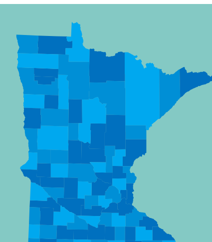
Groundwater quality

April 2025

The Condition of Minnesota's Groundwater Quality 2018 – 2023

An assessment of current water-quality conditions and trends in Minnesota's groundwater

MINNESOTA POLLUTION CONTROL AGENCY



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Introduction

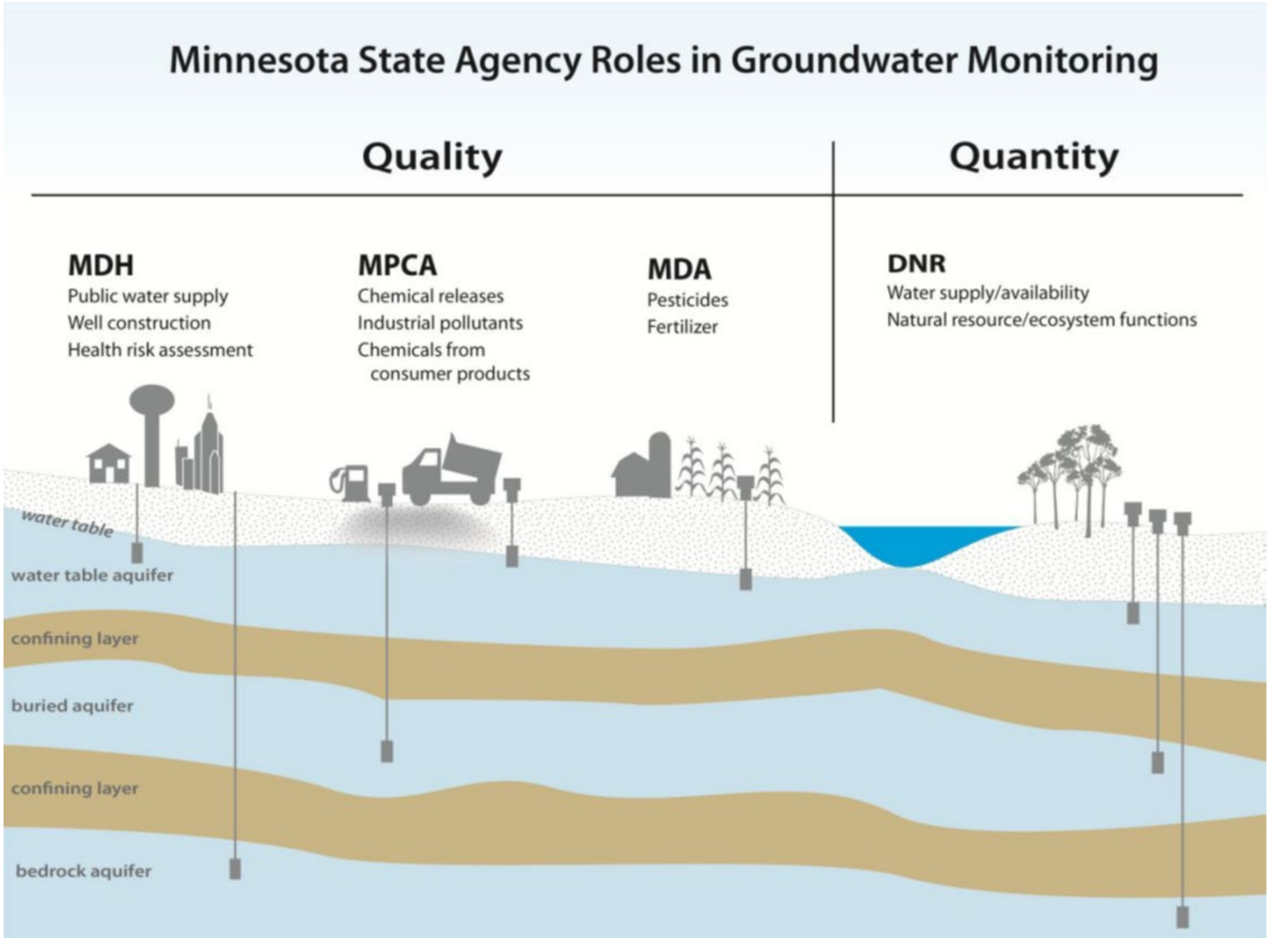
Enough clean groundwater is vital to the State of Minnesota. Groundwater supplies drinking water to about 75% of all Minnesotans and nearly 90% of the water used to irrigate the state's crops. Groundwater flowing into Minnesota's streams, lakes, and wetlands is also important to maintain their water levels, pollution assimilative capacity, and/or temperature.

To meet Minnesotans' needs, groundwater must be clean. The Minnesota Pollution Control Agency (MPCA) considers all groundwater as potential drinking water sources, and the agency's policy is to maintain it in its natural condition as nearly as possible (Minn. R. ch. 7060). Polluted groundwater often is unsuitable for drinking and usually is very expensive to clean up. In addition, it costs more to install water-supply wells in areas with contaminated groundwater because they often need to be drilled deeper to tap uncontaminated aquifers. In some areas, deep underlying aquifers are not available so treatment devices must be installed to clean the contaminated groundwater before use, which incurs additional expenses.

Minnesota state law splits the groundwater monitoring and protection responsibilities among several state agencies that have unique expertise. Each of the agencies involved handles a specific facet of groundwater monitoring and protection. It takes the concerted effort of all these agencies, along with local and federal partners, to build the comprehensive picture of the status of the state's groundwater resources.

The state statutory roles and responsibilities in protecting the quality of Minnesota's groundwater is shown in Figure 1. The MPCA and Minnesota Department of Agriculture (MDA) conduct statewide ambient groundwater quality monitoring for non-agricultural chemicals and agricultural chemicals, respectively. The Minnesota Department of Health (MDH) conducts monitoring to evaluate and address the human health risk of contaminants in groundwater that is used for drinking. In addition to these agencies, the Minnesota Department of Natural Resources (DNR) monitors groundwater quality in selected counties throughout the state as part of its County Geologic Atlas Program, and the Metropolitan Council conducts regional water supply planning using the information collected by the MPCA, MDA, MDH, and DNR. These agencies share many monitoring resources, including the computer database that stores the collected data, technical staff that manage this information, and occasionally field staff that collect the state's groundwater samples.

Figure 1. State agency roles in groundwater monitoring [Graphic courtesy of the Minnesota Department of Natural Resources].



In the last five years, the state agencies continued to collect information that allowed groundwater quality trends to be detected as well as analyzed samples for other chemicals that might adversely affect this resource. The MPCA and MDA continued to operate their ambient and private well monitoring networks, and MDA added chloride to its ambient monitoring program during this time frame. Monitoring for trace organic compounds that contaminate water supplies such as per- and poly-fluroalkyl substances (PFAS) continued, and analytical methods improved during this timeframe to permit more individual PFAS to be monitored in the groundwater, including replacement chemicals such as ADONA and HPFO-DA. Much of this monitoring by the MPCA and MDA was made possible by the Clean Water Land and Legacy Amendment.

Purpose and scope

This report describes the current condition of Minnesota's ambient groundwater quality and determines, to the extent possible, whether it changed over time. The term "ambient groundwater" refers to the parts of this water resource that are affected by the general, routine use of chemicals and are not affected by localized pollutant spills or leaks. Monitoring data from 2018-2023 were used to determine the current condition of the state's groundwater, and information from the last 10 years (2013-2023) was used to quantify whether any changes in groundwater quality occurred. Similar to the last MPCA assessment of the state's groundwater quality (Kroening and Vaughan, 2019), this report also focuses on the quality of aquifers that are often tapped for municipal and domestic water supplies and are vulnerable to human-caused contamination.

This report primarily focuses on water-quality conditions and trends in aquifers in the state's unconsolidated sand and gravel aquifers and the bedrock aquifers in the Twin Cities Metropolitan Area (TCMA) and southeastern Minnesota. These aquifers were the focus of this report for several reasons. First, they both yield good amounts of groundwater and are the drinking water source for about 75 percent of the state's population. Second, both aquifer systems are known to be vulnerable to human-caused contamination, especially where they are near the land surface and covered by thin deposits of permeable sandy sediments. Lastly, a considerable amount of routine ambient groundwater quality data is collected from these two aquifers by state ambient monitoring networks.

