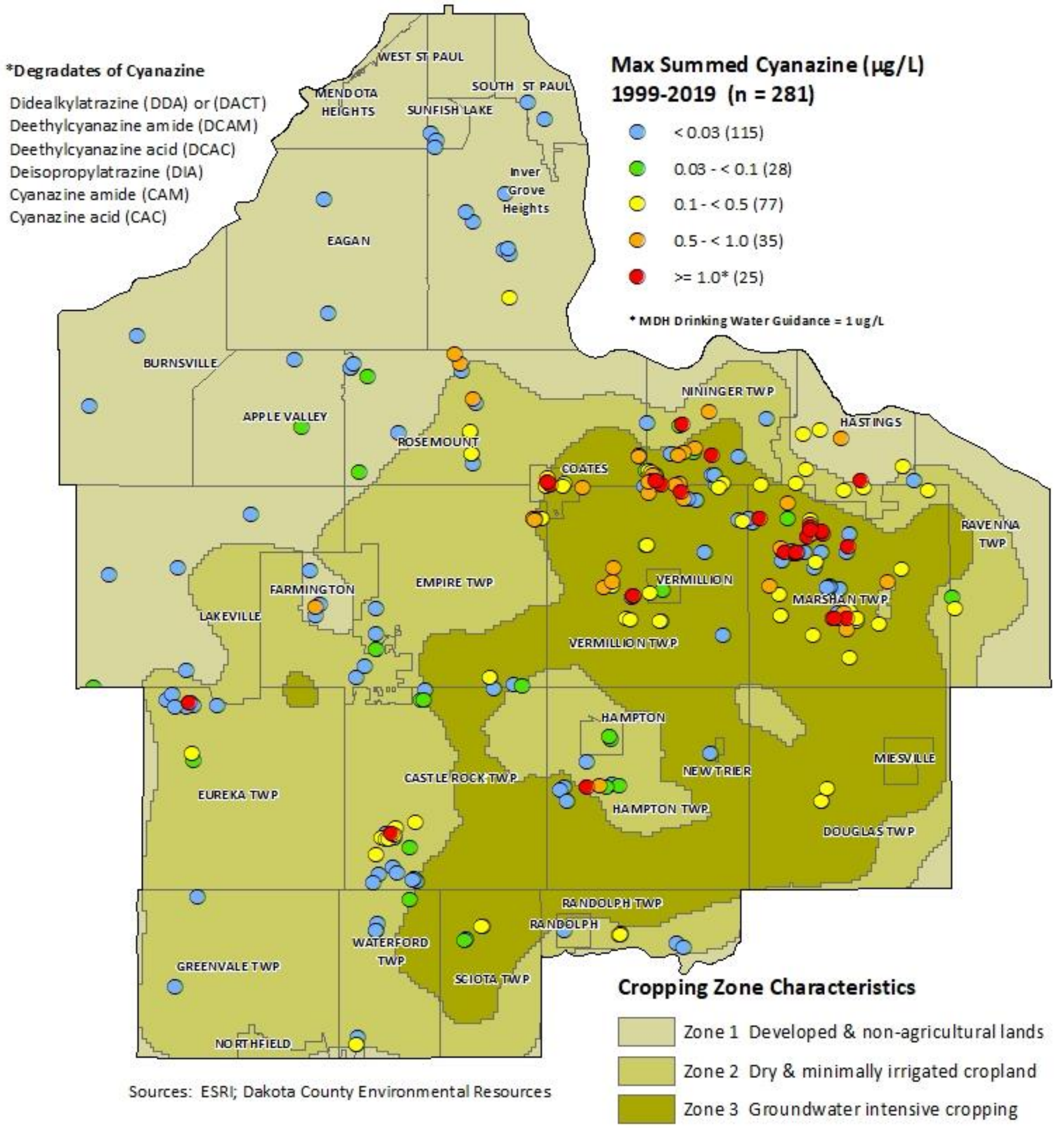
Sources: ESRI; MDA ; Dakota County Environmental Resources

Figure 51. 2019 Cyanazine Results.

In 2019, MDA sampling of surface water, groundwater and private wells outside of Dakota County included the cyanazine degradates (MDA 2019). The MDA ambient groundwater program sampled 166 springs, monitoring and private wells; cyanazine degradates were detected in three springs and three private wells in SE MN and a shallow well in central MN. Three of the sample points were in Dakota County and had no cyanazine over the MRL. The MDA surface monitoring program detected cyanazine breakdown product, DCAC in 15 percent of the 373 samples.

### vi. Maximum total cyanazine 1999–2019

Figure 52 includes all the cyanazine results for wells sampled throughout the County between 1999–2019. The locations of the results were spread and distributed to lessen overlap of results. The map shows that while many of the elevated results are concentrated in the eastern portion of the County, elevated levels are also found in areas where row crop agriculture is not the dominant land use, although at lower occurrence.



Sources: ESRI; Dakota County Environmental Resources

Figure 52. All Cyanazine Results (1999-2019).

### 4.2.8 Municipal well test results – pesticides and nitrate

In May 2005, as part of the Ambient Study sampling event, five City of Hastings municipal wells were sampled and tested for the same general chemistry parameters and herbicides as the private wells. Hastings had a new well, well number 8, go online until late 2006 and was not sampled by the County. Cyanazine and other herbicides were detected in all five wells, total cyanazine exceeded the existing MDH drinking water guideline (HBV) at that time of, 0.4 µg/L, in one well. In light of the results, the Hastings wells were tested quarterly by Dakota County for nitrate and pesticides the next four quarters; the maximum detects are reported in Appendix B and C for years 2005 and 2006. In December 2005, samples were collected from 28 municipal wells (includes the five Hastings wells) and analyzed for nitrate and nitrite by MVTL and analyzed by USGS OGRL for the same list of herbicides used for the private study wells, see Appendix A Table A.4 for list of analytes and method information. The parent cyanazine has only ever been detected one time in all the sampling by Dakota County, as of the date of this report, it was detected in a Hastings municipal well in 2006. The MDA conducts investigation of agricultural incidence sites that have found the detections of the parent cyanazine.

In 2019, the County requested that the State test the municipal wells for pesticides, to include breakdown products of cyanazine. A total of 13 wells were tested for 135 pesticides by Weck Lab, the results are in Appendix C. The construction details of the municipal wells are summarized in Appendix B Table B.1. and all municipal wells were assigned an alias name beginning with "Muni." MDH plans to test all nine of the City of Rosemount municipal wells in 2020.

Summary of municipal well detections by Total Herbicide parent and breakdown products (see Appendix C Tables C.1, C.10, C.27, C.36, C.44, C.51, and C.66 for insecticide – Imidacloprid):

<u>2019 Results</u>

- Herbicides were detected in 62 percent of wells (8 of 13 wells), none of the wells exceeded drinking water guidelines.
- All 8 wells with herbicides detected have total cyanazine detected; 38 percent (5 wells) exceed 0.5 µg/L, half the drinking water guideline.
- Forty-six percent (6 wells) have total cyanazine, atrazine and metolachlor detected.
- Both dimethenamid and acetochlor were introduced in 1994 and are detected in three of the same wells and acetochlor is detected in one additional. This suggests that activities on the surface may be impacting the water quality of these wells in as few as 25 years.
- The noenicitinoid, imidacloprid, was detected in Hastings Muni-26 below the guideline. This is the only well where imidacloprid was detected, it was not detected in any of the study private well or in other municipal wells. The registration of imidacloprid was cancelled effective May 2020 by the USEPA.

### 2019 Results Compared to 2005 Results

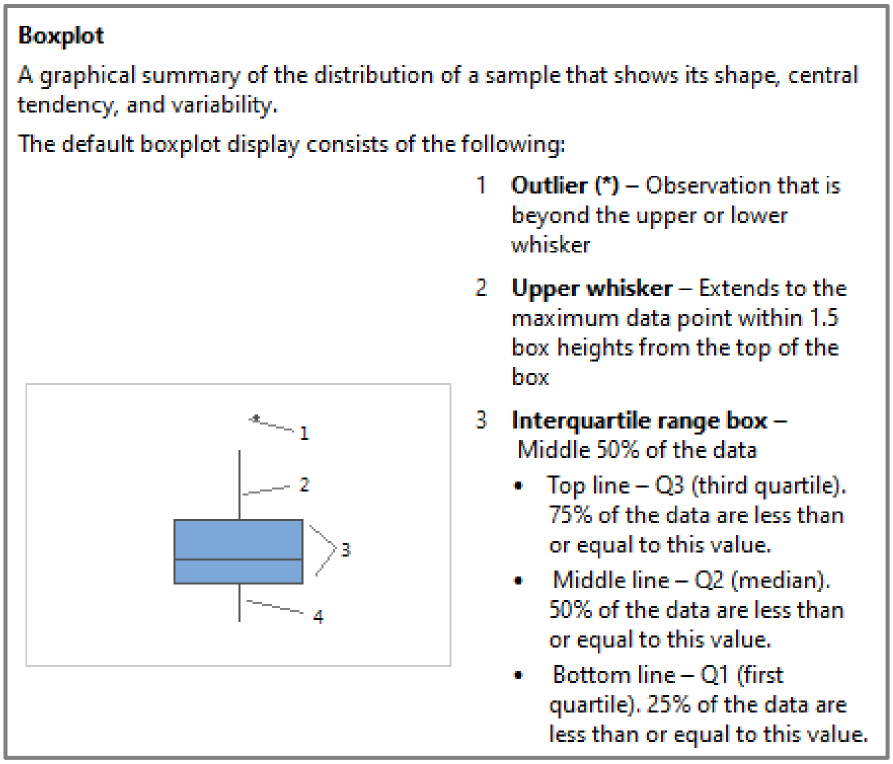
- Ten of the same wells were tested in both 2005 and 2019; four wells that had no herbicides detected above the MRL in both years.
- All total herbicide detects are higher in 2019 than 2005, except for Farmington well Muni-20, where both total atrazine and total alachlor are lower, less that the MRL in 2019.
- All wells with cyanazine detections, also had alachlor detections.
- Total atrazine is higher in 5 of the 7 wells, in 2019.
- Total alachlor is lower in 4 of the five wells in 2019. Alachlor was phased out between 1992 and 2016.
- Acetochlor is higher in all 4 wells in 2019, where detected in 2005.
- Metolachlor is higher in 2019 in all 6 wells where previously detected in 2005.

Since there are more detections of cyanazine and it is the herbicide detected that is closest to exceeding the drinking water guideline, statistical analysis was performed. There is no significant correlation between the 2005 (Kendall, p=0.12) and 2019 (Kendall, 1.00) total cyanazine results compared to well casing depth. The deepest well with total cyanazine detected in 2005 was in Apple Valley well, Muni-14, with a casing depth of 420 feet and a total depth of 516 feet. This well was not tested in 2019. In 2019, the deepest well with total cyanazine also had the highest total cyanazine of 0.86 µg/L was Farmington well, Muni-20, that has a well casing depth of 417 feet and a total depth of 512 feet. The 2005 and 2019 total cyanazine results by well casing depth category are summarized in Table 30. The average well casing depth in the 2005 sampling was 330 feet and the average in 2019 was 298 feet. The average well casing depth of the private wells in the study excluding the wells in the shallow well category was 186 feet. The municipal wells are, on average, much deeper than private wells.

**Table 27. Descriptive Statistics of 2005 and 2019 Total Cyanazine Results (mg/L) by Well Casing Depth Category (ft).**

| Year | Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|---|
| 2005 | Mid 125' to 250' | 7 | 0.17 | 0.18 | 0.03 | 0.03 | 0.05 | 0.35 | 0.46 |
| 2019 | Mid 125' to 250' | 4 | 0.45 | 0.29 | 0.03 | 0.15 | 0.53 | 0.66 | 0.70 |
| 2005 | Deep >250' | 21 | 0.10 | 0.15 | 0.03 | 0.03 | 0.03 | 0.10 | 0.59 |
| 2019 | Deep >250' | 9 | 0.23 | 0.31 | 0.02 | 0.03 | 0.03 | 0.48 | 0.86 |

Total cyanazine compared to total atrazine are positively statistically significant in both 2005 (Kendall, p <0.05) and 2019 (Kendall, p <0.05). In Figure 53, the 13 wells that were tested in both 2005 and 2019 are compared by well casing depth.



**Boxplot**

A graphical summary of the distribution of a sample that shows its shape, central tendency, and variability.

The default boxplot display consists of the following:

1 **Outlier (*)** – Observation that is beyond the upper or lower whisker

2 **Upper whisker** – Extends to the maximum data point within 1.5 box heights from the top of the box

3 **Interquartile range box** – Middle 50% of the data

- Top line – Q3 (third quartile). 75% of the data are less than or equal to this value.
- Middle line – Q2 (median). 50% of the data are less than or equal to this value.
- Bottom line – Q1 (first quartile). 25% of the data are less than or equal to this value.

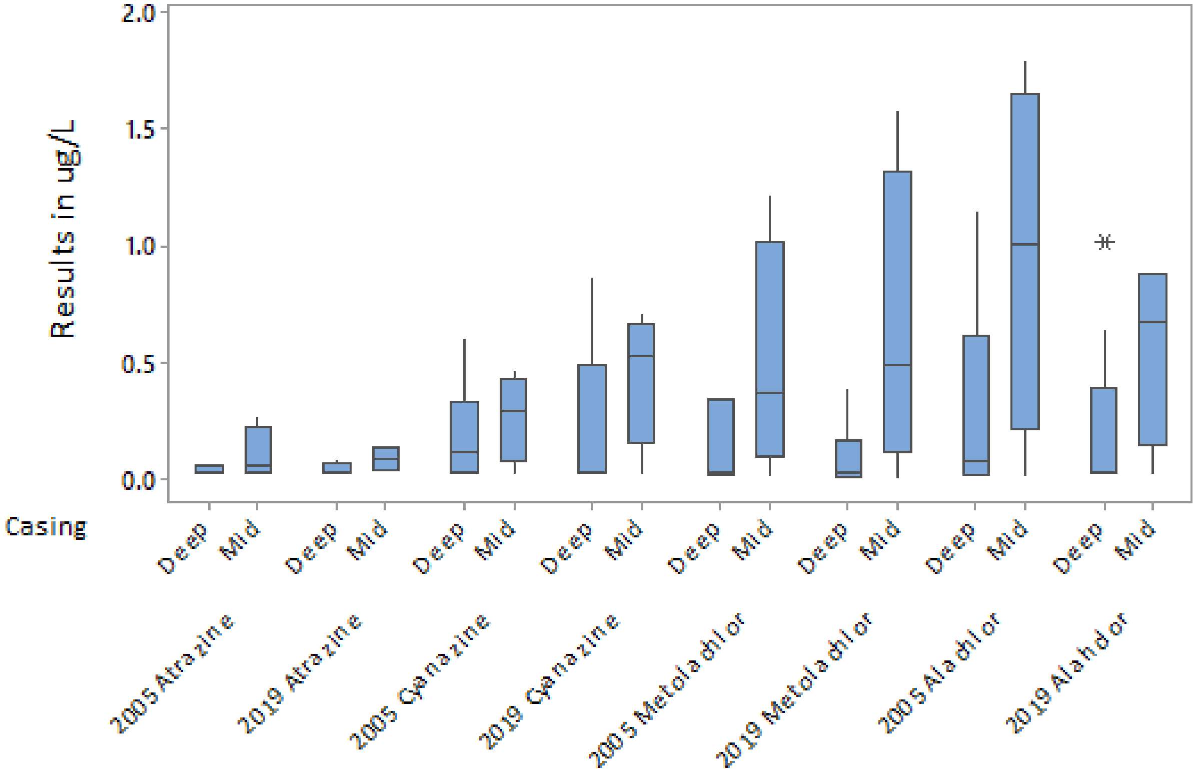


**Figure 53. Boxplot comparing total herbicides (sum of parent plus breakdown products) in 2005 and 2019 municipal well sampling by well casing category, n =13.**

Municipal wells have high capacity pumps and are operated for a long time, i.e. 8 hours. This can drawdown the aquifer water level and if contaminants are present at a shallower depth, then they can be drawn down to the depth of the well casing and pumped up the well. This is dependent on other factors such as rate of pumping and the permeability and porosity of the geologic material.

Figure 54 shows that both Rosemount and Hastings have nitrate over 5 mg/L in one or more wells. The MDA assigned the Hastings DWSMA a Mitigation Level 2 (high priority) and the Rosemount DWSMA Mitigation Level 1. Both cities are to adopt Best Management Practices to address the elevated nitrate.

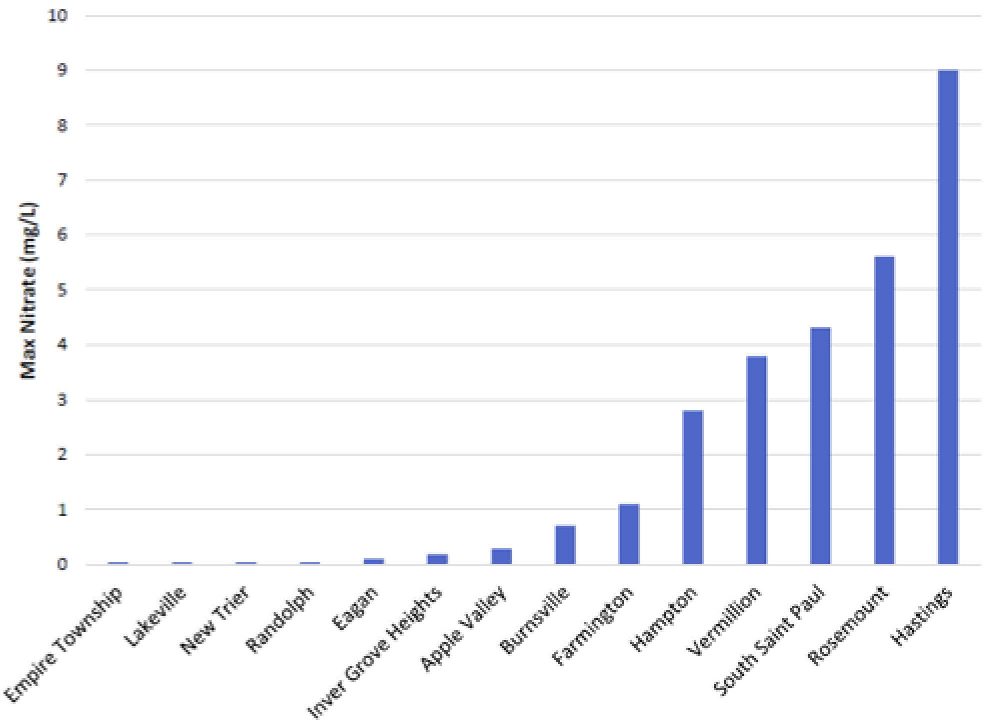


**Figure 54: Maximum Reported Nitrate Detection for Public Water Suppliers from 1998-2017. (Source: Dakota County Groundwater Plan, 8/4/2020)**

The average (mean) and maximum nitrate (NO3) from 1998 to 2015 are plotted in Figure 55. The nitrate maximum levels are increasing for both DWSMAs and Hasting is approaching 10 mg/L. The City of Hastings has a treatment plant that treats two of the city wells to reduce nitrate, this treatment process does not reduce pesticides.

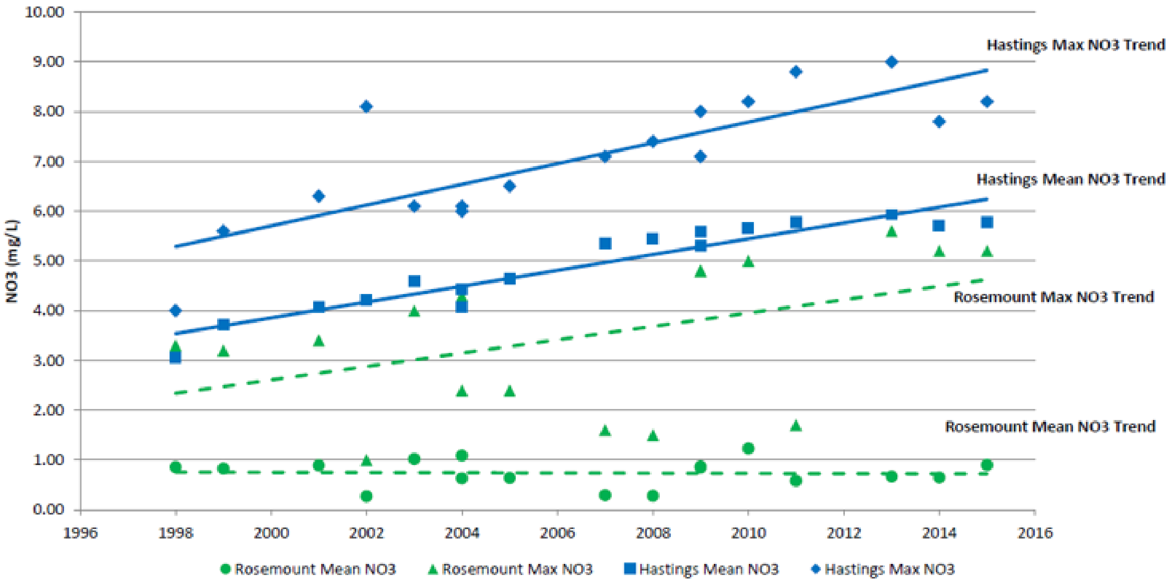


**Figure 55: Hastings and Rosemount Nitrate Levels, 1998-2015.**
**(Source: Dakota County Groundwater Plan, 8/4/2020)**

Nitrate results for the municipal well are summarized in Appendix Table B.17. The 2014 and 2019 nitrate results were provided by the MDH and the City of Hastings. The 2019 nitrate results are significantly correlated at 95% or higher (Kendall, $p < 0.05$) with total cyanazine, total atrazine, total alachlor, total dimethenamid and total metolachlor.

### 4.2.9. Drinking Water Treatment of Pesticides

In 2019, MDA conducted an observational field study of the effectiveness of home water treatment systems ability to remove pesticides summarized in Table 31 (MDA 2019). Household reverse osmosis systems (RO) performed well at reducing the total concentration of pesticides, the number of detectible pesticides, and nitrate (often found in combination with pesticides).

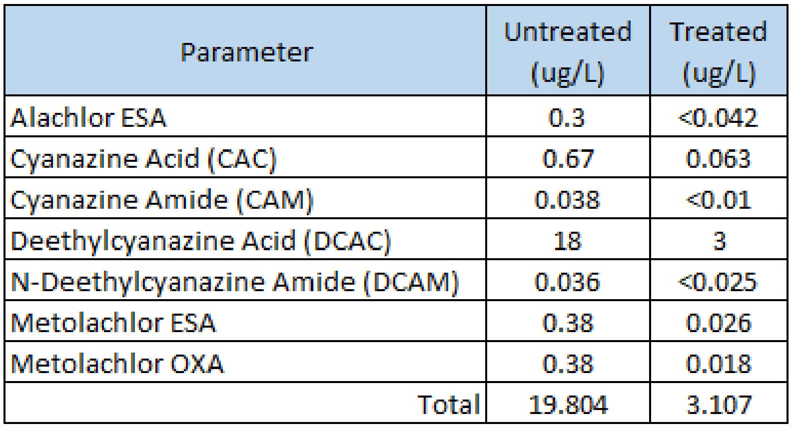
**Table 28. 2019 MDA Dakota County Preliminary Sampling Results (through October 23, 2019), Comparing Pre and Post treatment at Reverse Osmosis Systems.**

| Pre-treatment # of pesticide compounds detected | Post-treatment # of pesticide compounds detected | Pre-treatment Total Pesticide Concentration (µg/L) | Post-treatment Total Pesticide Concentration (µg/L) | Pre-treatment Nitrate (mg/L) | Post-treatment Nitrate (mg/L) |
|---|---|---|---|---|---|
| 15 | 2 | 8.7 | 0.081 | 23 | 3.1 |
| 15 | 1 | 5.884 | 0.06 | 25 | 3.8 |
| 14 | 1 | 3.7101 | 0.021 | 18 | 5.4 |
| 14 | 0 | 5.4358 | 0 | 13 | 2 |
| 14 | 0 | 5.1961 | 0 | 22 | 7.8 |
| 14 | 0 | 2.0969 | 0 | 12 | 1.4 |
| 13 | 1 | 2.2908 | 0.024 | 15 | 3 |
| 13 | 0 | 1.748 | 0 | 16 | 1.4 |
| 11 | 0 | 3.99 | 0 | 10 | 1.5 |
| 11 | 0 | 1.366 | 0 | 3 | 0.74 |
| 10 | 0 | 2.026 | 0 | 9.6 | 1.1 |
| 9 | 0 | 2.8222 | 0 | 12 | ND |
| 9 | 0 | 2.861 | 0 | 11 | 2 |
| 9 | 0 | 3.213 | 0 | 11 | 4.9 |
| 8 | 1 | 3.684 | 0.014 | 17 | 6.7 |
| 6 | 0 | 0.893 | 0 | 2.4 | 0.27 |
| 6 | 0 | 3.228 | 0 | ND | ND |
| 5 | 0 | 1.572 | 0 | ND | ND |
| 4 | 0 | 1.282 | 0 | 0.14 | ND |
| 4 | 0 | 1.618 | 0 | 0.84 | ND |
| 4 | 0 | 1.753 | 0 | 0.068 | ND |
| 4 | 0 | 0.747 | 0 | 0.63 | ND |
| 1 | 0 | 0.019 | 0 | ND | ND |

These findings were part of a wider evaluation by MDA of the removal efficiency of point-of-use treatment systems which included RO and carbon filtration treatment (MDA 2019). From 2017 through 2019, water samples were collected before (pre-treatment) and after (post-treatment) from 51 home water treatment systems across Minnesota, to evaluate pesticide and nitrate-nitrogen removal efficiency. An evaluation of 44 reverse osmosis treatment systems showed an average total pesticide concentration reduction of 99.7 percent and an average nitrate-nitrogen reduction of 78.9 percent. The MDA evaluated an additional seven home treatment systems (other than reverse osmosis) and found that the results ranged from poor to mixed for pesticide removal. This suggests that carbon filtration devices alone are not reliably effective at removing pesticide breakdown products from drinking water, but preliminary results suggest that RO treatment is effective at removing cyanazine breakdown products and nitrate to a level that meets drinking water guidelines (MDA 2019).

In the Ambient 2019 sampling event, two wells were sampled both from outside untreated spigots and inside from refrigerator carbon filters for pesticides (nitrate was not tested because carbon filters should have no effect on nitrate reduction). One of the wells selected had the highest total cyanazine from Dakota County's expanded 2017 sampling event located in Marshan Township and is not part of the Ambient Study set of 77 wells. The results from the well in Marshan Township are summarized in Table 32. The total pesticide concentration was reduced from 19.8 µg/L to 3.1 µg/L (85%) with the use of a refrigerator carbon filter. The sum of cyanazine breakdown products is 3.063 µg/L which is more than three times the drinking water guideline of 1 µg/L.

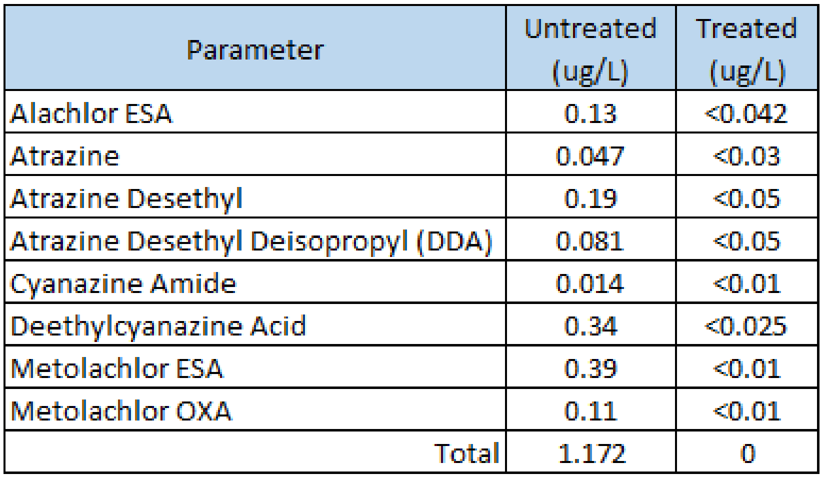
**Table 29. Comparison of Untreated and Treated Results from Well in Marshan Township.**



| Parameter | Untreated (ug/L) | Treated (ug/L) |
|---|---|---|
| Alachlor ESA | 0.3 | <0.042 |
| Cyanazine Acid (CAC) | 0.67 | 0.063 |
| Cyanazine Amide (CAM) | 0.038 | <0.01 |
| Deethylcyanazine Acid (DCAC) | 18 | 3 |
| N-Deethylcyanazine Amide (DCAM) | 0.036 | <0.025 |
| Metolachlor ESA | 0.38 | 0.026 |
| Metolachlor OXA | 0.38 | 0.018 |
| Total | 19.804 | 3.107 |

The second well, AGQS-54, had both an outside untreated sample and inside water treated with a refrigerator carbon filter; results are summarized in Table 33. The total pesticide concentration was reduced 100 percent with the use of a refrigerator carbon filter, however, the sum of pesticides in the untreated water was 1.172 µg/L, which is much lower than the sum of pesticides of 19.804 µg/L in the Marshan Township well.

**Table 30. Comparison of Untreated and Treated Results from Well AGQS-54.**



| Parameter | Untreated (ug/L) | Treated (ug/L) |
|---|---|---|
| Alachlor ESA | 0.13 | <0.042 |
| Atrazine | 0.047 | <0.03 |
| Atrazine Desethyl | 0.19 | <0.05 |
| Atrazine Desethyl Deisopropyl (DDA) | 0.081 | <0.05 |
| Cyanazine Amide | 0.014 | <0.01 |
| Deethylcyanazine Acid | 0.34 | <0.025 |
| Metolachlor ESA | 0.39 | <0.01 |
| Metolachlor OXA | 0.11 | <0.01 |
| Total | 1.172 | 0 |

Effectiveness of carbon filters is mixed and warrants more data if MDH is going to continue to list carbon filters as a treatment method on the MDH Home Water Treatment Factsheet located in Appendix E.1. See footnote related to carbon filters. “The substances that these technologies reduce or remove depends on the filter media or resin.” As demonstrated with the well in Marshan Township, a carbon filter can still leave pesticide levels in the water above drinking water guidelines. It is important to note that the homeowner is responsible to inspect and maintain the water treatment device depending on water conditions and manufacturer recommendations to ensure proper operation.

## 4.3. Chloride

### 4.3.1. Chloride Sources

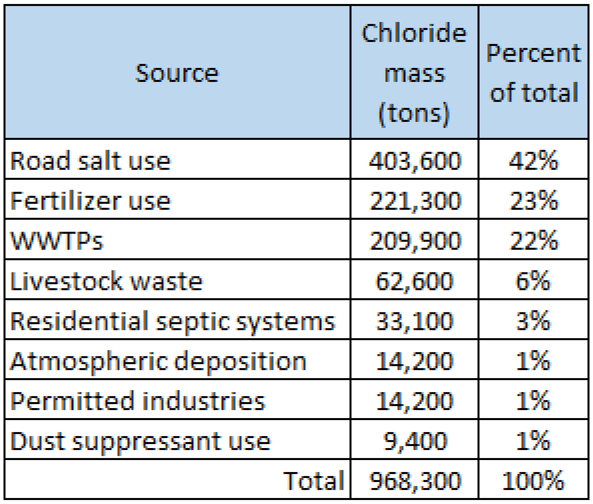
Chloride in nature is common in minerals in the form of sodium chloride (table salt or sea salt), potassium chloride or calcium chloride, but naturally occurring levels in Minnesota water resources are very low. Although chloride can get into groundwater from the weathering of soil and rock, when it is detected at levels above 3 mg/L in the three principal aquifers, it is from anthropogenic sources. Chemically, chloride is a conservative ion: it does not readily adsorb to soil particles, is not reactive in the environment and does not form common insoluble salts. Hence, chloride moves with infiltrating water and is an excellent tracer for the impact of human activities on groundwater.

At high levels, chloride is a pollutant in both drinking and surface waters. The USEPA does not consider chloride in drinking water a threat to human health and has assigned it a secondary maximum contaminant level (SMCL) of 250 mg/L. A SMCL applies to parameters in drinking water that affect the odor, taste or appearance. Drinking water with 250 mg/L or higher of chloride would taste salty. Reverse osmosis or distillation will reduce chloride in drinking water; the MDH Factsheet on home water treatment options is provided in Appendix E.

Chloride in surface water can be toxic to fish, aquatic bugs, amphibians and plants at 230 mg/L. Chloride corrodes road surfaces and bridges and damages reinforcing rods, increasing maintenance and repair costs. Since nearly all surface water features in the County interact with groundwater, pollution of groundwater can degrade surface water quality, and pollution of surface water can degrade groundwater quality.

Table 34 is a summary of the chloride sources in Minnesota, the largest of which are road salt, potash (aka muriate of potash (MOP), potassium chloride (KCl) and $K_2O$) fertilizer and wastewater treatment plant (WWTP) discharges (Overbo et al, 2019). The largest source of chloride to wastewater is water softener salt: water softener brine is either discharged to wastewater treatment plants (WWTPs) or, in non-sewered areas, to the subsurface from septic systems or direct discharge into the subsurface. WWTP processes do not remove chloride; chloride is in the effluent discharged to surface water and in the WWTP biosolids applied to the land.

**Table 31. Minnesota statewide annual chloride contributions from major point and nonpoint sources. (Overbo et al, 2019).**



| Source | Chloride mass (tons) | Percent of total |
|---|---|---|
| Road salt use | 403,600 | 42% |
| Fertilizer use | 221,300 | 23% |
| WWTPs | 209,900 | 22% |
| Livestock waste | 62,600 | 6% |
| Residential septic systems | 33,100 | 3% |
| Atmospheric deposition | 14,200 | 1% |
| Permitted industries | 14,200 | 1% |
| Dust suppressant use | 9,400 | 1% |
| Total | 968,300 | 100% |

## 4.3.2. Chloride Results

The 77 Ambient Study wells have been systematically sampled since 1999, with some wells sampled every sample event (16 times) and others only a few events (two to five times). The average number of samples per well is 10; some well owners have come and gone from the Ambient Study over time. All the chloride results by well and year are summarized in Appendix B Table B.7. Depending on the laboratory used, the chloride MRL ranged from 0.3 mg/L to 3 mg/L. This affects the calculated “low end” of the chloride concentration distribution(s). The MRL was 3 mg/L most years with the exception of years: 2009, 2011, 2013 and 2019 where it was 0.3 mg/L. The net effect is that the minimum, and even the lower quartile of chloride concentrations, are influenced by the detection limit over the early vs the later time frame.

Chloride results from 1999–2019 chloride study find that:

- Results range from non-detect (less than 0.3 mg/L or < 0.3 mg/L) to 292.0 mg/L

- All wells but two had chloride above the MRL
- One well exceeded the SMCL of 250 mg/L at least once
- Five wells exceeded half the SMCL of 125 mg/L

Comparison of the chloride results by well casing categories, summarized in Table 35, shows that chloride decreases with depth.

**Table 32. Descriptive Statistics of Average Chloride Results (mg/L) by Well Casing Depth Category (ft).**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26.0 | 32.5 | 43.9 | 3.6 | 7.5 | 18.9 | 30.4 | 213.0 |
| Mid 125' to 250' | 26.0 | 20.7 | 28.8 | 1.7 | 6.5 | 13.6 | 17.2 | 125.8 |
| Deep >250' | 25.0 | 6.0 | 6.7 | 1.9 | 2.5 | 3.4 | 7.4 | 32.8 |

### i. Chloride by aquifer versus well casing depth

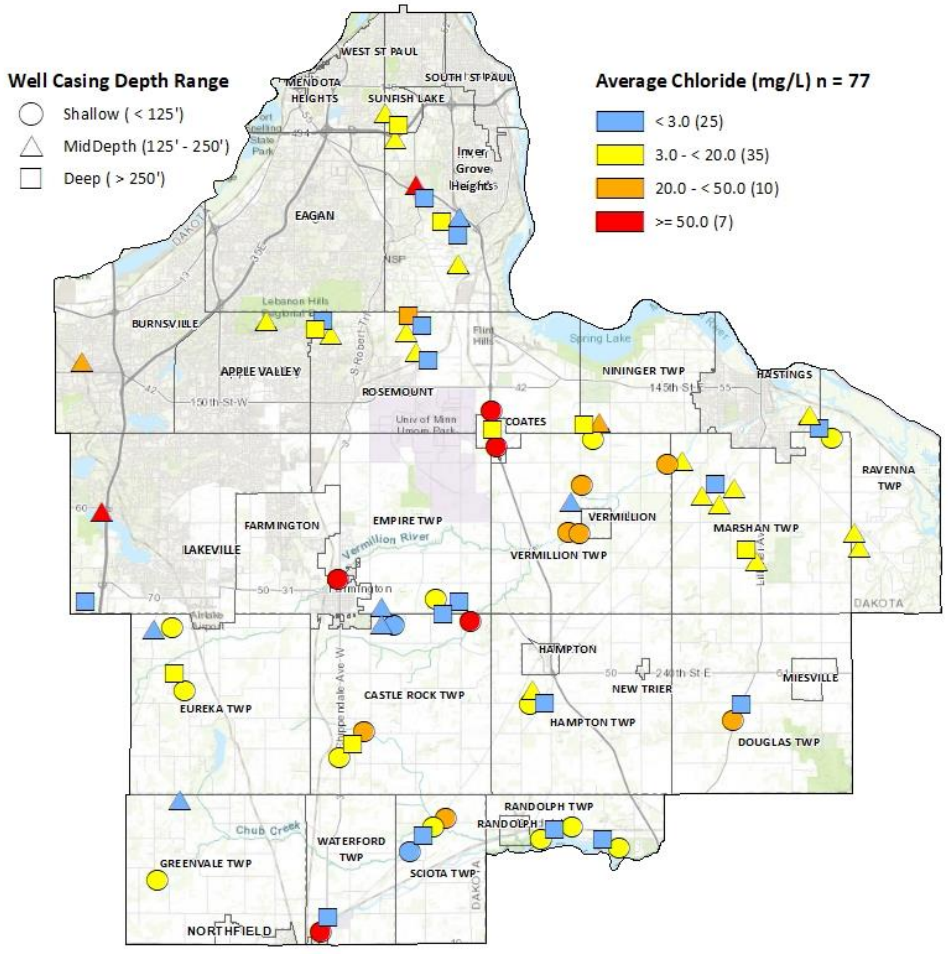
Table 36 is excerpted from Table 1 and Appendix D Tables D.2 and D.3. As previously stated, there is no statistical difference between Ucs and Opdc chloride results (Wilcoxon, p = 0.44). Aquifer does not appear to be necessarily the most import variable, at least down to the top of the Jordan. Chloride results are statistically different between all three well casing depth categories.

**Table 33. Statistical Significance of Median Chloride by Aquifer and Well Casing Depth.**

| **Median level by Aquifer** | | | **p-value for Aquifer Differences** | | |
|---|---|---|---|---|---|
| Cjdn | Opdc | Ucs | Opdc vs Cjdn | Opdc vs Ucs | Usc vs Cjdn |
| 3.0 | 12.8 | 15.4 | **0.000** | 0.44 | **0.000** |
| **Median level by Well Casing Depth Category** | | | **p-value for Well Casing Depth Differences** | | |
| Deep > 250 ft | Mid 125 ft to 250 ft | <125 ft | Mid vs Deep | Mid vs Shallow | Shallow vs Deep |
| 3.0 | 13.0 | 18.0 | **0.001** | 0.099 | **0.000** |

Shaded Cells > 95% statistical significance
Shaded Cells 90 to 95% statistical significance
No shading <90% statistical significance

Figure 56 shows the average chloride by the well casing depth. Geographically, wells with chloride above the MRL of 3. 0 mg/L are located both in agricultural and suburban settings. Most of the highest chloride results (more than 50 mg/L) are near major highways.