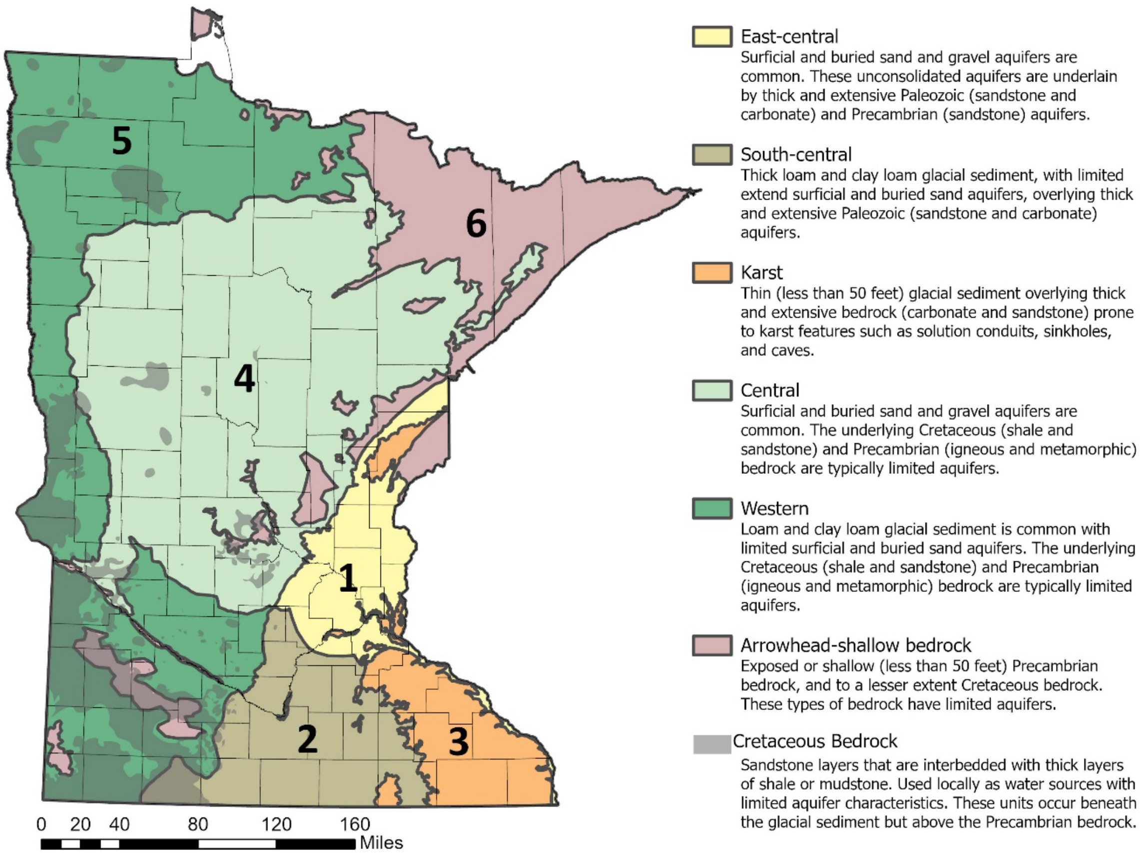
The data analyzed in this report primarily were from ambient monitoring networks operated by Minnesota state agencies, or previously published reports. The main sources of groundwater quality information used were the MPCA's Ambient Groundwater Monitoring Network; the MDA's Ambient Groundwater Monitoring Network, Central Sands Private Well Network (CSPWN), Southeast Volunteer Nitrate Monitoring Network (SEVMN), Township Testing Program, and the Private Well Pesticide Sampling (PWPS) Project; and the DNR's County Geologic Atlas Program. This assessment includes traditional pollutants known to adversely affect the potability of groundwater, such as nitrate and chloride, as well as trace organic compounds such as pharmaceuticals, PFAS, and organophosphate flame retardants.

Minnesota's groundwater resources

Minnesota's groundwater can be broadly classified as occurring in bedrock aquifers and unconsolidated deposits. Over 10 different bedrock aquifers have been recognized in Minnesota, and these generally are composed of crystalline and sedimentary rocks. Crystalline rocks underlie the entire state and typically yield small amounts of groundwater because these usually have low porosity and only form aquifers in places where the rocks are weathered and fractured. Sedimentary rocks such as sandstone, limestone, and dolomite are present in southeastern and extreme northwestern Minnesota. These rocks form very productive aquifers because groundwater can occur in the pore spaces between the sandstone grains and the dissolution features in the limestone as well as in the joints and fractures that occur in all sedimentary rocks. Unconsolidated glacial deposits overlie most of the bedrock in Minnesota, with the notable exceptions of northeastern and southeastern Minnesota where these deposits are known to be thin or absent. The unconsolidated deposits form productive aquifers when they are composed of permeable materials such as sand and gravel and can be buried within clay layers in parts of the state that were glaciated repeatedly.

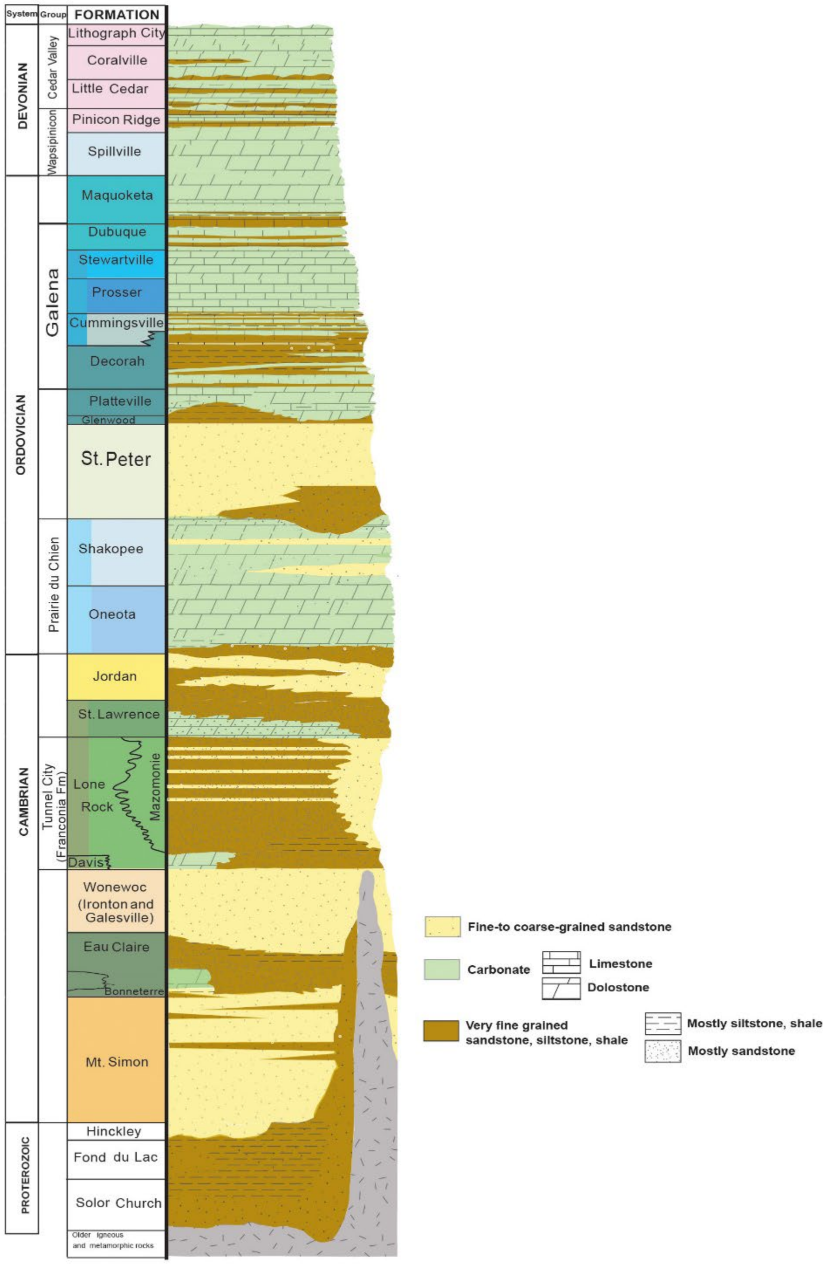
The DNR's groundwater province map (Figure 2) illustrates the uneven distribution of groundwater across the state. This map divides the state into six provinces based on the state's bedrock and glacial geology. Good amounts of groundwater are available from bedrock aquifers in provinces 1-3 due to these areas being underlain by thick sequences of sedimentary rocks. Similarly, good amounts of groundwater are available in province 4 in central Minnesota due to this area having thick glacial sediments, with sand and gravel aquifers commonly occurring in them. In contrast, northeastern Minnesota has very limited groundwater resources. This part of the state generally has thin soils which are underlain by crystalline bedrock that yields limited amounts of groundwater.

Figure 2. Minnesota's groundwater provinces



Southeastern Minnesota is underlain by a "layer cake" of aquifers that are separated by leaky confining units (Figure 3). Four aquifers in this system, whose quality will be discussed further in this report, are the Galena, St. Peter, Prairie du Chien and Jordan. The Galena is the uppermost and youngest of these aquifers and extends only about 80 miles north into Minnesota from the Iowa border. The St. Peter aquifer underlies the Upper Carbonate and extends as far north as the Twin Cities Metropolitan Area (TCMA). This aquifer consists of a white, crumbly, fine- to medium-grained sandstone. Most of the flow through it is intergranular or between the sand grains themselves. The Prairie du Chien and Jordan aquifers underlie the St. Peter and are a major source of water supplies. These two aquifers also extend into the TCMA. The Prairie du Chien Group is a sandy dolomite, and the Jordan is a sandstone. In southeastern Minnesota, the Prairie du Chien and Jordan aquifers form flat plateaus and mesas that are important recharge points because it is typically covered by less than 50 feet of unconsolidated deposits (described further in the next paragraph). In addition, when confining units are present, they often are breached by vertical fractures which allow water (and any associated pollution) to flow through it.

Figure 3. Stratigraphic column of the bedrock aquifers in southeastern Minnesota [Runkel et al, 2013].



Unconsolidated clay, silt, sand, or gravel deposits overlie most of the bedrock aquifers. These important sources of groundwater occur throughout Minnesota and are concentrated in the central part of the state, where they may either be near the land surface or buried within clays. The sediments that form these aquifers generally were deposited about two million to 12,000 years ago when Minnesota had a very cold climate and glaciers periodically advanced through the state. The composition of the sand and gravel aquifers varies depending upon the source area of the sediments comprising them, which geologists term provenance. These aquifers were formed from materials that originated from source areas northwest and northeast of Minnesota, that had very different types of bedrock (Meyer & Knaeble, 1996). The glaciers that traversed into Minnesota from northwest source area left loamy to clayey till deposits, some containing carbonate rock and shale. In contrast, glaciers entering the state from the northeast traversed igneous and metamorphic rocks and left sandy till that had a more siliceous composition and few carbonate pebbles.

Minnesota's monitoring strategy

Groundwater quality monitoring by the Minnesota state agencies primarily is a coordinated effort among the MDA, MPCA, and MDH. The Minnesota Groundwater Protection Act (Minn. Stat. Ch. 103H) splits the ambient groundwater quality monitoring responsibilities between the MDA and MPCA. The MDA is charged with assessing agricultural chemicals including pesticides and fertilizers, and the MPCA has the complementary charge to assess all other non-agricultural contaminants. The MDH's monitoring responsibilities focus on drinking water, as MDH is the state's Safe Drinking Water Act authority. The MDH works with the state's public water system suppliers to test their water for over 100 different contaminants. The agency also compiles the bacteria, nitrate, and arsenic data required from all newly installed water-supply wells before they are placed in service (Minn. R. ch. 4725.5650).

The MPCA and MDA each maintain their own ambient groundwater-monitoring network that, combined, provides good spatial coverage of groundwater quality conditions across the state. The MPCA's ambient groundwater monitoring primarily targets aquifers in urbanized parts of the state, and most of the MDA's monitoring is done in agricultural areas. The MDA also monitors private, domestic wells to assess the impact of agricultural chemicals reaching Minnesota's drinking water. Detailed descriptions of the MPCA's and MDA's ambient monitoring networks are given in the following sections of this report.

MPCA's ambient groundwater monitoring network

The MPCA's Ambient Groundwater Monitoring Network was designed to meet its statutory requirement to monitor for non-agricultural pollution in the groundwater. The network assesses the presence of non-agricultural chemicals from routine, normal practices and identifies any changes in groundwater quality. It does not assess groundwater quality conditions in the immediate vicinity of known chemical spills or releases because these locations already are monitored as part of the agency's cleanup and solid waste activities. The network mainly is comprised of shallow monitoring wells which intersect the water table but also includes some deep wells. The shallow wells, which have a median depth of 22 feet, comprise an "early warning system" and allows the agency to understand what chemicals can readily be transported to the groundwater as well as discern the effect land use has on groundwater quality and quickly identify any emerging trends. The deep wells, which primarily are domestic wells installed in the Prairie du Chien-Jordan aquifer, provide information on the quality of the water that is consumed by Minnesotans, plus it lets the agency know how quickly any contamination from the surface is percolating downward.

The shallow early warning system was designed to assess current groundwater quality conditions and trends in key urban settings. The wells in the "early warning system" were placed according to a strict protocol. For a well to be placed in this subnetwork, 75% of the land within a 500-meter circular buffer surrounding each well site was required to be in the targeted land use setting. Wells were not placed near potential chemical release sites, such as gasoline stations or dry cleaners.

Most of the wells that comprise the "early warning system" were installed near the water table in areas where the land use is either predominantly residential or commercial/industrial. The residential settings assessed by the network were further subdivided based on whether the neighborhood was served by a centralized sewage treatment system where municipal wastes are treated and typically disposed in a stream or river, or a SSTS, where wastewater is disposed to the soil for final treatment. To see how the information collected in these urban settings compares to background levels, the network also sampled aquifers in forested, undeveloped areas. Finally, all network wells were installed in aquifers that were vulnerable to contamination. These aquifers often were close to the land surface and were covered by permeable materials, such as sand or gravel, that allow water and any associated contamination to readily flow through it.

MDA groundwater monitoring

The MDA maintains several monitoring networks that target aquifers that are likely impacted by agricultural chemicals. The agency operates an ambient monitoring network that is like the MPCA's in that it primarily targets shallow sand and gravel aquifers that are near the water table; except MDA monitors those that underlie the agricultural parts of the state. Deeper parts of the groundwater system also are monitored by two long-term private well nitrate monitoring networks, the Private Well Pesticide Sampling (PWPS) Project and the Township Testing Program. The agency's ambient groundwater monitoring network added chloride analysis to its program beginning in 2022.

The design of MDA's ambient monitoring network is based on the state's ten pesticide-monitoring regions (PMRs), which represent different agricultural practices and/or hydrogeologic conditions. The network currently consists of about 170 monitoring sites. Most of these are monitoring wells that typically are located near the edge of farm fields; however, the network does include a small number of springs and domestic water-supply wells. About 80 of the network's monitoring sites are located in PMR 4 in central Minnesota, and the remaining sites are divided among most of the state's other PMRs. The wells sampled in PMR 10, which includes the TCMA, are primarily ten wells from the MPCA's Ambient Groundwater Monitoring Network. Although MDA's groundwater monitoring network was designed to assess the presence and distribution of pesticides in the groundwater, the staff also collects and analyzes water samples for nitrate to add to the body of information that relates to the potential environmental impact to groundwater associated with agricultural activities.

The MDA also continued to operate the CSPWM, SEVMN, and the Township Testing Program. The CSPWM and SEVMN are long-term private well monitoring networks, and their goal is to track nitrate trends in wells used to obtain household water supplies. In 2022, 282 private wells were tested by the CSPWM, and 376 wells were tested by the SEVMN. The Township Testing Program was conducted from 2013-2019 as required by the revised Nitrogen Fertilizer Management Plan (NFMP) (Minnesota Department of Agriculture, 2015). This program was like the CSPWM and SEVMN in that it targeted privately owned drinking water wells for nitrate sampling but focused on a finer, township scale compared to these two regional networks. The townships selected for sampling were based on the vulnerability of the groundwater to contamination from the land surface, the proportion of land in row crops, and other information that indicated the groundwater may be contaminated with nitrate. Over 32,000 private wells were tested by this program in 50 counties across the state.

Homeowner volunteers were the cornerstone of each of these sampling efforts. For all of them, the homeowners collected their own water sample and sent it by mail to be tested by a laboratory at no cost to them. This method was developed from years of collaboration with other state and local agencies through pilot projects testing different methods of collection and sample delivery.

To provide information about the occurrence and distribution of pesticides in private drinking water wells, the MDA started its Private Well Pesticide Sampling Project (PWPS) in 2014. This effort originally targeted wells that had nitrate detected in them as part of the agency's Township Testing Program. As part of the PWPS Project, well owners also were given an opportunity to have a low-level pesticide sample collected from their well. As the PWPS Project has matured, the MDA has focused the analytical list on pesticide chemicals detected in groundwater that pose the greatest risk to drinking water. Over 9,500 pesticide samples have been collected from private wells since the program began.

Minnesota's Groundwater Protection Rule (GPR): Chapter 1573 went into effect on June 24, 2019. Through this rule, the MDA is working to minimize potential sources of nitrate pollution to the state's groundwater and protect drinking water. Part 2 of the GPR responds to elevated nitrate + nitrite-nitrogen (nitrate) in community water supply wells and the associated Drinking Water Supply Management Areas (DWSMAs).

DWSMAs with public water supply wells that have exceeded 8.0 mg/L of nitrate-N in the previous 10 years were designated at Mitigation Level 2 under the GPR. In level 2 DWSMAs, the MDA will work with local farmers to adopt practices that can reduce nitrate levels in groundwater.

The MDA installed local groundwater monitoring networks at three Mitigation Level 2 DWSMAs: Hastings, Rock County Rural Water Supply (RCRW), and St. Peter. The purpose of these networks is to collect nitrate data from groundwater in the upper most aquifer and evaluate concentration changes over time. As of 2023, there are thirteen groundwater monitoring wells in the Hastings DWSMA, seven in the RCRW DWSMA, and seven in the St. Peter DWSMA.

MN DNR groundwater quality monitoring

The MN DNR's role in groundwater monitoring primarily is to collect static water-level information to determine the quantity of available water but collects water-quality data as part of their County Geologic Atlas program work. The DNR operates a cooperative groundwater monitoring program that currently consists of roughly 1,300 wells. This information is used by the agency to assess the status of the state's groundwater resources, determine long-term trends, interpret impacts of pumping and climate on the groundwater, plan for water conservation, and evaluate groundwater use conflicts. The DNR generally only collects groundwater quality information through its County Groundwater Atlas Program. Water chemistry data is collected to provide information on when the water entered the ground, pollution sensitivity, interaction with surface water, possible sources of contamination, and areas of concern for human health (Minnesota Department of Natural Resources, 2021). Typically, about 100 wells are sampled for inorganic constituents including nitrate and chloride for each county geologic atlas project.

Nitrate

Nitrate is a common source of groundwater contamination. Nitrogen-containing compounds are needed for all life to survive, but too much, especially in the form of nitrate, harms human and aquatic health. High nitrate concentrations in drinking water may cause methemoglobinemia, a blood disorder that typically affects infants and susceptible adults. In this potentially fatal disorder, the blood is unable to carry oxygen to the rest of the body, which results in the skin turning a bluish color. To protect human health, the U.S. Environmental Protection Agency established a Maximum Contaminant Level (MCL) of 10 mg/L for nitrate in drinking water. This is a legally enforceable standard that applies to public drinking water systems and is the highest concentration allowed. The MCL also was adopted as a state class 1 domestic consumption use standard and applies to all groundwater (Minn. R. ch. 7050, 7060). In surface waters, too much nitrate may stimulate the excessive growth of algae, and in some cases, this algal growth is so severe that it interferes with the decomposition process and can deplete all oxygen from the water resulting in fish kills.