Sources: ESRI; Dakota County Environmental Resources

**Figure 56. Average Chloride by Well Casing Depth.**

The graph in Figure 57 below plots the average chloride results by well casing depth; the correlation is statistically significant (Kendall, $p < 0.05$), and the line shows that chloride decreases with well casing depth. The line intercepts the x-axis at 450 feet and is the best statistical representation of the depth that we stop "seeing "chloride, and this depth is interpreted to represent the year when large scale use of chloride in Minnesota began (about 1955). Intercept depth of 450 feet divided by 54 years (2009–1955) equals 8.3 feet per year of infiltration. The year 2009 is used because it is the mid-point of the study years for 1999–2019.

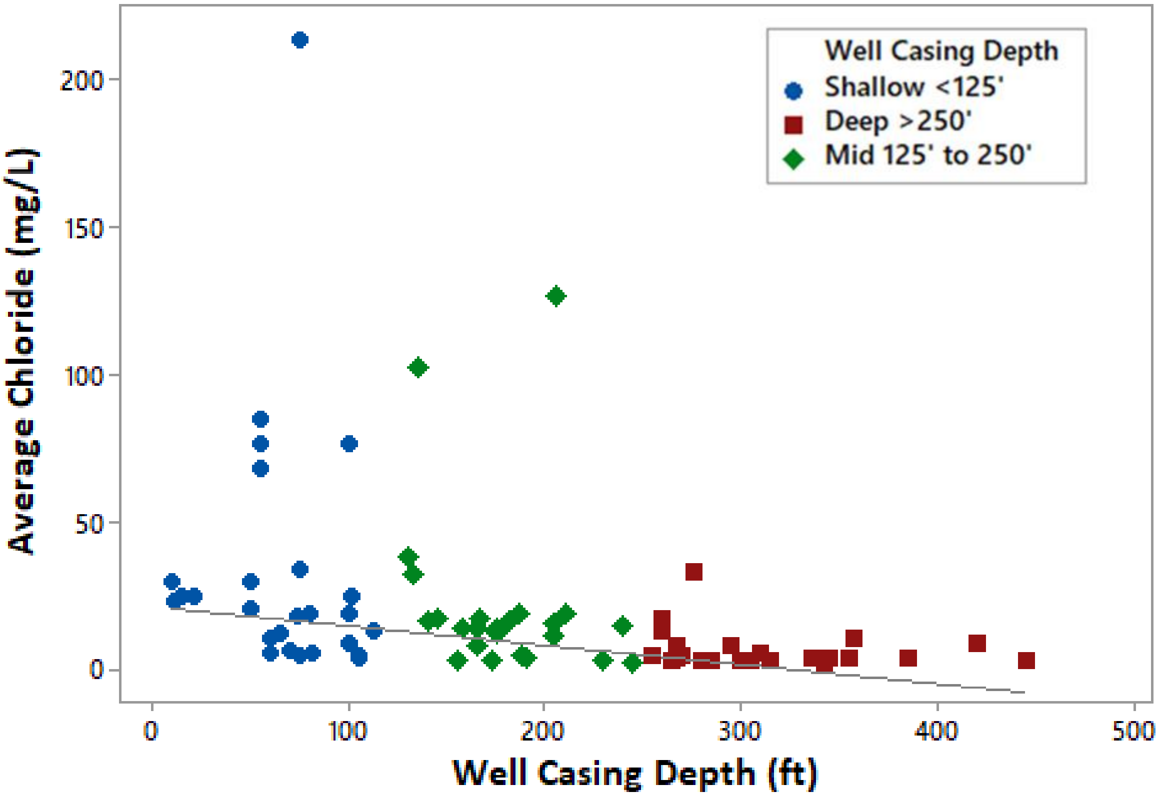


**Figure 57. Correlation of Average Chloride by Well Casing Depth—Kendall Line.**

### ii. Chloride by well cluster and aquifer

The Ambient Study "well clusters" are explained in Section 3.3. There are 60 Ambient Study wells included in 21 well clusters. The chloride levels in the well clusters were compared and the p-values (Wilcoxon) are tabulated in Appendix D Table D.5. Chloride was detected in all wells in every cluster. When chloride was examined across all 77 wells in the study, summarized in Table 36, no difference in chloride levels was found between Opdc and Ucs wells (Mann-Whitney, p = 0.44). The findings from Appendix D Table D.5. are summarized below:

- The Ucs vs Opdc wells are statistically significantly different (Wilcoxon, p <0.10) in 16 of the 17 clustered pairs.
    - In the 16 clusters that are statistically different, the estimated difference in medians is positive/higher chloride in nine Ucs wells and seven Opdc wells in clustered pairs.
- The Ucs vs Cjdn wells are statistically different (Wilcoxon, p <0.10) for 14 of the 16 clusters; 12 have a positive or higher chloride in the Ucs wells and two of the Cjdn wells are higher.
- The Opdc vs Cjdn wells are statistically different (Wilcoxon, p <0.10) in 20 of the 22 clustered pairs.

  - In the 20 clusters that are statistically different, the estimated difference in medians is positive or higher in chloride in the Opdc in 18 clustered pairs and higher in the Cjdn in 2 of the pairs.
- There are two clusters with two Opdc wells; both are statistically different (Wilcoxon, p <0.05).
- There are two clusters with two Ucs wells; one is significantly different and one is not.
- In general, the statistical pattern is the Ucs>Opdc, Opdc>Cjdn, and Ucs>Cjdn.

### 4.3.3. Chloride Trends

#### i. Trends for chloride with frequency analysis

The frequency of contaminant detection was also examined, following MDA's example in its "2018 Water Quality Monitoring Report" (MDA 2018). In the Ambient Study well data set from 1999 to 2019, not all years had samples for all wells or the same wells in each sampling event. Analysis of the frequency with which chloride was detected at different levels allows the overall results to be compared from year to year, even though the exact wells used varied somewhat.

The data set was filtered to capture the group of wells that have consistently been tested for chloride. Figure 58 shows the 15 sample events where 30 or more wells were sampled and the 61 wells that have been sampled at least 9 times were put into three categories:

- Over 20 mg/L
- Between 10 mg/L to 20 mg/L
- Between 3.0 and 10 mg/L; 3.0 mg/L is the laboratory minimum reporting level (MRL)
- 3.0 mg/L, the MRL

Table 37 shows that chloride has been increasing in Ambient Study wells. For chloride concentrations over 20 mg/L, the frequency trend has increased from 13 percent to 36 percent. In general, as chloride levels increase, the wells move from a lower concentration category to a higher chloride concentration category. There is a decrease in the percent of wells with chloride of less than 3 mg/L: from 53 percent in 1999 to 23 percent in 2019.

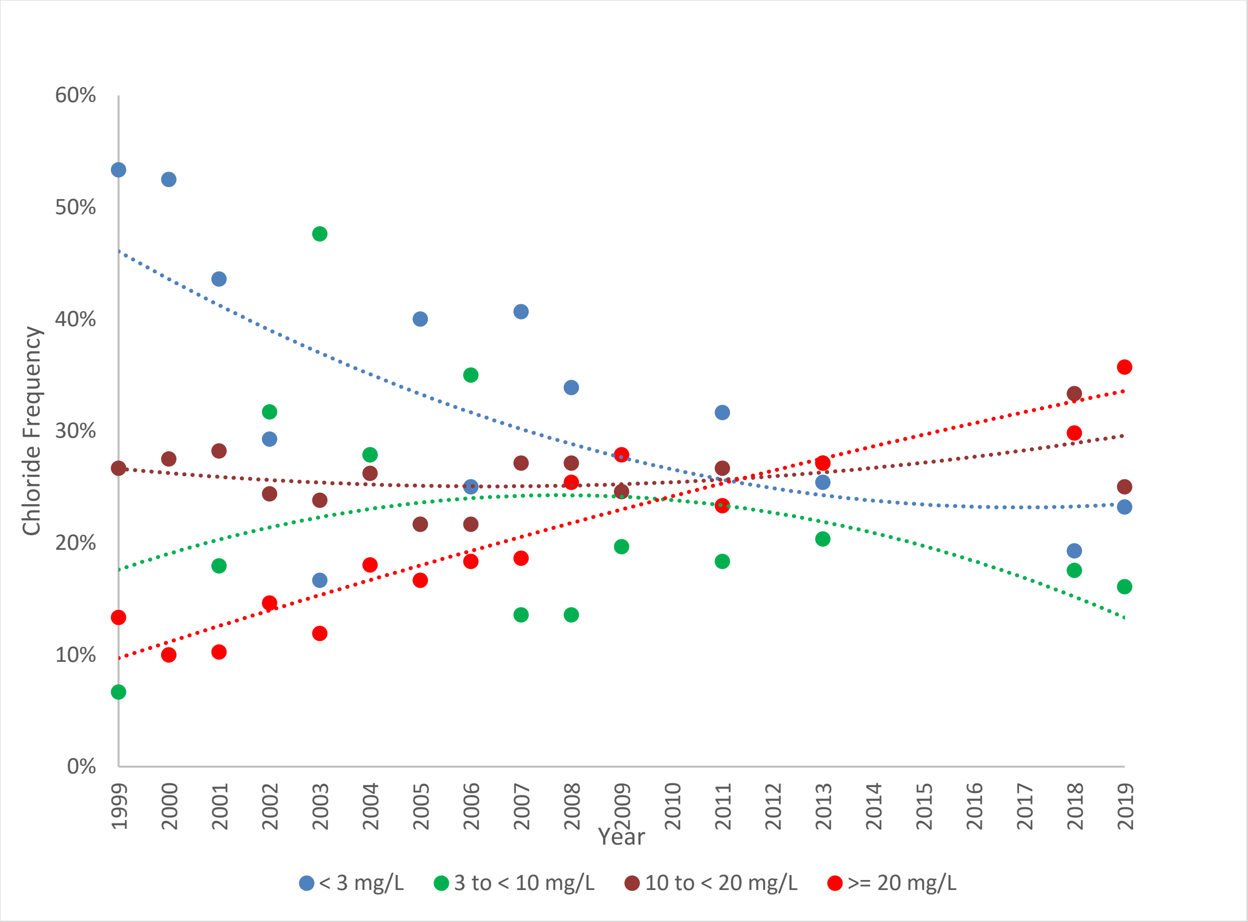


**Figure 58. Chloride Concentration Frequency by Year.**

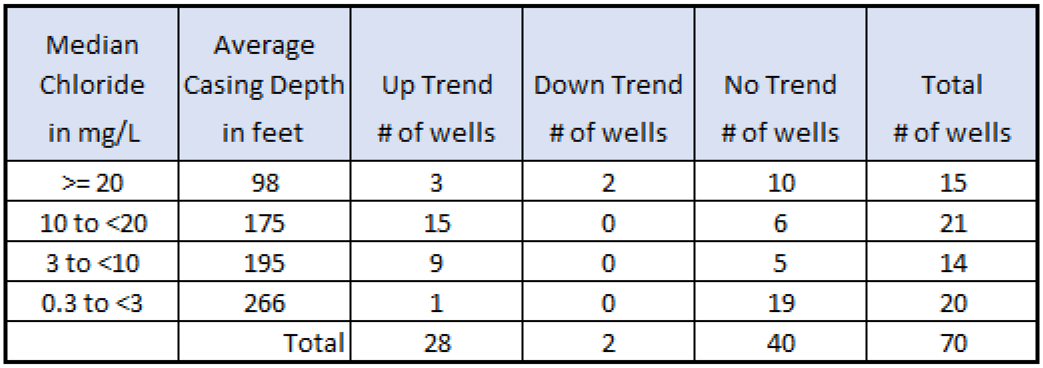
### Table 34. Chloride Frequency by Year and Concentration Category.

| Chloride Category | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 | 2006 | 2007 | 2008 | 2009 | 2011 | 2013 | 2018 | 2019 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| < 3 mg/L | 53% | 53% | 44% | 29% | 17% | 28% | 40% | 25% | 41% | 34% | 28% | 32% | 25% | 19% | 23% |
| 3 to < 10 mg/L | 7% | 10% | 18% | 32% | 48% | 28% | 22% | 35% | 14% | 14% | 20% | 18% | 20% | 18% | 16% |
| 10 to < 20 mg/L | 27% | 28% | 28% | 24% | 24% | 26% | 22% | 22% | 27% | 27% | 25% | 27% | 27% | 33% | 25% |
| >= 20 mg/L | 13% | 10% | 10% | 15% | 12% | 18% | 17% | 18% | 19% | 25% | 28% | 23% | 27% | 30% | 36% |

### ii. Trends for chloride and well casing depth

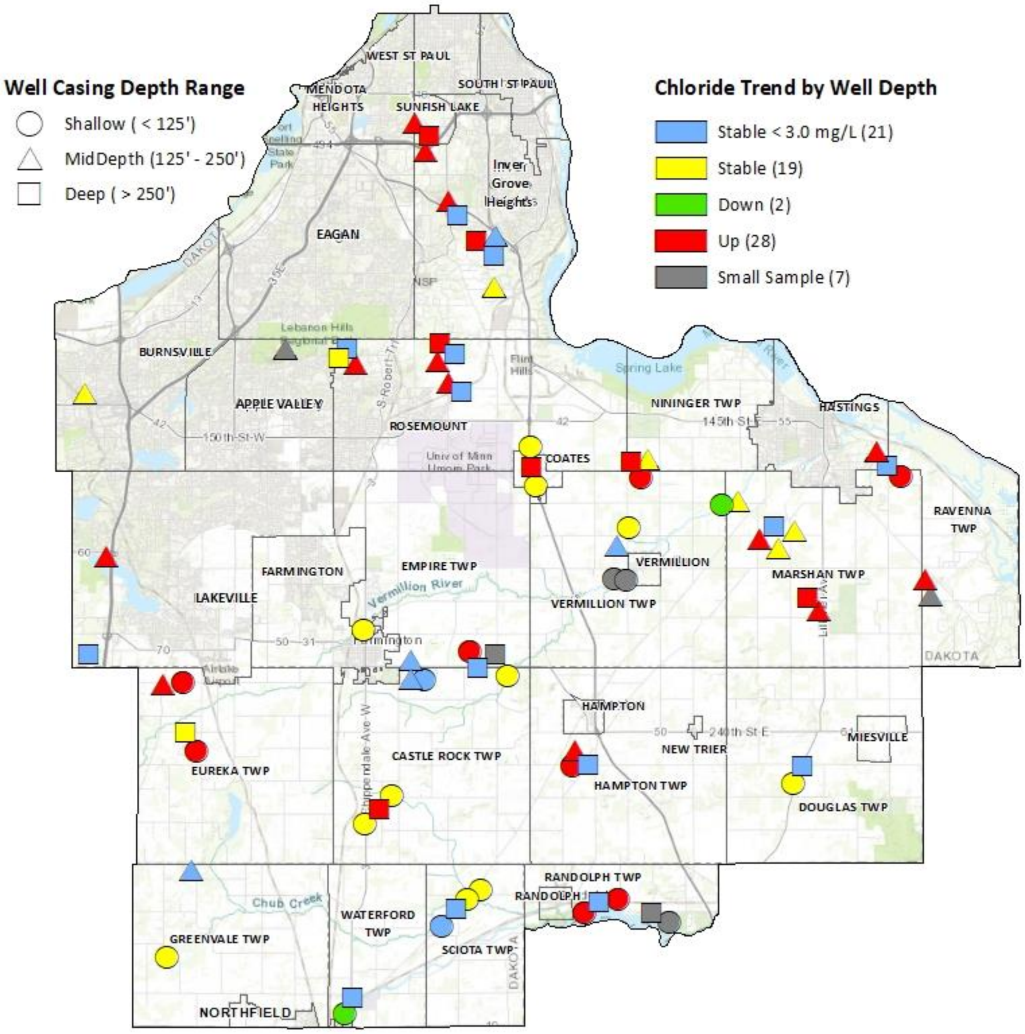
Chloride trend patterns are listed by well in Appendix B Table B.7. and are summarized by median well casing depth in Table 38. The median chloride was divided into four categories: 0.3 mg/L to 3 mg/L, greater than 3 mg/L to 10 mg/L, greater than 10 mg/L to 20 mg/L, and greater than 20 mg/L. Seven wells were sampled less than five times, so valid trend analysis could not be performed. Forty percent (28 wells) of the wells have an upward trend, 3 percent (2 wells) have a downward trend, and 57 percent (40 wells) have no trend. The category of 20 mg/L and higher has 15 wells: three wells with an upward trend and two wells with a downward trend. This category also has the shallowest well casing depth of 98 feet. The median chloride decreases as the well casing depth gets deeper. There are 20 wells (29 percent) with chloride less than 3 mg/L, 19 of which are stable with no trends. The other 11 wells without trends are likely in equilibrium with the chloride sources on the surface.

**Table 35. Chloride Trends by Median Chloride Concentration (mg/L) and Average Well Casing Depth.**



| Median Chloride in mg/L | Average Casing Depth in feet | Up Trend # of wells | Down Trend # of wells | No Trend # of wells | Total # of wells |
|---|---|---|---|---|---|
| >= 20 | 98 | 3 | 2 | 10 | 15 |
| 10 to <20 | 175 | 15 | 0 | 6 | 21 |
| 3 to <10 | 195 | 9 | 0 | 5 | 14 |
| 0.3 to <3 | 266 | 1 | 0 | 19 | 20 |
|  | Total | 28 | 2 | 40 | 70 |

There is no clear geographic pattern regarding well location among the wells with upward trends in Figure 59, presumably because the sources of chloride are varied and widespread.



Sources: ESRI; Dakota County Environmental Resources

**Figure 59. Chloride Trends.**

### 4.3.4. Chloride and Land Use

There are many sources of chloride that can impact aquifers, as shown in Table 34 above. Every property is near a road that may be treated with salt for deicing or for suppressing dust in the summer.

Fertilizer use (potash-potassium chloride) is the second highest use of chloride in Minnesota. (Overbo et al, 2019) mainly on row-crop agriculture but is also present in common lawn and turf fertilizers. Groundwater chloride results were statistically evaluated against the percentage of land in row crop agriculture in a one-mile section as determined by the Public Land Survey (PLS) proximate to the wells sampled. The concentration and distribution of cropland is evaluated as a general indication of where fertilizers would be applied. There is not a significant correlation between chloride and the percentage of row crop agriculture depth (Kendall, p = 0.29).

The location and density of cultivated row crop agriculture was derived from GIS files produced by the Dakota County Soil and Water Conservation District. The cultivated row cropland data represents cleared and tilled acreage used to produce adapted crops for harvest. This coverage represents a snapshot of the land use occurring at a specific time. Only the areas classified as agricultural were used for analysis because of the nitrogen inputs employed in modern row crop agriculture. Figure 60 shows elevated chloride levels at both where there is zero percent land in agriculture and 85 percent agriculture, which indicates chloride sources across the landscape.

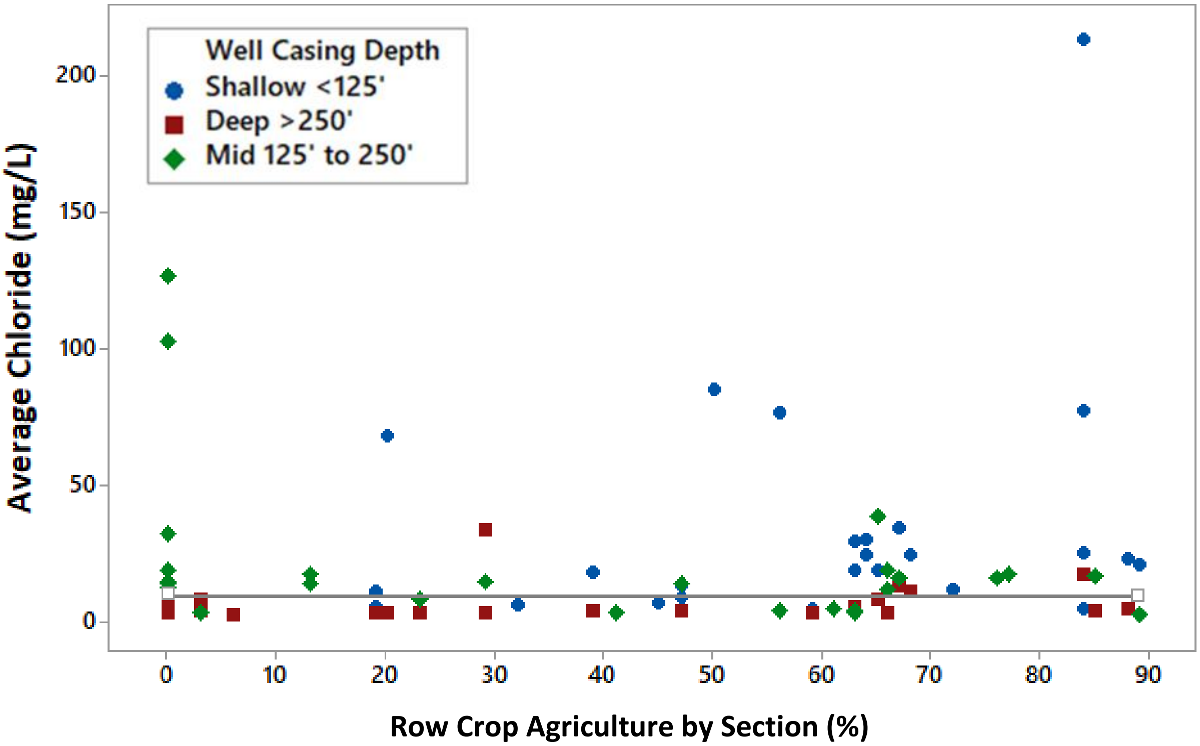


**Figure 60. Correlation of Average Chloride by Percent of Agriculture by Section—Kendall Line.**

Table 39 compares the percentage of land in agriculture by section (75 percent is the highest) into categories compared to average chloride level. It appears chloride increases with higher percentage of agriculture according to the average and median columns, but this relationship is not statistically significant as previously stated (Kendall, p = 0.29).

**Table 36. Descriptive Statistics of Average Chloride (mg/L) by Row Crop Agriculture by Section (%).**

| Agriculture by Section | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| <25% | 25 | 19.6 | 31.6 | 1.9 | 3.1 | 8.6 | 15.2 | 125.8 |
| 25% -50% | 13 | 15.7 | 22.3 | 2.3 | 3.2 | 8.0 | 15.5 | 84.3 |
| 50% -75% | 26 | 15.6 | 16.4 | 2.2 | 3.5 | 11.1 | 23.8 | 76.1 |
| >75% | 13 | 33.3 | 57.3 | 1.7 | 3.8 | 16.6 | 23.2 | 213.0 |

### 4.3.5. Chloride in Inver Grove Heights (WIISE STUDY) and Community-Focused Sampling

Community-focused sampling of private wells began in 2018; in this initiative, all water samples collected from outside faucets were tested for chloride but no samples from the inside primary drinking water tap were tested for chloride. In 2018, 66 private wells in Burnsville were tested for chloride. Burnsville had the highest average, median and maximum detected chloride of all the sampling events. The highest chloride result of 451 mg/L in Burnsville was in a well located 65 feet from a county road where road salt is used for winter maintenance and there is a water softener in use in the household on the property. There is essentially no agriculture remaining in Burnsville, so no agricultural sources of chloride (potash fertilizer) are expected. Sixty-eight percent of the Burnsville well sampling project participants report having a water softener. Since the households in the Burnsville sampling are rural residential, they are not connected to city sewer; the water softener brine is discharged into septic systems or the subsurface, both of which leach to the groundwater. See Table 40.

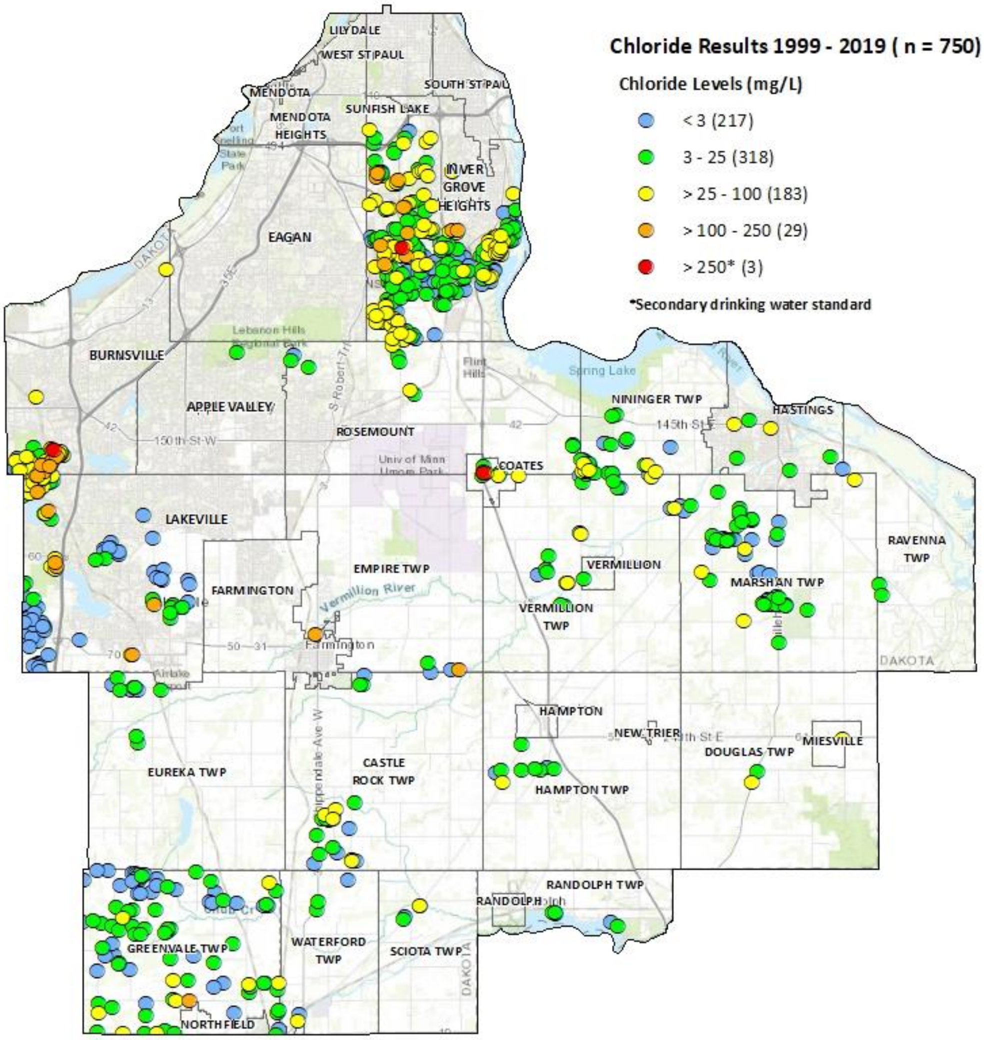
Surveys of well owners who participated in the community-focused well sampling (which are wells in rural residential setting), show that softener use by community ranges from a low of 60 percent of participants in Inver Grove Heights to a high of 96 percent of Lakeville participants.

**Table 37. Summary of Chloride Results (mg/L) Comparing Datasets.**

| Sample Events | Year | # of Samples | # of Samples with Detections | # of Samples above SMCL 250 mg/L | Average | Median | Max |
|---|---|---|---|---|---|---|---|
| Ambient Study outside untreated | 1999-2019 | 77 | 77 | 1 | 20.2 | 10.9 | 292 |
| Inver Grove Heights outside untreated | 2016 | 274 | 274 | 1 | 26.6 | 15.6 | 288 |
| Burnsville outside untreated | 2018 | 66 | 58 | 2 | 55.3 | 34.4 | 451 |
| Greenvale outside untreated | 2019 | 94 | 52 | 0 | 9.9 | 3.3 | 110 |
| Lakeville outside untreated | 2019 | 100 | 51 | 0 | 21.9 | 3.8 | 225 |

### 4.3.6. All Chloride Results

The median chloride from 750 private well water tests, including 77 Ambient Study wells, in the County are mapped in Figure 61. Seventy-one percent of the results are above the MRL of 3 mg/L for chloride which indicate the aquifers are impacted by anthropogenic uses of chloride.



Sources: ESRI; Dakota County Environmental Resources

**Figure 61. All Dakota County Private Well Chloride Results.**

## 4.3.7. Chloride and Other Anthropogenic Parameters

### i. Chloride and sodium ferrocyanide

Sodium ferrocyanide is used in as an anticaking agent in road salt; it and can decompose by certain bacteria or exposure to sunlight and release free cyanide to the environment. The elevated chloride and increasing upward trends for chloride in the Ambient Study wells, which may be related to the application of road salt, raise concerns about potential cyanide contamination. In 2018, 20 Ambient Study wells that have elevated chloride levels were sampled and analyzed for free cyanide. No free cyanide was detected above the method reporting limit of 0.005 mg/L. The drinking water guideline for free cyanide is 0.1 mg/L, so all the samples were orders of magnitude below that.

### ii. Chloride compared to nitrate and sodium

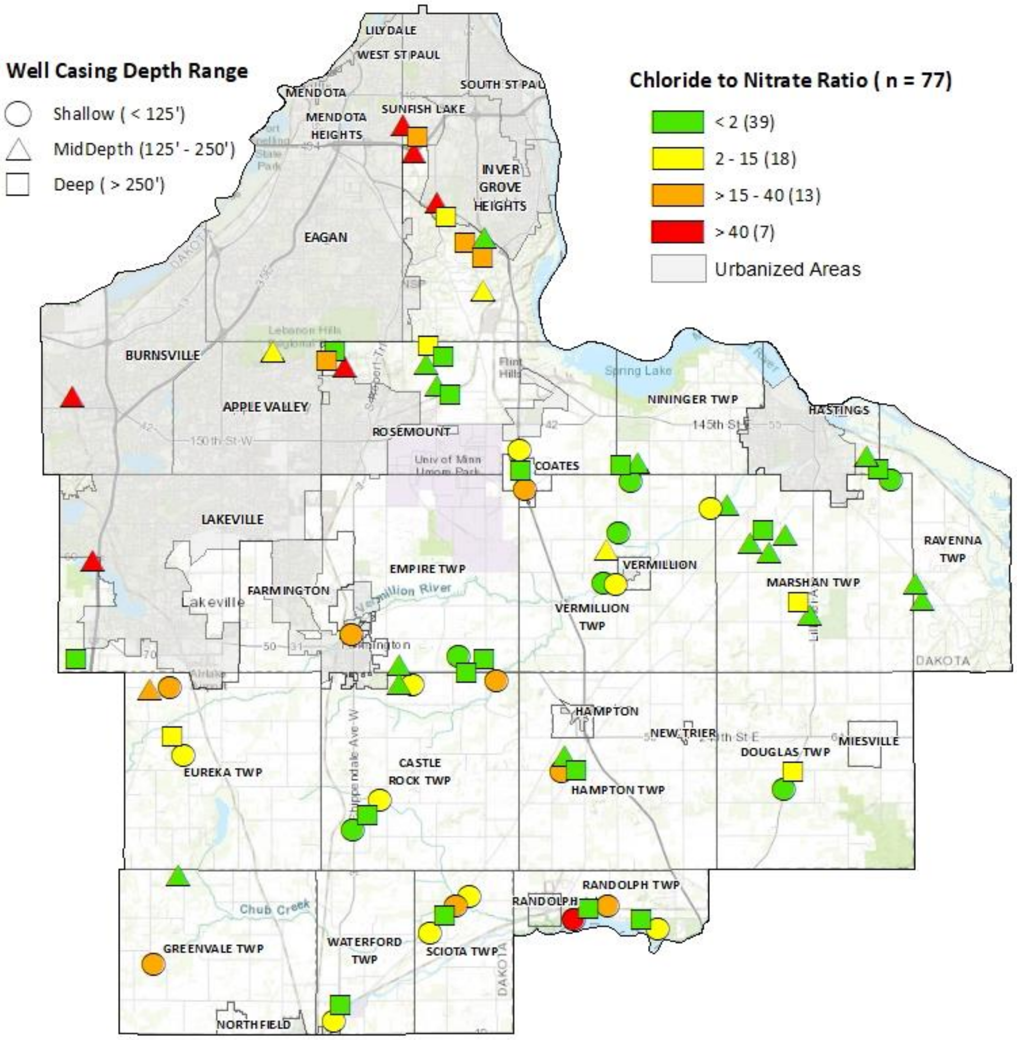
Large-scale commercial use of nitrogen fertilizer began in 1960 in southeast Minnesota; road salt application began to be widely used in 1955; and water softeners began to be installed as early as the 1950s. If either nitrate or chloride is detected in a private well above the background level of 3 mg/L, then the water in the well is younger than the date the chemical was introduced into the environment.

Septic systems leach both chloride from water softener brine and nitrate from human waste into the groundwater. Septic systems, where present, are estimated to contribute four to 17 pounds of nitrogen per acre per year to the groundwater (MPCA, 2013, D1–15). By contrast, row crop agriculture, in sensitive geologic areas like Dakota County, is estimated to contribute 20 to 37 pounds of nitrogen per acre per year to the groundwater (MPCA, 2013, D1–15).

The chloride to nitrate ratio is a good indicator for the relative source contributions of the anthropogenic parameters. In the Ambient Study results, the chloride to nitrate ratio correlates negatively with the percent of land use in row crop agriculture by section (Kendall, $p < 0.05$).

In agricultural settings, the ratio is approximately two, due to potash (potassium chloride fertilizer) as the dominant source for chloride, and nitrogen fertilizer applied to crops as the dominant source of nitrate. In the Ambient Study the ratio of chloride to nitrate is approximately two for wells where the percent of row crop agriculture is over 60 percent. The WIISE study also indicated that in rural residential suburban settings with little agriculture, the ratio of chloride to nitrate is approximately ten or more. There can be specific wells in rural settings with higher chloride to nitrate ratios – these wells are usually near highways and may be impacted by road salt for deicing. This pattern is seen elsewhere in southeast Minnesota (e.g. Olmsted County), with high ratios in the Rochester metro area (over 10) and ratios closer to two in dominantly agricultural townships/sections (SEMWAL dataset).

Figure 62 shows wells in suburban areas have a chloride to nitrate ratio much higher than wells in agricultural settings (red and orange shapes), because the chloride sources are relatively higher, and the nitrate sources are much lower. The ratio is closer to two in the agricultural areas (green and yellow shapes). For deeper wells where *both* chloride and nitrate can be quite low, the ratio can also be much higher than two (orange squares).



Sources: ESRI; Dakota County Environmental Resources

Figure 62. Median Chloride to Median Nitrate Ratio.

The sodium data separately supports the analysis that potash is contributing chloride in agricultural areas. Chloride moves essentially with water, and the background concentration of chloride is about 1 mg/L. If all chloride is anthropogenic and comes from sodium chloride and not potassium chloride and there is also no removal mechanism for sodium, then the molar sodium to chloride slope would be approximately 1. Atomic weight of chloride is 35.5 and sodium is approximately 23. Thus, NaCl by weight is approximately 61 percent chloride and 39 percent sodium, but the molar ratio is 1:1. If all sodium were from NaCl the molar ratio should be 1:1, and the weight ratio should be approximately 23/35.5. However, in the study data, the empirical slope is approximately 0.2. Figure 63 indicates that some sodium is missing; removed – retained by clay soils or that some of the chloride, is not from NaCl but from KCL, or both.

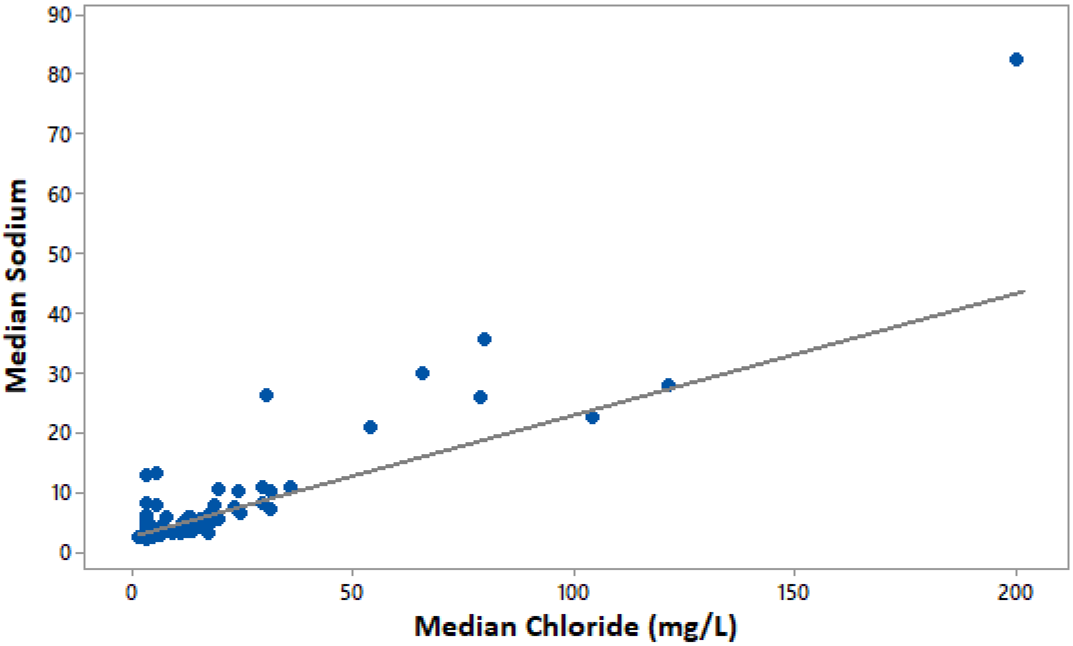
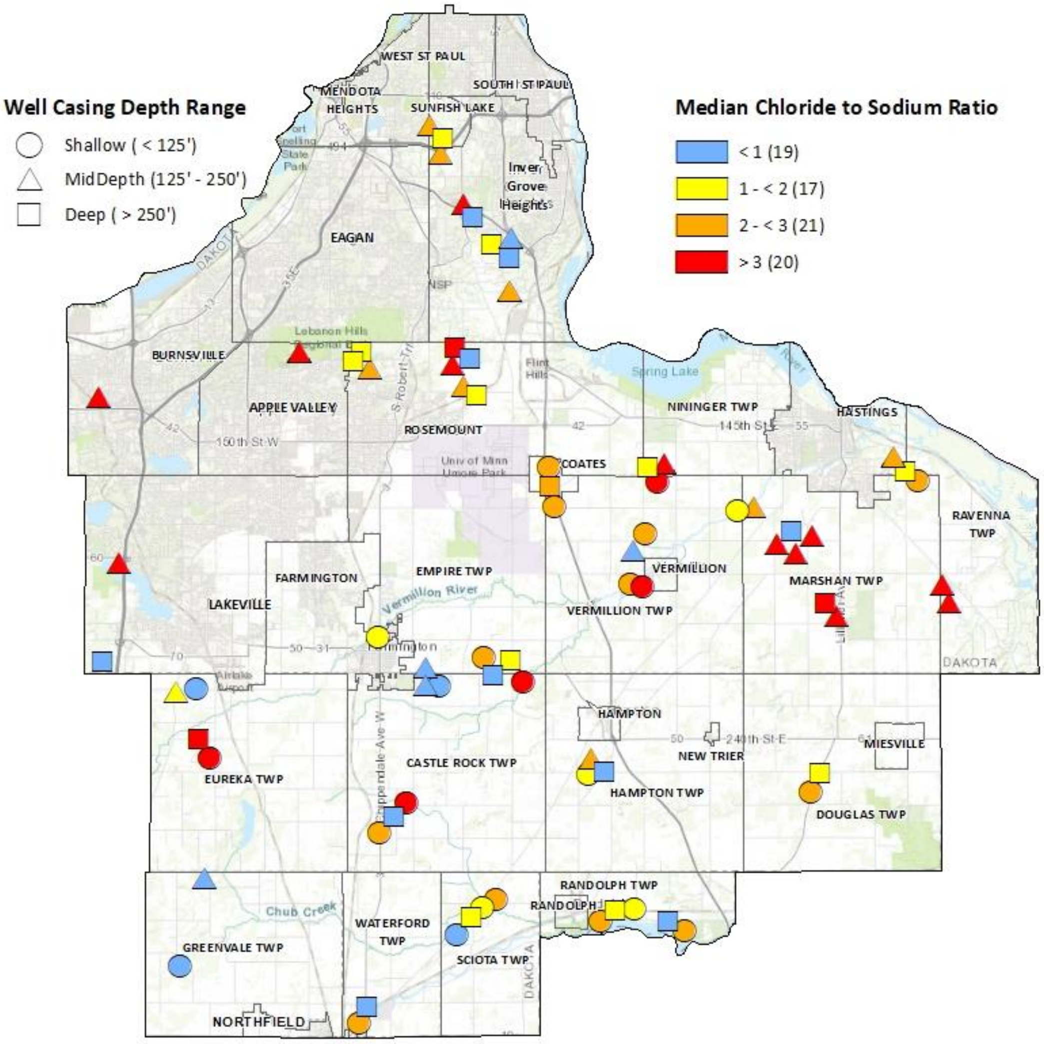


Figure 63. Correlation of Median Sodium to Median Chloride.