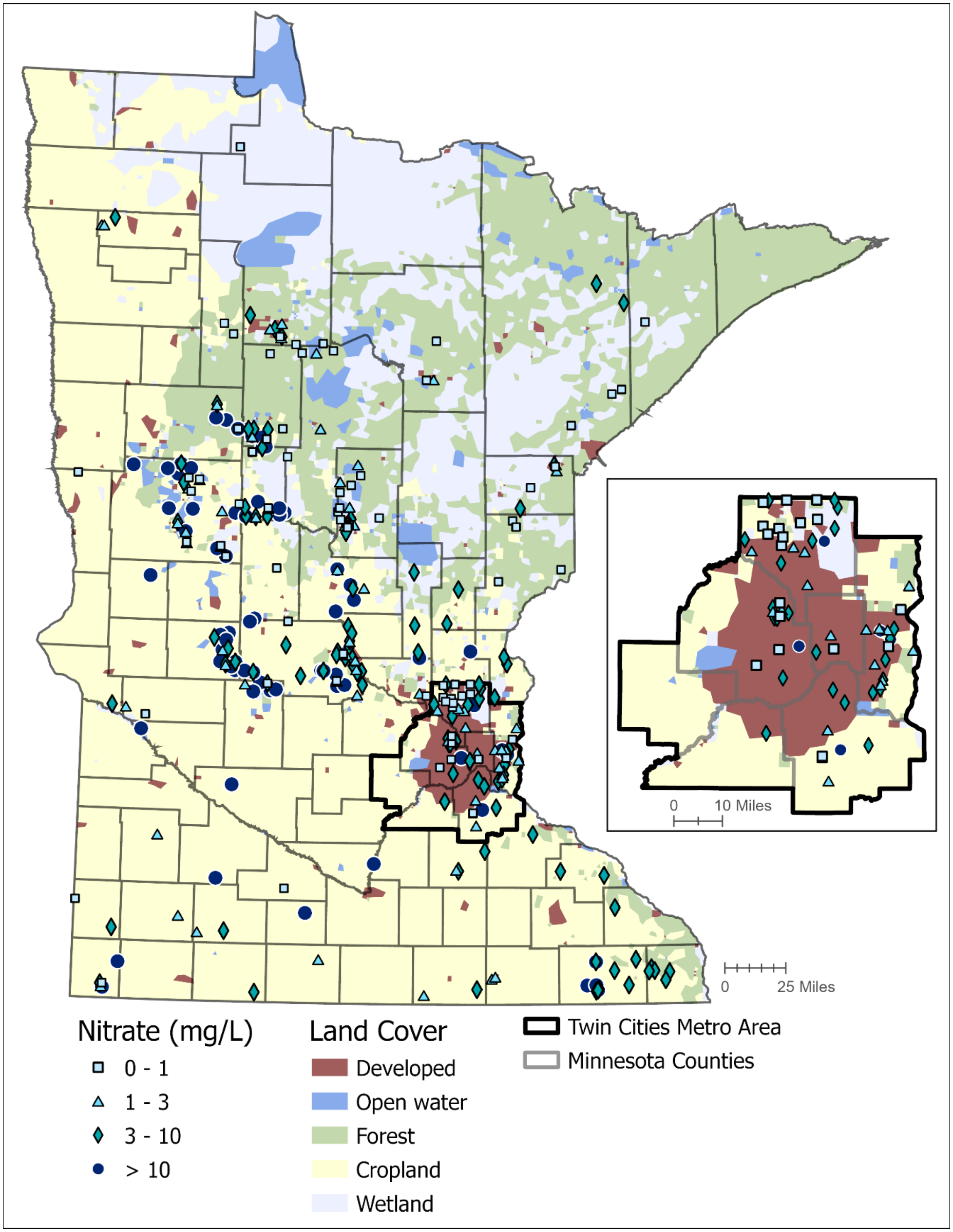
Fertilizer, animal waste, and septic systems are some common sources of nitrate pollution to the groundwater (Minnesota Department of Health, n.d.; Minnesota Pollution Control Agency, 2013). Wells may be vulnerable to nitrate contamination from these and other sources if they are shallow, installed in sandy aquifers, or constructed with casings that are not watertight or are damaged. A MPCA report estimated that commercial fertilizer and livestock manure were the largest sources of nitrogen applied in the state, except for the mineralization of naturally occurring organic matter in the state’s soils (Minnesota Pollution Control Agency, 2013). In Minnesota, the MDA is the lead state regulatory agency for nitrogen fertilizer and has the authority to regulate the use of nitrogen fertilizer to protect groundwater, if necessary. As part of their work, the MDA develops the NFMP, as required by state law (Minnesota Statutes, section 103H), which is the state’s blueprint for addressing nitrate impacts to groundwater that are related to fertilizer use. The MPCA is the lead state regulatory agency that responds to elevated nitrate concentrations in surface waters and regulates the collection, transportation, storage, processing, and land application of manure and other livestock operation wastes and develops rules for how septic systems are designed, installed, and managed.

Groundwater monitoring data collected by the state agencies continue to show that nitrate concentrations are highest near the water table in agricultural areas and are lower in the underlying aquifers. This result is consistent with several other past assessments of Minnesota's groundwater quality (Anderson, 1993; Fong, 2000; Trojan, Maloney, Stockinger, Eid, & Lahtinen, 2003; Kroening & Ferrey, 2013; Kroening & Vaughan, 2019). Nitrate data collected by the MPCA and MDA near the water table in the surficial sand and gravel aquifers showed that the highest median and maximum concentrations measured typically are found in wells installed in agricultural settings (table 1, figure 4). Median nitrate concentrations near the water table in agricultural areas were 4-8 times higher compared to those found in the state's urban lands. Almost 40 percent of the water table wells tested in the agricultural areas exceeded the state's class 1 domestic consumption use standard of 10 mg/L. The percentage of wells exceeding the class 1 standard was much less in the urban and undeveloped settings. Six percent of the water table wells in the residential areas that rely on SSTS for wastewater treatment and disposal and almost 2.5 percent of the water table wells in commercial industrial areas had nitrate concentrations exceeding 10 mg/L. No water table wells in the residential areas that use centralized wastewater treatment or in the undeveloped areas had nitrate concentrations that exceeded the class 1 domestic consumption use standard.

Table 1. Summary statistics of nitrate nitrogen concentrations in the groundwater with land use, 2018-2023 [statistics based upon the most recent sampling event during this period at each well]

Land Use	Number of Wells Sampled	Median Well Depth (ft)	Median Concentration (mg/L)	Concentration Range (mg/L)
Agricultural	215	20.8	6.94	<0.2 – 35.7
Sewered Residential	48	19.0	1.45	<0.05 – 9.9
Residential SSTS	50	24.0	0.89	<0.05 – 34
Commercial/Industrial	42	19.0	1.50	<0.05 – 17
Undeveloped	52	18.0	0.05	<0.05 – 3.4

Figure 4. Nitrate concentrations in the surficial sand and gravel aquifers, 2018-2023 [concentrations are expressed as nitrogen].



Monitoring in the underlying bedrock aquifers and deeper parts of the sand and gravel aquifers continued to show that nitrate concentrations typically are lower in these parts of Minnesota's groundwater system compared to near the water table. The MDA's Township Testing Program collected nitrate concentration data from over 30,000 wells in agricultural areas throughout the state from 2013-2019. These wells tap deeper parts of the groundwater system compared to the ambient monitoring networks, with the median depths ranging from 54 feet in Hubbard County in north-central Minnesota to 410 feet in Fillmore County in southeastern Minnesota. This dataset showed that the median nitrate concentration and percentage of wells exceeding the class 1 domestic consumption use standard was about 4 times lower in the deeper parts of the groundwater system compared to near the water table. The median nitrate concentration for all wells sampled by the Township Testing Program was 1.7 mg/L, and 9.1% of the tested wells had concentrations of 10 mg/L or greater. If only the wells potentially impacted by commercial nitrogen sources were considered, the concentrations were even lower. For these wells, the median concentration was 0.6 mg/L, and 4.7% of the wells exceeded by the class 1 standard. Nitrate data from the MDA's SEVMN and CSPWM and MPCA's limited ambient bedrock aquifer monitoring showed similar results. The 2022 data from the SEVMN showed that the median nitrate concentration in southeastern Minnesota was less than 0.25 mg/L, and 8.2% of the concentrations in the sampled wells exceeded the class 1 domestic use standard of 10 mg/L (Minnesota Department of Agriculure, 2023). The CSPWM had similar results. In 2022, the median nitrate concentration from this network was less than the reporting limit of 0.03 mg/L, and 2.1 percent of the wells had concentrations of 10 mg/L or more (Minnesota Department of Agriculture, 2023). The MPCA monitored 43 bedrock aquifer wells during the 2018-2023 period. A substantial number of these wells were in Washington County in the southeastern TCMA, and the majority number of them were installed in the Prairie du Chien or Jordan aquifers. The median nitrate concentration in these wells (1.4 mg/L) was similar to the concentrations measured near the water table in urban parts of the state, and almost seven percent of the wells had concentrations exceeding the class 1 domestic consumption use standard of 10 mg/L.

The nitrate data generated by the MDA's monitoring programs identified where the highest concentrations typically occur in aquifers used for drinking water supplies, and which groundwaters are affected by nitrogen fertilizer applications. Monitoring conducted by the both the Township Testing Program and SEVMN showed that at least 10 percent of wells in a considerable number of townships in Wabasha, Winona, and Fillmore Counties had concentrations at or exceeding the class 1 standard of 10 mg/L (Figure 5). This also was the case for most of the tested townships in Rock and Pipestone Counties in southwestern Minnesota and in Morrison County in Central Minnesota. Some of these high concentrations may be due to non-fertilizer sources of nitrogen like livestock feedlots or septic systems, or the result of well construction issues such as broken cap or not being installed according to the state well construction code. MDA's final Township Testing Program dataset, which excluded wells near potential non-fertilizer nitrogen sources or with construction concerns, indicated that high concentrations in southeastern Minnesota, especially those measured in wells located on the Prairie du Chien Plateau, and in north Central Morrison County and other parts of Central Minnesota may be related to the use of nitrogen fertilizers (Figure 6).

Figure 5. Initial township testing results for nitrate in Minnesota's groundwater, 2013-2019 [from (Minnesota Department of Agriculture, 2022)]

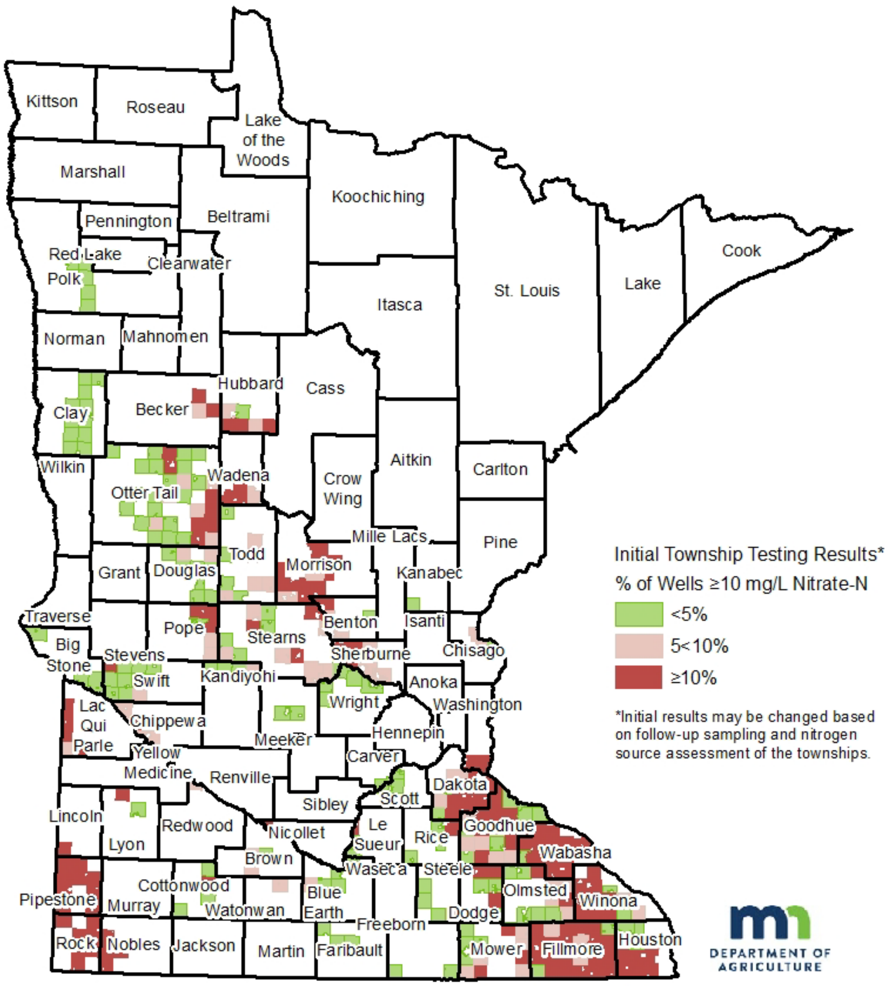
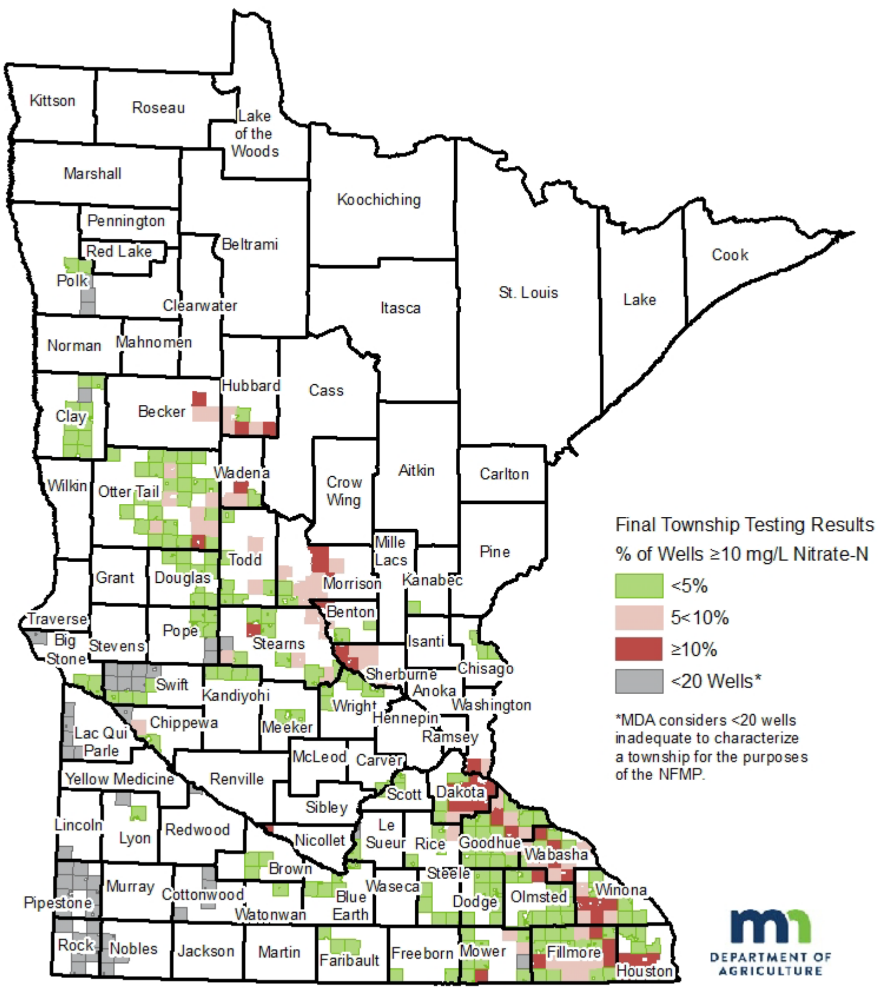


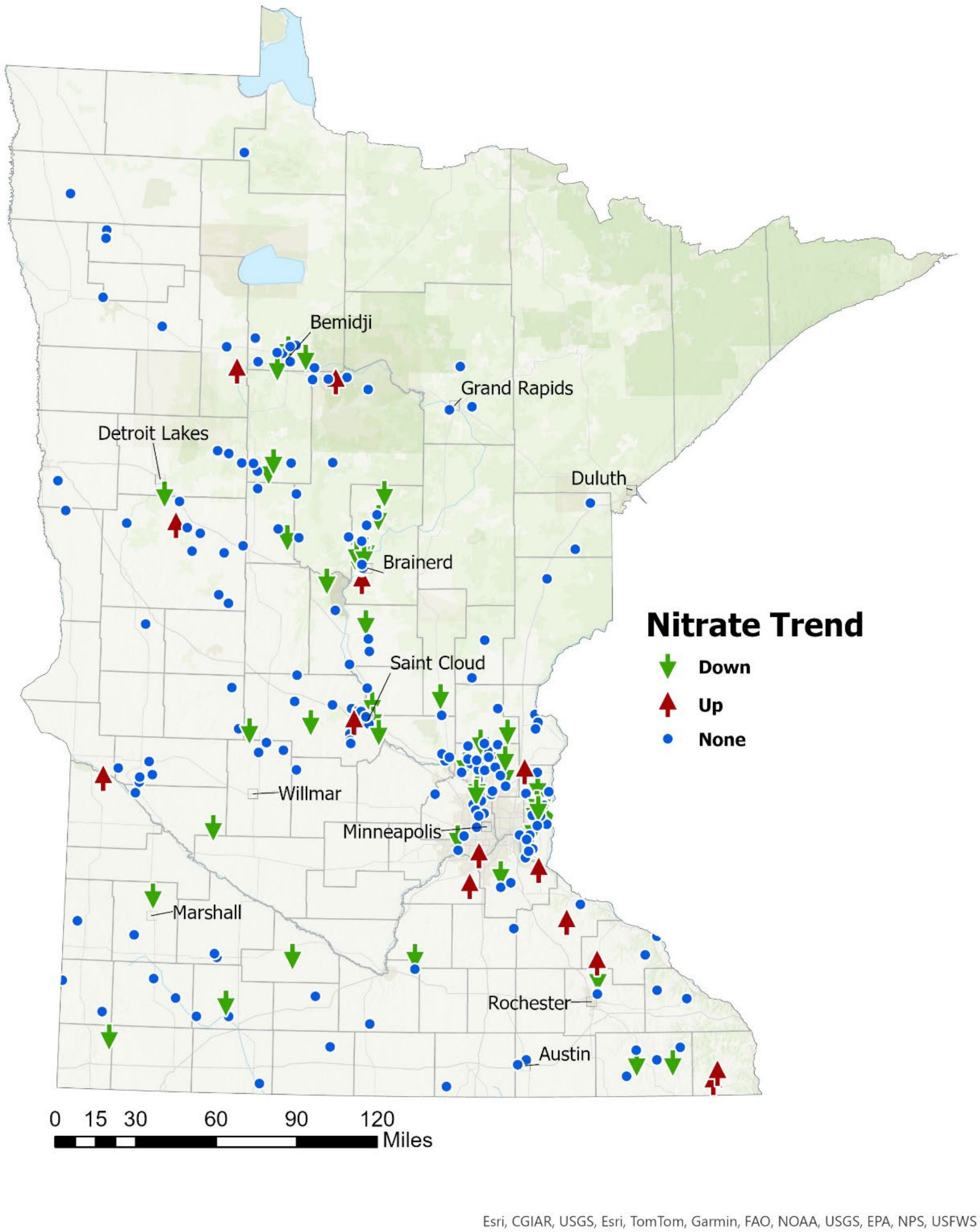
Figure 6. Final township testing results for nitrate in Minnesota's groundwater, 2013-2019 [from (Minnesota Department of Agriculture, 2022)]



Nitrate concentrations near the water table generally continued to remain stable. For this report, nitrate trends were analyzed for the 2013-2023 period and included over twice as many wells and springs compared to the last assessment (Kroening & Vaughan, 2019). Two hundred fifty-three wells and 14 springs from MPCA and MDA's ambient monitoring networks had sufficient information to calculate temporal trends. About 60 percent of these sites were sampled by the MPCA's ambient monitoring network, and the remainder were sampled by MDA's monitoring program. Sites were included in the trend analysis if there were at least five samples collected from 2013-2023. Trends were calculated using the Mann-Kendall test, and the statistical test accounted for both ties and censored data (Helsel, 2005). The criterion for statistical significance was the 0.05 significance level. The dominant finding from the trend testing was that most sites continued to exhibit no change in nitrate concentrations from 2013-

2023. Three-quarters of the sites had no statistically significant trend in nitrate concentrations (Figure 7). When trends were detected, they typically were downward. Wells and springs with downward trends in nitrate concentrations were fairly evenly divided between areas with urban, agricultural, and undeveloped land use and land cover. Downward trends, while a good sign, also should not be interpreted to mean that concentrations are below the class 1 domestic consumption use standard. Several sites, primarily in the state's agricultural areas, have downward trends in nitrate from 2013-2023, but the most recent concentration measured still was above 10 mg/L. For example, one monitoring well tested for trends in Morrison County had one of largest decreases in concentrations from 2013-2023, with an average decrease of about 5 mg/L each year, but the most recently measured nitrate concentration was 33 mg/L which is over three times the class 1 standard.

Figure 7. Nitrate trends in Minnesota's groundwater, 2013-2023 [Data from the MPCA and MDA ambient groundwater monitoring networks].



Trend analyses of the MDA's private well networks, which tap deeper parts of the groundwater system, showed similar results. The most recent published trend analyses of the Southeast Minnesota Volunteer Network and Central Sands Private Well network data were for the 2008-2018 period (Kaiser, Schaefer, & VanRyswyk, 2019). This work also used the Mann-Kendall test and aggregated the network results by percentile. The results showed that there was no significant trend in nitrate concentrations in the Southeast Minnesota Volunteer Network from 2008-2018. The trend analysis for the Central Sands Private Well Network was similar. There was no significant change in the median or 75th percentile concentrations measured by the network from 2011-2018, but there was a statistically significant decrease in the 90th percentile concentration measured by this network.