Figure 64 below maps the chloride to sodium ratio by well casing depth category. The wells with excess chloride compared to sodium (red and orange shapes) in the north and western areas of the county where clay soils are more prevalent and retain the sodium as compared to wells  with a chloride to sodium ratio over 2 on the eastern side of the county where there are coarse textured soils where potash use is prevalent on agricultural fields.



Sources: ESRI; Dakota County Environmental Resources

Figure 64. Median Chloride to Median Sodium Ratio

### iii. Well grout analysis for chloride and nitrate

Prior to the 1974 Minnesota Well Code, Mn. Rule 4725, well contractors were not required to complete and submit water wells records documenting the well's construction and geology encountered to the MDH. Appendix B Table B.1. lists the well construction details where well records were obtained. Most drinking water wells drilled in Dakota County are rotary drilled which creates an open annular space between the borehole and the well casing where grout must be placed as a sealing material; 40 percent of the wells in the Ambient Study are either rotary drilled wells and likely not grouted with bentonite, cement, or neat cement or are drilled by cable tool and ungrouted. Wells in the study that are completed in the Cjdn aquifer, and the Opdc is present above it, have been required since 1975 to be full length grouted with neat cement. In principle, grout prevents surface contaminants from migrating down the well casing. Until the most recent revision to the Well Code in 2008, only the top 30 feet of the annular space in a well was required to be grouted in wells that are screened or completed in the first bedrock encountered. The revised Well Code requires the top 50 feet to be grouted and cuttings can be used to fill the annular space below 50 feet.

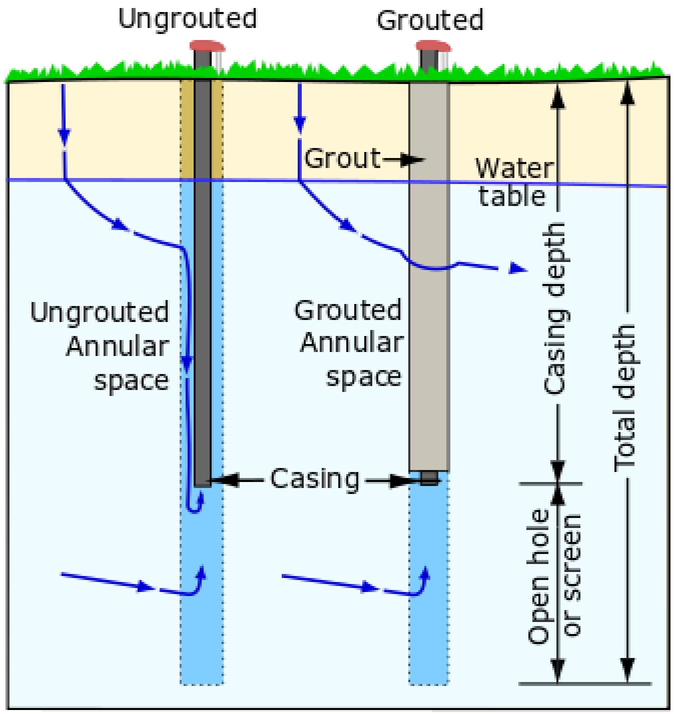


**Figure 65. Diagram of Simplified Groundwater Flow Affected by Ungrouted and Grouted Wells.**

Ungrouted wells in the study are statistically shallower than grouted wells (Mann-Whitney, $p < 0.01$) by approximately 120 feet. It was expected that an ungrouted well would have higher levels of the anthropogenic chemicals chloride and nitrate, and the data support these assumptions. For both nitrate and chloride, comparison of the grouted vs ungrouted wells in the Opdc and Ucs showed that levels were higher in the ungrouted wells. The median nitrate concentrations were higher in ungrouted than in grouted wells (Mann-Whitney, $p < 0.05$) by approximately 6.1 mg/L, and the median chloride concentrations were higher (Mann-Whitney, $p < 0.05$) by 8.7 mg/L.

Appendix D Table D.6. compares median nitrate, median chloride, grout and well casing category by well cluster.

Findings:

- 18 of the 21 clusters: the shallow well has the higher median nitrate and chloride.
    - 11 clusters have a shallow ungrouted well; 8 of those have higher chloride and nitrate.
    - Cluster 9 has two shallow ungrouted wells; one has higher chloride and the other higher nitrate.
    - Cluster 18 has two shallow wells: the ungrouted one has higher chloride and the grouted one has higher nitrate.
- 20 of 21 clusters: the deeper well had lower nitrate and chloride.
    - 19 of 21 clusters: the deeper well is neat cement grouted.

- 6 of 21 clusters have chloride detected but no nitrate. In five of these clusters, the chloride is highest in the shallower well; in one well, chloride is only detected in the shallowest well.
- 15 of 21 clusters have both nitrate and chloride detected. In 11 of the 15, the higher levels of nitrate and chloride are in the same well.

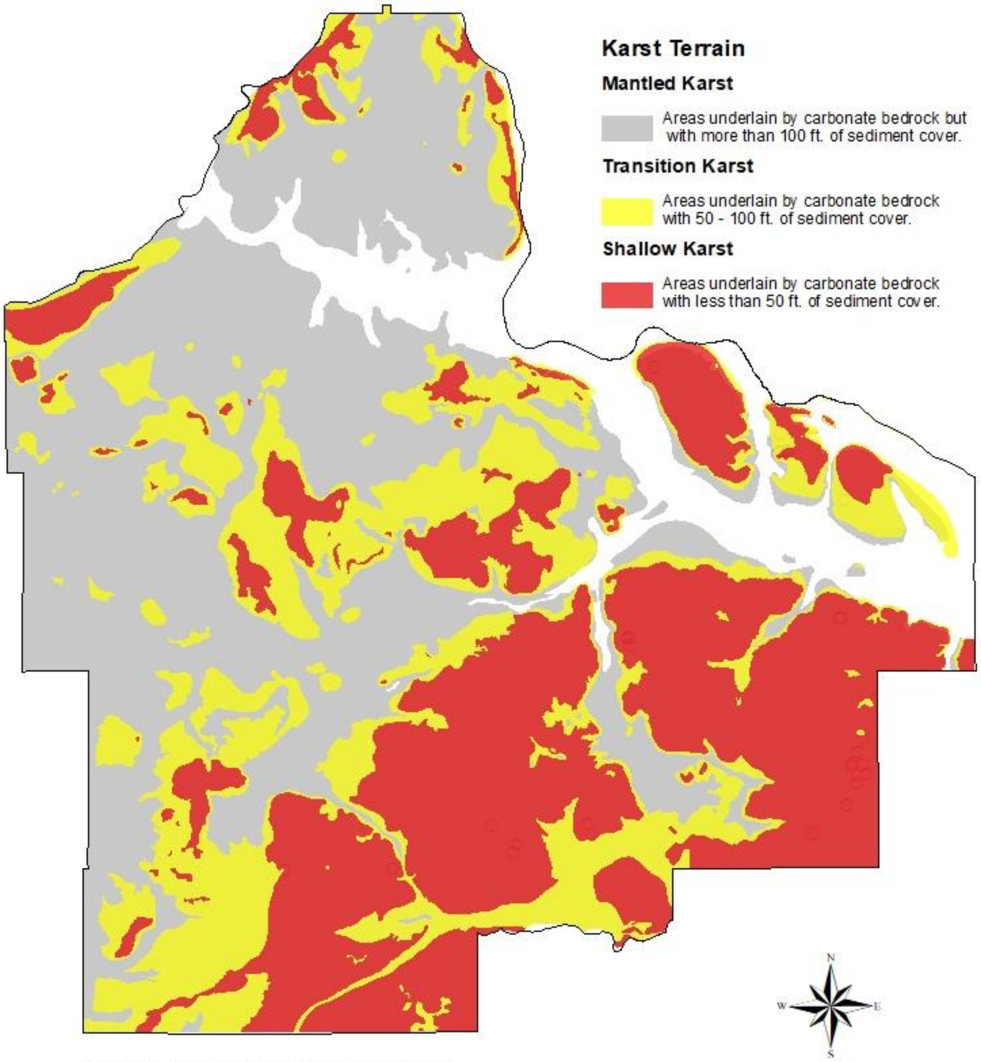
It is not clear from these results whether casing depth or grout is the dominant variable explaining the differences in nitrate and chloride concentrations. Cluster 12 is interesting in that the Ucs well is the shallowest in the cluster and is neat cement grouted; it has higher nitrate and chloride levels than the deeper ungrouted Jordan well. This suggests either, where anthropogenic chemicals are present at the ground surface, well casing depth is more indicative than grout of whether those chemicals will be detected in the well water or there is no sources in the infiltration area to this well. In addition, grouting practices are not uniform among well contractors and self-reported grouting data may not be accurate. For grout, the relatively small sample size within aquifers may allow these inaccuracies to be overrepresented.

The difference in findings regarding grout compared to ungrouted wells suggests one possible explanation regarding grout effectiveness. Where shallow groundwater contains nitrate but deeper groundwater does not, grouting may provide protection to a deep well by preventing the annular space of the deep well from acting as a conduit for shallow contaminated water to travel vertically to the deeper aquifer. However, properly installed grout is only effective at reducing the entry of surface water or shallow groundwater into deeper aquifers. Once an aquifer is contaminated to the depth that the specific well draws water from, the presence of grout is no longer relevant. For example, where deep groundwater already contains elevated nitrate, grouting will not prevent the nitrate-contaminated water from entering a deep well. Nonetheless, grouting wells does help to impede the movement of nitrate from shallow to deeper aquifers.

### iv. Chloride and nitrate in karsted areas

The widespread presence of karst contributes to Dakota County's geologic sensitivity, as described above in the section on Dakota County geology. The Opdc contains karst features such as fractures, sinkholes, solution channels and fissures where the top of the Opdc is closer to the surface and is covered with coarse-textured soils. These soils tend to be excessively drained and irrigation is widely used in karst areas in the County. Karst features provide conduits that can quickly transport surface water to the groundwater and water wells.

In the County, 66 percent of all cropland and 82 percent of the irrigated cropland is in karst areas. Figure 66 indicates the mapped location of sinkholes on a base map indicating three different karst conditions; mantled karst (carbonate rock with more than 100 feet of sediment cover), transition karst (carbonate rock with 50 to 100 feet of sediment cover) and shallow karst (carbonate rock with less than 50 feet of sediment cover).



Source: E. Calvn Alexander Jr. and Yongli Gao,
Minnesota Geologic Survey, 2001

**Figure 66. Dakota County Karst Lands.**
**(Source: Gao et al., 2002)**

Sixteen of the 28 Ambient Study Opdc wells are in karst areas. The karst versus non-karst wells were examined to see if two major anthropogenic parameters, nitrate and chloride, differ for the two situations. Both average nitrate (Mann-Whitney, $p < 0.05$) and average chloride (Mann-Whitney, $p < 0.05$) are higher in karst settings than in non-karst. These results suggest that karst is a factor relating to higher levels of these ions. However, because the County's karst is generally in areas with coarse-textured soils and irrigated agricultural land use, it is difficult to separate the effects of these different conditions on water quality.

### 4.3.8. Age of Water from Select Anthropogenic Parameters, Analysis in 2013

In general, when anthropogenic chemicals are applied to the land surface, some amount will be held up in the soil and some infiltrate past plant roots and into the aquifers. If the amount is large enough to be detected, then the date that a particular chemical is first detected in a well indicates how old the water in the well might be. Estimating the age of well water in this way is useful because it gives an estimate of when changes in practices at the land surface can produce changes in drinking water quality in similar wells. Fourteen parameters were selected; the analysis is summarized in Table 41. Water in wells is thought to be a mixture of water ages as illustrated in Figure 3 of Appendix H. The analysis below is an exercise to date the water based on anthropogenic compounds detected in the study.

% Significance Column

Kendall correlation between the median parameter concentration and well casing depth. All correlations are statistically significant ($p < 0.05$).

Year of Introduction Column

Wells that contain nitrate above, 0.2 mg/L, indicate that the water is younger than 1960 when widespread use of commercial fertilizer began+. When chloride is detected above 3 mg/L and when sodium is detected above 4 mg/L, the water is younger than 1955 when road salt (sodium chloride) began. For specific herbicides, the years in which they were introduced are known, so detections of those herbicides or their breakdown products can be used to estimate dates for a well water sample. For example, the herbicide acetochlor was first registered for use in 1994, so detection of its breakdown products indicated the water is more recent than 1994. As in the case for commercial fertilizer and road salt, the actual amount herbicides used on any given piece of land is not known, it is assumed that some users started applying these commercial products soon after they were introduced. Triazine herbicides were introduced in the late 1950s, while cyanazine and metolachlor were introduced in the early 1970s. Chlorinated herbicides dimethenamid and acetochlor were introduced in the early 1990s.

Statistical Maximum Column

A regression of parameter concentration versus well casing depth was estimated. The Statistical Maximum column lists the depth where the regression line reaches zero concentration (x-axis) and is the depth that the chemical parameter would be expected to reach by the middle of the sampling period, which was year 2006 (2013-1999), this analysis was conducted in 2013.

Calculated Age of Water Column

Dividing the depth in the Statistical Maximum column by the number of years before 2006 a parameter was introduced, results in the Calculated Age of Water value. Example for chloride: 2006 minus 1955 the Year of Introduction equals 51 years.

Calculated Vertical Velocity column

When the specific herbicide or chemical parameter first became widely used, gives an average vertical velocity for the herbicide or ion over the measured depth listed in the Calculated

Vertical Velocity column. Example for chloride: The statistical maximum for chloride of 392 feet divided by 51 years (2006-1955) equals 7.7 feet per year.

**Table 38. Correlation of Select Ions and Herbicides and Casing Depth: Calculated Age of Water and Vertical Velocity for Selected Parameters**

| Parameter | % Significance | Year of Introduction * | Statistical Max Casing Depth | Calculated Age of Water (years) | Calculated Vertical Velocity (ft/year) |
|---|---|---|---|---|---|
| General Chemistry | | | | | |
| Chloride | > 95% | 1955** | 392 | 51 | 7.7 |
| Sodium | > 95% | 1955** | 325 | 51 | 6.4 |
| Nitrate | > 95% | 1960** | 304 | 46 | 6.6 |
| Herbicides | | | | | |
| Deethylatrazine (DEA) | > 95% | 1957 | 240 | 49 | 4.9 |
| Atrazine | > 95% | 1957 | 221 | 49 | 4.3 |
| Alachlor ESA | > 95% | 1969 | 307 | 47 | 8.3 |
| Didealkylatrazine (DDA) | > 95% | 1971 | 238 | 35 | 6.8 |
| Deethylcyanazine acid (DCAC) | > 95% | 1971 | 244 | 35 | 7.0 |
| Cyanazine acid (CAC) | > 95% | 1971 | 169 | 35 | 4.8 |
| Cyanazine amide (CAM) | > 95% | 1971 | 188 | 35 | 5.4 |
| Metolachlor ESA | > 95% | 1974 | 263 | 32 | 8.2 |
| Metolachlor OXA | > 95% | 1974 | 245 | 35 | 7.1 |
| Acetochlor/ Metolachlor ESA 2nd Amide | > 95% | 1994 | 206 | 12 | 17.2 |
| Acetochlor ESA | > 95% | 1994 | 204 | 12 | 17.0 |

*Year used to represent start of widespread use of product.

**Year is an approximation

These results are consistent with the findings regarding aquifers: deeper cased wells tend to have fewer detections, either because the water is entirely older or because younger water is a smaller fraction of the water entering the well, and the chemicals are diluted below MRLs. The calculated vertical flow rates are also consistent with independent estimates of net infiltration rates for the broader TCMA of 8.5 inches/year (with a range of 5–12 depending on yearly precipitation).

The approximate porosity of the overall aquifer media is 10 percent (commonly assumed in groundwater flow models). Thus, 8.5 inches/year corresponds to 0.7 feet/year; at 10 percent porosity, downward movement is around 7 feet/year, a number consistent with the above statistical calculations.

The higher rates for the more recently introduced substances are consistent with the theory that vertical flow rates are a maximum closest to the land surface and decrease with depth. The interpretation of the statistical results for both the anthropogenic substances is consistent with the general physical geology and hydrology of Dakota County.

In 2003, County staff collected samples from 15 private wells, selected to be representative of typical County groundwater conditions, and had them analyzed at the University of Rochester (New York) Laboratory for tritium (an isotope of hydrogen) and helium to estimate the age of the groundwater. The helium-tritium results are discussed in the 1999–2003 Ambient Groundwater Quality Study Report, see www.dakotacounty.us, search *Ambient Groundwater Quality Study*. To summarize, the isotope analysis found a median groundwater age of 20.3 years, results range from older than 1950 to less than one year. However, evaluation of the results indicated that domestic wells are not ideal for this type of isotope analysis, because drinking water wells usually draw from a wide cross-section of the aquifer and therefore contain a mix of ages of water.

## 4.4. Sodium

### 4.4.1. Sodium Sources and Health Concerns

Although sodium is commonly found in soils and rocks, it is often used as an indicator of anthropogenic impacts to shallow groundwater (MPCA, 1999). The most common anthropogenic sources of sodium affecting groundwater are the use of road salt (sodium chloride) for deicing or dust control. Other local or point sources of sodium include water softener discharge to WWTPs or septic systems, salt storage, landfills and feedlots.

There are no health-based drinking water guidelines for sodium, although sodium intake may contribute to hypertension and be a concern for people with heart conditions (MPCA, 1999). The USEPA established a Drinking Water Equivalency Level or guidance level of 20 mg/L for sodium. Reverse osmosis or distillation will reduce 90 to 95 percent of sodium in drinking water.

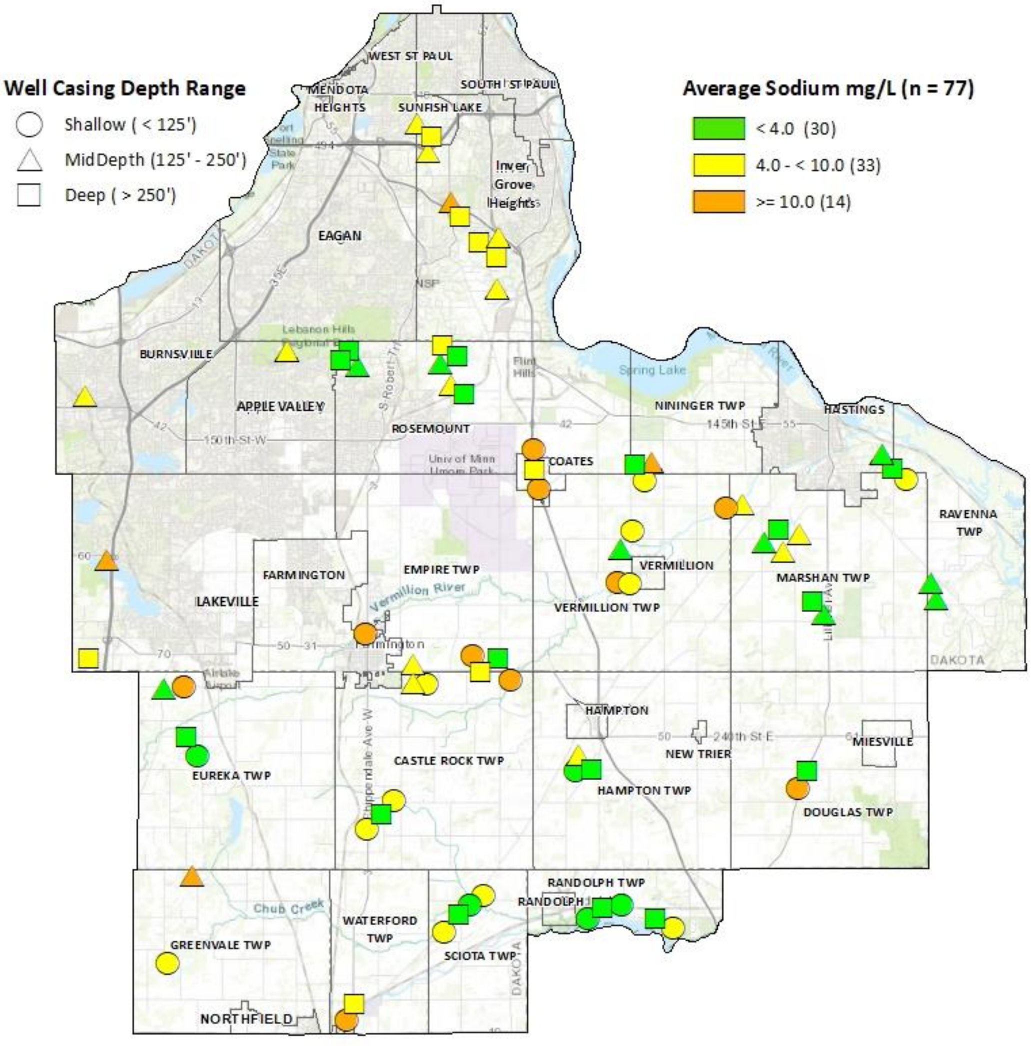
In this report, 4.0 mg/L sodium or lower is considered “background.” For Ambient Study wells with chloride below 3.0 mg/L and nitrate below 0.2 mg/L (below laboratory detection) and presumably free from anthropogenic impacts, the average sodium level has a range of 2–4 mg/L. When chloride is equal to or above 3.0 mg/L, the average (mean) sodium levels range 4–6 mg/L.

### 4.4.2. Sodium Results

Sodium levels over the study period of 1999–2013 range from a low of 0.5 mg/L to a high of 91.5 mg/L. All the sodium results by well and year are summarized in Appendix B Table B.22. Comparison of the sodium results by well casing categories, summarized in Table 42 show that sodium decreased with well casing depth from an average of 14.1 mg/L in the shallow well casing category to 3.8 mg/L in the deep well casing category; this is the same pattern for chloride and nitrate.

**Table 39. Descriptive Statistics of Average Sodium Results (mg/L) by Well Casing Depth Category (ft).**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26 | 14.1 | 17.1 | 2.3 | 4.4 | 7.8 | 19.3 | 83.9 |
| Mid 125' to 250' | 26 | 6.4 | 5.8 | 2.1 | 3.2 | 4.2 | 6.0 | 26.1 |
| Deep >250' | 25 | 3.8 | 1.5 | 1.8 | 2.6 | 3.1 | 4.6 | 7.9 |



Sources: ESRI; Dakota County Environmental Resources

**Figure 67. Average Sodium by Well Casing Depth.**

Figure 68 plots the average sodium results by well casing depth; the correlation is statistically significant (Kendall, p <0.05), and the line shows that sodium decreases with well casing depth.

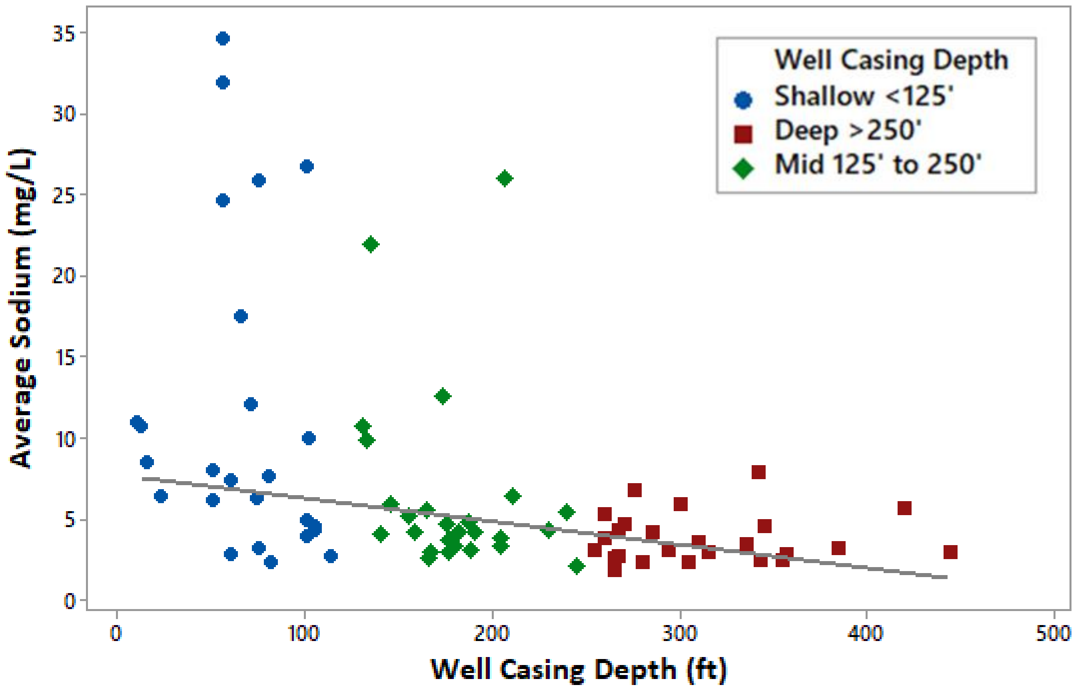


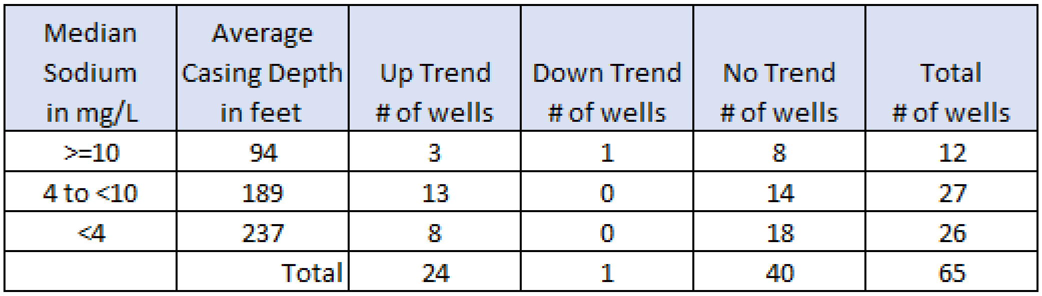
**Figure 68. Correlation of Average Sodium by Well Casing Depth—Kendall Line.**

The data point for the highest average sodium of 83.25 mg/L was removed from the graph for improved readability. This well is AGQS-66 is in the shallow well casing category with a well casing of 75 feet deep.

### 4.4.3. Sodium Trends

Sodium trends per well are listed in Appendix B Table B.22. and are summarized by average well casing depth in Table 44. The median sodium was divided into three categories: less than 4 mg/L, greater than 4 mg/L and less than 10 mg/L, and greater than 10 mg/L. The wells without trends are in the steady-state with the sodium sources on the surface. Twelve wells were sampled less than five times, so valid trend analysis could not be performed. Thirty-four percent (24 wells) have an upward trend compared to 43 percent (28 wells) have an upward trend for chloride. Well AGQS-67 is the one well with a downward trend, and it has a downward trend for chloride. Sixty-two percent (40 wells) have no trend for sodium compared to 57 percent (40 wells) have no trend for chloride. The average sodium decreases as the well casing depth gets deeper. Forty percent (26 wells) have less than 4.0 mg/L of sodium compared to 29 percent (20 wells) with chloride detected less than 3.0 mg/L. Whereas, 37 percent (24) of wells have an upward trend for sodium and 40 percent (28) have upward trends for chloride.

**Table 40. Trends by Median Sodium Concentration and Average Well Casing Depth.**



| Median Sodium in mg/L | Average Casing Depth in feet | Up Trend # of wells | Down Trend # of wells | No Trend # of wells | Total # of wells |
|---|---|---|---|---|---|
| >=10 | 94 | 3 | 1 | 8 | 12 |
| 4 to <10 | 189 | 13 | 0 | 14 | 27 |
| <4 | 237 | 8 | 0 | 18 | 26 |
|  | Total | 24 | 1 | 40 | 65 |

The sodium-to-chloride correlation slope (molar basis) for sodium compared to chloride is around 0.3, which suggests either more than half of the chloride in Ambient Study wells is not from sodium chloride, or that part of the sodium is not moving through groundwater along with chloride. Either could be the case, since in agricultural settings (without major roads) most of the chloride likely comes from potash, and it is known that sodium is partially held up by cation exchange reactions in soils.

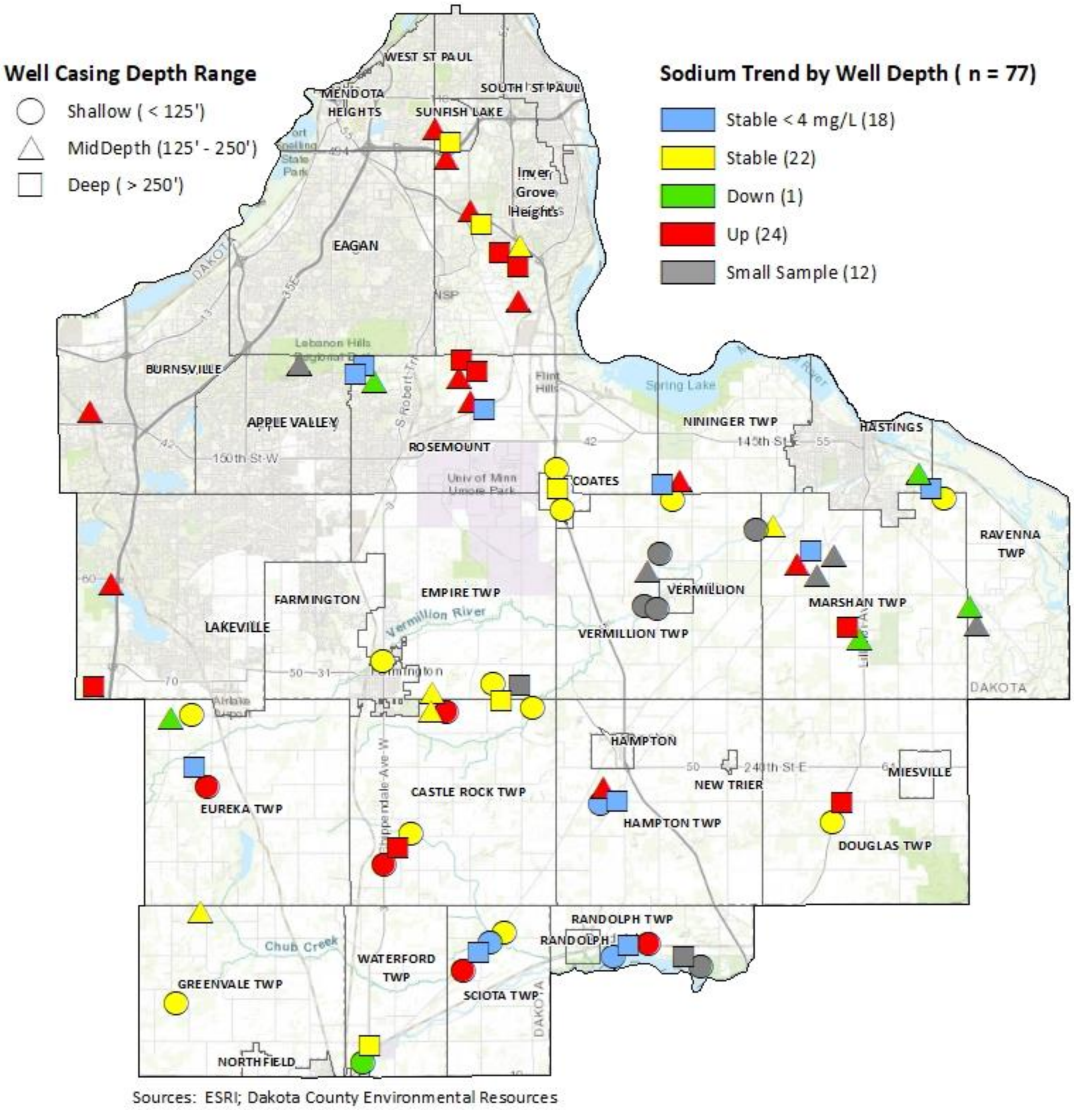


Figure 69. Average Sodium Trends by Well Casing

# 4.5. Sulfate

## 4.5.1. Sulfate Sources and Health Concerns

Sulfate is both a geologically-sourced and anthropogenic chemical in the aquifers in the study. Natural sources of sulfate in the County are the weathering of sulfur from igneous and sedimentary rocks — typically pyrite ($FeS_2$) and gypsum ($CaSO_4$), which dissolve in groundwater and surface water. The sulfur is converted to sulfate when it comes into contact with air. Anthropogenic sources include burning of fossil fuels, processing of metals, mining and wastewater treatment plants discharging sulfur compounds. When fossil fuels combust, the sulfur dioxide emissions react with other chemicals in the atmosphere to form sulfur salts (SOx) that make acid rain. The sulfate in precipitation contributes to increased sulfate levels in surface and groundwater. Sulfate moves readily with water.

At high levels, sulfate is a pollutant for both groundwater and surface waters. Drinking water with 250 mg/L or more of sulfate may taste bitter and cause diarrhea; however, the USEPA does not consider sulfate in drinking water a threat to human health and has assigned sulfate a SMCL of 250 mg/L. MDH recommends that water with a sulfate level exceeding 500 mg/L should not be used in preparation of infant formula, since infants may be more sensitive to sulfate than adults (MDH Sulfate, 2019). Sulfate can be removed from drinking water; an MDH Factsheet on home water treatment options is provided in Appendix E.1.

### 4.5.2. Sulfate Results

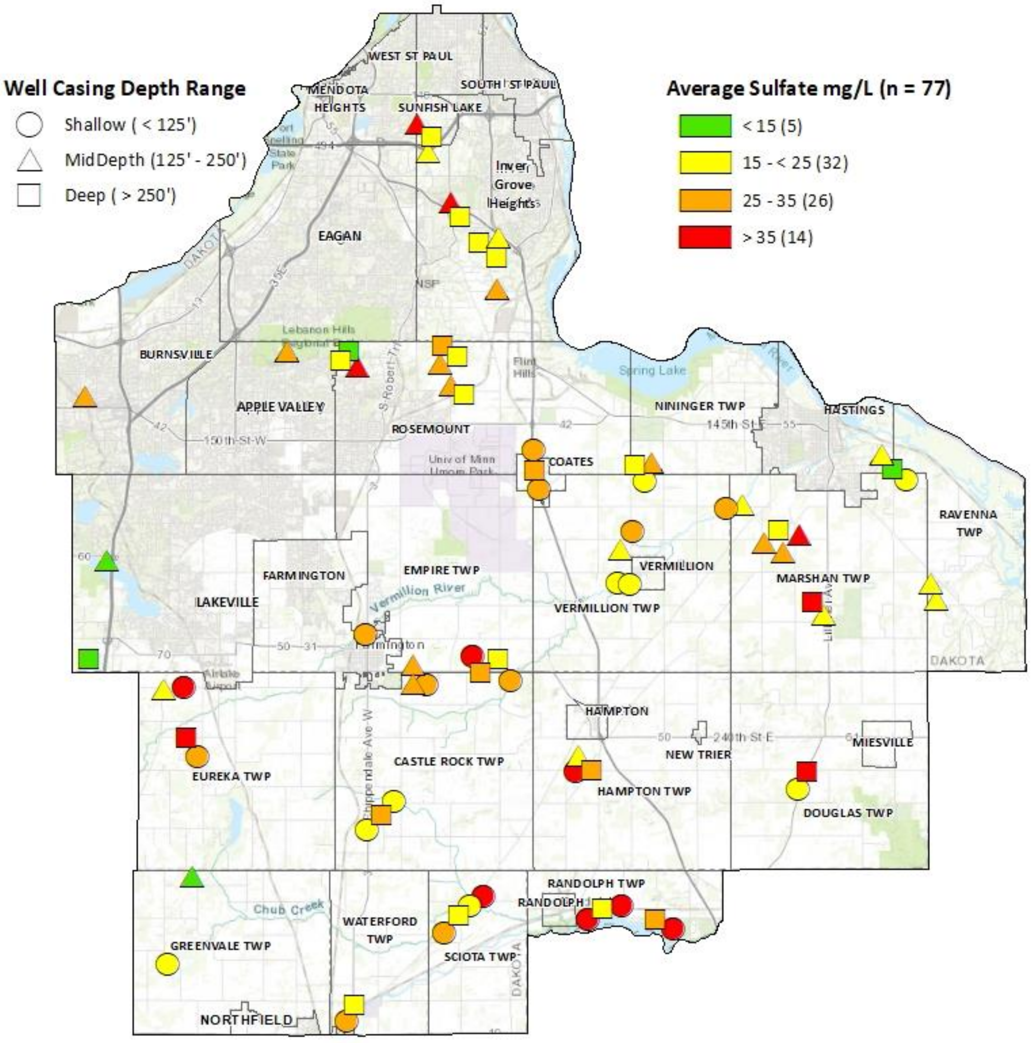
Sulfate levels over the study period of 1999–2019 range from a low of 3.98 mg/L to a high of 75.1 mg/L. All sulfate results by well and year are summarized in Appendix B Table B.24. A comparison of average sulfate results by well casing categories, summarized in Table 44, show average sulfate is similar in all casing categories and both median and average sulfate is highest in the middle well casing depth category.

**Table 41. Descriptive Statistics of Average Sulfate Results (mg/L) by Well Casing Depth Category.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26 | 26.8 | 11.6 | 10.4 | 18.0 | 23.6 | 31.4 | 63.7 |
| Mid 125' to 250' | 26 | 27.9 | 6.9 | 15.8 | 22.6 | 27.3 | 31.9 | 41.6 |
| Deep >250' | 25 | 25.4 | 11.3 | 6.7 | 16.9 | 24.1 | 32.8 | 49.0 |

Some natural sulfate from the weathering of minerals such as pyrite, appears to be in the County’s groundwater, since all median sulfate levels were above the MRL of 4.0 mg/L. Some, or perhaps most of the sulfate now measured in water extracted from the study wells may have originated as atmospheric deposition of SOx from fossil fuel combustion. Such SOx emissions had been increasing in Midwestern US until the Clean Air Act of 1970, with decreasing atmospheric loading since the 1970s. Atmospheric deposition still occurs, but it is much lower than in the period preceding the 1970s.

Figure 70 shows widespread geographic and vertical distribution ( in all casing categories) of the elevated average sulfate results by well casing depth.



Sources: ESRI; Dakota County Environmental Resources

Figure 70. Average Sulfate by Well Casing Depth

The graph in Figure 71 plots the average sulfate results by well casing depth; the correlation is statistically significant (Kendall, p <0.01), and the line shows that sulfate decreases with well casing depth. The observed scatter in the data is the result of the source of sulfate derived from both the geologic materials in the aquifer and inputs from the atmospheric deposition of sulfate.

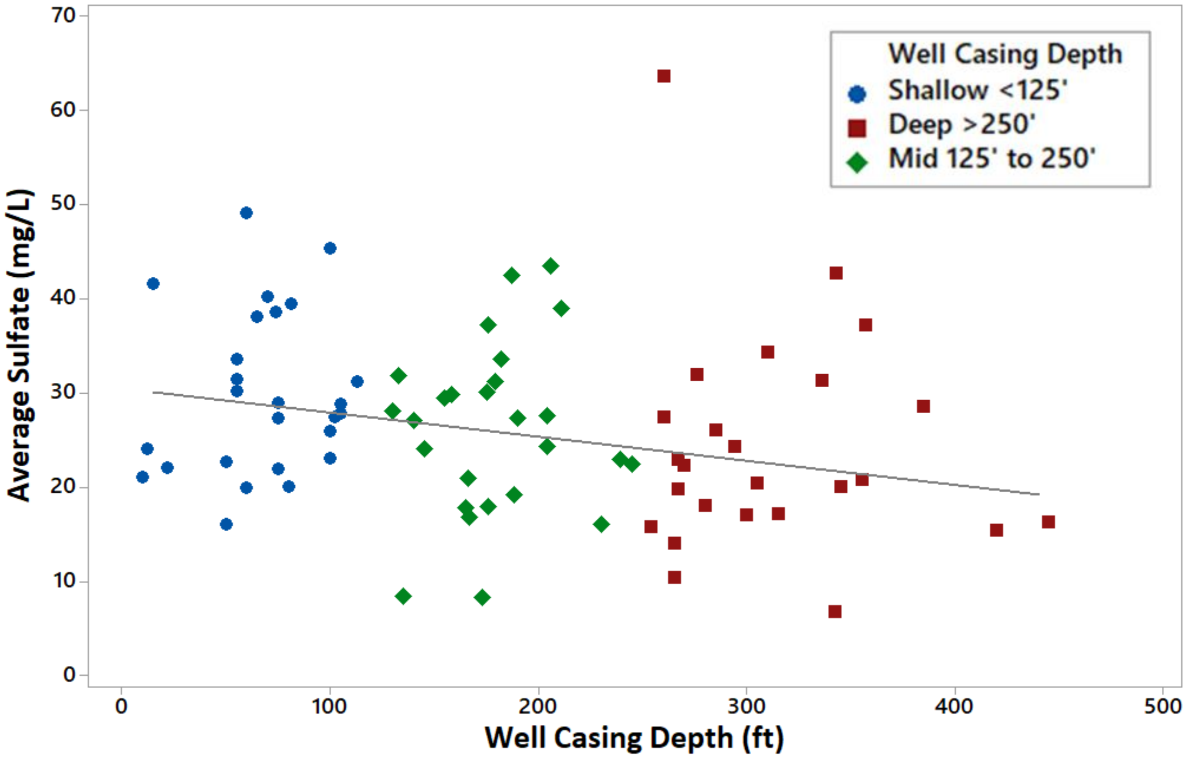


**Figure 71. Correlation of Average Sulfate by Well Casing Depth—Kendall Line.**

### 4.5.3. Sulfate trends

#### i. Trends for sulfate with frequency analysis

Analysis of the frequency with which sulfate was detected at different levels allows the overall results compared from year to year, even though the exact wells used varied somewhat. The data set was filtered to capture the group of wells that have consistently been tested for chloride. Figure 72 shows the 15 sample events where 30 or more wells were sampled and the 61 wells that have been sampled at least nine times were put into three categories:

- Over 25 mg/L
- Between 15 mg/L to 25 mg/L
- Less than 15 mg/L

Table 45 shows the trend frequency pattern for sulfate. Sulfate is above the MRL in all wells. Thus, the sulfate above any natural contribution in wells depends on the age of the water. For wells with water more recent than about 40 years, downward trends might be expected, while an upward pattern would be more likely for 50 to 60-year-old water. Some peaking would be in the middle of the age distribution: wells with average sulfate over 25 mg/L. The relative rate of increase for sulfate greater than 25 mg/L is about 1.5 percent until the peak in about 2007 and 2008. Table 45 and Figure 72 shows that, in 2019, sulfate returned to the 1999 levels across the data set.

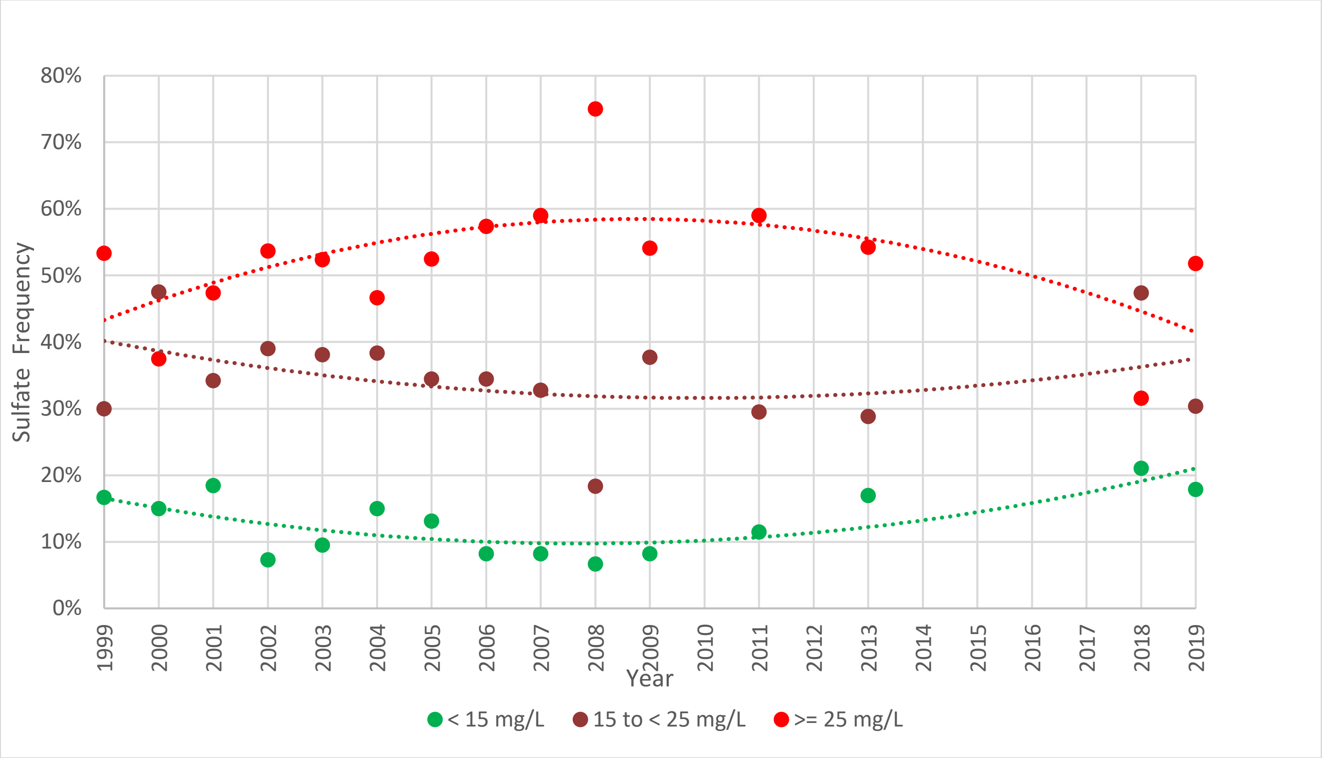


**Figure 72. Sulfate Concentration Frequency by Year.**

**Table 42. Sulfate Frequency by Year and Concentration Category**

| Sulfate Category | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 | 2006 | 2007 | 2008 | 2009 | 2011 | 2013 | 2018 | 2019 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| < 15 mg/L | 17% | 15% | 18% | 7% | 10% | 15% | 13% | 8% | 8% | 7% | 8% | 11% | 17% | 21% | 18% |
| 15 to < 25 mg/L | 30% | 48% | 34% | 39% | 38% | 38% | 34% | 34% | 33% | 18% | 38% | 30% | 29% | 47% | 30% |
| >= 25 mg/L | 53% | 38% | 47% | 54% | 52% | 47% | 52% | 57% | 59% | 75% | 54% | 59% | 54% | 32% | 52% |

### ii. Trends for sulfate and well casing depth

Like nitrate and chloride, sulfate has many upward trends. Sulfate trend patterns are listed by well in Appendix B Table B.24. and are summarized by average well casing depth in Table 46. The median sulfate was divided into four categories: less than 15 mg/L, between 15 mg/L and 25 mg/L, between 25 mg/L and 35 mg/L, and over 35 mg/L. Eleven wells were sampled less than five times, so valid trend analysis could not be performed. The average well casing is shallowest (162 feet) in the highest median sulfate concentration category, over 35 mg/L, and deepest (236 feet) where sulfate is less than 15 mg/L. Sulfate trends differ from the nitrate and chloride trend patterns in that sulfate has 10 wells over the past 20 years of the study in which the sulfate levels increased (peaked) and then began declining. The approximate year that the decline began is listed in Appendix B Table B.24. next to the label of “Peaked” in the Trend column. There were more wells with either a downward trend (7) or having peaked (10), totaling 17 wells, than wells with an upward trend (14).

**Table 43. Trends by Median Sulfate Concentration and Average Well Casing Depth.**

| Average Sulfate in mg/L | Average Casing Depth in feet | Up Trend # of wells | Down Trend # of wells | Peaked # of wells | No Trend # of wells | Total # of wells |
|---|---|---|---|---|---|---|
| >= 35 | 162 | 3 | 0 | 4 | 5 | 12 |
| 25 to <35 | 167 | 5 | 3 | 4 | 10 | 22 |
| 15 to <25 | 214 | 4 | 3 | 2 | 18 | 27 |
| <15 | 236 | 2 | 1 | 0 | 2 | 5 |
|  | Total | 14 | 7 | 10 | 35 | 66 |

Since sulfate in precipitation has been decreasing since the Clean Air Act of 1970 and sulfate associated with leaching in soils has been decreasing in recent years due to crop removal, farmers need to apply sulfur containing fertilizers because the amount of free sulfur from precipitation is decreasing. Natural sulfur containing substances (e.g., pyrites) in glacial till and/or sedimentary rocks may be experiencing more rapid weathering in the presence of increased salt and nitrate loading from anthropogenic sources (Kaushal, et.al.). This would be reflected in increases in sulfate in shallower aquifers and shallow well casing depth wells in decades since about 1970. The anthropogenic weathering process has been identified to explain observed changes in stream water chemistry throughout the US over the last few decades. Anthropogenic-induced weathering changes the salinity and alkalinity in subject waters (Kaushal, et.al.), and the same underlying process seem likely to be at play in Minnesota groundwater.

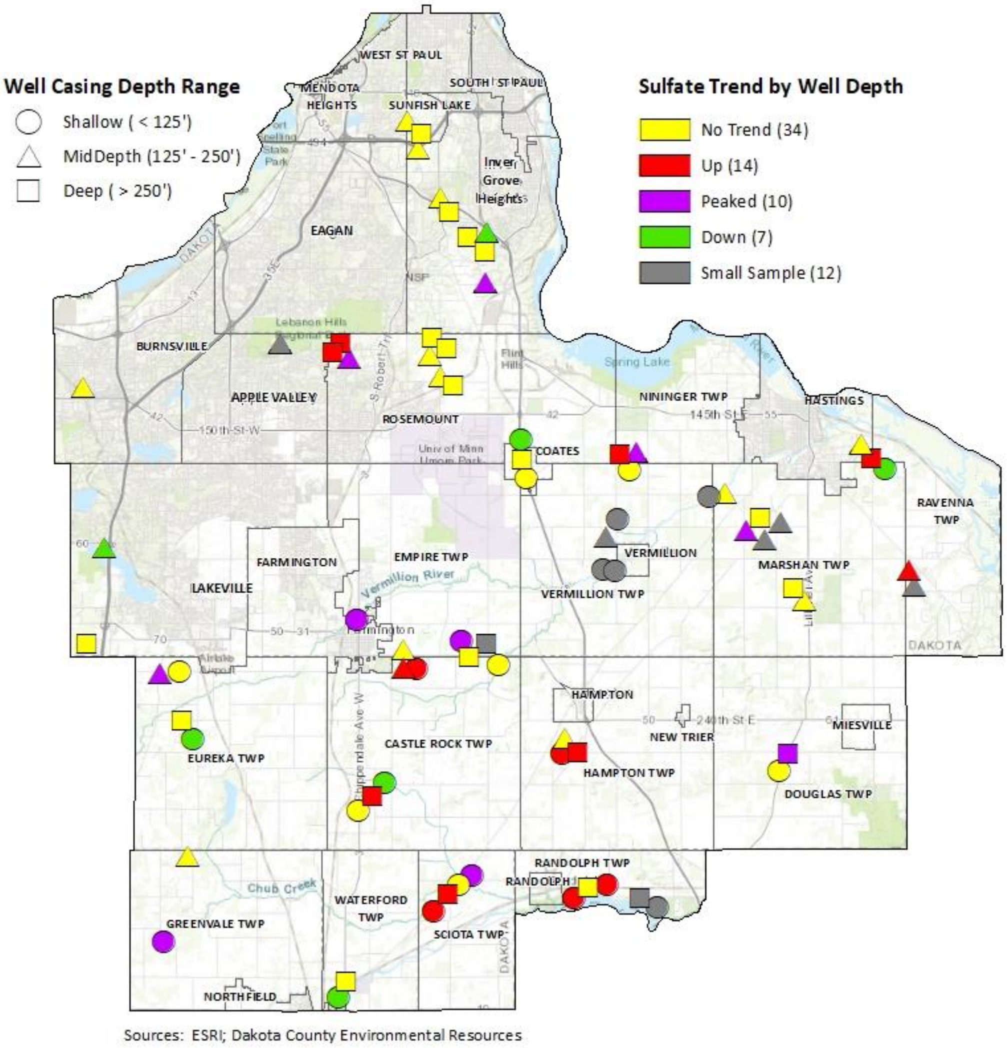


Figure 73. Sulfate Trends by Well Casing Depth.

## 4.6. Ammonium Nitrogen – Sources and Results

Ammonium is part the nitrogen cycle. Ammonia quickly converts to ammonium in the soil, which binds to soil particles. Ammonia and ammonium fertilizers are the most commonly used. Feedlots can also be a source of ammonium. It is likely to be a surface water contaminant and not usually found in groundwater, however, ammonium was detected in 23 of the 72 study wells that were tested. Results range from the MRL of 0.02 mg/L to 2.0 mg/L. The highest result of 2.0 mg/L is from AGQS-31 in 2008 and the corresponding nitrite and nitrate were 0.2 mg/L. This well is completed in the Ucs in the middle well casing category located in Lakeville. There is no drinking water guideline for ammonium nitrogen. Ammonia can be removed from drinking water; an MDH Factsheet on home water treatment options is provided in Appendix E.1. It is assumed that the same methods would reduce ammonium nitrogen.

Ammonium Nitrogen is negatively correlated (Kendall, $p < 0.05$) with the percent of land in agricultural use and positively correlated with well casing depth (Kendall, $p < 0.05$). Correlations with selected parameters are summarized in Table 47.

**Table 44. Average Ammonium nitrogen Correlations with Select Chemical.**

| Ammonium Nitrate Correlations | Direction | P Value* |
|---|---|---|
| Nitrite | N/A | 0.21 |
| Nitrate | N/A | 0.98 |
| Dissolved Oxygen | N/A | 0.43 |
| Percent of Land in Row Crop Ag | Decreasing | <0.05 |
| Well Casing Depth | Increasing | <0.05 |

*Kendall nonparametric correlation

A comparison of the ammonium nitrogen results by well casing categories is summarized in Table 48. The elevated ammonium nitrogen in AGQS-31 is evident in the high average in the middle well casing category where the maximum ammonium nitrogen is 1.93 mg/L.

**Table 45. Descriptive Statistics of Average Ammonium Nitrogen Results (mg/L) by Well Casing Depth.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 24 | 0.03 | 0.05 | <0.02 | <0.02 | <0.02 | 0.02 | 0.23 |
| Mid 125' to 250' | 23 | 0.13 | 0.40 | <0.02 | <0.02 | <0.02 | 0.06 | 1.93 |
| Deep >250' | 25 | 0.06 | 0.09 | <0.02 | <0.02 | <0.02 | 0.06 | 0.38 |

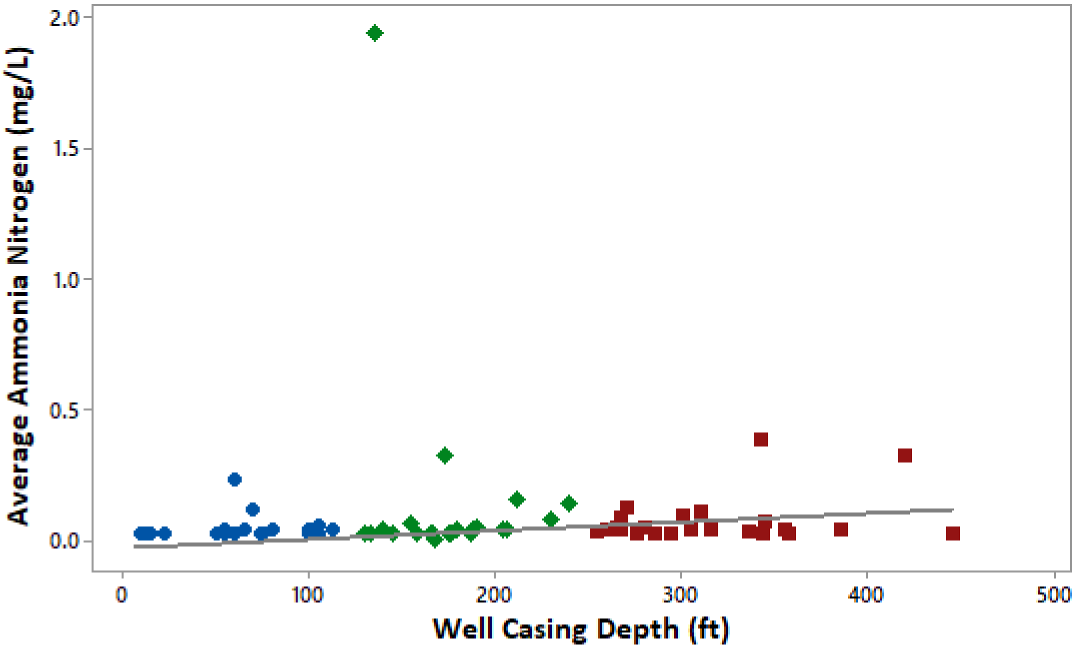


**Figure 74. Correlation of Average Ammonium Nitrogen by Well Casing Depth.**

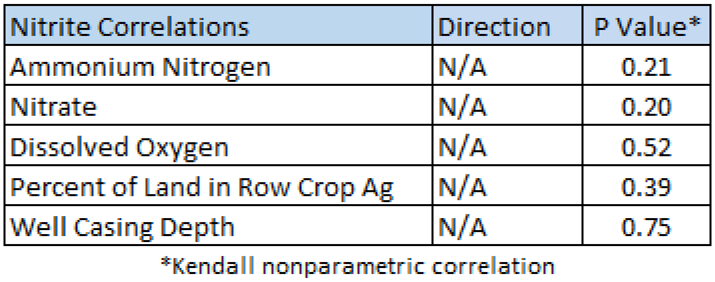
## 4.7. Nitrite – Sources and Results

Nitrite is part of the nitrogen cycle and is an intermediate product in the conversion of ammonium to nitrate in the soil. When detected in groundwater, nitrite may indicate a recent source that may be nitrogen fertilizer, denitrification, animal or manure waste or septic system effluent. Nitrite can occur naturally in food such as vegetables or added preservative in the form of sodium nitrite to cure meats. The drinking water guideline is 1 mg/L for infants 6 months and younger that consume the water because they are at risk for developing methemoglobinemia or “blue baby syndrome.” Nitrite can be removed from drinking water; an MDH Factsheet on home water treatment options is provided in Appendix E.1.

The 77 Ambient Study wells have been tested for nitrite in 13 sampling events since 1999. All the nitrite results by well and year are summarized in Appendix B Table B.18. The results range from non-detect (less than the lowest MRL of 0.1 mg/L) to a maximum detect of 0.52 mg/L which is more than half the drinking water guideline of 1.0 mg/L. This was detected in AGQS-25, a Jordan well in the deep well casing category, located in Eureka Township. Nitrite has been detected at least once above the MRL in 44 percent of the wells (34 wells). The data for statistical analysis censored and excluded the data from 1999, 2011 and 2013 where the MRL was 0.5 mg/L, 0.3 mg/L, and 0.3 mg/L, respectively.

There are no significant correlations between average nitrite results and any of the selected parameters summarized in Table 49.

**Table 46. Correlations of Average Nitrite with select chemical.**



| Nitrite Correlations | Direction | P Value* |
|---|---|---|
| Ammonium Nitrogen | N/A | 0.21 |
| Nitrate | N/A | 0.20 |
| Dissolved Oxygen | N/A | 0.52 |
| Percent of Land in Row Crop Ag | N/A | 0.39 |
| Well Casing Depth | N/A | 0.75 |

*Kendall nonparametric correlation

Comparison of the nitrite results by well casing categories summarized in Table 50. The elevated nitrite in AGQS-25 affected the average, median and maximum nitrite levels which are the highest in the deep well casing category and evident in Figure 75 depicted as the well in the deep well category with average of 0.213 mg/L.

**Table 47. Descriptive Statistics of Average Nitrite Results (mg/L) by Well Casing Depth Category.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26 | 0.049 | 0.027 | <0.01 | 0.026 | 0.033 | 0.069 | 0.100 |
| Mid 125' to 250' | 26 | 0.044 | 0.026 | <0.01 | 0.020 | 0.033 | 0.067 | 0.100 |
| Deep >250' | 25 | 0.058 | 0.040 | <0.01 | 0.026 | 0.066 | 0.069 | 0.213 |

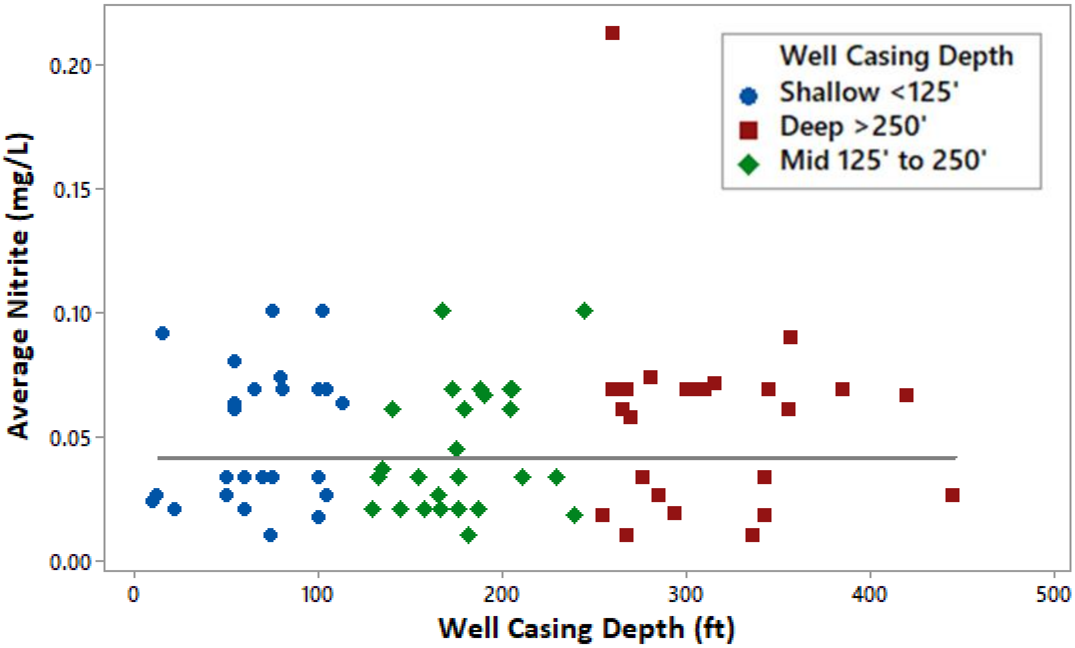
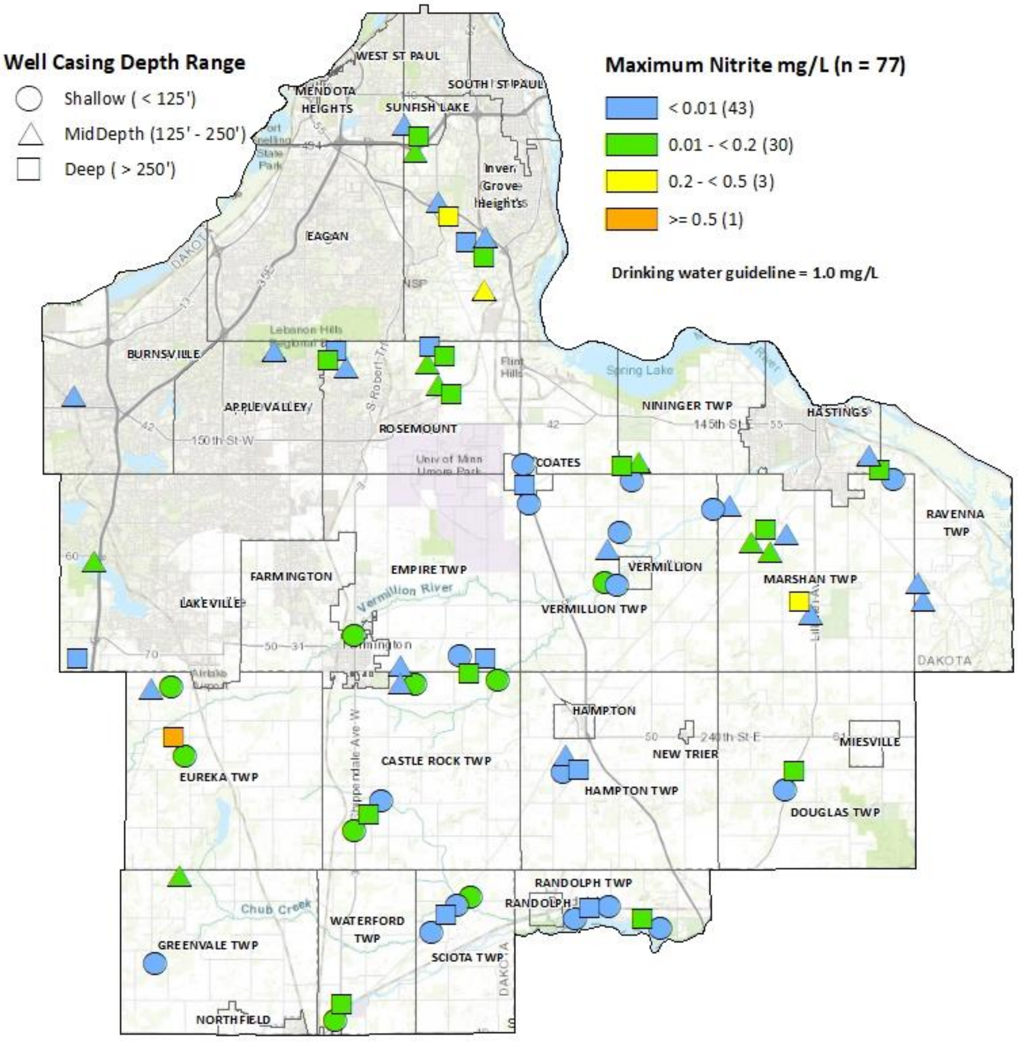


**Figure 75. Correlation of Average Nitrite by Well Casing Depth – Kendall Line.**

Figure 76 depicts average nitrite by well casing depth category. There is no spatial pattern to wells with nitrite detected above the MRL. They occur in both rural residential and row crop agricultural areas.



Sources: ESRI; Dakota County Environmental Resources

**Figure 76. Maximum Nitrite Result by Well Casing Depth.**

## 4.8. Potassium

### 4.8.1. Potassium Sources, Health Concerns and Drinking Water Treatment

Potassium, like sodium, is an important ion for assessing groundwater quality and identifying groundwater sources (MPCA, 1999). Potassium is commonly found in soils and rocks and is released slowly by the dissolution of rock materials. It is a primary plant nutrient (along with nitrogen and phosphorus). Although potash fertilizer (predominantly potassium chloride and potassium carbonate) is widely applied to cropland, the potassium is general removed with the crops or is retained in the soil rather than leaching into groundwater. There are no negative health effects associated with potassium in drinking water and therefore no drinking water guidelines. Distillation may reduce potassium concentrations in water.

### 4.8.2. Potassium Results

Potassium results from 1999 to 2008 are summarized in Appendix B Table B.20. Potassium ranges from 1.0 to 5.0 mg/L for all study wells except for AGQS-57, whose results ranged from 4.19 mg/L in 2006 to 24 mg/L in 2008. For comparison, an MDH survey of domestic wells in southeast Minnesota reported median potassium concentrations of 1.14 mg/L and a maximum concentration of 15.40 mg/L (MDH, 2016, p. 28). The elevated potassium in one Ambient Study well could be related to historical burning of wood, leaves or garbage in the well's infiltration area. Statistical analysis found that potassium is not correlated with well casing depth, aquifer, agricultural land use, chloride or sodium in study wells.

## 4.9. Contaminants of Emerging Concern

"Contaminants of emerging concern" describes pollutants that have been detected in groundwater or surface water that may cause ecological or human health impacts and that typically are not regulated under current environmental laws (Wikipedia). Some examples are perfluoroalkyl substances (PFAS or "3M" chemicals), manganese which occurs naturally but whose health risks have only recently been understood (Section 5.1.1.), organic wastewater compounds or pharmaceutical compounds.

### 4.9.1. Per- and Polyfluoroalkyl Substances (PFAS)

#### i. PFAS sources, health concerns and drinking water treatment

PFAS chemicals, formally known as perfluorochemicals (PFCs), were introduced in the 1940s for their ability to repel oils, stains, grease, heat and water in products such as stain-resistant carpet and fabrics (Scotchgard™), nonstick cookware (Teflon™), coatings on some food packaging, fire-fighting foam and other applications. Thousands of PFAS have been manufactured.

**Water Treatment**
Testing for PFAS is expensive and is not easily accessible to private well owners. Either a carbon filter or reverse osmosis system are recommended to reduce PFAS levels in drinking water. The NSF lists 76 water treatment devices certified to reduce PFOA and PFOS to below 70 ng/L. Read more information from MDH about PFAS at https://www.health.state.mn.us/communities/environment/hazardous/topics/pfcs.html.

3M produced PFAS since the 1950s at the 3M Chemolite Plant in Cottage Grove, Minnesota, located north across the Mississippi River from Dakota County. The plant treats its wastewater and discharges it to the Mississippi River. The stretch of the Mississippi River below the facility is listed as "impaired" under the federal Clean Water Act due to the presence of perfluorooctane sulfonate (PFOS) in the tissue of fish. Until 2011, there were no limits on the level of PFOS in discharges from the 3M facility wastewater treatment plant. Historically, disposal of the treatment plant sludge occurred both onsite in a sludge disposal area and in disposal sites in Washington County (MDH, 2010). The sludge is currently incinerated and disposed of in an approved industrial landfill. Incineration may or may not destroy PFAS compounds.

3M ceased production of perfluoro-n-butyric acid (PFBA) in 1998 and phased out manufacturing of eight-carbon PFAS including PFOS and PFOA in 2002. 3M continues to produce perfluorobutane sulfonate (PFBS), a four-carbon chain that can breakdown to PFOS in the environment and produces one- to three-carbon PFAS at the Cottage Grove facility (3M, 2010a).

PFAS are stable compounds, resistant to breakdown, and found in soil, surface water, groundwater, air, precipitation, humans and animals. The compounds can accumulate in the body and may have adverse health outcomes. Studies on two prevalent PFAS compounds, PFOS and perfluorooctanoic acid (PFOA), found reproductive and developmental, liver and kidney, and immunological effects and tumors in lab animals (EPA, PFAS). Increased cholesterol levels are the most consistent finding, and less consistent is low infant birth weights, immune system effects, cancer (PFOA exposure) and thyroid disruption (PFOS exposure) (EPA, PFAS).

### ii. PFAS results

In 2008, PFBA was detected in 25 of 64 study wells that were sampled by MVTL and analyzed by the MDH Laboratory for a list of seven PFAS chemicals (Appendix A Table A.5.- methods). Results were reported by the laboratory as estimated, when detected below MRL of 300 ng/L (nanograms per liter equivalent for parts per trillion) and above the method detection level of 50 ng/L. The PFBA results ranged from 50 ng/L to 500 ng/L, all below the 2008 drinking water guideline of 7000 ng/L. Results are listed by well in Appendix B Table B.29.

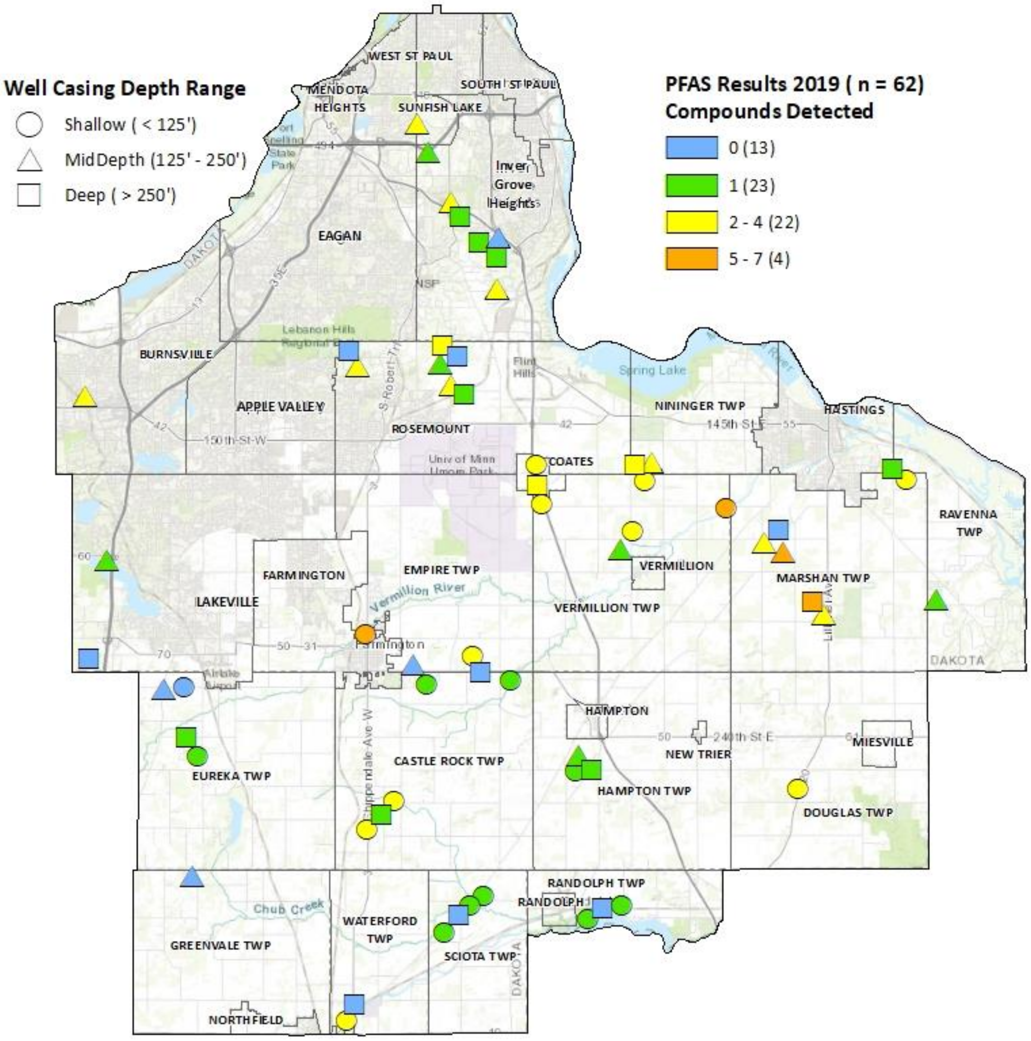
In 2018, 46 study wells, excluding the deeper wells in the Cjdn Aquifer, were analyzed for 21 PFAS, with lower detection levels than were available during the 2008 sampling event (Appendix A Table A.9.- methods). In 2019, 17 wells were tested for 32 PFAS -Appendix A Table A.10.-methods): 16 wells were in the Cjdn and one in the Ucs, well AGQS-20. AGQS-20 was previously tested in the 2018, it had the most PFAS compounds detected, seven. This well was resampled and tested in 2019, the average results from the two sample events is reported in the table. The results were consistent, the well had the same seven PFAS detected in both years and two different labs were used in each year. All of the results, by well, from the 2008, 2018 and 2019 sample events are combined in Appendix B Table B.29.

Fifty-four of the study wells were tested in both 2008 and 2018–2019. Twenty wells had PFBA detected in both sample events, and 23 had PFBA detected in the 2018–2019 that were not detected in the 2008 sample event. The same well, AGQS-55, had the highest PFBA level in both sample events: 500 ng/L in 2008 and 280 ng/L in 2018.

Eight different PFAS chemicals were detected, with PFBA as the most frequently detected compound, found in 79 percent of the tested wells. MDH has established drinking water guidelines for five of the eight PFAS chemicals detected, and none of the well results exceeded the guidelines. Detections are summarized in Table 51 and Figure 77 depicts the study wells by number of different compounds detected. Appendix G contains maps of the eight individual compounds detected.

## Table 48. Descriptive Statistics of 2018-2019 PFAS Detections (ng/L) from Ambient Study Wells.

| PFAS Compounds | PFBA | PFPeA | PFOA | PFHxS | PFHxA | PFOS | PFBS | PFHpA |
|---|---|---|---|---|---|---|---|---|
| % Detects | 79% | 34% | 24% | 19% | 10% | 8% | 2% | 2% |
| # of Detects | 49 | 21 | 15 | 12 | 6 | 5 | 1 | 1 |
| Minimum | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Maximum | 280 | 8 | 6 | 12 | 6 | 5 | 4 | 3 |
| Average | 67.1 | 4.0 | 3.5 | 3.9 | 3.2 | 3.7 | 4.3 | 3.1 |
| Median | 48.0 | 3.7 | 3.5 | 3.2 | 2.5 | 3.5 | 4.3 | 3.1 |
| Drinking Water Guideline | 7000 | None | 35 | 47 | None | 15 | 2000 | None |
| Year Guideline Established | 2011 HRL | -- | 2018 HRL | 2019 HBV | -- | 2019 HBV | 2017 HBV | -- |



Sources: ESRI; Dakota County Environmental Resources

Figure 77. Number of PFAS Detections by Well Casing Depth.

### iii. PFAS and well casing depth

The negative correlation between casing depth and select PFAS are statistically significant: PFBA is (Kendall, p <0.05), PFHxS (Kendall, p <0.05), and PFPeA (Kendall, p <1.0). Table 53 summarizes PFBA compared with well casing depth. PFBA is the most detected PFAS with 49 detections as compared to the next highest number of 21 detections of PFPeA.

**Table 49. Descriptive Statistics of 2018-2019 PFBA Results (ng/L) by Well Casing Depth.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 22 | 54.4 | 64.7 | 2 | 13 | 29 | 71.8 | 280 |
| Mid 125' to 250' | 20 | 74.5 | 61.3 | 2 | 6.5 | 84 | 120 | 200 |
| Deep >250' | 20 | 31.1 | 49 | 1 | 1 | 6.2 | 47.5 | 170 |

All three casing depth categories are impacted by PFBA; average PFBA decreases with depth, and median and average PFBA is highest in the middle well casing depth category. The graph in Figure 78 shows that there is a lot of scatter in the data and a slightly decreasing line with depth.