Starting in 2021, each of the MDA DWSMA groundwater well networks were sampled for nitrate in the spring, summer, and fall. In 2023, the sampling frequency was increased in the RCRW DWSMA network, and the wells were monitored monthly during the sampling season. In the Hasting DWSMA, the median groundwater nitrate results, per sampling event, ranged from 9.87 to 12.5 mg/L. In the Rock County DWSMA the median groundwater nitrate results, per sampling event, ranged from 6.67 to 13.7 mg/L. In the St. Peter DWSMA, the median groundwater nitrate results, per sampling event, ranged from 10.0 to 14.3 mg/L. The MDA will continue monitoring groundwater in these three networks and use the data to help evaluate nitrate trends in the DWSMAs.

Chloride

Chloride is often referred to as a "permanent" pollutant in the groundwater and is present due to both human use and because it occurs naturally in some aquifers. Chloride pollution is called "permanent" because once it is in the groundwater, the element is not broken down and any chloride will remain there until it is transported either downward to deep aquifers (which typically are used for drinking water) or to streams, lakes, and wetlands as groundwater inflow. Common anthropogenic sources of chloride that contaminate the groundwater are de-icing salt application to maintain roadway safety in the winter and water softener salt use. Several aquifers in Minnesota contain naturally high chloride concentrations, including the Red River-Winnipeg aquifer in northwestern Minnesota, some buried sand and gravel aquifers in southwestern Minnesota, and the North Shore Volcanics aquifer that is present along Lake Superior and the Upper St. Croix River Basin (Albin & Brummer, 1987; Morton & Ameel, 1985; Winter, 1974; McClay, Winter, & Bidwell, 1972). In western Minnesota, these naturally high concentrations are attributed to the presence of very soluble, chloride-containing minerals in the rocks that make up the aquifers and the movement of saline groundwater from the Dakotas (Paulson, 1983; McClay & Winter, 1967). Naturally occurring chloride also may be present if the aquifer still contains connate water, which is the water that was initially trapped in a rock when it was formed in a marine environment. In Minnesota, the aquifers composed of sedimentary rock, like the Prairie du Chien-Jordan, were formed in an ocean environment and likely contained high chloride concentrations when they were formed.

Excessive chloride in groundwater restricts its use for drinking and may degrade aquatic habitat if it is transported to surface waters. High chloride concentrations adversely affect drinking water not due to human toxicity but because it imparts a salty taste that consumers find objectionable. High concentrations also change the chemistry of the water and can result in lead and copper being leached from plumbing and fixtures (Edwards, Jacobs, & Dodrill, 1999; Nguyen, Stone, Dudi, & Edwards, 2010; Nguyen, Stone, & Edwards, 2011). To minimize taste problems with public drinking water supplies, the U.S. Environmental Protection Agency (EPA) set a Secondary Maximum Contaminant Level (SMCL) for chloride of 250 mg/L. SMCLs are not enforced by the EPA; they are a guideline to assist public drinking water suppliers in managing their systems for aesthetic considerations. However, the SMCL was adopted as Class 1 domestic consumption use standard in Minnesota and applies to all groundwater (Minn. R. ch. 7050, 7060). Additionally, high chloride concentrations are toxic to aquatic life. Streams and lakes with high chloride concentrations may have decreased biological integrity or even may be limited to just salt-tolerant species. To protect these plants and animals from water with high chloride concentrations, the State of Minnesota set a chronic water quality standard of 230 mg/L and an acute water quality standard of 850 mg/L (Minn. R. ch. 7050).

The number of wells monitored for chloride in the ambient groundwater was smaller compared to the nitrate dataset. The MPCA and MDA ambient networks and the DNR's County Geologic Atlas Program sampled over 1,900 wells for chloride from 2018-2023. The two ambient networks generally focused on sampling wells located near the water table. The DNR's County Geological Atlas Program sampled deeper wells located in the 15 counties where geologic atlases were being prepared during 2018-2023. The median depths of these wells ranged from 67 feet in Wadena County to 368 feet in Washington County.

These data showed that chloride concentrations continued to be highest in the surficial sand and gravel aquifers. This is illustrated in Figure 8 which shows the median concentrations in the aquifers sampled most frequently by the state monitoring programs. In this figure, the median concentrations were calculated by aquifer using the most recent sample collected from each of the wells. The aquifer was assigned to each well based on the aquifer code information in the state's County Well Index, which is maintained by the Minnesota Geological Survey in partnership with MDH. Like the results from the last groundwater condition report (Kroening & Vaughan, 2019), the highest median chloride concentration was in the quaternary water table aquifers. Median concentrations in the quaternary water table aquifers were at least twice as high compared to the other sampled aquifers in Figure 8 and Table 2, except for the Cretaceous aquifers in southwestern Minnesota. The maximum chloride concentration measured in the state's groundwater also was reported to occur in the quaternary water table aquifers (table 2).

Figure 8. Median chloride concentrations in Minnesota's groundwater, 2018-2023, by aquifer [based on the latest observation collected from each well].

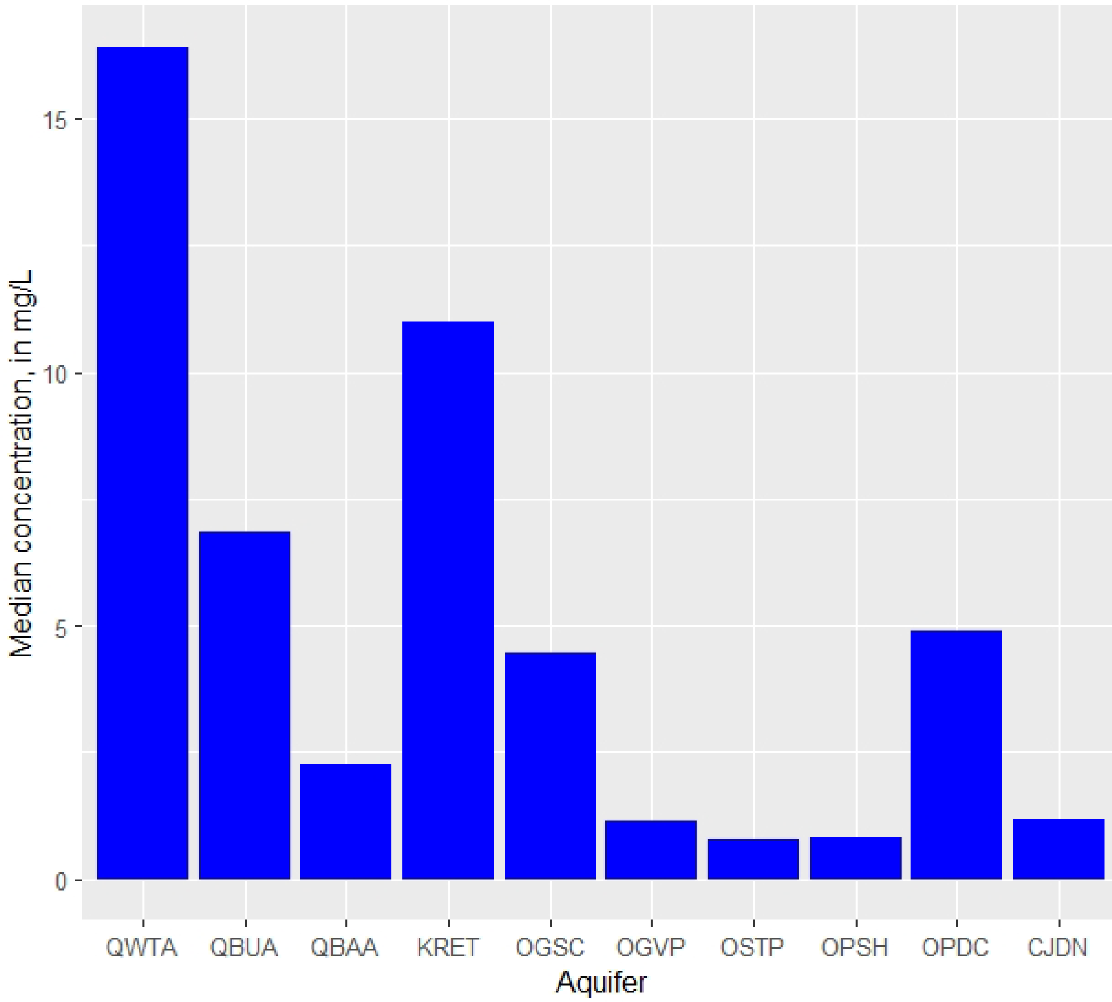


Table 2. Summary statistics for chloride concentrations in Minnesota's groundwater, 2018-2023 by aquifer (based on the latest observation collected from each well).

Aquifer	Number of wells	Median depth of wells	Median concentration	Minimum concentration	Maximum concentration
Quaternary water table (QWTA)	463	25 feet	16.4 mg/L	<0.5 mg/L	1,370 mg/L
Quaternary buried unconfined aquifer (QBUA)	76	75.5 feet	6.9 mg/L	<0.5 mg/L	294 mg/L
Quaternary buried artesian aquifer (QBAA)	875	98 feet	2.3 mg/L	<0.5 mg/L	451 mg/L
Cretaceous aquifers (KRET)	21	426 feet	11 mg/L	1.3 mg/L	52.8 mg/L
Galena – Stewartville-Cummingsville members (OGSC)	21	183 feet	4.5 mg/L	<0.5 mg/L	86.2 mg/L
Galena – Stewartville – Prosser members (OGVP)	23	183 feet	1.2 mg/L	0.5 mg/L	19.8 mg/L
St. Peter (OSTP)	51	283 feet	0.8 mg/L	<0.5 mg/L	78.9 mg/L
Prairie du Chien – Shakopee Formation (OPSH)	24	355 feet	0.8 mg/L	<0.5 mg/L	131 mg/L
Prairie du Chien Group (OPDC)	55	271 feet	4.9 mg/L	<0.5 mg/L	128 mg/L
Jordan (CJDN)	38	358 feet	1.2 mg/L	<0.5	62.1 mg/L

High chloride concentrations in the quaternary water table aquifers resulted from both their natural sensitivity to contamination combined with overlying land use settings that contributed chloride to the environment such as salt applied to deice pavement in the winter and potassium chloride applied to cropland as a fertilizer. Most of the wells tapping the quaternary water table aquifers that were sampled for chloride had a high to moderate sensitivity to pollution. Overlaying the groundwater sensitivity map of the near surface materials produced by the Minnesota Department of Natural Resources (Adams, 2016) with the sampled quaternary water table wells showed that the vertical travel time to a depth of 10 feet ranged from hours to weeks for over 80 percent of the sampled wells. Monitoring near the water table in urban and agricultural settings by the MPCA and MDA also continued to show that the highest chloride concentrations were in the shallow groundwater underlying urban areas, especially commercial/industrial and sewered residential areas (table 3).

Table 3. Summary statistics of chloride concentrations in the groundwater with land use, 2018-2023 [statistics based upon the most recent sampling during this period at each well]

Land Use	Number of wells sampled	Median well depth	Median concentration	Range in concentrations
Commercial/Industrial	42	19 feet	106.0 mg/L	1.6 - 1,370 mg/L
Sewered Residential	48	19 feet	68.8 mg/L	0.5 – 443 mg/L
Residential areas using SSTS	50	24 feet	28.0 mg/L	0.6 – 825 mg/L
Agricultural	134	20.5 feet	14.8 mg/L	<0.5 – 471 mg/L
Undeveloped	52	18 feet	1.0 mg/L	<0.5 – 133 mg/L

Distinguishing chloride sources in groundwater

Chloride to bromide (Cl/Br) ratios are used by many researchers to distinguish among the various sources of human-caused and natural contamination in the groundwater. Cl/Br ratios are a useful tool to discriminate between sources because chloride is about 40-8000 times more abundant than bromide. As a result, small differences in bromide concentrations in the various chloride sources yield vastly different Cl/Br ratios. Pristine groundwater has Cl/Br ratios that are less than 200 (Davis, Whittemore, & Fabryka-Martin, 1998). In contrast, domestic sewage has ratios ranging from 300-600, and groundwater affected by the dissolution of halite (commonly known as rock salt) has ratios that are greater than 1,000.

The chemical signature and annual variations in chloride concentrations were consistent with a de-icing chemical source in the shallow groundwater underlying all three urban land use settings. Chloride to bromide ratios (Davis, Whittemore, & Fabryka-Martin, 1998) were used in this report to distinguish chloride sources in the groundwater (see sidebar). Bromide data was available from all sites in the urban and undeveloped land use settings used to calculate summary statistics in Table 3, but this information was more limited for the sites located in the agricultural areas where only 14 of the wells had associated bromide concentration data. Over 70 percent of the wells located in the residential settings and over 80 percent of the wells in the commercial/industrial areas had a chloride/bromide ratio at or exceeding 1,000 mg/L which indicated a halite source of chloride. This is the type of chloride that is used for pavement de-icing or water softening. It is likely that a considerable amount of this chloride originated from de-icing chemical applications. About one-half of the wells in the residential areas and most of the wells in commercial/industrial areas were in communities where any chloride resulting from water softening would likely be discharged to a centralized sewer systems and would not be transported to the groundwater. In addition, many of the wells in residential and commercial/industrial areas also showed large annual fluctuations in chloride concentrations. For example, one monitoring well in Hennepin County had a chloride concentration of 90 mg/L in 2022 but the concentration measured in 2023 was over 150 mg/L. Fluctuations like these likely result from the application of pavement deicers, which varied with the winter conditions. Chloride primarily resulting from water softener use was expected to be more consistent since household water use generally does not fluctuate as much annually.

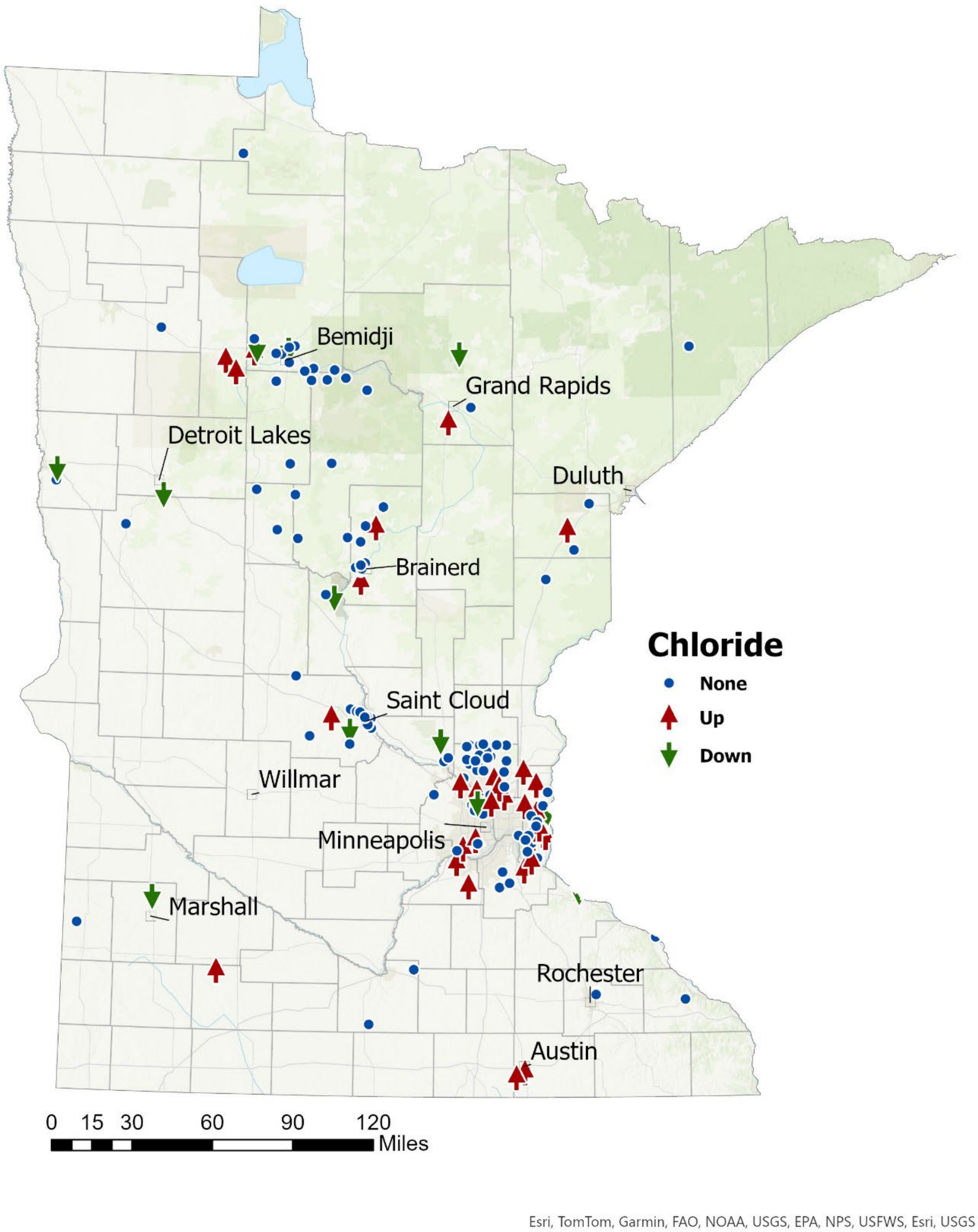
Similar to the results from the last groundwater condition report, median chloride concentrations generally became progressively lower in the underlying aquifers with a few exceptions. The median chloride concentrations in the state's groundwater generally are related to the depth of the sampled wells (Figure 8, table 2). Concentrations are generally lower in deeper wells because the aquifers they tap typically contain older water and had less contamination in it that originated from the land surface. This again can be illustrated by examining the chloride/bromide ratios in a few of these aquifers. The quaternary buried unconfined aquifers had a median chloride concentration that was about one-half of what was measured in the overlying QWTA aquifers (Figure 8, Table 2), and the Cl/Br ratios showed that 40 percent of the chloride measured in the QBUA aquifers were from a natural source. Median chloride concentrations were even lower in the underlying QBAA aquifers that were sampled, which generally were about 25 feet deeper than the QBUA aquifers. There also are clay confining layers separating the QBAA from the overlying aquifers such as the QBUA and QWTA. The QBAA aquifers contained even more natural chloride, and the calculated Cl/Br ratios indicated that almost 70 percent of the chloride in them originated from natural sources. In the Prairie du Chien Group and Cretaceous aquifers, chloride concentrations did not follow the pattern of decreasing with aquifer depth and generally were higher compared to some of the overlying aquifers.

The higher median concentration in the Prairie du Chien Group was an artifact of the uneven regional distribution of chloride in this aquifer, with higher concentrations occurring in the wells sampled within the TCMA compared to other parts of southeastern Minnesota. The high median concentrations in the Cretaceous aquifers resulted from naturally occurring chloride rather than an anthropogenic source. This again can be illustrated by examining the chloride/bromide ratios. For the sampled Cretaceous aquifer wells, over 90 percent of the measured concentrations were associated with a Cl/Br ratio less than 200 which indicated it originated from a natural source.

Very few of the sampled wells exceeded the Class 1 domestic consumption use standard of 250 mg/L, and exceedances typically were in shallow monitoring wells that were not used as drinking water sources. About two percent of the wells compiled for this study contained at least one chloride concentration of 250 mg/L or greater during 2018-2023. Almost 90 percent of the wells with exceedances of the Class 1 domestic consumption use standard were shallow monitoring wells with a median depth of less than 25 feet. The chloride/bromide ratios indicated that most of these exceedances were associated with chloride that had a halite source.

Like the nitrate trend results, chloride concentrations in the ambient groundwater continued to generally remain stable from 2013-2023. The chloride concentration trend analyses conducted for this report included over four times as many wells and springs compared to the last assessment (Kroening & Vaughan, 2019). One hundred seventy-one wells from MPCA's ambient monitoring networks had sufficient information to calculate temporal trends. The same procedure used to evaluate for nitrate trends was followed for the chloride analysis. Sites were included in the trend analysis if there were at least five samples collected in the period beginning in 2013 and ending in 2023. Trends were calculated using the Mann-Kendall test, and the statistical test accounted for both ties and censored data (Helsel, 2005). The dominant finding from the trend testing was that most sites continued to exhibit no change in nitrate concentrations from 2013-2023. Over 70 percent of the sites had no statistically significant trend in chloride concentrations (Figure 9).