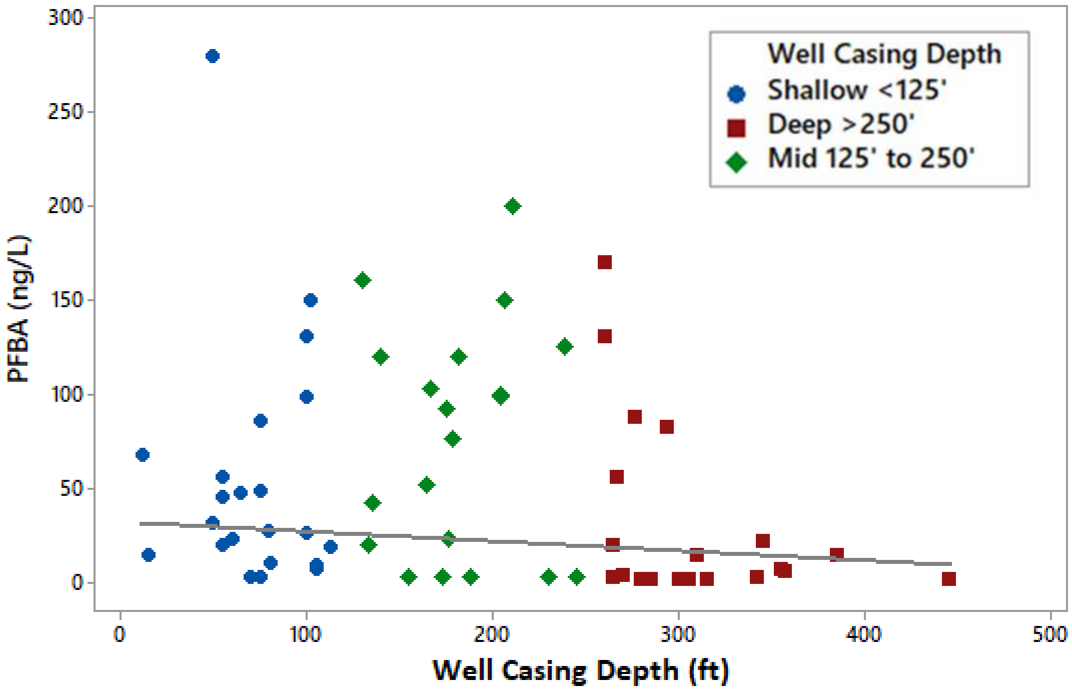


Figure 78. 2018-19 Correlation of PFBA by Well Casing Depth—Kendall Line.

The number of PFAS compounds detected by well by casing depth is summarized in Table 53 where the summary statistics decrease with well casing depth category.

Table 50. Number of PFAS Compounds Detected in 2018-19, by Well Casing Depth.

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 22 | 2.5 | 1.74 | 0 | 1 | 2.5 | 4 | 7 |
| Mid 125' to 250' | 20 | 1.9 | 1.60 | 0 | 1 | 1.5 | 3 | 6 |
| Deep >250' | 20 | 1.0 | 1.19 | 0 | 0 | 1 | 1 | 5 |

Figure 79 shows the negative correlation between number of PFAS and well casing depth that is statistically significant (Kendall, $p < 0.05$).

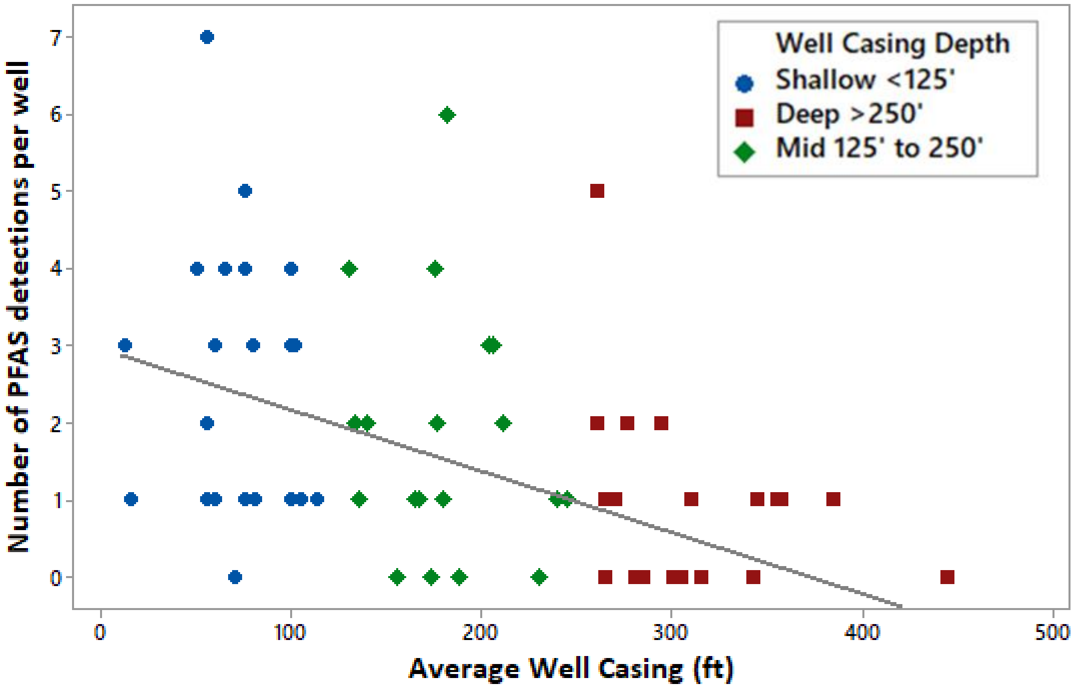


Figure 79. Correlation of Number of PFAS detects by Well Casing Depth—Kendall Line.

PFBA and percent of land use in row crop agriculture by section is not significant (Kendall, $p = 0.21$), but the correlation between the number of PFAS and percent of land use in row crop agriculture by section is >90 percent significant (Kendall $p < 0.10$).

### iv. Statewide PFAS testing by MPCA and MDH

The State of Minnesota's ambient groundwater sampling program, conducted by MPCA, sampled for PFAS statewide in 2013 and limited follow-up sampling in 2017. The statewide results were comparable to what Dakota County found, although PFAS above the drinking water guidelines were found outside of Dakota County. Comparable to what Dakota County found in its sampling, PFBA was the most common PFAS chemical detected statewide, in 70 percent of its wells sampled in 2013. The highest PFBA detection was 1,680 ng/L (below the drinking water guideline of 7000 ng/L), in a domestic well in Washington County. Also, in 2013, PFOA was detected in 30 percent of the wells tested, with the highest detection at 74 ng/L (above the guideline of 34 ng/L) in a domestic well near Wabasha. PFOS was detected in 12 percent of the wells tested, with the highest detections at 98.0 and 98.8 ng/L (above the guideline of 15 ng/L) in two shallow monitoring wells in Anoka and Hennepin counties. PFHxS was detected in about 11 percent of the wells tested, with three wells above the guideline of 47 ng/L: two monitoring wells in the Twin Cities area and one monitoring well near Brainerd. The MPCA noted that PFAS detections were much higher in urban areas than in rural areas. The 2017 sampling event re-sampled wells tested earlier; the PFAS concentrations had decreased markedly. (MPCA, July 2019)

### v. PFAS and WWTPs

PFAS are present in WWTP influent and effluent as well as sewage sludge that has historically been applied to agricultural fields in Dakota County. Twice a year, the Empire WWTP plant spreads biosolids on nearby farm fields on land owned by Metropolitan Council that is leased to local farmers (MCES Empire). There is no complete inventory of sewage sludge land application locations, application rate or source in the County. Dakota County will be sampling private wells near known biosolid application sites in the fall of 2020 for PFAS and other wastewater compounds.

In 2007 and 2009, sample results of the effluent at Flint Hills Resources Refinery in Rosemount found 8 of the 13 PFAS detected in the WWTP effluent. PFOS was detected at 0.057 µg/L, exceeding the drinking water guideline of 0.015 µg/L. This water is discharged to the Mississippi River.

### vi. PFAS testing by MPCA and MDH in Dakota County

#### WASTE DISPOSAL SITES

PFAS are found in disposal sites which can impact the soil and groundwater. As part of its statewide investigation of PFAS, the MPCA sampled the groundwater using existing monitoring wells, effluent at landfills and dumps in the County.

- MPCA tested landfill effluent from the Waste Connection’s Rosemount Landfill and Waste Management’s Pine Bend Landfill in Inver Grove Heights for nine PFAS, eight of which were detected above the 2019 drinking water guidelines.
- Between 2006 and 2019, MPCA tested monitoring well samples at Dakhue Landfill in Hampton Township for seven PFAS and detected five below guidelines, guidelines do not exist for two of the PFAS that were detected. Surrounding residential properties rely on private drinking water wells and it is unknown if they are impacted.
- In 2015 and 2019, MPCA tested eight monitoring wells at Freeway Landfill for seven PFAS. Drinking water guidelines were exceeded for PFOA, PFOS and PFBA. The contaminant plume from the landfill travels north and discharges into the Minnesota River. It is unknown if drinking water wells in the vicinity are impacted.
- In 2011 and 2012, PFAS was detected in all 16 monitoring wells sampled at Pine Bend Landfill. The 2019 drinking water guidelines were exceeded for PFOA, PFOS, PFHxS and

PFBA. The contaminant plume from the landfill travels east and discharges into the Mississippi River. There are no known drinking water supply wells that in the path of the plume.

### PFAS TESTING OF MUNICIPAL WELLS

Since 2007, MDH has sampled a subset of community (municipal) and non-community water supply wells in Hastings, Nininger Township, Rosemount, Inver Grove Heights, Vermillion, Eagan and South St. Paul. PFAS have been detected but none have exceeded established drinking water guidelines.

### FIREFIGHTING LOCATIONS

In 2009, MDH sampled locations where Class B Aqueous Film Forming Foam for firefighting may been used and impacted municipal wells. Trace level detections were identified in Burnsville and Apple Valley.

As of November 2019, MPCA is planning additional PFAS sampling in Dakota County and other metro counties to evaluate possible PFAS releases from specific industries to the groundwater or surface water (Star Tribune, November 2019).

## 4.9.2. Volatile Organic Compounds (VOCs)

### i. Volatile organic compounds: sources, health concerns, and drinking water treatment

“Volatile organic compounds are chemicals that contain carbon and have a high vapor pressure and low water solubility. Many VOCs are anthropogenic chemicals that are used and produced in the manufacture of paints, pharmaceuticals and refrigerants. VOCs typically are industrial solvents, such as trichloroethylene; fuel oxygenates, such as methyl tert-butyl ether (MTBE); or by-products produced by chlorination in water treatment, such as chloroform. VOCs are often components of petroleum fuels, hydraulic fluids, paint thinners and dry-cleaning agents. VOCs are common groundwater contaminants” (EPA, 12/19/19).

Tetrachloroethene (PCE) is a solvent used in industrial processes, metal cleaning, dry cleaning and textile processing. It is a common groundwater contaminant. Drinking water with levels of PCE that are higher than the MDH guidance value of 4.0 µg/L over several years could increase the risk of some types of cancer and kidney damage. If a private well has known PCE contamination, the well owner should contact the MDH or MPCA for more information about water treatment or alternative sources of drinking water (MDH, 2014).

Tribromomethane (bromoform) in drinking water is usually a byproduct of water chlorination. In the past, bromoform was used by industry to dissolve dirt and grease and to make other chemicals (ATSDR, 2005). The MDH Health Risk Limit for bromoform is 40.0 µg/L.

### ii. Volatile organic compound results

Samples from Ambient Study wells have been analyzed for VOCs by both MVTL and the USGS NWQL. MVTL analyzed samples from 47 Opdc and Cjdn wells in 2000, 21 Ucs wells in 2004, and two Ucs wells in 2005. The parameter list and method reporting limits are listed in Appendix A Table A.3. No VOCs were detected.

The 2008 Ambient Study and Hastings Area Nitrate Study (HANS) sampling for organic wastewater compounds, analyzed by the USGS NWQL, discussed at length below, included VOCs in the analytes. Sixty-six Ambient Study and 31 HANS wells were tested for common wastewater compounds. Five of the 97 wells (5 percent) had VOC detections. PCE was detected in four wells, at levels ranging from “detected but not quantifiable” to 0.05 µg/L (1.25 percent of the MDH drinking water guideline). Bromoform was detected in one well at “estimated 0.01 µg/L” (0.025 percent of the MDH drinking water guideline). The USGS NWQL detection limits were lower than those of MVTL.

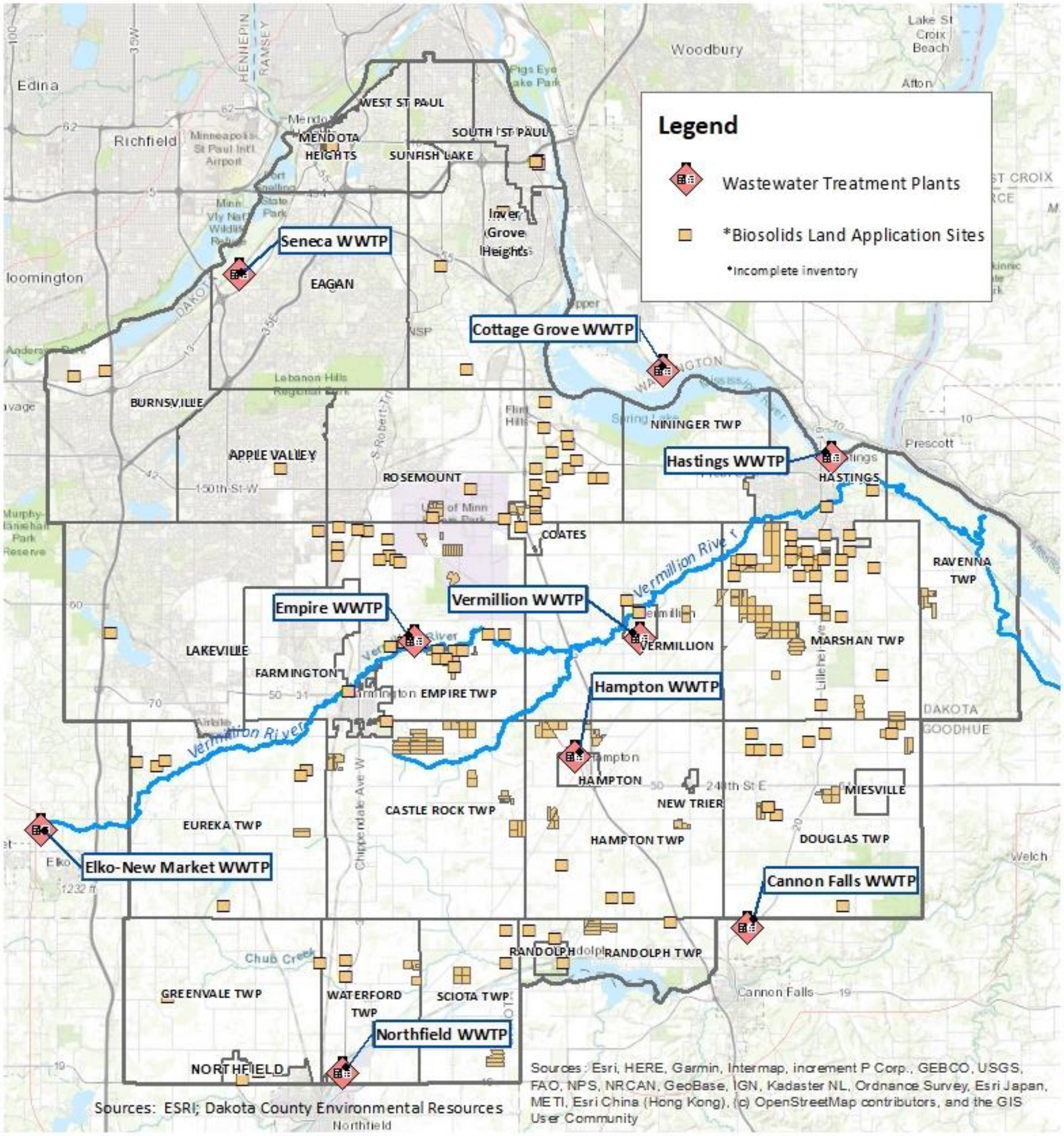
## 4.9.3. Organic Wastewater Compounds (OWWC)

In 2008, a total of 97 wells (66 Ambient Study wells and 31 Hastings Area Nitrate Study (HANS) wells) were tested for 69 common wastewater effluent compounds Schedule 4433 at the USGS National Water Quality Laboratory (Appendix A Table A.6.).

### i. OWWC sources, health concerns, and drinking water treatment

OWWC compounds are also referred to as anthropogenic organic compounds (AOCs), which are anthropogenic and introduced into the air, water and soil through industrial or individuals using pesticides, medications, personal care products, household products, cleaners and manufacturing ingredients. Many of these contaminants are classified as CECs and may be biologically active compounds (BACs).

Effluent and solids from both septic systems and WWTPs can contaminant the soil, and surface and groundwater with OWWC. There are an estimated 8,000 septic systems located in Dakota County that are required to be inspected and may be pumped every three years. The pumped septage is disposed of at a WWTP or directly land-applied. There are nine WWTPs located in or near the County boundary (Figure 80).



Sources: ESRI; Dakota County Environmental Resources

**Figure 80. WWTP locations in or near Dakota County.**

Releases of WWTP effluent to waterways can introduce low concentrations of metals and metalloids into receiving waters (MPCA, 2016) and OWWCs some of which are CECs. When used together, reverse osmosis membranes, ultraviolet light and advanced oxidation processes can successfully remove CECs from WWTP effluent to be used as recharge to drinking water aquifers (Bloetscher et.al, 2014). However, current practices at the nine WWTPs do not include these processes to treat the effluent that could become drinking water downstream. The fate and transport of contaminants in surface water and their interaction with sediments is complex. The properties of a chemical contaminant determine what portion of a chemical will adsorb and desorb to become a nonpoint source and recontaminate water (Kolok et al., 2014). In general, the distribution of a chemical in the environment can be predicted based on the octanol-water partition coefficient ($K_{ow}$); chemicals with a low $K_{ow}$ tend to be more water soluble and less likely to bioaccumulate in organisms. Conversely chemicals with high $K_{ow}$ tend to adsorb to organic matter in sediment, transport of these chemicals may be retarded in the groundwater (MPCA, January 2012), and they have more potential to bioaccumulate in living organisms (ChemSafetyPro). Thirty-one percent of the 16 OWWCs detected have $K_{ow}$ values greater than 4.5, an indicator that bioaccumulation is a greater concern. They are likely to persist after the source is removed.

The USGS collected samples from landfill leachate at three Dakota County landfills: Burnsville SLF, Pine Bend SLF and SKB Industrial Waste Landfill. A total of 46 OWWCs were detected (Lee, 2004). The effluent is treated at the Metropolitan Council Metro WWTP in St. Paul and discharged to the Mississippi River, upstream from Dakota County. The treatment efficiency of OWWCs by the Metro WWTP are unknown. The USGS collected a sample from below Vermillion River below the Empire WWTP in 2001 and detected 17 OWWC; 3 antibiotics, 4 pharmaceuticals, 10 household, industrial and agricultural use compounds (Lee, 2004). Both the Elko-New Market WWTP (deactivated in 2011 and routed to the Empire WWTP) and the Empire WWTP (rerouted to the Mississippi River in 2008) historically discharged treated wastewater to the Vermillion River. Immediate improvement in water quality and temperature were observed downstream of the Empire WWTP outfall on the Vermillion River (MPCA, 2012) after rerouting. Currently, two WWTPs discharge to the Vermillion River, the Vermillion WWTP, 11 million gallons discharged in 2017, and the Hampton WWTP, 22 million gallons discharged to a tributary of the South Branch Vermillion River in 2017.

Dakota County monitoring and groundwater modeling determined the segment of the Vermillion River from the west city boundary of Hastings — east to the Vermillion River Falls is a losing reach and supplies a major portion of groundwater to Hastings municipal wells (Dakota County, 2003). The Vermillion River Watershed is the largest watershed in the County which drains 335 square miles of Dakota and Scott counties and includes 49 miles of MN DNR designated trout stream. Continued efforts to improve the water quality in the Vermillion River watershed will benefit consumers of Hastings municipal water. Contaminants can be tied up in river sediments and may be released overtime, serving as a source of contaminants to both surface and groundwater that enters the City of Hastings DWSMA.

WWTP sewage sludge is applied to agricultural fields throughout the County and on the 400 acres at the Empire WWTP along the Vermillion River. The Northfield WWTP discharges treated effluent to the Cannon River and land applies sewage sludge. The location of all land applications sites, source of material and application rates are unknown.

The effect of chronic exposure to low levels of these chemicals to human and aquatic life is unknown (MPCA, January 2012). Toxicity data are lacking, and health risk guidelines have not been established for many of these parameters. Appendix A Table A.6a, a USGS table, lists the possible uses of each compound tested, as well as the known and suspected endocrine-disrupting potential (EDP) for each compound to interfere with human and wildlife’s endocrine systems. Endocrine effects can include disturbances in the immune and nervous system function, developmental malformations, interference with reproduction and increased cancer risk (EPA endocrine website).

### ii. OWWC results

Five of the 69 parameters are pesticides; four were detected; atrazine, metolachlor, prometon and pentachlorophenol; metalaxyl was not detected. No detections were over the drinking water guidelines. All results were estimated (E) except for the two highest results for atrazine which were 0.22 µg/L and 0.25 µg/L, the method reporting level is 0.20 µg/L. The results are summarized in Table 54. The Ambient study wells are routinely tested for atrazine, metolachlor and prometon see the herbicide section of this report for more data related to these herbicides.

**Table 51. OWWC Herbicide Results Summarized from Ambient and Hastings Area Nitrate Studies.**

| Compound Name | Possible Use or Source | # of Detects (n=97) in 2008 | Min (ug/L) & MRL | Max (ug/L) | MDH Drinking Water Guideline (µg/L) in 2018 |
|---|---|---|---|---|---|
| Atrazine | Herbicide | 31 | <0.20 | 0.25 | 3 |
| Metolachlor | Herbicide | 8 | <0.20 | E 0.11 | 300 |
| Pentachlorophenol | Herbicide, fungicide, wood preservative | 1 | <0.8 | E 0.1 | 0.3 |
| Prometon | Herbicide (noncrop), applied prior to blacktop | 1 | <0.20 | E 0.4 | 100 |

*EPA MCL Goal is zero µg/L.

A summary of the OWWC detections for 2008 are provided in Table 56. The following is a summary of OWWC results excluding herbicides:

- All analytes detected are below drinking water guidelines (where guidelines are available).
- There were 33 detections: 16 different OWWCs detected across 24 wells. Seven of the 33 (21 percent) detections are reported values; 26 are estimated values or too low to quantify.
- Of the wells with detections, 18 were part of the Ambient Study and six were part of the HANS.
- Six of the chemicals detected are known endocrine disrupters.
- Nine of the 16 compounds detected have established drinking water guidelines.
- Diethyl phthalate was the most frequently detected, found in five wells.
- One well had four different OWWCs detected, which was the most for any well.
- Bis(2-ethylhexyl) phthalate was found at the highest concentration of all 66 analytes, at 5.0 µg/L.

Bisphenol A, diethyl phthalate, and bis(2-ethylhexyl) phthalate are plasticizers that could be present in the garden hoses used in the water sampling, which may have contaminated the water samples. Sample collection procedures involved purging the outside spigot at the homes with a garden hose to direct the water away from the foundation. The well water is purged through a garden hose for 15 minutes or more while field parameters are collected, the hose is then unscrewed from the spigot and samples are collected from the same spigot. The sample technician would use the well owner's hose if one was available; if not, the technician will use MVTL's garden hose. Whether the well owner's or MVTL's hose was used was not documented. A recommendation for future sampling is to resample the wells where plasticizers were detected and to clean the spigot with Alconox detergent, or similar solution, after hose removal and prior to sample collection.

Drinking water guidelines are provided for reference in Table 55 and the results are depicted on maps in Appendix G. An asterisk indicates compounds that the USEPA has determined that zero or none of the amount of the contaminant should be consumed. Many of the results were estimated and flagged with the letter "E" meaning the compound was detected and the concentration is estimated. Results flagged with the letter "M" means the compound was detected but at concentrations too low to quantify.

### Table 52. Wastewater Compound detections from Ambient and Hastings Area Nitrate Studies.

| Compound Name | Possible Use or Source | # of Detects (n=97) | MRL (µg/L) | Min (µg/L) | Max (µg/L) | Lowest Applcable Drinking Water Guideline (ug/L) 2018 |
|---|---|---|---|---|---|---|
| Diethyl phthalate (DEP) (known EDP) | Plasticizer in polymers & resins | 5 | 0.2 | E 0.6 | 1.8 | 6000 (MDH) |
| Bis(2-ethylhexyl) phthalate aka. Diethylhexyl phthalate (DEHP) (known EDP) | Plasticizer in PVC and pesticides | 4 | 2 | M | 5 | 6* (EPA) |
| Bisphenol A (known EDP) | Polycarbonate plastic & flame retardant | 4 | 0.4 | E 0.05 | 0.78 | 20 (MDH) |
| Tetrachloroethylene (PCE) | Solvent, degreaser, & vet med for parasites | 4 | 0.4 | M | 0.05 | 4 (MDH) |
| Tri(2-butoxyethyl) phosphate | Flame retardant | 4 | 0.2 | E 0.20 | 0.33 | None |
| Caffeine | Beverages and diuretic | 2 | 0.2 | <0.20 | E 0.05 | None |
| *beta* -Sitosterol | Plant sterol used in medicines | 1 | 0.8 | <0.8 | E 3.3 | None |
| Carbaryl (known EDP) | Insecticide - crop or garden use | 1 | 0.2 | <0.20 | E 0.04 | 400 (EPA) |
| 2-Methylnaphthalene | Gasoline, diesel fuel or crude oil | 1 | 0.2 | <0.20 | E 0.02 | 8 (MDH) |
| 3-Methyl-1H-indole (skatol) | Fragrance, stench in feces & coal tar | 1 | 0.2 | <0.20 | E 0.01 | None |
| 4-n-Octylphenol (known EDP) | Detergent | 1 | 0.2 | <0.20 | E 0.01 | None |
| 4-Nonylphenol (total NP) (known EDP) | Detergent | 1 | 1.6 | <1.6 | E 0.4 | 20 (MDH) |
| Phenol | Disinfectant and oral care products | 1 | 0.2 | <0.20 | E 0.1 | 2000 (EPA) |
| Bromoform | Wastewater ozonation byproduct & explosives | 1 | 0.2 | <0.20 | E 0.01 | 40 |
| Tributyl phosphate | Antifoaming agent, flame retardant | 1 | <0.200 | <0.200 | E0.012 | None |
| Triphenyl phosphate | Plasticizer, resin, wax, flame retardant | 1 | 0.2 | <0.20 | E 0.03 | None |

*EPA MCL Goal is zero µg/L.
EDP= endocrine disrupting potential

In the State of Minnesota’s 2013–2017 ambient groundwater sampling program, CECs were detected in 124 of 262 wells sampled (47 percent). Detections were much lower in other wells. (MPCA, July 2019).

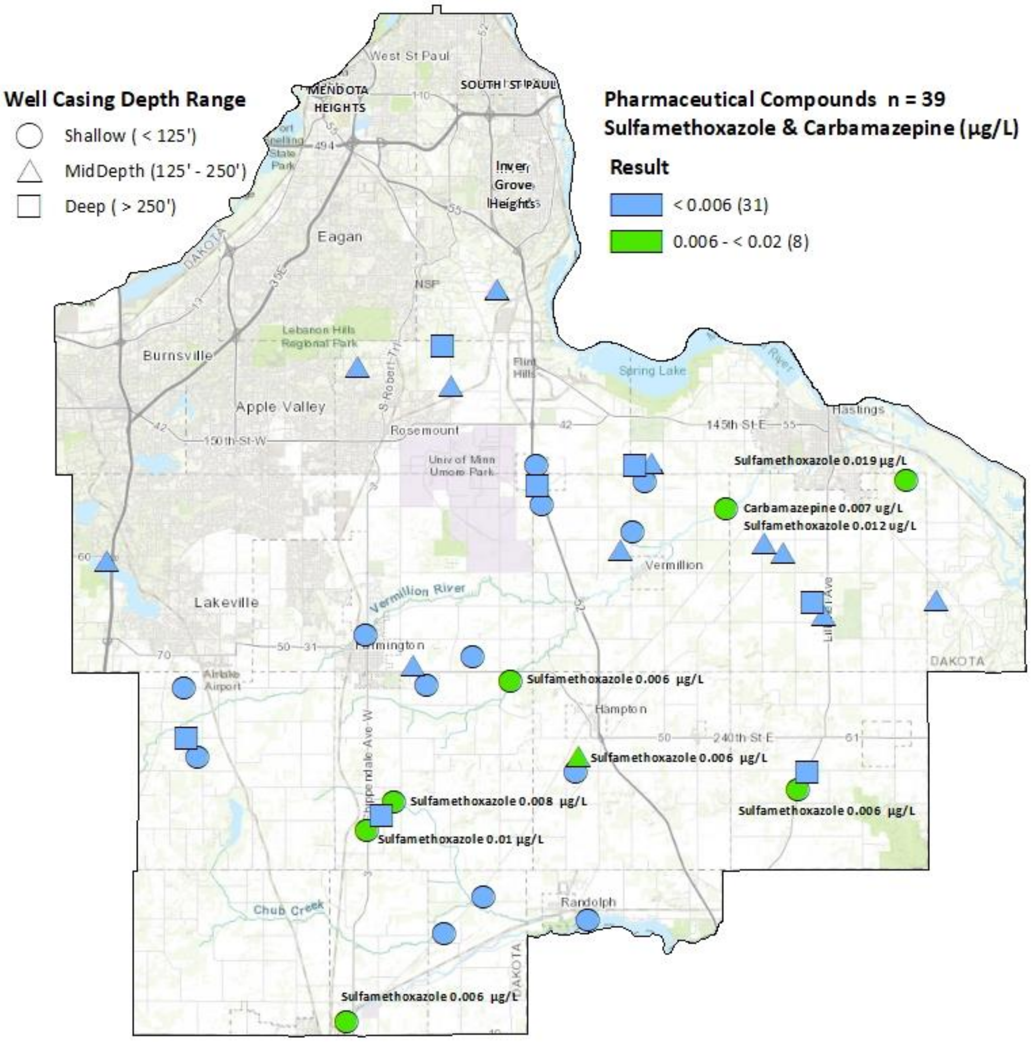
## 4.9.4. Pharmaceuticals

### i. Pharmaceutical sources, health concerns, and drinking water treatment

Pharmaceuticals are medicines that are available in stores or by prescription and are used to treat illnesses in humans and animals. The presence of pharmaceuticals in water is of increasing concern because they may cause harm to humans. Antibiotics in the environment may also contribute to the development of antibiotic-resistant pathogens. Pharmaceuticals enter rivers, lakes and groundwater when human waste, animal waste or discarded medications move from storm water systems, sewer systems or septic tanks into water. Pharmaceuticals in water may break down but can be constantly replenished. Wastewater and drinking water treatment may not completely remove pharmaceuticals. As a result, these chemicals can be found in drinking water sources for Minnesotans (MDH, undated website). Land application of biosolids from WWTP can also be a source of pharmaceuticals in the groundwater.

### ii. Pharmaceutical results

In 2013, eight of the 40 (20 percent) Ambient Study wells tested for a list of 27 pharmaceuticals, and six pharmaceuticals breakdown products (Appendix A Table A.8 - method) had detections. Due to budgetary constraints not every Ambient Study well was tested. Only wells that had more than one herbicide detected in prior sampling events were tested for both herbicides and the pharmaceuticals list in 2013. A surface water sample collected from the Vermillion River, above the Vermillion Falls, during the 2013 well sampling event, had no pharmaceuticals detected.

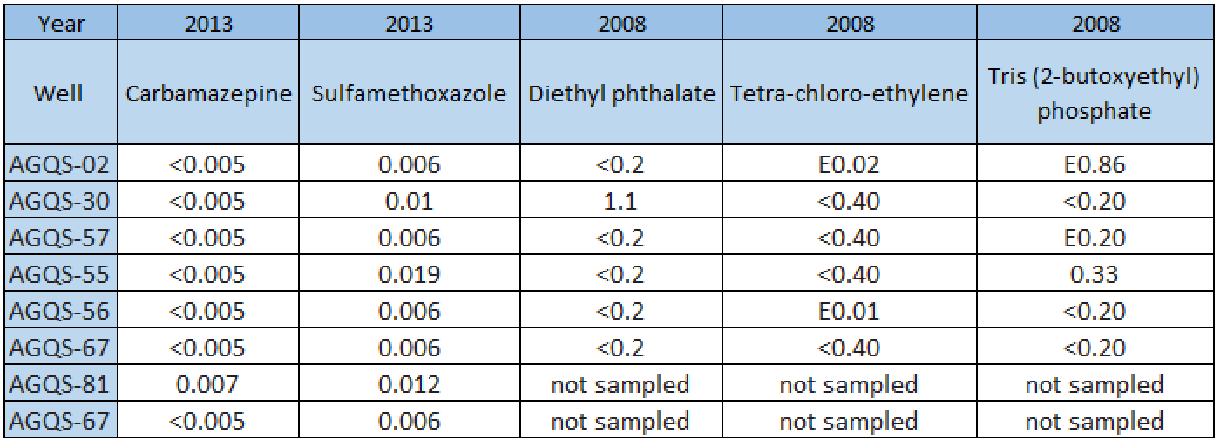


Sources: ESRI; Dakota County Environmental Resources

Figure 81. Pharmaceutical Results by Well Casing Depth

Two of the 33 pharmaceuticals and pharmaceutical breakdown products tested were detected: sulfamethoxazole, an antibiotic used for both humans and animals, and carbamazepine, an anticonvulsant used to reduce seizures and nerve pain. Sulfamethoxazole was detected in seven wells, plus both sulfamethoxazole and carbamazepine were detected in one well, depicted in Figure 81. All the detections are below the drinking water guidelines. The highest sulfamethoxazole result was 0.01 µg/L, which is below the guideline of 100 µg/L. Thirty-four of the 40 wells tested for pharmaceuticals in 2013 were previously tested for OWWC in 2008. Six of the eight wells with sulfamethoxazole in 2013 were tested for OWWC in 2008; five had had OWWCs detected (Table 56). In addition to be used as a human and veterinary antibiotic to treat infection, sulfamethoxazole has been used as a feed additive to promote growth in animals and as a preventative and treatment of diseases (Rade et al, 2008). This practice is now discouraged. Carbamazepine of 0.007 µg/L was detected, which is below the drinking water guideline of 40 µg/L.

**Table 53. Pharmaceutical Detections and OWWC detected in same wells if applicable.**



| Year | 2013 | 2013 | 2008 | 2008 | 2008 |
|---|---|---|---|---|---|
| Well | Carbamazepine | Sulfamethoxazole | Diethyl phthalate | Tetra-chloro-ethylene | Tris (2-butoxyethyl) phosphate |
| AGQS-02 | <0.005 | 0.006 | <0.2 | E0.02 | E0.86 |
| AGQS-30 | <0.005 | 0.01 | 1.1 | <0.40 | <0.20 |
| AGQS-57 | <0.005 | 0.006 | <0.2 | <0.40 | E0.20 |
| AGQS-55 | <0.005 | 0.019 | <0.2 | <0.40 | 0.33 |
| AGQS-56 | <0.005 | 0.006 | <0.2 | E0.01 | <0.20 |
| AGQS-67 | <0.005 | 0.006 | <0.2 | <0.40 | <0.20 |
| AGQS-81 | 0.007 | 0.012 | not sampled | not sampled | not sampled |
| AGQS-67 | <0.005 | 0.006 | not sampled | not sampled | not sampled |

In the State of Minnesota’s 2013–2017 ambient groundwater sampling program, sulfamethoxazole was found in nearly 14 percent of the wells sampled and was the most commonly detected Contaminant of Emerging Concern (MPCA July 2019) compared to being detected in 20 percent of the Ambient Study wells.

# 5. Naturally Occurring Parameters

## 5.1 Toxic Heavy Metals

### 5.1.1. Manganese

#### i. Manganese sources and health concerns

Manganese occurs naturally in the groundwater in the County; it is an essential nutrient to maintain health. The EPA's Health Advisory guideline for manganese, which applies to public water suppliers, is 0.300 mg/L based on neurological symptoms and concerns. However, in 2012, MDH staff became concerned that this recommendation was too high for young infants, especially those who are fed formula mixed with water high in manganese. Epidemiology and toxicology studies reviewed by MDH suggested that manganese in drinking water may cause subtle changes in neurodevelopmental endpoints in infants and children. Infants younger than 12 months of age who consume water with too much manganese may develop learning and behavior problems. Children older than 12 months and adults who consume water with high levels of manganese for a long time may have problems with memory, attention and motor skills. In 2012, MDH created a tiered drinking water guidance applicable to manganese in private drinking water wells:

- 0.100 mg/L for bottle-fed infants 12 months and younger who are drinking the well water; and
- 0.300 mg/L for children older than 12 months and adults.

In 2018, MDH removed the tiered Risk Assessment Advice. MDH continues to support the EPA Health Advisory levels of 0.300 mg/L of manganese for children one year of age and adults (MDH, March 2018) and the Short-term Health Based Value of 0.100 mg/L for bottle-fed infants less than one year of age. Manganese can be removed from drinking water; see the MDH Factsheet on home water treatment options is provided in Appendix E.1.

#### ii. Manganese results

There are 74 wells in the Ambient Study tested for manganese in the sampling events that occurred between 2005 and 2013, summarized in Appendix B Table B.16. Twenty-five (34 percent) of the wells exceeded the infant drinking water guideline of 0.100 mg/L at least one time and 19 percent of those wells exceeded 0.300 mg/L at least once. The distribution for manganese is highly skewed reflecting a few wells with very high manganese levels. Since manganese is not anthropogenic, trends over time would not be expected; however, there are two wells with an upward trend and one that is peaking, which means over the study, manganese was decreasing, and it is now increasing in that well.

Nonparametric statistical tests indicate that median manganese is not different between Opdc, Cjdn and Ucs aquifers (Table 4). Variability within an aquifer is greater than the variability across aquifers across the County. Nonparametric statistical tests comparing paired Ambient Study wells in 20 well clusters also indicate no systematic pattern of manganese in one aquifer versus another. This suggests that even when wells are in proximity, aquifer is not a key variable. Manganese level is not related to whether a well is grouted or not (Kruskal Wallis, p =

0.16). Also, manganese is not correlated with well casing depth (Kendall, p=0.11) depicted in Figure 82 and is positively correlated with total well depth (Kendall, p <0.10). Table 57 compares median manganese with well casing depth. The middle depth range has lower median and average manganese, suggesting there is a geologic source for manganese in the deeper and shallower aquifers.

**Table 54. Descriptive Statistics of Median Manganese Results (mg/L) by Well Casing Depth Category.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 25 | 0.130 | 0.261 | 0.005 | 0.005 | 0.005 | 0.089 | 1.010 |
| Mid 125' to 250' | 26 | 0.109 | 0.203 | 0.005 | 0.005 | 0.005 | 0.112 | 0.795 |
| Deep >250' | 23 | 0.144 | 0.224 | 0.005 | 0.008 | 0.040 | 0.183 | 0.791 |

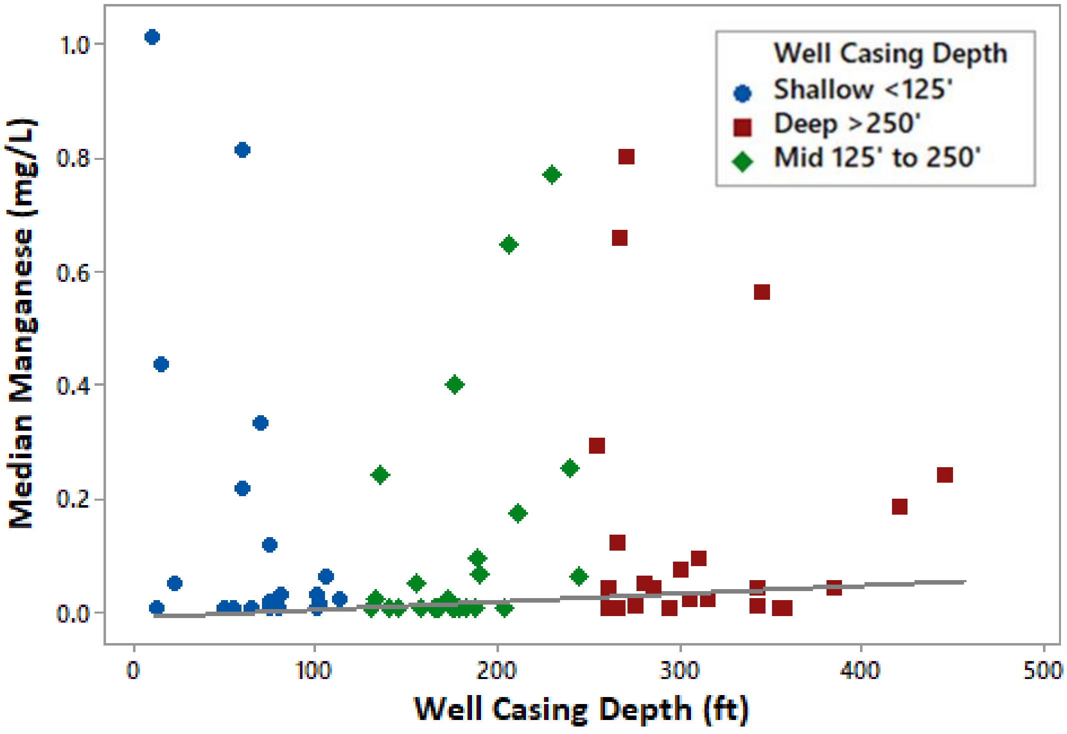


**Figure 82. Correlation of Median Manganese by Well Casing Depth—Kendall Line.**

The presence of manganese and iron in a groundwater sample is influenced by chemical reactions of oxidation or reduction (redox). Manganese is positively correlated with Iron (Kendall, p <0.05). When iron is above 0.7 mg/L, manganese is likely to be above 0.05 mg/L. Both iron and manganese are negatively correlated with dissolved oxygen (Kendall, p <0.05). The more dissolved oxygen present, lower levels of manganese and iron are expected (Figure 83).

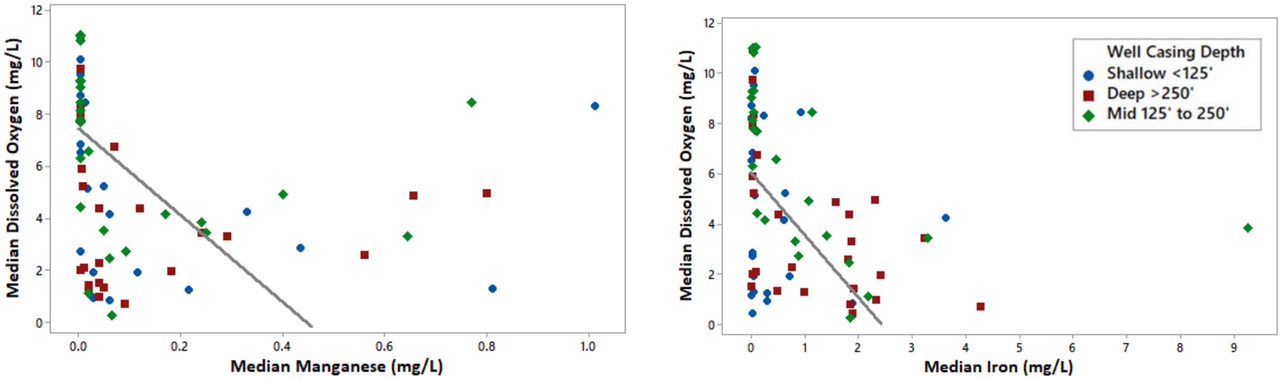


**Figure 83. Correlation of Median Dissolved Oxygen by Median Manganese — Kendall Line & Correlation of Median Dissolve Oxygen by Median Manganese — Kendall Line.**

In contrast, iron is negatively correlated with sulfate (Kendall, p <0.05), while manganese is not correlated (Kendall, p=0.58). This suggests that geologic sources of manganese in groundwater differ from those for iron. Table 58 summarizes the manganese and iron correlations between parameters.

**Table 55. Correlations of Manganese and Iron with Select Parameters.**

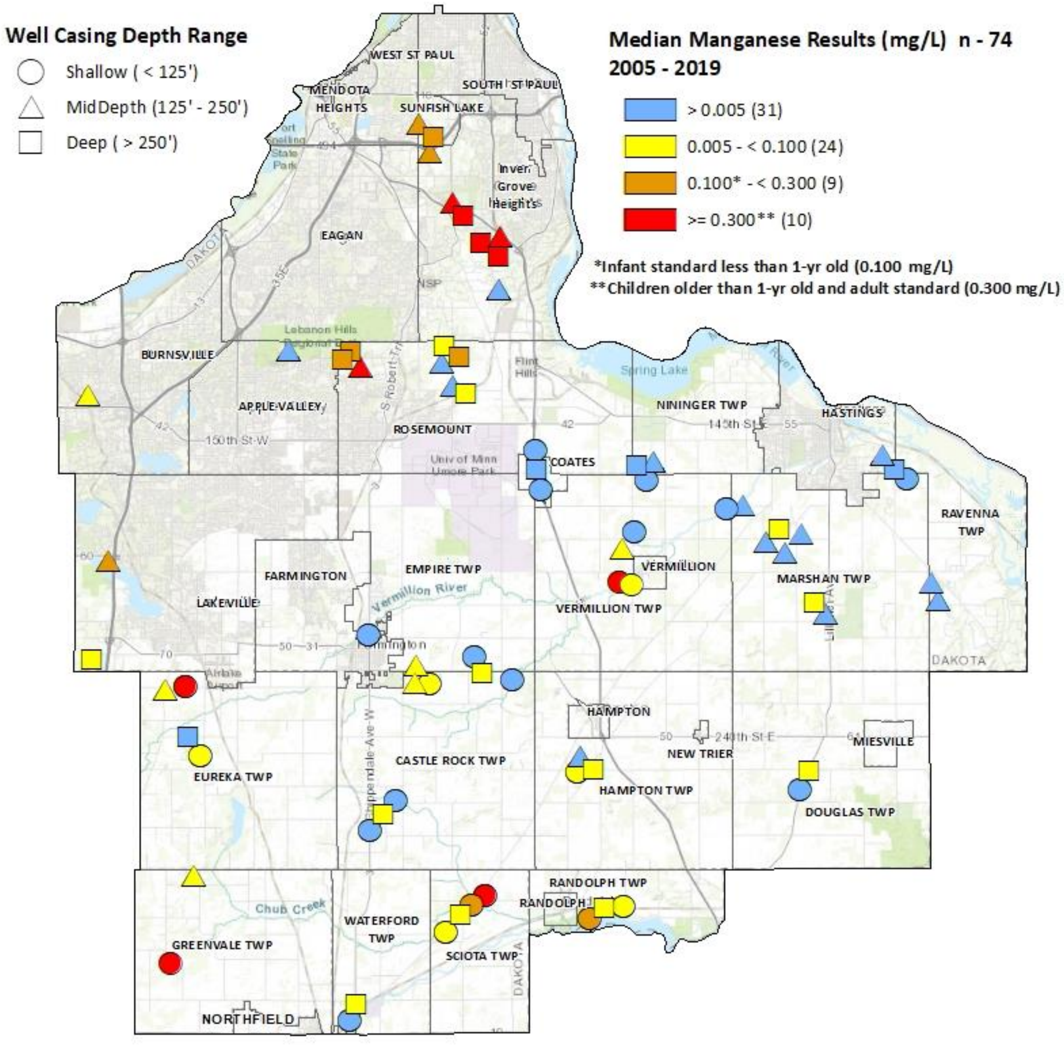
| Manganese Correlations | Direction | P Value* |
|---|---|---|
| Arsenic | Increasing | <0.05 |
| Barium | Increasing | <0.05 |
| Dissolved Oxygen | Decreasing | <0.05 |
| Iron | Increasing | <0.05 |
| Sulfate | N/A | 0.54 |
| Well Casing Depth | N/A | 0.11 |

| Iron Correlations | Direction | P Value* |
|---|---|---|
| Arsenic | Increasing | <0.05 |
| Barium | Increasing | <0.05 |
| Dissolved Oxygen | Decreasing | <0.05 |
| Manganese | Increasing | <0.05 |
| Sulfate | Decreasing | <0.05 |
| Well Casing Depth | Decreasing | <0.05 |

*Kendall nonparametric correlation

A different situation occurs with iron (Fe), which is not related to human activity. Fe(II) increases statistically with depth (Mann-Whitney, p <0.05). As dissolved oxygen decreases with depth, lower oxidation state Fe(II) becomes more soluble, as Fe(III) is almost entirely insoluble. Note that although chemical states for manganese are somewhat similar to Fe, there is no statistical relationship with aquifer for manganese (Mann-Whitney, p >0.10).

Geographically, manganese levels are higher for Ambient Study wells in the north and western part of the County than in the other areas (Figure 84) where geologic till is prevalent. Manganese is negatively correlated with agricultural land use (Kendall, p <0.05). Twenty-five percent of the study wells do not have a well construction record; 68 percent of these are Ucs wells. Well records that have been located often lack detail in the reporting of the geologic materials encountered therefore analysis of the water quality results compared to presence or absence of till units was not performed.



Sources: ESRI; Dakota County Environmental Resources

Figure 84. Median Manganese by Well Casing Depth.

### iii. Manganese in Inver Grove Heights (WIISE STUDY) and community-focused sampling

Dakota County Environmental Resources offered a free manganese test to all the participants in the MDA Township Testing program in 2014. Of the 739 samples submitted, 155 (21 percent) exceeded 0.100 mg/L and 76 of those (10 percent) exceeded 0.300 mg/L.

In 2015, Dakota County Environmental Resources partnered with MDH to conduct a study of private wells in Inver Grove Heights: Wells and Increased Infant Sensitivity and Exposure (WIISE) Study (Scher and Demuth, 2017). This was a pilot project, one of the first in the state to evaluate private well users' exposure to manganese and other contaminants of concern for children's health. Dakota County staff collected untreated water samples from outside faucets at the homes of 274 private well owners in Inver Grove Heights to test for manganese, nitrate, nitrite, chloride, sulfate, fluoride, lead and coliform bacteria. Of the 274 water samples collected, 194 (71 percent) exceeded MDH’s drinking water guidance for manganese of 0.100 mg/L for infants 12 months and younger; of those, 153 of the samples (56 percent) exceeded MDH’s drinking water guidance for manganese of 0.300 mg/L for everyone older than 12 months. The median manganese level in the WIISE study of 0.340 mg/L is much higher than the Countywide Ambient Study manganese median of 0.020 mg/L.

In 2018, Dakota County began its community- focused sampling projects where all private well owners are provided a water test kit for well owners to collect an untreated water sample from an outside faucet and a second sample from the primary drinking water tap within the residence, which can be treated. The participant was asked to complete a form describing the water treatment devices present.

If the outside sample result exceeded 3.0 mg/L for nitrate, 0.05 µg/L for arsenic or 0.090 mg/L for manganese, then the sample collected from the inside tap was tested for that chemical parameter. Table 59 summarizes the results from the outside and inside samples. The WIISE study found that water softeners are very effective at reducing manganese, so all water test kits include two hardness test strips for the well owner to test both sample locations and are to report the result of the test strip. Surveys of well owners who participated in the community-focused well sampling, which are wells in rural residential settings, show that softener use by community ranges from a low of 60 percent of participants in Inver Grove Heights to a high of 96 percent of Lakeville participants. Reverse osmosis systems are effective at reducing manganese, but they most often receive softened water where the manganese would have first been reduced by the softener; the water softeners were most likely responsible for the reduction of manganese in the inside drinking water samples.

Note the number of well owners drinking water (inside sample) with manganese above the drinking water guideline of 0.100 mg/L ranges from a high of 36 percent from the Ambient Study well participants (small sample size, 11 samples) to a low of four percent in Inver Grove Heights (68 samples).

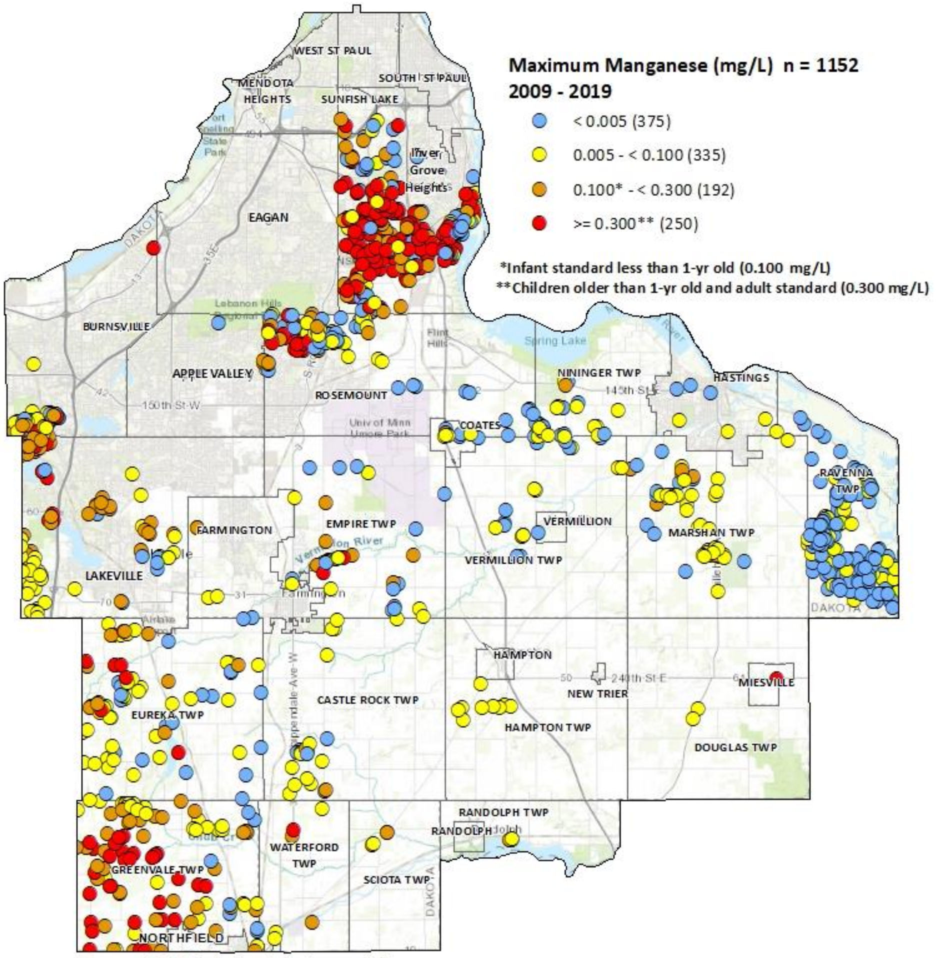
**Table 56. Summary of Manganese Results (mg/L) Comparing Datasets.**

| Sample Events | Year | # of Samples | # of Samples with Detections MRL <0.005 mg/L | # of Samples above Standard 0.100 mg/L | # of Samples above Standard of 0.300 mg/L | Average | Median | Max |
|---|---|---|---|---|---|---|---|---|
| Ambient Study outside untreated * | 2018-19 | 11 | 10 (90%) | 10 (90%) | 5 (45%) | 0.347 | 0.250 | 0.800 |
| Ambient Study inside drinking water * | 2018-19 | 11 | 4 (36%) | 4 (36%) | 5 (45%) | <0.005 | <0.005 | 0.542 |
| Inver Grove Heights outside untreated | 2016 | 274 | 216 (79%) | 194 (71%) | 153 (56%) | 0.361 | 0.347 | 1.790 |
| Inver Grove Heights inside drinking water** | 2016 | 68 | 12 (18%) | 3 (4%) | 2 (3%) | 0.028 | <0.005 | 1.140 |
| Burnsville outside untreated | 2018 | 66 | 48 (73%) | 26 (39%) | 12 (18%) | 0.136 | 0.069 | 0.754 |
| Burnsville inside drinking water | 2018 | 27 | 14 (52%) | 9 (33%) | 4 (15%) | 0.115 | 0.007 | 0.793 |
| Greenvale outside untreated | 2019 | 94 | 88 (94) | 59 (63%) | 25 (27%) | 0.220 | 0.150 | 1.020 |
| Greenvale inside drinking water | 2019 | 59 | 17 (29%) | 13 (22%) | 13 (22%) | 0.084 | <0.005 | 0.769 |
| Lakeville outside untreated | 2019 | 100 | 90 (90%) | 51 (51%) | 10 (10%) | 0.127 | 0.106 | 0.539 |
| Lakeville inside drinking water | 2019 | 58 | 8 (14%) | 3 (5%) | 2 (3%) | 0.020 | <0.005 | 0.383 |

*Only 11 Ambient Study wells with manganese known to be greater than 0.090 from the most recent sample collected from the outside faucet were teste inside water for manganese

** Only 68 of the 194 well owners in IGH with manganese over 0.100 mg/L brought a water sample from an inside faucet to a sample drop off event for a manganese test

Figure 85 displays all the of manganese results from other studies and focused sampling; some parts of the County are more represented than others. Future sampling is expected to provide a more comprehensive picture of manganese levels throughout the County's groundwater. Geographically, manganese is elevated in the heavier (high clay content) loamy soils and where glacial till is more prevalent, from Inver Grove Heights south along the west side of the County to Greenvale Township at the southern border.



*Infant standard less than 1-yr old (0.100 mg/L)

**Children older than 1-yr old and adult standard (0.300 mg/L)

Sources: ESRI; Dakota County Environmental Resources

Figure 85. Manganese Results (mg/L).

#### iv. Actions related to manganese

In response to the presence of elevated manganese in the drinking water aquifers, Dakota County approved an amendment to Ordinance No. 114 Well and Water Supply Management to require all newly constructed domestic private supply wells to be tested for manganese. In addition, at the time of property transaction a manganese test result from the private water supply must be shared with the buyer. A well owner is not required to treat to reduce manganese if it is elevated.

### 5.1.2. Arsenic

#### i. Arsenic sources and health concerns

Arsenic occurs naturally in rocks and soil across Minnesota and can dissolve into groundwater. Consuming water with even low levels of arsenic over a long time is associated with diabetes and increased risk of cancers of the bladder, lungs, liver and other organs. Ingesting arsenic can also contribute to cardiovascular and respiratory disease, reduced intelligence in children, and skin problems such as lesions, discoloration and the development of corns. Health impacts of arsenic may take many years to develop. The maximum level of arsenic the USEPA allows in community water systems is 10 µg/L. However, no level of arsenic in drinking water is considered safe (MDH).

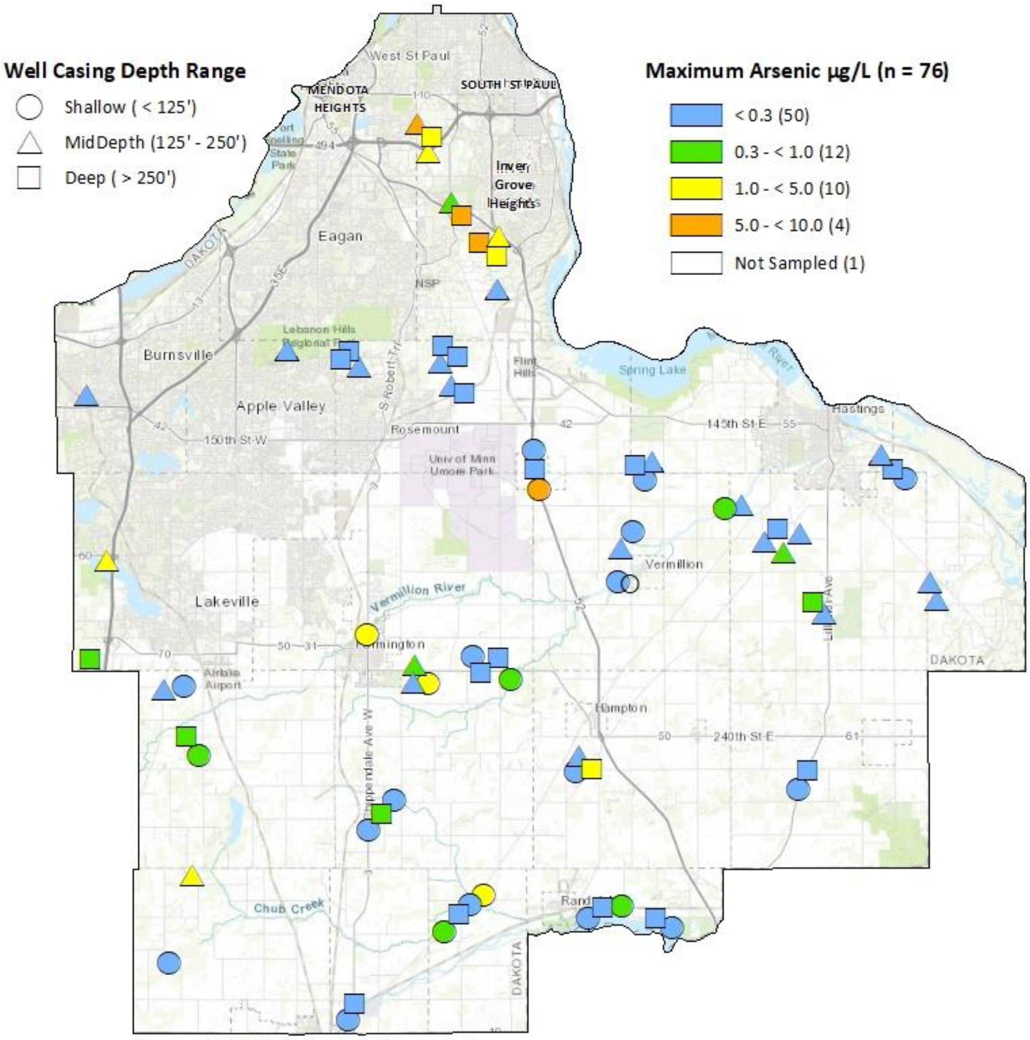
Since 2009, all newly constructed potable water wells must be tested for arsenic in accordance with Minnesota Rules 4725, the state Well Code. In November 2019, the Dakota County approved an amendment to Ordinance No. 114 Well and Water Supply Management to require a water test for arsenic to be shared with the buyer at the time of property transaction. A well owner is not required to treat to reduce arsenic if elevated.

#### ii. Arsenic results

When wells are added to the study, they are tested for arsenic. In 2018, all 62 sampled Ambient Study wells were again tested for arsenic. The highest result in the study was 9.9 µg/L. Arsenic was detected above the MRL (0.5 µg/L) in 24 of 77 wells (31 percent). None exceeded the drinking guideline of 10 µg/; however, as noted above, MDH does not consider any level of arsenic to be safe.

The median arsenic levels are higher in the Opdc and the Cjdn than in the Ucs. Statistically there is a difference in arsenic between the Ucs and Opdc (Mann-Whitney $p < 0.05$) and the Ucs and the Cjdn (Mann Whitney $p < 0.05$), Table 4. The two highest arsenic results are wells located in Inver Grove Heights, one well in the Ucs and one in the Opdc; both are in the deep well casing category.

Arsenic in drinking water wells is highly variable spatially (Figure 86). As of 2020, Dakota County does not have sufficient arsenic results to define “high arsenic” versus “low arsenic” areas. As with manganese, the County’s community-focused well sampling program will produce county-wide information about the prevalence of arsenic in private drinking water wells.



Sources: ESRI; Dakota County Environmental Resources

Figure 86. 2018 Arsenic Results.

Average arsenic by well casing depth is summarized in Table 60. There is not much variation in average arsenic by well casing depth.

Table 57. Descriptive Statistics of Average Arsenic Results (µg/L) by Well Casing Depth Category.

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 25 | 1.0 | 0.6 | 0.5 | 0.5 | 1.1 | 1.3 | 3.0 |
| Mid 125' to 250' | 26 | 1.1 | 0.8 | 0.5 | 0.5 | 0.8 | 1.3 | 3.4 |
| Deep >250' | 25 | 1.8 | 1.5 | 0.5 | 1.3 | 1.3 | 2.0 | 7.0 |

Average arsenic is not correlated with well casing depth (Kendall, p = 0.18) depicted in Figure 87.

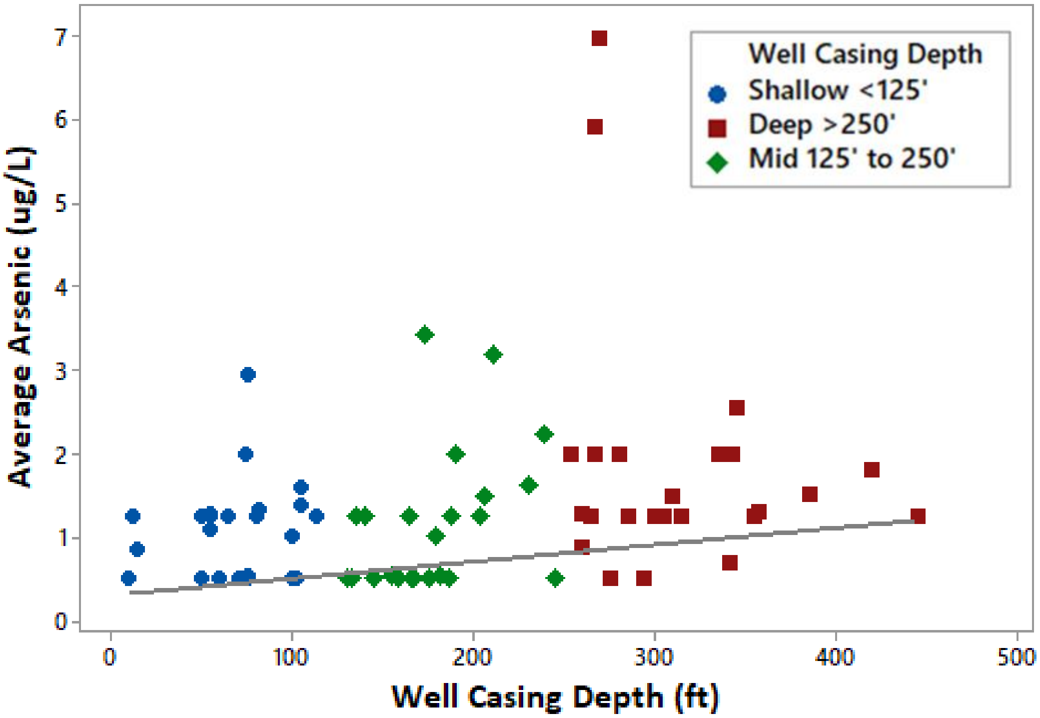


Figure 87. Correlation of Median Arsenic by Well Casing Depth—Kendall Line.

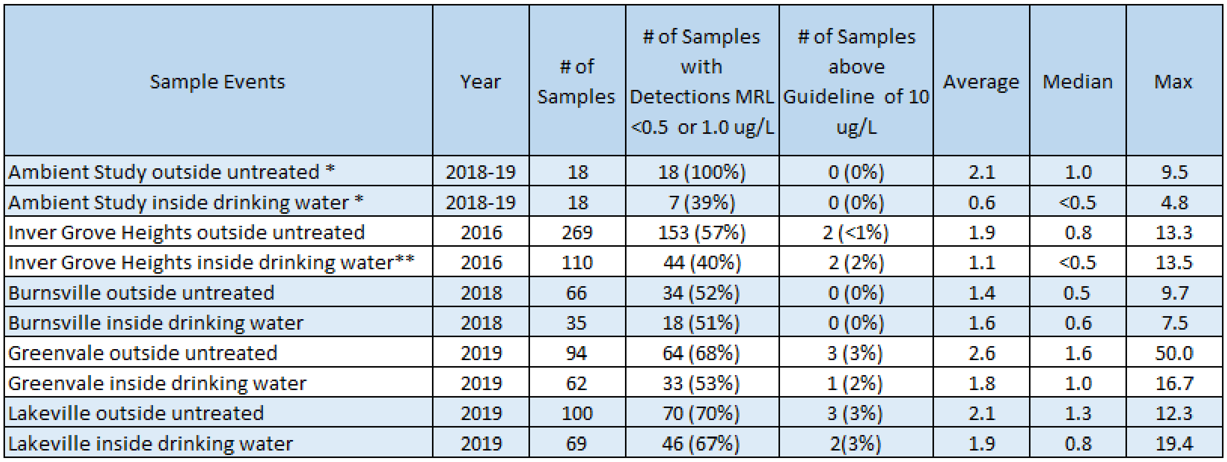
### iii. Arsenic in Inver Grove Heights (WIISE STUDY) and community-focused sampling

Arsenic was analyzed in outside water samples in all of the focused sampling events. In Burnsville, Greenvale and Lakeville, inside samples were tested for arsenic if it was detected above the MRL in the outside sample. In Inver Grove Heights, County staff collected the outside untreated water sample as part of the WIISE. WIISE study participants could bring a sample they collected from their drinking water tap for arsenic analysis. Eighteen of the Ambient Study wells that had a previous outside untreated water test for arsenic above the MRL had the inside samples analyzed for arsenic. The results from all the focused studies are summarized in Table 61. The maximum arsenic detected from inside drinking water ranged from a minimum of 4.8 µg/L in Ambient Study wells to 19.4 µg/L in Lakeville. Lakeville has the highest percent of results above the MRL, 67 percent in inside drinking water. According to the MDH, there is no safe level of arsenic.

The highest levels of arsenic detected was 50 µg/L in a well of unknown depth in Greenvale Township. County staff consulted with the USGS Minnesota Water Science Center (Melinda Erickson, Ph.D.) about potential sources of elevated arsenic, which can be attributed to legacy use, sale and storage of pesticides that contain arsenic, petroleum spills or leak sites, dumps or landfills, or large wetlands. Dr. Erickson suggested that the source of the elevated arsenic may be clay layers within the Des Moines Lobe outwash. Figure 86 shows the arsenic results in relation to the surficial geology map. Compared to other glacial materials, the Des Moines Lobe tends to be finer grain material with higher organics and is more biochemically active and conducive to mobilizing arsenic into groundwater than other geologic conditions. Geochemical conditions at the boundary of an aquitard to the aquifer are especially geochemically reactive.

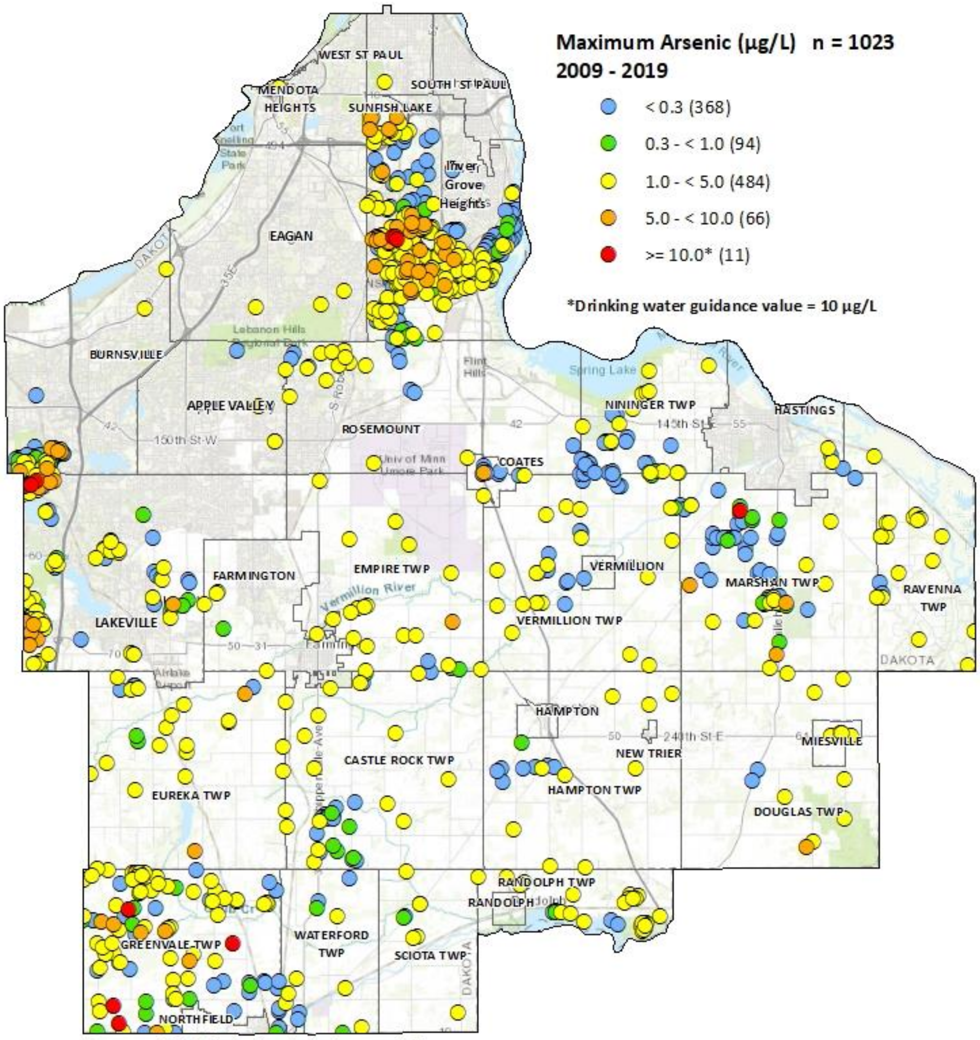
In hydrogeologic settings where arsenic source material is present, Dr. Erickson has shown a high likelihood of the occurrence of mobile arsenic in wells screened a short interval away from the lower geologic contact of the clay till confining layer. This suggests that screen placement is a control on the occurrence of arsenic in well water: screen placement at depths that maximize the distance from the clay till contact could minimize the creation of geochemical conditions that mobilize arsenic (Erickson et al., 2005).

**Table 58. Summary of Arsenic Results Comparing Datasets.**



| Sample Events | Year | # of Samples | # of Samples with Detections MRL <0.5 or 1.0 ug/L | # of Samples above Guideline of 10 ug/L | Average | Median | Max |
|---|---|---|---|---|---|---|---|
| Ambient Study outside untreated * | 2018-19 | 18 | 18 (100%) | 0 (0%) | 2.1 | 1.0 | 9.5 |
| Ambient Study inside drinking water * | 2018-19 | 18 | 7 (39%) | 0 (0%) | 0.6 | <0.5 | 4.8 |
| Inver Grove Heights outside untreated | 2016 | 269 | 153 (57%) | 2 (<1%) | 1.9 | 0.8 | 13.3 |
| Inver Grove Heights inside drinking water** | 2016 | 110 | 44 (40%) | 2 (2%) | 1.1 | <0.5 | 13.5 |
| Burnsville outside untreated | 2018 | 66 | 34 (52%) | 0 (0%) | 1.4 | 0.5 | 9.7 |
| Burnsville inside drinking water | 2018 | 35 | 18 (51%) | 0 (0%) | 1.6 | 0.6 | 7.5 |
| Greenvale outside untreated | 2019 | 94 | 64 (68%) | 3 (3%) | 2.6 | 1.6 | 50.0 |
| Greenvale inside drinking water | 2019 | 62 | 33 (53%) | 1 (2%) | 1.8 | 1.0 | 16.7 |
| Lakeville outside untreated | 2019 | 100 | 70 (70%) | 3 (3%) | 2.1 | 1.3 | 12.3 |
| Lakeville inside drinking water | 2019 | 69 | 46 (67%) | 2(3%) | 1.9 | 0.8 | 19.4 |

Figure 88 depicts all the arsenic results including arsenic from newly constructed domestic wells since 2009.



Sources: ESRI; Dakota County Environmental Resources

**Figure 88. All Arsenic Results.**

## 5.1.3. Lead

### i. Lead sources, health concerns and drinking water treatment

In most cases, when lead is found in drinking water it has leached from the pipes or some component of the plumbing. Lead is a naturally occurring element but is not very soluble in water or mobile in soil and, therefore, not likely to be present in drinking water aquifers in the County. The biggest impact the groundwater has on lead levels is from the water chemistry: water with a relatively low pH (more acidic) may leach lead from the plumbing into the drinking water.

The two most significant sources of lead in Minnesota drinking water are lead service lines and indoor plumbing fixtures (MDH and University of MN). The regulation of lead content in plumbing and well fixtures has the following history:

- June 1986: Safe Drinking Water Act (SDWA), Section 1417, prohibited the use of any lead pipe, pipe or plumbing fitting, or fixture, solder or flux.
- January 1995: all United States well pump manufactures have agreed not to use leaded-brass components in submersible pumps.
- 2008: In Minnesota, materials to be used in the construction of drinking water wells, where the material will be in contact with water, must not exceed an average of eight percent lead by weight for pipes, pipe fittings, plumbing fittings and fixtures, and 0.2 percent lead for solder and flux (MDH and University of MN).
- 2014: Section 1417 of the Safe Drinking Water Act defines “lead free” as the 0.25 percent lead weighted average for pipes, pipe fittings, plumbing fittings and fixtures, and 0.2 percent lead for solder and flux.

All people, whether they have city water or use a private well, are advised to test their primary drinking water faucet for lead if any part of their water pipes, plumbing, or drinking water faucet pre-dates the 2014 “lead free” guideline.

Exposure to lead poses a variety of health concerns for adults, women who may become pregnant, and children. Children absorb lead at higher rates than the average adult and the damage from lead exposure in children is permanent. Lead can be either dissolved in the water or in particulate form or both. The USEPA has set a maximum contaminant level of 15 µg/L for municipal water supplies, but there is no safe level of lead exposure. Lead can be removed from drinking water; an MDH Factsheet on home water treatment options is provided in Appendix E.1.

### ii. Lead in Inver Grove Heights (WIISE STUDY) and community-focused sampling

The Ambient Study well samples are collected from outside untreated water spigots and were <u>not</u> tested for lead.

In 2018–2019, study participants were provided with a sample bottle to collect and mail a water sample to the laboratory from a water sample they collect from the primary inside drinking water tap which could be water treated by a water treatment system. Samples from 48 primary taps were analyzed; lead above the MRL of 0.5 µg/L was detected in 13 (27 percent) of the wells; the maximum detected was 2.16 mg/L.

Community-focused sampling began in 2018 where all participants where only the inside water samples collected from their primary drinking water tap were tested for lead. No amount of lead is safe. Lead above the MRL of 0.5 µg/L ranged from a low in Greenvale and Lakeville of seven percent of samples to a high of 27 percent of samples in the Ambient Study wells. None of the samples exceeded the drinking water guideline of 15 µg/L; the maximum detected was 5.42 µg/L.

**Table 59. Summary of Lead Results (µg/L) Comparing Datasets.**

| Sample Events | Year | # of Samples | # of Samples with Detections MRL <0.5 or 1.0 ug/L | # of Samples above Guideline 15 ug/L | Average | Median | Max |
|---|---|---|---|---|---|---|---|
| Ambient Study inside drinking water | 1999-2019 | 48 | 13 (27%) | 0 | 0.32 | <0.5 | 2.16 |
| Inver Grove Heights inside drinking water | 2016 | 32 | 4 (13%) | 0 | 0.10 | <0.5 | 1.14 |
| Burnsville inside drinking water | 2018 | 66 | 5 (8%) | 0 | 0.09 | <0.5 | 2.13 |
| Greenvale inside drinking water | 2019 | 94 | 7 (7%) | 0 | 0.12 | <0.5 | 5.42 |
| Lakeville inside drinking water | 2019 | 100 | 7 (7%) | 0 | 0.12 | <0.5 | 5.20 |

### iii. Wells and Increased Infant Sensitivity and Exposure Study (WIISE)

In 2014–15, the County and MDH conducted a joint study of private wells in Inver Grove Heights. Lead was not a targeted parameter, but the lab notified the County of elevated lead in one sample; the County then acquired the lead results from all 274 wells. Lead was detected in 53 percent of the outside spigots where the water samples had been collected. The highest lead detected was 111.1 µg/L. Subsequent pre-purge and purge samples were collected by the well owners at their primary inside drinking water faucets (some of which had been through a treatment system). Although five samples from outside faucets exceeded 15 µg/L for lead, none of the purged samples exceeded the MRL of 0.5 µg/L. One sample had 3.04 µg/L of lead in the pre-purge sample, which was the highest.

## 5.1.4. Copper

### i. Copper sources, health concerns and drinking water treatment

Copper may occur naturally in groundwater, but it can also leach from copper pipes into drinking water. Over time, plumbing parts with copper in them usually build up a natural coating that prevents copper from being dissolved into the water. Plumbing systems with copper parts newer than three years old usually have not had time to build up this protective coating. Copper is an essential nutrient in small amounts and necessary in our diet for good health but eating or drinking too much copper can cause vomiting, diarrhea, stomach cramps, nausea, liver damage and kidney disease. People with Wilson's disease and some infants (under one year old) are extra sensitive to copper. Drinking water with more than 1.3 mg/L of copper can be a health risk for everyone. Infants and people with Wilson's disease may need water with an even lower level of copper to stay safe (MDH, August 2018). Copper can be removed from drinking water; an MDH Factsheet on home water treatment options is provided in Appendix E.1.

### ii. Copper results

The Ambient Study well samples are collected from outside untreated water spigots that were not tested for copper.

In 2018–2019, study participants were provided with a sample bottle to collect and mail a water sample to the laboratory from a water sample they collect from the primary inside drinking water tap which could be water treated by a water treatment system. Samples from 46 primary taps were analyzed; copper above the MRL of 0.005 mg/L was detected in 22 (48 percent) of the wells; the maximum detected was 1.28 mg/L, just below the guideline. Despite concerns that copper and lead in drinking water may occur together, there was no lead above the MRL of 0.5 µg/L is this same water sample.

In 2018, 66 samples collected from the community-focused Burnsville sampling from the primary inside drinking water tap found copper detected in 30 wells (45 percent) above the MRL of 0.005 mg/L; the highest result was 0.113 mg/L, and no lead was detected in that sample. Chloride can make water corrosive and possibly leach metals, such as copper or lead, from plumbing into the drinking water. The outside chloride results from the Burnsville water samples were not correlated with the inside copper results (Kendall, p = 0.36).

## 5.2. Radionuclides

### 5.2.1. Radionuclide Sources and Health Concerns

Radionuclides are unbalanced atoms that emit ionizing radiation in the form of alpha particles, beta particles and/or gamma rays. Radionuclides are geologically sourced and can dissolve into groundwater and drinking water. Radionuclides are also present in food and in the air; they have no odor or taste.

Consuming drinking water containing these contaminants at high levels for a short time and lower levels every day for many years increases the risk of cancer. Radium behaves like calcium and can replace calcium in bones which increases the risk of developing bone cancer and blood cancer. The USEPA goal, known as the MCLG, is the level where there is no known or expected risk to health. The MCLG for all radioactive contaminants is zero.

Municipalities are required to test for radionuclides and to meet the following maximum contaminant levels (MCLs):

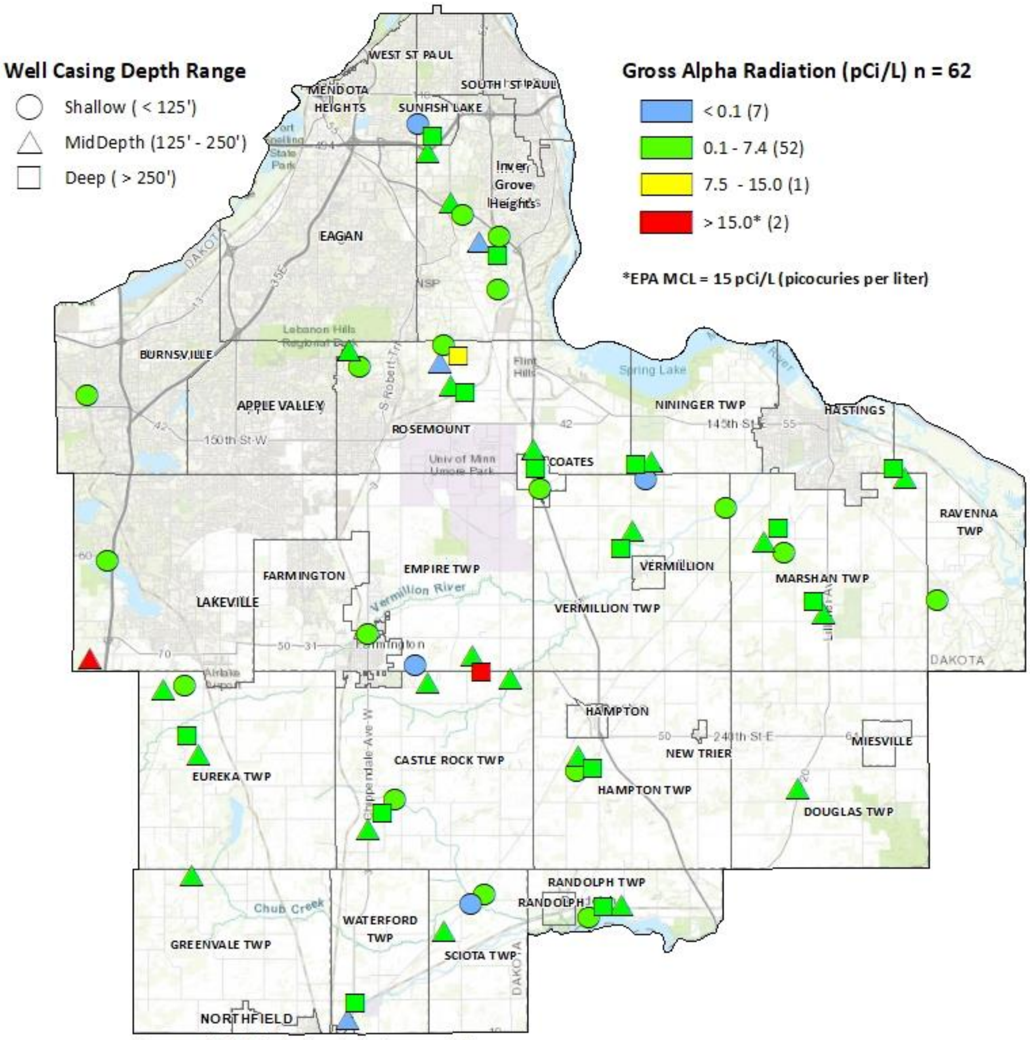
- Alpha particles (includes gross alpha): 15.0 picocuries per liter of water (pCi/L) or less
- Combined radium-226 plus radium-228: 5.0 pCi/L or less
- Uranium: 20.0 pCi/L or less
- Beta particles/photon emitters: 4.0 millirem per year (mrem/yr) or less (MDH, August 2019)

Private wells are not required to be tested for radionuclides, but the testing is available through MDH certified laboratories. (States such as Vermont and Wisconsin recommend private well owners test their water for gross alpha.) When gross alpha is above 5.0 pCi/L, it is recommended that testing for radium-226 and radium-228 occur. There are treatment options available to reduce radionuclides in drinking water; the MDH factsheet on home water treatment options is provided in Appendix E.1. Testing of the treated water to determine the effectiveness of the treatment devices is important.

According to the MDH, there is an inverse relationship between radionuclides in water and indoor radon levels (Conversation with Karla Peterson at MDH Community Water Systems Drinking Water Standards). The Ambient Study well samples were not tested for radon and neither was radon in the indoor air. All homes should be tested for airborne radon, especially in the basement level because radon levels above the USEPA action level of 4.0 pCi/L exist in households in the County.

### 5.2.2. Radionuclide Results

Radium-226 has a half-life of 1,600 years and emits alpha particles. Radium-228 has a half-life of 5.75 years and emits beta particles. The presence of gross alpha in water is an indication that there is radioactive decay related to radium-226, an alpha emitter. In 2018, 62 of the Ambient Study wells were tested for gross alpha, and two exceeded the drinking water guideline of 15 pCi/L. The two wells have nothing apparent in common: they are not located geographically close to each other, and they differ in total well depth by 184 feet and well casing depth by 57 feet. They are completed in different aquifers: one in the Cjdn and the other in the Opdc. See Figure 89 of gross alpha results by well casing depth.



Sources: ESRI; Dakota County Environmental Resources

**Figure 89. Gross Alpha by Well Casing Depth.**

In 2019, 61 of the Ambient Study wells were tested for radium-226 and radium-228. Sixty of the same wells were tested in 2018-2019; the results are summarized in Table 64 in relation to well casing depth category. Per a conversation with Pace laboratory, negative results are where sample count rates are lower than the background count rates. Negative results are treated as non-detects and are reported in in Appendix B Table B.28. of all the gross alpha and radium results by well.

**Table 60. Descriptive Statistics of Radionuclides 2018–2019 Sample Events (picocuries per liter).**

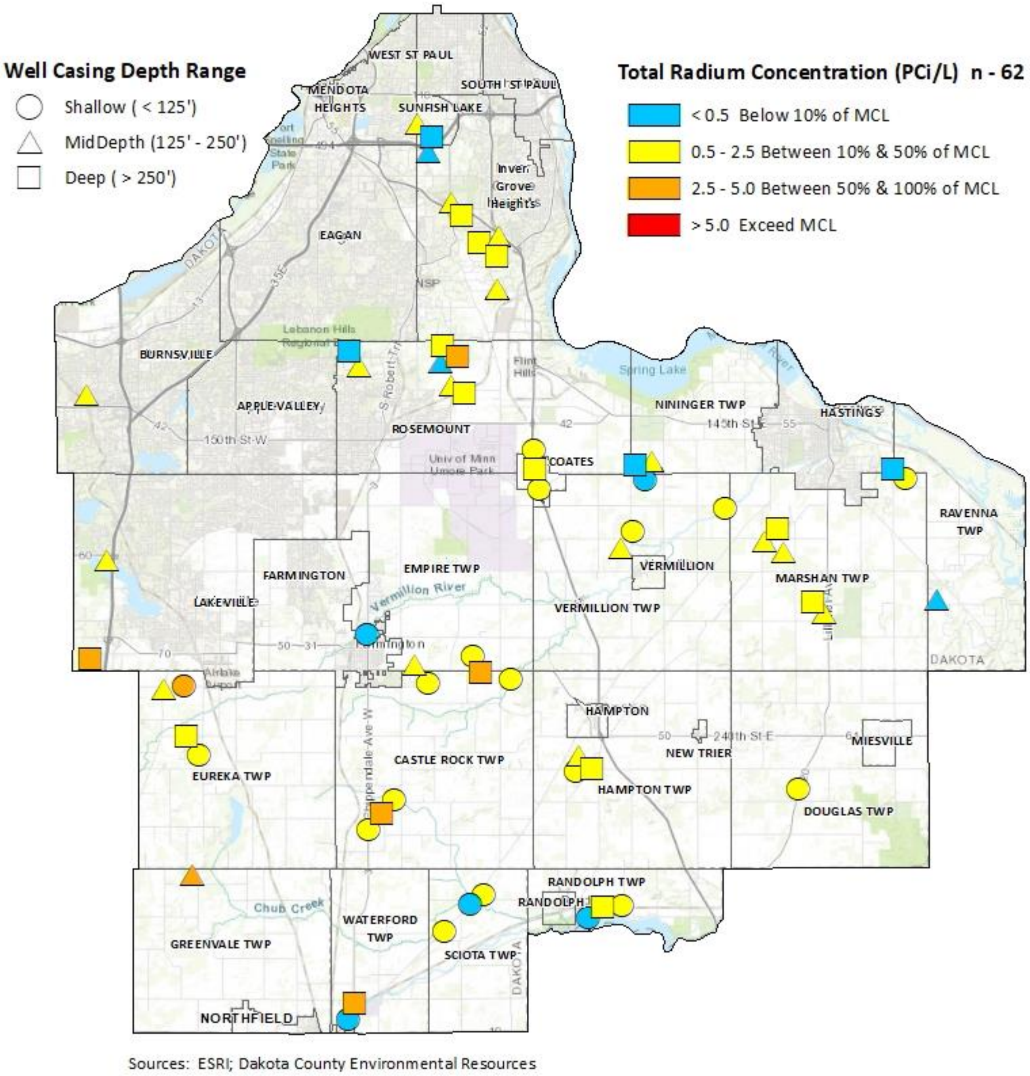
| Parameter | Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|---|
| Gross Alpha | Shallow <125' | 22 | 2.554 | 3.549 | Non-detect | 0.597 | 1.175 | 3.840 | 16.200 |
| | Mid 125' to 250' | 20 | 2.690 | 2.787 | Non-detect | 0.813 | 2.120 | 3.550 | 11.900 |
| | Deep >250' | 20 | 3.257 | 3.542 | Non-detect | 0.899 | 2.000 | 5.550 | 15.200 |
| Radium 226 | Shallow <125' | 22 | 0.475 | 0.559 | Non-detect | 0.056 | 0.208 | 0.730 | 2.010 |
| | Mid 125' to 250' | 19 | 0.482 | 0.761 | Non-detect | 0.140 | 0.255 | 0.390 | 3.350 |
| | Deep >250' | 20 | 0.891 | 1.067 | 0.051 | 0.115 | 0.446 | 1.120 | 3.360 |
| Radium 228 | Shallow <125' | 22 | 0.525 | 0.311 | Non-detect | 0.348 | 0.493 | 0.679 | 1.170 |
| | Mid 125' to 250' | 19 | 0.724 | 0.395 | 0.165 | 0.396 | 0.640 | 0.942 | 1.560 |
| | Deep >250' | 20 | 0.849 | 0.541 | 0.144 | 0.385 | 0.783 | 1.348 | 1.950 |

Of the 60 wells tested in 2019, 59 wells (97 percent) had either radium-226 (Figure 91) or radium-228 (Figure 92) detected. Radioactivity measurements are statistical measurements that have a certain amount of inherent uncertainty. All the results were provided from the laboratory with the calculated uncertainty value. When the uncertainty is calculated and added to the combined radium-226 and radium-228 result, there are four bedrock wells in the southwest area of the County (two in the Prairie du Chien and two wells in the Jordan Aquifer) with measurable probability of exceeding the combined drinking water guideline of 5.0 pCi/L; two of these wells also exceeded the guideline for gross alpha in 2018. The wells are listed in Table 64 summarize the wells where the percent probability of exceeding 5.0 pCi/L is considered as possibly over the drinking water guideline of 5.0 picocuries per liter.

**Table 61. Wells that Exceed Guideline for Combined Radium 226 and Radium 228.**

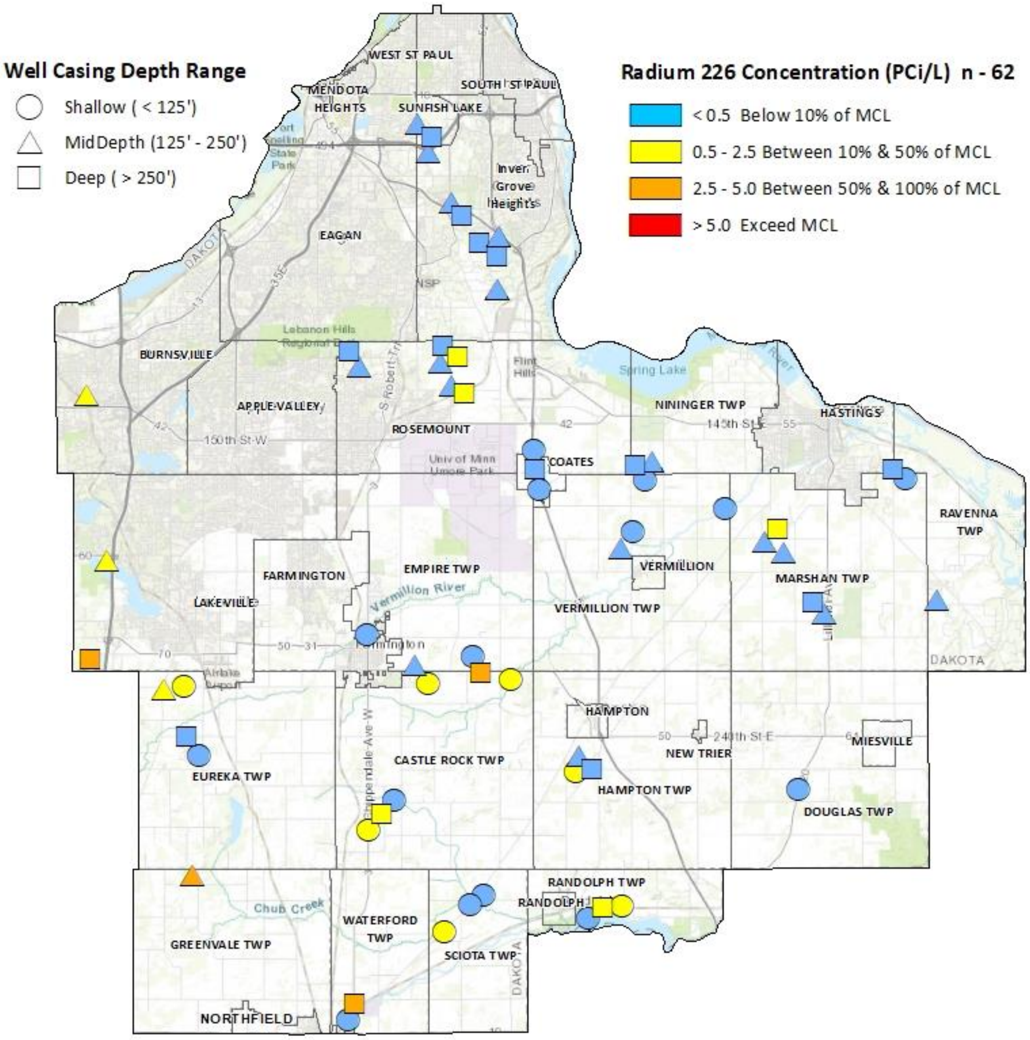
| Alias | Casing Category | Casing Depth | Total Depth | Aquifer | Municipality | Grout | Probablity of exceeding 5 pCi/L |
|---|---|---|---|---|---|---|---|
| AGQS-26 | Deep | 342 | 360 | Opdc | Lakeville | No grout | 38% |
| AGQS-28 | Deep | 285 | 300 | Cjdn | Castle Rock Twp | Neat cement | 1% |
| AGQS-40 | Deep | 300 | 320 | Cjdn | Waterford Twp | Neat cement | 29% |
| AGQS-50 | Mid | 173 | 181 | Opdc | Greenvale Twp | Bentonite | 29% |

The results of radium-226 and radium-228 are combined (added) and depicted in Figure 90.



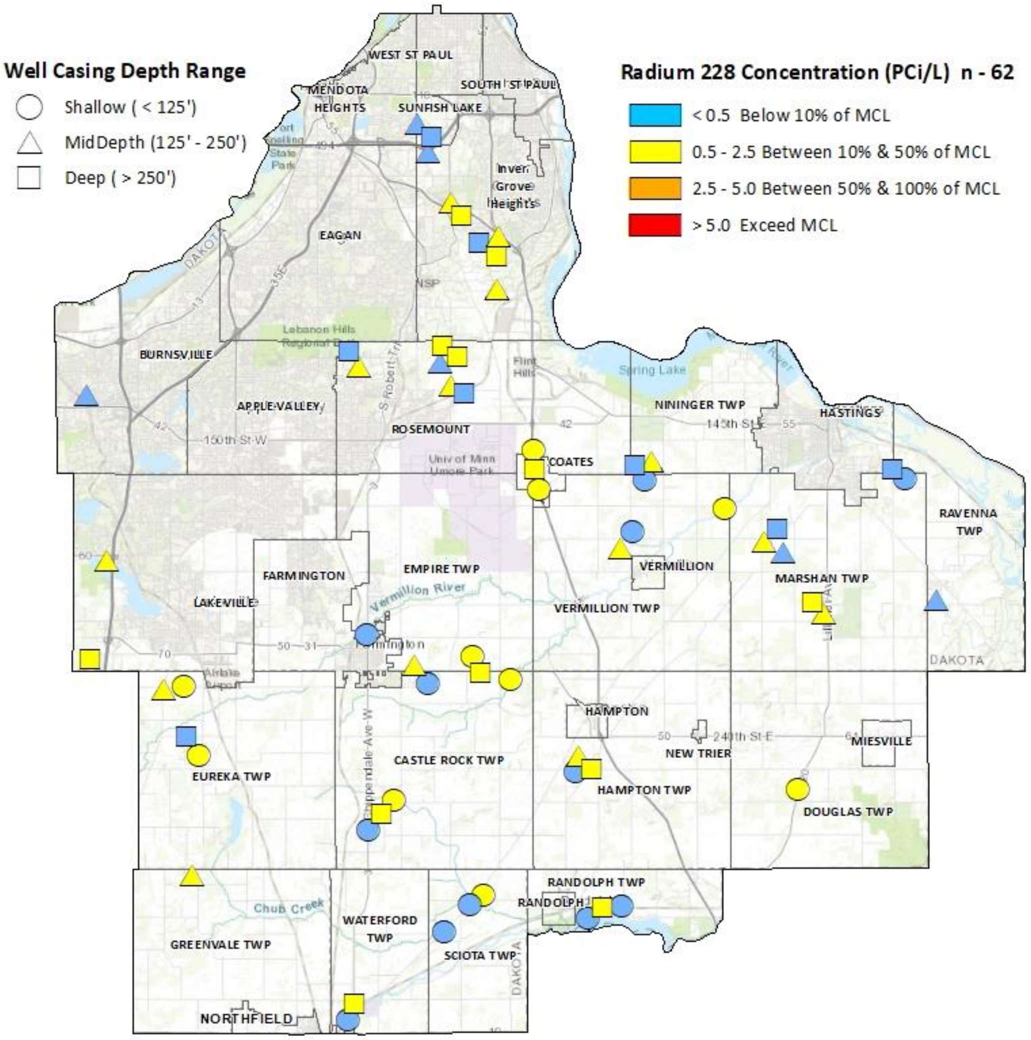
Sources: ESRI; Dakota County Environmental Resources

Figure 90. Combined Ra 226 & Ra 228.



Sources: ESRI; Dakota County Environmental Resources

**Figure 91. Radium-226 by Casing Depth Category.**

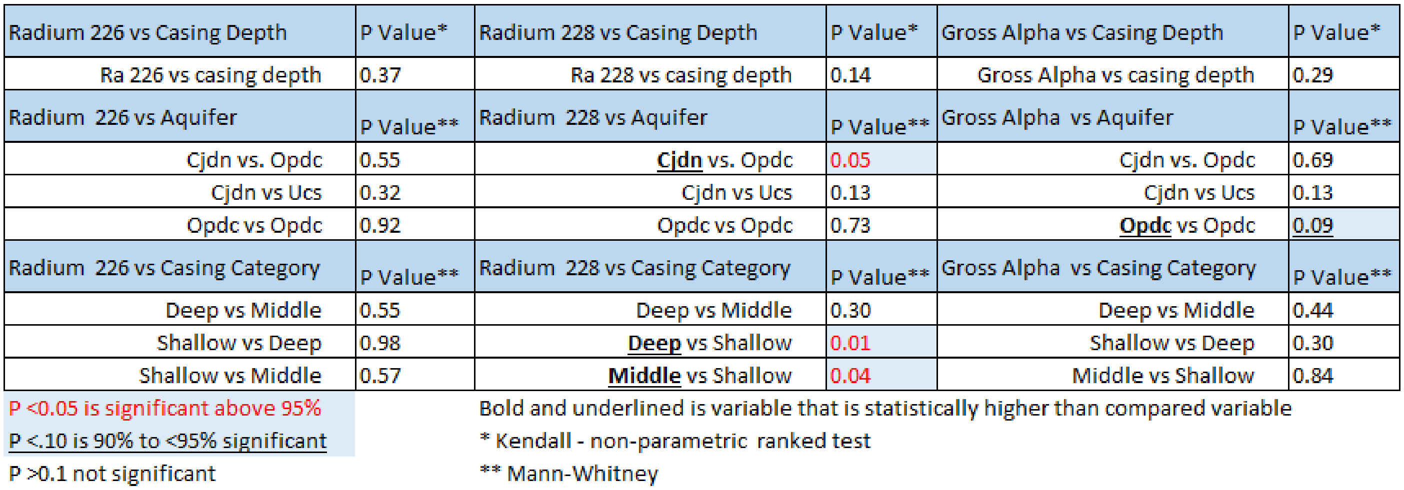


Sources: ESRI; Dakota County Environmental Resources

**Figure 92. Radium-228 by Casing Depth Category.**

Non-parametric statistics were utilized to examine the data. When radionuclide activity results were less than the laboratory calculated minimum detection concentration (MDC), the result was treated as a non-detect at the MDC. There is a high statistical correlation between radium-226 and gross alpha (Kendall, p <.001). This is useful because it means well owners can test their water for gross alpha to inform them about the probability of having radium-226, which is available at local labs and is more affordable than testing for radium-226. Correlation between radium-226 and radium-228 was not significant (Kendall, p = 0.11). Radionuclides individually were compared to well casing depth, aquifer, and well casing depth categories and are summarized in Table 65.

**Table 62. Summary of Radionuclides Statistical Correlations.**



| Radium 226 vs Casing Depth | P Value* | Radium 228 vs Casing Depth | P Value* | Gross Alpha vs Casing Depth | P Value* |
|---|---|---|---|---|---|
| Ra 226 vs casing depth | 0.37 | Ra 228 vs casing depth | 0.14 | Gross Alpha vs casing depth | 0.29 |
| Radium 226 vs Aquifer | P Value** | Radium 228 vs Aquifer | P Value** | Gross Alpha vs Aquifer | P Value** |
| Cjdn vs. Opdc | 0.55 | **<u>Cjdn</u>** vs. Opdc | 0.05 | Cjdn vs. Opdc | 0.69 |
| Cjdn vs Ucs | 0.32 | Cjdn vs Ucs | 0.13 | Cjdn vs Ucs | 0.13 |
| Opdc vs Opdc | 0.92 | Opdc vs Opdc | 0.73 | **<u>Opdc</u>** vs Opdc | <u>0.09</u> |
| Radium 226 vs Casing Category | P Value** | Radium 228 vs Casing Category | P Value** | Gross Alpha vs Casing Category | P Value** |
| Deep vs Middle | 0.55 | Deep vs Middle | 0.30 | Deep vs Middle | 0.44 |
| Shallow vs Deep | 0.98 | **<u>Deep</u>** vs Shallow | 0.01 | Shallow vs Deep | 0.30 |
| Shallow vs Middle | 0.57 | **<u>Middle</u>** vs Shallow | 0.04 | Middle vs Shallow | 0.84 |

P <0.05 is significant above 95%

<u>P <.10 is 90% to <95% significant</u>

P >0.1 not significant

Bold and underlined is variable that is statistically higher than compared variable

* Kendall - non-parametric ranked test

** Mann-Whitney

Two correlations are significant at 95 percent: radium-228 is higher in deep versus shallow cased wells (Mann-Whitney, p <0.05) and in the middle casing depth versus shallow wells (Mann-Whitney, p <0.05). Two correlations are significant at 90 percent: radium-228 is higher in Cjdn wells when compared to Opdc wells (Mann-Whitney, p <0.05), and gross alpha is higher in Opdc wells compared to Ucs (Mann-Whitney, p <0.10). In general, shallow wells less than 125 feet deep (shallow well casing depth category) or screened in the Ucs are less likely to have elevated radium-228. This differs from the anthropogenic compounds that are most prevalent and elevated in shallower wells in both the Ucs and Opdc. There is no pattern for radium-226, so all wells are regardless of aquifer or casing depth could have elevated radium-226; this could be due to the long half-life of radium 226 of 1600 years.

## 5.3. Barium

### 5.3.1. Barium Sources, Health Concerns and Drinking Water Treatment

Barium can occur naturally in food and Minnesota groundwater from the dissolution of the mineral barite, but it is not very soluble in water. In most groundwater settings, the presence of sulfate limits the solubility of barium. Barium can also be associated with mine tailings or copper smelting, in areas where those occur.

The health effects of different barium compounds depend on how well the compound dissolves in water. Barium compounds that do not dissolve well in water are not generally harmful and are often used by doctors for medical purposes. If the sulfate concentration in the water is high, then the precipitation of barium as a sulfate salt reduces its potential for adverse health effects. Elevated levels of soluble barium can cause difficulties in breathing, increased blood pressure, changes in heart rhythm, stomach irritation, brain swelling, muscle weakness, and damage to the liver, kidney, heart and spleen. The drinking water guideline for barium is 2.0 mg/L.

Barium can be removed from household drinking water by cation exchange, reverse osmosis, or distillation (Water Quality Association, 2013).

### 5.3.2. Barium Results

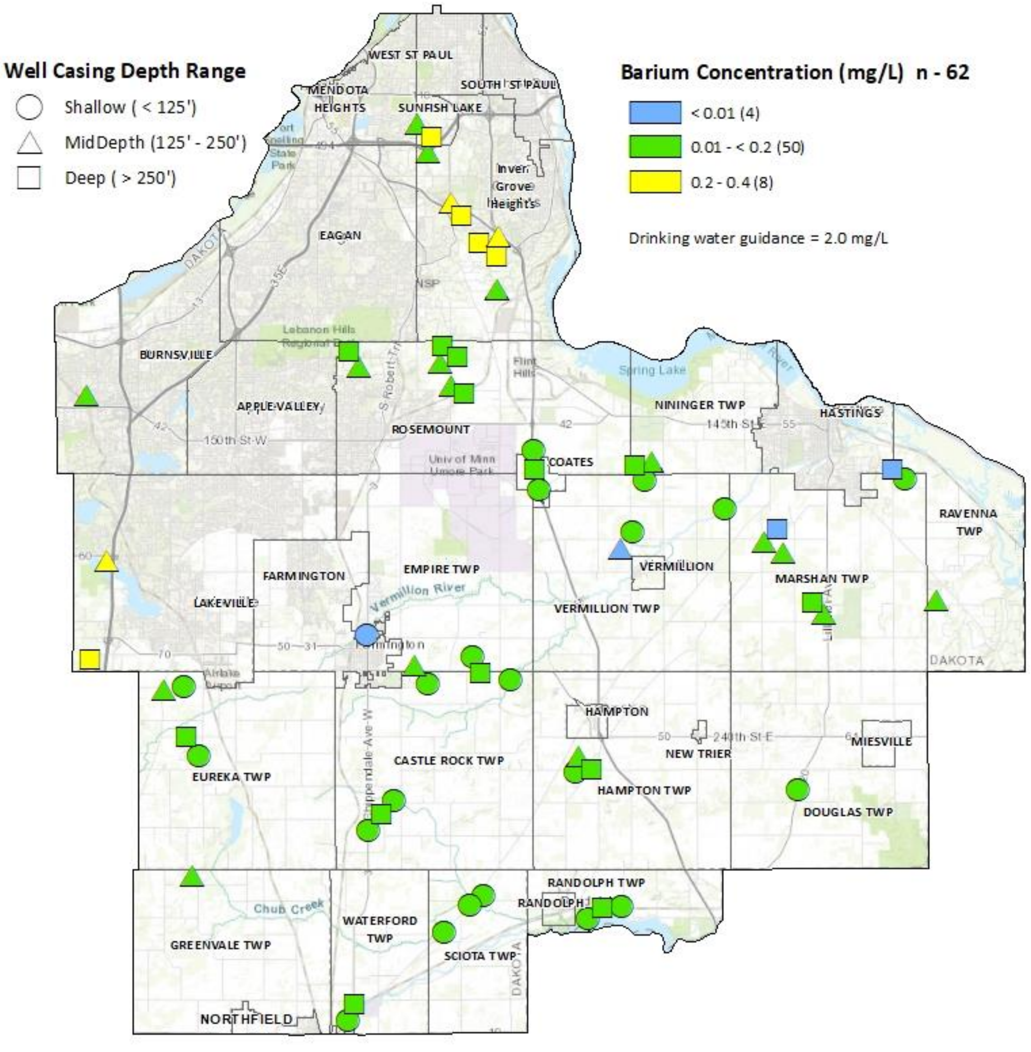
In 2018, the 62 Ambient Study wells were tested for barium to align with the parameters of the MDH sampling program of private wells for radioactive contaminants. The hypothesis is that barium may help to determine the occurrence and source of radium in the groundwater, should the barium results correlate with the 2019 Ambient Study radium testing. The maximum level detected was 0.374 mg/L, which is below the drinking water guideline of 2.0 mg/L.

The barium results are summarized in Table 66 by well casing depth. The average, median and maximum barium are in the middle well casing category. There is no correlation between barium and well casing depth (Kendall, p = 0.90).

**Table 63. Descriptive Statistics of Barium (mg/L) Results by Well Casing Depth Category.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 22 | 0.063 | 0.034 | <0.005 | 0.034 | 0.059 | 0.086 | 0.134 |
| Mid 125' to 250' | 20 | 0.110 | 0.102 | 0.009 | 0.031 | 0.074 | 0.156 | 0.374 |
| Deep >250' | 20 | 0.098 | 0.113 | 0.008 | 0.016 | 0.048 | 0.183 | 0.326 |

Glacial till is prevalent in the north and west areas of the County where detections of barium above the MRL are detected (Figure 93). The shales and clay in the till may be the source of barium; they also tend to be a source of arsenic and manganese.



Sources: ESRI; Dakota County Environmental Resources

Figure 93. Barium Results by Well Casing Depth.

The correlations between barium and manganese, arsenic and iron are all statistically significant (Kendall, p <.001). There is no statistical correlation between barium and sulfate (Kendall, p = 0.47), gross alpha (Kendall, p = 0.54), radium-226 (Kendall, p = 0.23) and radium-228 (Kendall, p = .32). Table 67 summarizes the correlations.

**Table 64. Barium Correlations with Select Chemical.**

| Barium Correlations | Direction | P Value* |
|---|---|---|
| Arsenic | Increasing | <0.05 |
| Iron | Increasing | <0.05 |
| Manganese | Increasing | <0.05 |
| Radium 226 | N/A | 0.11 |
| Radium 228 | N/A | 0.32 |
| Gross Alpha | N/A | 0.54 |
| Sulfate | N/A | 0.47 |
| Well Casing Depth | N/A | 0.90 |

*Kendall nonparametric correlation

Figure 94 depicts barium results by well casing depth; there is more scatter in the data in the middle and deep well casing depth categories.

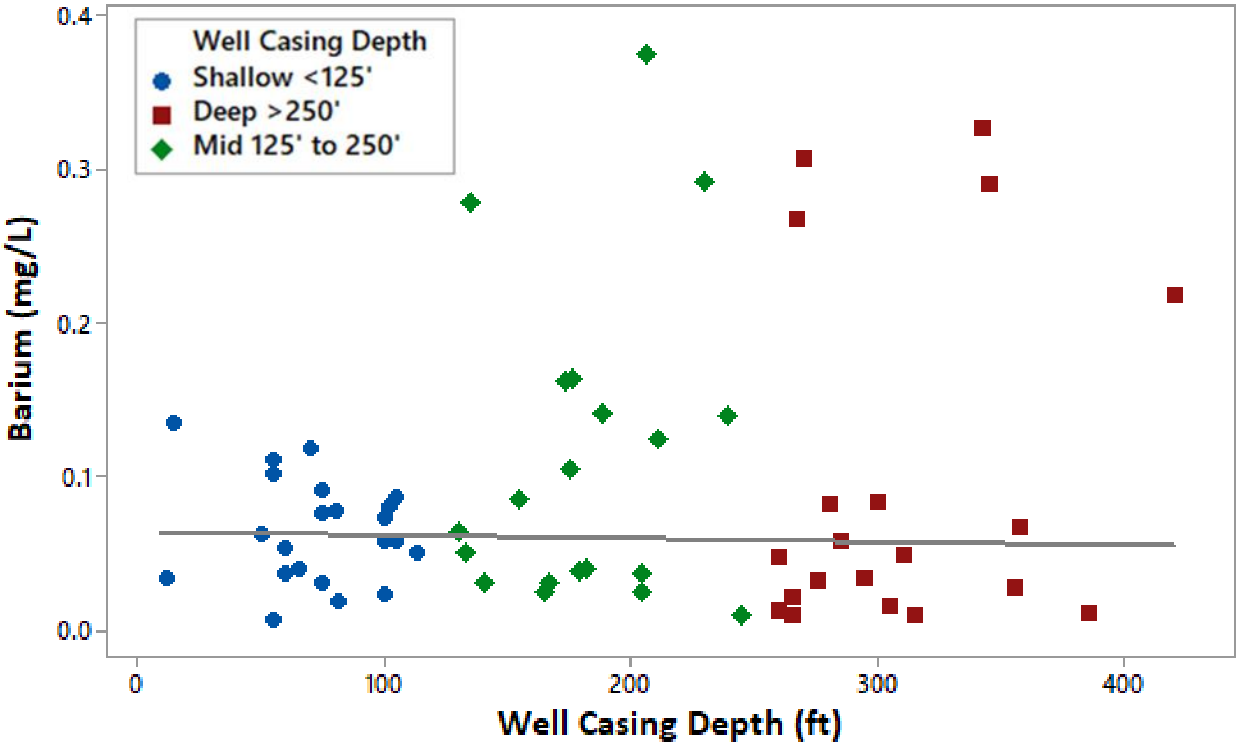


**Figure 94. Correlation of Barium and Well Casing Depth.**

# 5.4. Other naturally-occurring parameters

## 5.4.1. Fluoride

### i. Fluoride sources and health concerns

Fluoride is a naturally-occurring element found in water, air and soil across Minnesota. Fluoride can help prevent tooth decay, but too much fluoride can damage teeth, bones and joints. The recommended fluoride level in drinking water for good oral health is 0.7 mg/L. The USEPA has an established drinking water guideline of 4.0 mg/L for fluoride.

Knowing the natural levels of fluoride in your well can help you decide if fluoride supplements are right for your family’s dental health. If fluoride levels in your drinking water are lower than 0.7 mg/L, your child's dentist or pediatrician should evaluate whether your child could benefit from daily fluoride supplements.

### ii. Fluoride results

In the Ambient Study data set, no wells have a median fluoride level higher than 0.7 mg/L. Only three wells have ever tested higher than 0.7 mg/L over the course of 14 to 15 sampling events; the highest fluoride result was 0.94 mg/L. Most well water does not contain enough fluoride for dental health in the County. All the fluoride results are in Appendix B Table B.10.

### iii. Fluoride and well casing depth

Fluoride is not correlated with aquifer (Table 4), but it is positively correlated with well casing depth (Kendall, p <0.05). Comparison of the fluoride results by well casing categories are summarized in Table 68.

**Table 65. Descriptive Statistics of Average Fluoride Results (mg/L) by Well Casing Depth Category.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26 | 0.10 | 0.07 | 0.03 | 0.04 | 0.09 | 0.12 | 0.28 |
| Mid 125' to 250' | 26 | 0.12 | 0.08 | 0.03 | 0.06 | 0.11 | 0.15 | 0.41 |
| Deep >250' | 25 | 0.12 | 0.05 | 0.03 | 0.08 | 0.13 | 0.16 | 0.21 |

Figure 95 shows that fluoride increases with well casing depth.

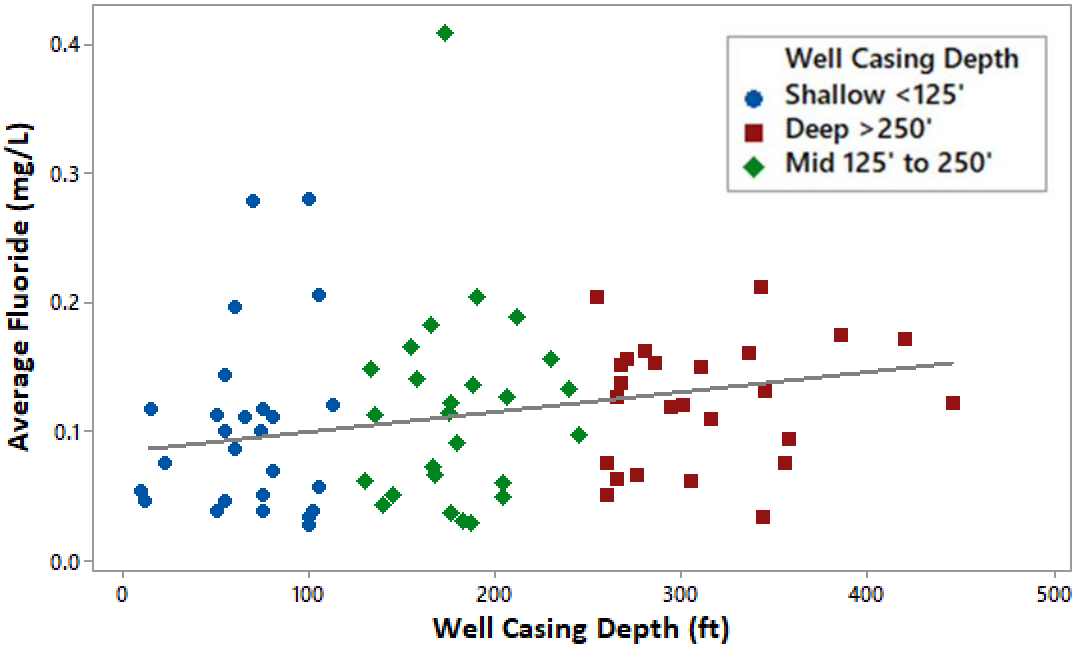


**Figure 95. Correlation of Fluoride and Well Casing Depth—Kendall Line.**

## 5.4.2. Dissolved Oxygen

### i. Dissolved Oxygen Sources

Dissolved Oxygen (DO) in groundwater is derived from atmospheric oxygen ($O_2$). The typical temperature of groundwater in the County is 10–13°C, and the solubility of $O_2$ in water at equilibrium with the atmosphere at these temperatures is 12–13 mg/L DO. Water infiltrating soil initially is in approximate equilibrium with the atmosphere regarding $O_2$. Microbes in organic matter consume $O_2$ and produce carbon dioxide in the soil and vadose zones. Above the water table, $O_2$ can be added to infiltrating water from the gas phase. Below the water table, no gas phase is present, and no reactions generate $O_2$. As a result, DO generally decreases with depth in most aquifers as dissolved and solid phase organic materials breakdown. DO in the infiltrating water is consumed by organic matter in the soil. Shallow water should have higher DO than deeper water; if it does not, then the water is warmer, the $O_2$ has been consumed by microbes in organic matter or in a wetland, sulfide minerals, or the $O_2$ has been consumed by contamination such as from septic systems, manure, wastewater discharge or a contaminant spill.

### ii. Dissolved Oxygen Results and Well Casing Depth

To collect a well water sample with representative, DO concentrations, contact between the water and the atmosphere must be minimized. Many Ambient Study wells show a lot of variability for DO over the 13 sampling years (Appendix B Table B.8.); some of this is likely attributable to accidental introduction of air when the samples were collected. This is especially likely if a sample is collected directly from an outside faucet into a sample vessel. A better procedure is to run a flexible tube from the faucet into the bottom of a bucket, then allow water to gently flow into the bottom and overflow the top. Since the guideline procedure is to purge the well system of water until a stable temperature is obtained, the “bucket” method produces a sample of water representing the well system with minimal contact with atmosphere. When this “bucket” procedure was used in the 2009, 2011 and 2013 sample events, the results are different from previous years (Kendall, $p < 0.05$).

DO levels in the Ambient Study wells ranged from 0.01 mg/L to 25.5 mg/L; the median DO level for all Ambient Study wells is 3.9 mg/L. The 20 wells in the Cjdn have a lower median DO level of 2.9 mg/L — lower than either the 28 wells in the Opdc, which have a median of 4.9 mg/L, or the 28 wells in the Ucs, which have a median of 5.8 mg/L (Table 4). The Cjdn water is older and deeper than the other aquifers, so there has been more time for biologic breakdown of organic material originating at the surface to consume the DO. Opdc and Ucs levels for DO are not statistically different from each other.

DO is negatively correlated with well casing depth (Kendall, $p < 0.05$). Comparison of the median DO results by well casing categories are summarized in Table 69.

**Table 66. Descriptive Statistics of Median Dissolved Oxygen Results (mg/L) by Well Casing Depth Category.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26 | 5.36 | 3.60 | 0.42 | 1.72 | 5.16 | 8.48 | 11.03 |
| Mid 125' to 250' | 26 | 6.31 | 3.16 | 0.25 | 3.48 | 7.10 | 9.06 | 11.00 |
| Deep >250' | 25 | 3.51 | 2.62 | 0.41 | 1.34 | 2.54 | 5.05 | 9.70 |

Figure 96 shows that DO increases with depth.

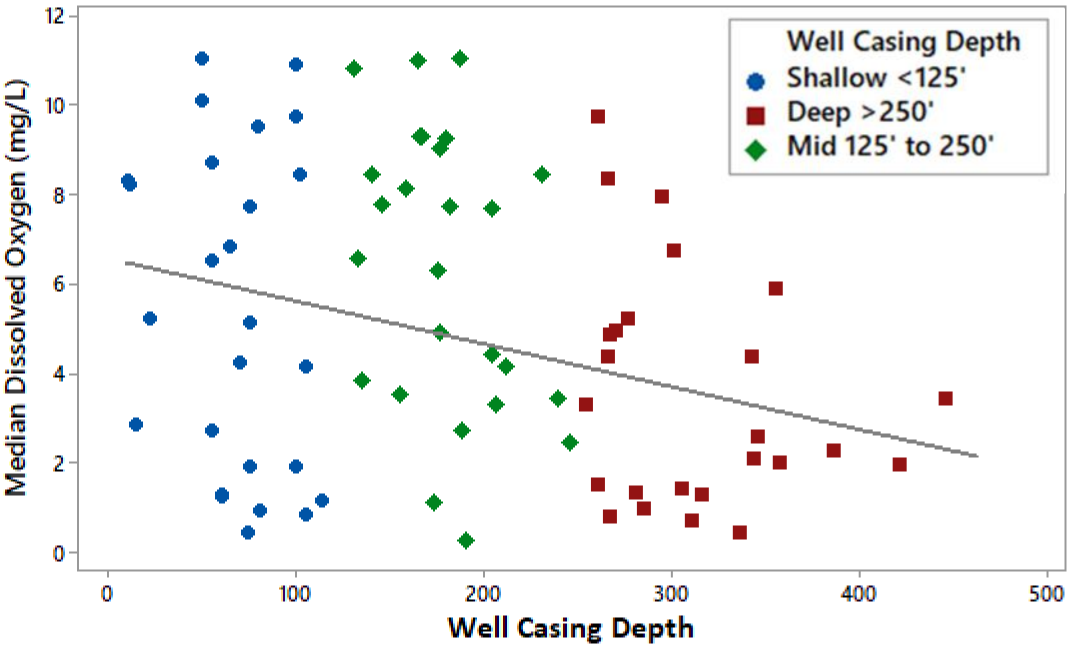


Figure 96. Correlation of Dissolved Oxygen and Well Casing Depth—Kendall Line.

### iii. Nitrate and Dissolved Oxygen

Nitrate is positively correlated with DO (Kendall, p <0.05) depicted in Figure 97. Most all wells (60) have median DO above about 2 mg/l. Field and lab studies for *denitrification* indicate that a DO below 2 mg/l is one of several *necessary conditions* for this reaction. In addition, temperature above about 45-degrees F or ~13 degrees C, all average temperatures are below 13 degrees C, see Appendix B. Table B.25. With typical nitrate levels in the infiltrating water ranging from 10 to 20 mg/L in high percent of row crop agriculture, Total Organic Carbon (TOC) would need to be in the same concentration range of 10 to 20 mg/L to support denitrification on a continuous, ongoing basis. See Appendix B. Table B.27 for TOC results. TOC only exceeded 10 mg/L in four wells in 1999, subsequent testing show TOC levels were dramatically lower than the 1999 sampling event. None of the conditions for denitrification exist in the Ambient Study wells.

For 33 wells with nitrate level at or below detection of 0.2 mg/L, the DO levels are almost all below the median DO of 1.0 mg/L for those wells and only 2 wells have DO levels above 4.0 mg/L. There are two possible reasons why wells with low DO have low nitrate: 1) there are no sources of nitrate in the water that infiltrate to the well; or 2) the well is deep and the nitrate has not reached the depth of the well casing yet.

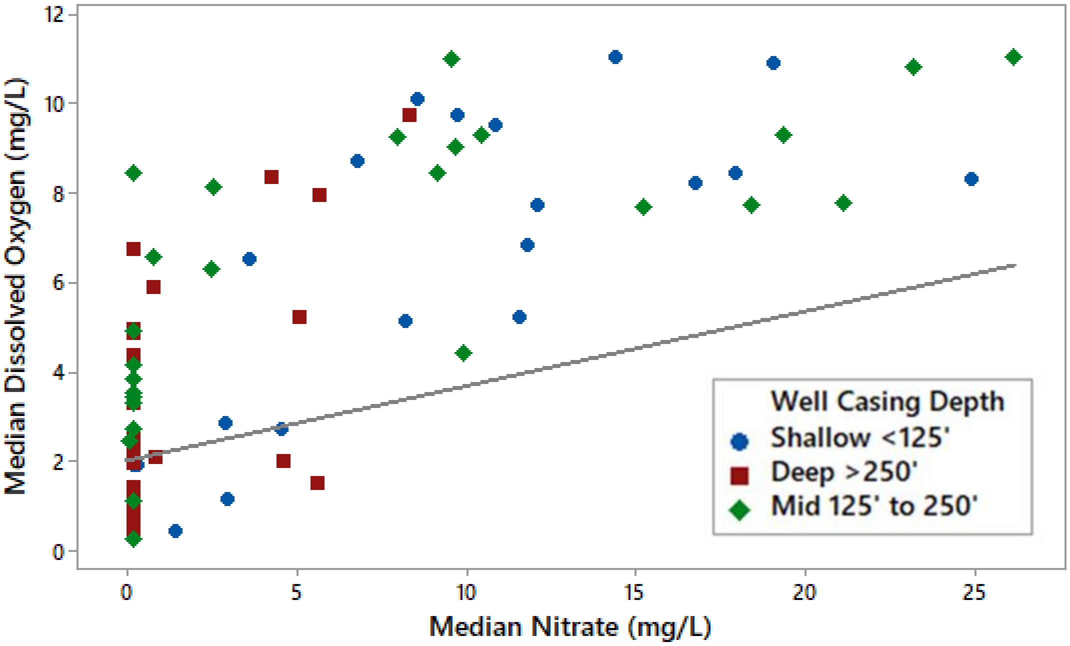


Figure 97. Correlation of Median Dissolved Oxygen to Nitrate—Kendall Line.

### 5.4.3. Iron

#### i. Iron sources, concerns and water treatment

Iron in the plus-2 oxidation state, Fe(II), is the major form of iron found in uncontaminated groundwater where carbonate geology dominates, like Dakota County's geology. In such carbonate environments, natural waters are almost always slightly alkaline. Fe(III) is only present in very small amounts due to the quite limited solubility of $Fe(OH)_3$ under alkaline conditions. Soluble Fe(III) can occur under more acid conditions, such as with acid mine drainage. Common analytical procedures do not necessarily distinguish between oxidation states for iron. It is usually assumed that under neutral to alkaline conditions, Fe(II) is the dominant ion present. Fe(III) oxide is known to be a cementing agent in limestones and sandstones and is not appreciably soluble in alkaline environments.

The USEPA has established a SMCL for iron of 0.3 mg/L for the aesthetic quality of the water. There are no drinking water guidelines related to health for iron. Water with iron concentrations exceeding 0.3 mg/L may be rusty in color, contain sediment, have a metallic taste or cause red to orange staining on plumbing fixtures. Water softeners remove a small amount of iron from well water, but a specialized iron removal system may be needed in situations where the iron is a significant nuisance.

### ii. Iron results and well casing depth

The iron results are summarized by well in Appendix B Table B.13. Iron concentrations range from <0.2 mg/L to 73.1 mg/L, with a median level of 0.02 mg/L. Iron levels are positively correlated with well casing depth (Kendall, p <0.05). Iron is negatively correlated with DO (Kendall, p <0.05); that is, iron decreases as DO increases. The iron in the Cjdn groundwater today is suspected to be derived internally from the Fe(III) oxides converted to Fe(II) under low DO conditions. Potential sources for the iron could be from the cementing material of the Cjdn bedrock or from soil that has subsequently infiltrated to the Cjdn. Because there is so much DO in the shallower aquifers, it is not likely that soils are the source of the iron. It is more probable that the iron is geologically sourced from the Cjdn. Comparison of the average iron results by well casing categories are summarized in Table 70.

**Table 67. Descriptive Statistics of Average Iron Results (mg/L) by Well Casing Depth Category.**

| Casing Category | # of Wells | Average | Std Deviation | Minimum | 25th Percentile | Median | 75th Percentile | Maximum |
|---|---|---|---|---|---|---|---|---|
| Shallow <125' | 26 | 1.35 | 3.72 | 0.02 | 0.05 | 0.12 | 0.83 | 18.40 |
| Mid 125' to 250' | 26 | 1.07 | 1.87 | 0.01 | 0.07 | 0.21 | 1.55 | 9.16 |
| Deep >250' | 25 | 1.36 | 1.24 | 0.03 | 0.07 | 1.37 | 2.21 | 4.46 |

Figure 98 shows that average iron increases with depth and there are elevated median iron results above 5.0 mg/L in both the shallow and middle well casing categories.

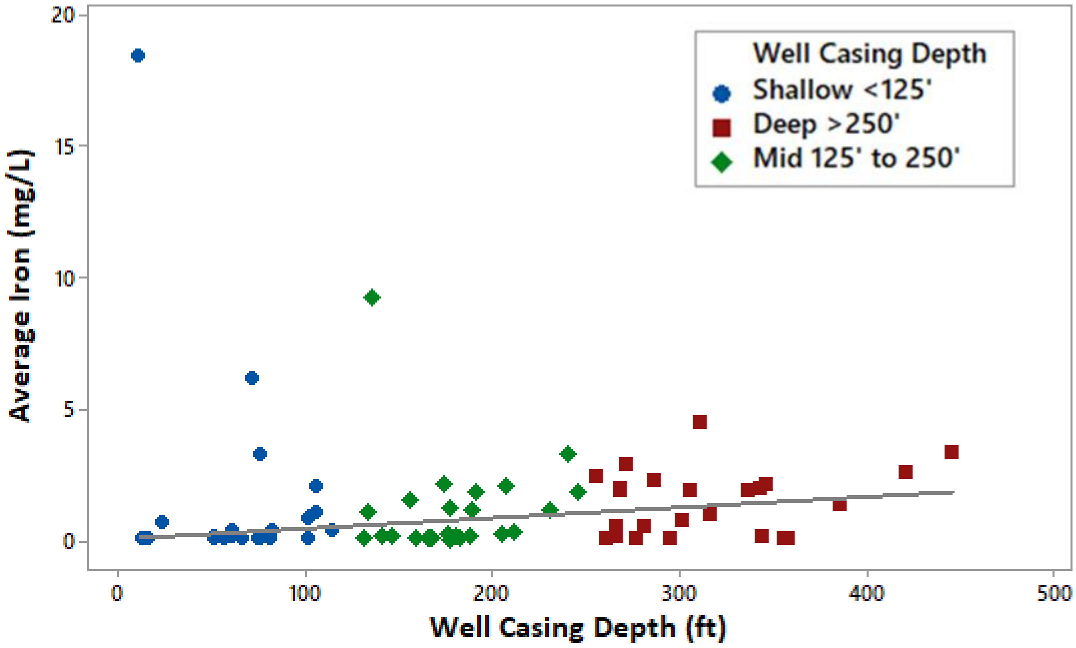


**Figure 98. Correlation of Iron and Well Casing Depth—Kendall Line.**

### 5.4.4. Other Parameters

Other parameters were analyzed and may be referred to in this report, but a section discussing the results was not warranted. See Appendix A for summary tables of results from the following parameters:

- Alkalinity
- Calcium
- Eh
- Hardness
- Noncarbonate hardness
- Magnesium
- Silica
- Temperature
- Total Dissolved Solids
- Specific conductance
- pH
- Total Organic Carbon

# 6. Ambient Study Conclusions

Private drinking water wells are not generally monitored or regulated by public agencies for water quality concerns. Private well owners are responsible for the safety of their own wells and often have no control over the contaminants that impact the aquifer water. From 1999 to 2019, Dakota County has monitored private drinking water wells to characterize the County's ambient groundwater conditions over time, using wells selected to represent the three main drinking water aquifers—Ucs, Opdc and Cjdn—and conditions throughout the County. The result is a unique collection of data about the County's groundwater conditions.

The Ambient Study results indicate that about two-thirds of the County's households that rely on private wells may exceed a drinking water guideline for at least one contaminant. The County's soils and geology make much of the County's groundwater susceptible to contamination from any pollution source at the surface.

In rural Dakota County, the major issues are nitrate from fertilizer and agricultural herbicides—especially the breakdown products of cyanazine, which have proved to be persistent in groundwater despite cyanazine being discontinued as of 2002. Nitrate levels are rising or have reached equilibrium or stable levels above the drinking water guideline. Herbicide trends vary according to the individual chemical and its history of use.

Countywide, rising levels of chloride in Ambient Study wells, while not health concern for drinking water, demonstrate the sensitivity of the groundwater to contamination from the surface. Chloride can change the geochemistry of the water and potentially mobilize other, more toxic, contaminants (such as lead).

In the eastern and northern parts of the County, the major issues are naturally-occurring contaminants like manganese and arsenic. However, manganese and arsenic levels are difficult to predict; every well owner should test their well for these contaminants at least once.

In the private wells Dakota County has sampled, 1) anthropogenic contamination follows groundwater movement deeper in the groundwater, and 2) natural- occurring contaminants are not related to specific well depths or aquifers. In the early years of the Study, anthropogenic contamination was rarely found in deeper, Cjdn wells. By 2019, it is no longer unusual to find elevated nitrate or cyanazine breakdown products in deeper wells. The deepest well cyanazine was detected was in a municipal well in Farmington, where the casing depth is at 417 feet. Because of these issues with both anthropogenic and naturally-occurring contaminants, it is no longer prudent to assume that using a deeper well will be a long-term solution to water contamination issues.

The Ambient Study results confirm MDH and MPCA studies that CECs such as PFAS, organic wastewater compounds and pharmaceuticals are present in Dakota County groundwater. Although, in drinking water, CEC detections are below current health guidelines, their presence, sources and health effects are not adequately understood. For example, the PFAS chemical, PFBA, was detected in 79 percent of the wells tested, but at levels below the recommended health guideline. The PFAS chemicals, PFPeA, PFOA, and PFHxS, were detected in 34 percent, 24 percent, and 19 percent of the wells tested, respectively; these detections were also below the health guideline.

The large number of PFAS chemicals in the environment and their health risks, especially in mixtures with each other or other contaminants, are not well understood. When two chemicals have the same toxic endpoint, each chemical can be below a recommended guideline; but, if both chemicals are in the water, the sum can be above the guideline and the water unsafe to drink. Some PFAS chemicals have the same toxic endpoints as each other or as other contaminants that may be in the same well water.

In addition to PFAS chemicals, the Ambient Study also found organic wastewater compounds and pharmaceuticals in private wells. The sources of these CECs are not known, but old dumps or land application of biosolids from wastewater treatment plants are suspected. Additional information is needed to better understand the health risks that CECs pose in drinking water.

# 7. Actions Taken in Response to Dakota County Groundwater Research Findings

## 7.1. Private Well Water Testing and Treatment

### 7.1.1. Dakota County Ordinance 114, Well and Water Management

In November 2019, the Dakota County Board adopted a revised Ordinance No. 114 Well and Water Management. New provisions include the following:

- When a new drinking water well is constructed, MDH requires that the water be tested for nitrate, coliform bacteria and arsenic. Dakota County now requires manganese testing as well.
- The County previously required that, if a new well's pre-completion water sample exceeded the nitrate drinking water guideline, the well contractor had to drill the well deep enough to avoid the contamination. Now, the new well's owner has the option to install a water treatment system instead of having the well drilled deeper.
- At the time of property transfer, Dakota County previously required that the well be tested for nitrate and coliform bacteria. The County has added arsenic and manganese to the required testing.

### 7.1.2. Expanded Free Water Testing

- In 2019, Dakota County was in the process of updating its Groundwater Plan. As part of the Groundwater Plan's Stakeholder Engagement Process, the County partnered with MDA to provide free nitrate testing clinics. The County has also hosted free lead testing events for residents, regardless of whether they use city water or a private well.
- In conjunction with the Groundwater Plan update, County staff is implementing a program to provide, over the course of five years, every residence that uses a private well the opportunity to receive a free test for nitrate, arsenic, manganese, lead and chloride.
- County staff is exploring ways to subsidize water treatment systems for low-income residents with contaminated wells.

## 7.2. Agricultural Chemicals

### 7.2.1. Cyanazine Breakdown Products

In 2019, because of Dakota County's persistence in sampling private wells for cyanazine breakdown products in cooperation with the USGS, and because of the number of wells that continue to exceed the drinking water guideline for cyanazine, MDA has:

- Contracted with two companies to create “standards” (standardized chemical solutions) for cyanazine breakdown products, which have been difficult to obtain because cyanazine is no longer manufactured.
- Obtained the USGS analytical method for cyanazine breakdown products, implemented it in their own lab, and shared it with a commercial lab, Weck Laboratories, so Weck can do the testing on a fee-for-service basis.
- Added cyanazine breakdown products to their statewide pesticide monitoring program.
- With Dakota County’s cooperation, provided 166 private well owners that the County had previously tested for cyanazine breakdown products with the opportunity to have their wells re-tested in 2019.
- In 2019–2020, tested 13 municipal wells in Dakota County for pesticides which included the cyanazine breakdown products.

### 7.2.2. Nitrate

- Independent of Dakota County’s sampling program, MDA is in the process of implementing its Nitrogen Fertilizer Management Plan, adopted in 2015 to reduce nitrate contamination of groundwater in Minnesota. In July 2019, the State adopted a Groundwater Protection Rule that restricts the fall use of nitrogen fertilizer in easily contaminated parts of the state, like Dakota County. The Rule contains additional measures to protect groundwater for the Drinking Water Supply Management Areas of public water suppliers that have elevated nitrate in their wells, such as Hastings.
- As a follow-up to the Groundwater Plan update, County staff will work with stakeholders to develop and implement an Agricultural Chemical Reduction Effort (ACRE) to address agricultural contamination of groundwater, beyond the MDA’s efforts.

### 7.2.3. Naturally Occurring Geologically Sourced Contaminants

- MDH is using the results of the joint MDH-Dakota County WIISE Study as the basis for its water treatment advice for manganese.
- The County’s proposed five-year sampling program for all County well owners will provide a more complete picture of the distribution of manganese and arsenic in the County’s groundwater.
- The County added required testing for new drinking water wells and manganese and arsenic testing at the time of property transaction; see discussion of Ordinance No. 114 above.

# 8. Ambient Groundwater Quality Study Recommendations

## 8.1. Assistance and Education

- Increase and improve education and outreach efforts. Develop, implement and update groundwater contamination maps, develop explanatory factsheets and other information on the County website to help inform private well owners and municipalities.
- To the extent appropriate and possible, collect demographic data to evaluate if water quality problems disproportionately impact specific populations and to address those inequities.
- Develop and implement a sampling schedule that will provide every well owner in the County the opportunity to have their well tested for nitrate, arsenic, manganese, lead and chloride, and will support the Agriculture Chemical Reduction Effort implementation.
- Communicate water test results and health risk.
- Ensure information for well owners is available in multiple languages and accessible formats.
- Develop a program promoting the installation and maintenance of household treatment systems (RO) where groundwater contaminants are elevated or exceed drinking water guidelines or are elevated above 50 percent of the drinking water guidance.
- Develop opportunities to work with State and County public health departments to inform local health care providers on the existence and risks associated with elevated nitrate, manganese, arsenic and herbicide concentrations in private water supply wells.
- Support feasibility studies to determine if a rural water supply system or expansion of public water systems are practical.

## 8.2. Agricultural Chemicals

- Work with MDA to ensure private well sampling schedules will also support implementation of the Groundwater Protection Rule and Nitrogen Fertilizer Management Plan.
- Partner with MDA to develop a long-term groundwater monitoring network to evaluate effectiveness of the Groundwater Protection Rule, the Nitrogen Fertilizer Management Plan and the Dakota County Agriculture Chemical Reduction Effort.
- Work with MDA and MDH to implement their response to cyanazine breakdown product contamination in Dakota County.

## 8.4. Research and Analysis

- Work with state agencies, watershed organizations and others to further research of the groundwater/surface water interface.
- Conduct research and analysis to determine the influence of irrigated agriculture on groundwater contaminated with nitrate and pesticides.
- Work with MDA, MDH and the City of Hastings to evaluate the threat to Hastings water supply for non-point agricultural chemicals. Expand sampling within the buried bedrock valley to determine to better understand infiltration and groundwater flow.
- Retain a researcher to conduct an epidemiological analysis that would assess agricultural chemical contamination of drinking water (e.g., complex agricultural chemical mixtures) with health outcomes among Dakota County residents.
- Develop and implement a project to sample private wells for pathogens (viruses, bacteria and protozoan parasites), which MDH detected in 70 percent of a sampling of non-community and community wells statewide as part of their recent study of pathogen study (MDH Pathogens).
- Evaluate impact of land application of sewage sludge and other biosolids on County groundwater quality.
    - Review published literature to identify characteristics of groundwater impacted by land application of sludge and biosolids vs. groundwater not impacted.
    - Identify known locations of sludge, biosolids, and manure applications.
    - With well owner permission, sample potentially impacted and presumably non-impacted wells for pathogens, PFAS and organic wastewater compounds.

## 8.5. Contaminants of Emerging Concern

- Work with MPCA to evaluate the source(s) of  PFAS in groundwater beginning with an analysis of PFAS near WWTP biosolid application sites in Dakota County.
- When new CECs are identified that could be a risk for County residents, sample private wells to screen the County’s drinking water supplies for detections and concentrations of the contaminant.

# 9. References

3M, 2010a. Comments of 3M Company on Minnesota Department of Health's Draft Public Assessment on Perfluorochemicals in Southern Washington County, Northern Dakota County, and Southeast Ramsey County, Minnesota. October 12, 2010.

Bloetscher, F., F. Pleitez, J. Hart, D. Stambaugh, J. Cooper, K. Kennedy, L. Sher Burack. 2014. Comparing Contaminant removal costs for aquifer recharge with wastewater with water supply benefits. JAWRA-Vol. 50, No. 2, P: 324-333.

ChemSafetyPro, n-Octanol/Water Partition Coefficient ($K_{ow}$/log$K_{ow}$) https://www.chemsafetypro.com/Topics/CRA/n_Octanol_Water_Partition_Coefficient_Kow.html.

Clark, G.M., Goolsby, D.A.. 1999. Trends in Annual Herbicide Loads from the Mississippi River Basin to the Gulf of Mexico. https://toxics.usgs.gov/pubs/wri99-4018/Volume2/sectionC/2404_Clark/pdf/2404_Clark.pdf

Dubrovsky, N.M., Burow, K.R., Clark, G.M., Gronberg, J.M., Hamilton P.A., Hitt, K.J., Mueller, D.K., Munn, M.D., Nolan, B.T. Puckett, L.J., Rupert, M.G., Short, T.M., Spahr, N.E., Sprague, L.A., and Wilber, W.G. 2010. The quality of our Nation's waters—Nutrients in the Nation's streams and groundwater, 1992–2004: U.S. Geological Survey Circular 1350.

EPA, Endocrine. https://www.epa.gov/endocrine-disruption/what-endocrine-disruption. (Accessed July 24, 2020).

EPA, Basic Information on PFAS. https://www.epa.gov/pfas/basic-information-pfas#health. (Accessed July 14, 2019).

Erickson ML and Barnes RJ. 2005. Well characteristics influencing arsenic concentrations in ground water. Elsevier Water Research 39: 4029-4039

Kaushal, S.S., G.E. Likens, M.L. Pace, R.M. Utz, S. Haq, J. Gorman, and M. Grese. 2017. Freshwater salinization syndrome on a continental scale. Proceedings of the National Academy of Sciences, January 2018, 115 (4) E574-E583; DOI: 10.1073/pnas.1711234115. https://www.pnas.org/content/115/4/E574.

Gao, Yongli, Alexander, Calvin E. Jr., Tipping, Robert G. The Development of a Karst Feature Database for Southeastern Minnesota. Journal of Cave and Karst Studies. April 2002. https://caves.org/pub/journal/PDF/V64/v64n1-Goa.pdf.

Kolok, A.S., M.K. Sellin, L. Knight, D.D. Snow, and S.L. Bartelt-Hunt. 2014. The Hourglass: a conceptual framework for the transport of biologically active compounds from agricultural landscapes. JAWRA-13-0060-P:266-274.

International Agency for Research on Cancer, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 94. 2010. Ingested Nitrate and Nitrite and Cyanobacterial Peptide Toxins. https://monographs.iarc.fr/ENG/Monographs/vol94/index.php.

Madison, R.J. and Brunett, J.O. 1985. Overview of the occurrence of nitrate in ground water of the United States, in National Water Summary 1984-Hydrologic Events, Selected Water-Quality Trends, and Ground-Water Resources: U.S. Geological Survey Water-Supply Paper 2275, pp. 93-105.

Mark J. VanGessel, "Glyphosate-Resistant Horseweed from Delaware," Weed Science, Vol. 49, No. 6, Nov-Dec. 2001

Metropolitan Council, (MCES) Empire Wastewater Treatment Plant. https://metrocouncil.org/Wastewater-Water/Publications-And-Resources/WASTEWATER/TREATMENT-PLANTS/Empire-Wastewater-Treatment-Plant.aspx. (Accessed June 14, 2019).

Metropolitan Council, 2018, Water Efficiency Potential Project. https://metrocouncil.org/Wastewater-Water/Planning/Water-Supply-Planning/Studies-Projects-Workgroups-(1)/Completed-Studies-Projects/Water-Efficiency-Potential-Project.aspx (Accessed June 25, 2020).

MN Department of Agriculture (MDA) 2019. 2019 Water Quality Monitoring Report. https://wrl.mnpals.net/islandora/object/WRLrepository%3A3580/datastream/PDF/view

MN Department of Agriculture (MDA). 1999. 1999 Survey of Farmers within the Perham Wellhead Protection Area. https://www.mda.state.mn.us/sites/default/files/inline-files/1997PerhamWellheadArea.pdf.

MN Department of Agriculture (MDA). 2013. Pesticide Usage on Four Major Crops in Minnesota September 2016. https://www.mda.state.mn.us/sites/default/files/inline-files/2013pesticiderpt.pdf.

MN Department of Agriculture (MDA). 2015. Pesticide Usage on Corn and Hay Grown in Minnesota. March 5, 2019. https://www.mda.state.mn.us/sites/default/files/inline-files/pesticideoncornhay2015.pdf.

MN Department of Agriculture (MDA). 2017. Final Township Testing Nitrate Report: Dakota County 2013-2015. Updated February 2018. https://www.mda.state.mn.us/sites/default/files/inline-files/dakotaoverallfinal_1.pdf

MN Department of Agriculture (MDA). Removal of pesticides and nitrate-nitrogen from private well water using in-home reverse osmosis. February 2020. https://wrl.mnpals.net/islandora/object/WRLrepository%3A3523/datastream/PDF/view

MN Department of Health (MDH) 2010. Public health assessment: Perfluorochemical contamination in southern Washington, northern Dakota County, and southeastern Ramsey County, Minnesota. Public comment release available at https://www.health.state.mn.us/communities/environment/hazardous/docs/pfas/pha3m0112.pdf.

MN Department of Health (MDH) July 2014. Tetrachloroethylene (PCE) and Drinking Water, https://www.health.state.mn.us/communities/environment/risk/docs/guidance/gw/tetpercinfo.pdf.

MN Department of Health (MDH). March 2016. Southeast Minnesota Domestic Well Network 2016 Data Report. https://www.health.state.mn.us/communities/environment/water/docs/swp/no3report.pdf.

MN Department of Health (MDA) 2018. Toxicological Summary for : Cyanazine. https://www.health.state.mn.us/communities/environment/risk/docs/guidance/gw/cyanazine.pdf

MN Department of Health (MDH). March 2018. Toxicological Summary for: Manganese https://www.health.state.mn.us/communities/environment/risk/docs/guidance/gw/manganese.pdf.

MN Department of Health (MDH). August 2018. Copper in Drinking Water. https://www.health.state.mn.us/communities/environment/water/docs/contaminants/copperfactsht.pdf.

Minnesota Department of Health (MDH). December 21, 2018. Cumulative Risk Assessment for 2017 Dakota County Pesticide Data.

Minnesota Department of Health and University of Minnesota (MDH and University of Minnesota). February 2019. Lead in Minnesota Water Assessment of Eliminating Lead in Minnesota Drinking Water.

Minnesota Department of Health (MDH). August 2019. Manganese in Drinking Water. https://www.health.state.mn.us/communities/environment/water/contaminants/manganese.html

Minnesota Department of Health (MDH). August 2019. Manganese in Drinking Water. Radionuclides (Radium) in Drinking Water. https://www.health.state.mn.us/communities/environment/water/contaminants/radionuclides.html#Protect

Minnesota Department of Health (MDH). August 2019. Sulfate in Well Water. https://www.health.state.mn.us/communities/environment/water/docs/wells/waterquality/sulfate.pdf.

Minnesota Department of Health (MDH). Undated. Rapid Assessments for Pharmaceuticals. https://www.health.state.mn.us/communities/environment/risk/guidance/dwec/pharmproj.html (Accessed July 16, 2019).

Minnesota Department of Health (MDH). Undated. Pathogens in Public Drinking Water Wells. (Accessed July 8, 2020) https://www.health.state.mn.us/communities/environment/water/docs/cwf/virusfs.pdf.

Minnesota Department of Natural Resources. (MN DNR). Climate Trends. (Accessed June 25, 2020) https://www.dnr.state.mn.us/climate/climate_change_info/climate-trends.html.

Minnesota Pollution Control Agency (MPCA) 1999. Baseline Water Quality of Minnesota's Principal Aquifers—Region 5, Southeast MN.

Minnesota Pollution Control Agency and Minnesota Department of Agriculture (MPCA & MDA). December 1991. Nitrogen in Minnesota Groundwater.

Minnesota Pollution Control Agency (MPCA). January 2012. Endocrine Active Chemical and Other Contaminants of Emerging Concern in Minnesota's Groundwater, 2009-2010. https://www.pca.state.mn.us/sites/default/files/wq-cm4-03.pdf.

Minnesota Pollution Control Agency (MPCA). 2016. Ambient Sediment Quality Conditions in Minnesota. https://www.pca.state.mn.us/sites/default/files/tdr-g1-19.pdf.

Minnesota Pollution Control Agency (MPCA), 2019. Best Management Practices and Data Needs for Groundwater Protection. https://www.pca.state.mn.us/sites/default/files/wq-gw1-08.pdf.

Minnesota Pollution Control Agency (MPCA), July 2019. "The Condition of Minnesota's Groundwater Quality, 2013-2017."

Mossler, J.H., 2013, Bedrock geology of the Twin Cities ten-county metropolitan area, Minnesota: Minnesota Geological Survey Miscellaneous Map M-194, scale 1:125,000.

Overbo, Alycia, S. Heger, S. Kyser, B. Asleson, and J. Gulliver. 2019. "Chloride Contributions from Water Softeners and Other Domestic, Commercial, Industrial, and Agricultural Sources to Minnesota Waters." Ph.D. Thesis, St. Paul, MN: University of Minnesota. https://www.wrc.umn.edu/sites/wrc.umn.edu/files/overbo_finaldraftchloridebudgetreport_jan2019_1.pdf.

Rade, I., N. Kocevar, B. Strukelj. 2008. Optimized method for determination of amoxicillin, ampicillin, sulfamethoxazole, and sulfacetamide in animal feed by micellar electrokinetic capillary chromatography and comparison with high-performance liquid chromatography. Croatica Chemica ACTA 82 (3) (2009) 685-694.

Scher D., and V. Demuth, 2017. Wells and Increased Infant Sensitivity and Exposure (WIISE) Study https://www.co.dakota.mn.us/Environment/WaterResources/WellsDrinkingWater/Documents/WellsIncreasedInfantSensitivityExposureStudy.pdf.

United States Department of Agriculture (USDA). Pesticide Use in U.S. Agriculture: 21 Selected Crops, 1960-2008. https://www.ers.usda.gov/webdocs/publications/43854/46734_eib124.pdf?v=41830.

United States Department of Agriculture (USDA NASS). https://www.nass.usda.gov/Charts_and_Maps/Field_Crops/soyyld.php and https://www.nass.usda.gov/Charts_and_Maps/Field_Crops/cornyld.php. Accessed July 30, 2020.

United States Environmental Protection Agency (USEPA) Cyanazine-Special Review Position Document 1- 1985

United States Environmental Protection Agency (USEPA) Chemicals Evaluated for Carcinogenic Potential Annual Cancer Report -2018 http://npic.orst.edu/chemicals_evaluated.pdf

United State Geological Survey (USGS). Estimated Annual Agricultural Pesticide Use. https://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2012&map=ALACHLOR&hilo=L&disp=Alachlor

United States Geological Survey (USGS). Water Quality Benchmarks for Contaminants. https://www.usgs.gov/mission-areas/water-resources/science/water-quality-benchmarks-contaminants?qt-science_center_objects=0#qt-science_center_objects.

United States Geological Survey (USGS). Waterwatch. Accessed August 2020. https://waterwatch.usgs.gov/.

United States Geological Survey (USGS). Walter, Donald A., Starn, Jeffrey J. The Use of process Models to Inform and Improve Statistical Models of Nitrate Occurrence, Great Miami River Basin, Southwestern Ohio. USGS Scientific Investigation Report 2012.

Ward, M.H., Jones, R.H., Brender, J.D., de Kok, T. M., Weyer, P. J., Nolan, B. T., Villanueva, C. M., and van Breda, S. G. 2018. Drinking Water Nitrate and Human Health: An Updated Review. International Journal of Environmental Research and Public Health. 2018 July; 15(7): 1557. Published online 2018 Jul 23. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6068531/.

Water Quality Association. 2013. Barium Fact Sheet. https://www.wqa.org/Portals/0/Technical/Technical%20Fact%20Sheets/2014_Barium.pdf.

Weedscience. International Herbicide-Resistant Weed Database. Accessed. September 1, 2020. http://weedscience.org/Pages/Case.aspx?ResistID=5333

Wikipedia contributors. (Wikipedia). Contaminants of emerging concern. In *Wikipedia, The Free Encyclopedia*. Accessed 16:00, July 11, 2019, https://en.wikipedia.org/wiki/Contaminants_of_emerging_concern.

Wikipedia contributors. (Wikipedia). Denitrification. In *Wikipedia, The Free Encyclopedia*. Accessed 07:23, July 14, 2019, https://en.wikipedia.org/wiki/Denitrification.

# List of Appendices

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Appendix B (Tables B.1. to B.29.): Table Results by Well – General Chemistry, Radionuclide, and PFAS

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Appendix F: Visualizing aquifer nitrate observations in space and time

Appendix G: Additional Maps

Appendix H: Groundwater modeling and land use factor analysis