Figure 9. Chloride trends in Minnesota's groundwater, 2013-2023 [Data from the MPCA ambient groundwater monitoring network].



When trends in chloride concentrations in the groundwater did occur, they were predominately upward. Statistically significant trends in chloride were found in about one-quarter of the analyzed wells from 2013-2023. In the small number of wells with significant trends, three-quarters of them were upward. Most of the wells with upward trends in chloride concentrations were installed in the quaternary water table aquifers (47 percent), Prairie du Chien Group (14 percent), or Jordan aquifer (17 percent). The quaternary water table aquifer wells with trends generally were installed near the water table and had a median depth of 22 feet.

Chloride trends in the shallow groundwater underlying the state's urban areas generally were not concentrated in any particular land use setting, with the exception of residential areas using SSTS for wastewater treatment and disposal. Chloride trends were quantified by land use setting using data from wells intersecting the water table from the MPCA's network. All trends were determined using data from 2013-2023 and the Regional Kendall test (Helsel & Frans, 2006). There were no significant temporal trends in the shallow groundwater underlying the commercial/industrial areas (p=0.1650) or sewered residential areas (p=0.1639). The only statistically significant trends were in the shallow groundwater underlying the residential areas using SSTS for wastewater treatment and disposal (p=0.0201, slope=0.3786) and the undeveloped areas (p=0.0180, slope=0). However, the slope of zero was inconsistent with a significant temporal trend and likely was an artifact that almost 25 percent of the chloride values in this dataset were below the laboratory's method reporting limit. Most of the shallow monitoring wells with upward trends in residential areas using SSTS were located in Anoka and Washington Counties.

PFAS

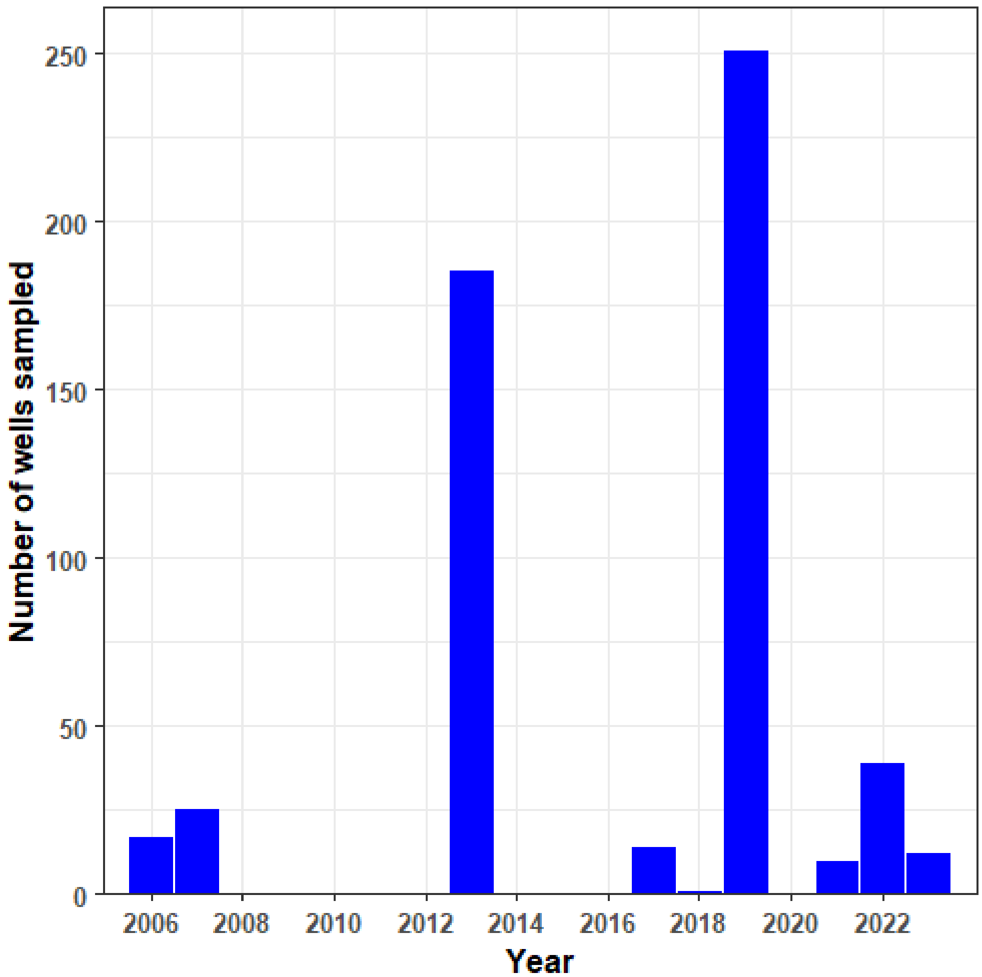
PFAS are a large family of synthetic fluorinated chemicals that are used throughout the world because of their water- and grease resistant properties. PFAS were invented in the 1930s and are defined by the EPA as organic chemicals that contain at least one fully fluorinated carbon atom that is adjacent to a partially fluorinated carbon as well as some fluoroethers or branched carbon chains (U.S. Environmental Protection Agency, 2022). Some fluorinated organic chemicals, such as the refrigerant R32 (also called dichlorofluoromethane), do not meet this definition and are not considered PFAS. Because of their unique properties, PFAS are used in a large number of products including non-stick cookware; fire-fighting foams; coatings for clothing, upholstery, and carpeting; lubricants; and as an insulator where materials are needed that are non-reactive and heat resistant. PFAS are very desirable in many these applications because of their extreme durability. Unfortunately, this durability also means that these chemicals do not readily break down over time under environmental conditions and are not easily removed through conventional wastewater treatment. This persistence of this suite of chemicals in the environment has led to them being given the nickname of “forever chemicals.”

PFAS are frequently found in the environment due to their widespread use and persistence to degradation. A global study of PFAS in soils found detections of PFAS in every sample, including samples collected from remote locations in every continent on the planet. PFAS also are known to occur in the Arctic, where they have been found to accumulate in high concentrations in snow and biota due to patterns of long-range atmospheric transport (Joerss, et al., 2020). The U.S. Centers for Disease Control and Prevention (CDC) regularly conducts the National Health and Nutrition Examination Survey (NHNES), which, among other objectives, measures levels of environmental contaminants in the blood and urine of Americans. The NHNES has included PFAS in its blood and urine monitoring since its 1999-2000 survey cycles and finds that exposure to 2 PFAS, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), is “universal”, even for Americans who were born after these two chemicals were phased out of production in the US. For most people, the main sources of PFAS exposure are consumer products that are grease, oil, and stain resistant (Minnesota Department of Health, n.d.), although drinking water can be a major source for people where these resources are contaminated with high concentrations of PFAS.

The resulting PFAS exposure is a concern because several of them are known to be toxic. The various types of PFAS likely impact health in different ways. Most PFAS health studies have focused on only two of the chemicals in this vast family—PFOA and PFOS. The most consistently observed and strongest evidence for harmful human health impacts is immune suppression (such as decreased vaccination response), changes in liver function (such as high cholesterol, and elevated liver enzymes), and low birth weight (Minnesota Department of Health, n.d.). PFOA also has been associated with kidney cancer.

The MPCA has monitored PFAS intermittently in the ambient groundwater for about the last 20 years, with the largest sampling events occurring in 2013 and 2019 (Figure 10). Since 2006, almost 300 individual wells representing ambient groundwater conditions were sampled for PFAS, and over 80 percent of these wells were last sampled from 2019-2023. Most of the wells sampled from 2019-2023 were specifically installed to monitor the groundwater (over 80 percent), and the remaining ones primarily served as private drinking water supplies for residences. The sampled monitoring wells were shallow, with an average depth of 26.7 feet, and the sampled domestic drinking water supply wells were more than five times deeper, with an average depth of 139 feet.

Figure 10. Number of wells monitored for PFAS by the MPCA's ambient groundwater monitoring program, 2006-2023.



All wells sampled for PFAS by the MPCA's ambient groundwater monitoring have been tested for the well-known chemicals, PFOA and PFOS, along with 10 other similarly structured chemicals (table 4). These PFAS are from a class called perfluoroalkyl acids. These are some of the simplest types of PFAS and generally consist of a fluorinated carbon chain with a charged functional group such as carboxylate or sulfonic acid group attached to it. PFAS like these were formerly used in some fire-fighting foams (Wang, Cousins, Scheringer, & Hungerbuhler, 2013) and as surfactants (Prevedouros, Cousins, Buck, & Korzenioski, 2006; Buck, et al., 2011). PFOA also was historically used as a processing aid in the production of fluoropolymers, and PFOS historically was used as a wetting agent and mist suppressant in metal plating (Wang, Cousins, Scheringer, & Hungerbuhler, 2013).

Table 4. PFAS analyzed in the ambient groundwater, 2019-2023

Perfluoroalkyl acids	**Perfluoroalkane sulfonamides**
Perfluorobutane sulfonate	Perfluorooctanesulfonamide
Perfluorobutanoic acid	2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (N-EtFOSE)[1]
Perfluoropentane sulfonate[1]	2-(N-methylperfluoro-1-octanesulfonamido)-ethanol (N-MeFOSE)[1]
Perfluoropentanoic acid	N-ethylperfluoro-1-octanesulfonamide (N-EtFOSA)[1]
Perfluorohexane sulfonate	N-methylperfluoro-1-octanesulfonamide (N-MeFOSA)[1]
Perfluorohexanoic acid	N-ethyl perfluorooctanesulfonamidoacetic acid (N-EtFOSAA)[1]
Perfluoroheptane sulfonate[1]	N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA)[1]
Perfluoroheptanoic acid	
Perfluorooctane sulfonate	Fluorotelomers
Perfluorooctanoic acid	FtS 4:2 ion[1]
Perfluorononane sulfonate[1]	FtS 6:2 ion[1]
Perfluorononanoic acid	FtS 8:2 ion[1]
Perfluorodecane sulfonate[1]	FTCA 3:3 ion[2]
Perfluorodecanoic acid	FTCA 5:3 ion[2]
Perfluoroundecanoic acid	FTCA 7:3 ion[2]
Perfluorododecane sulfonate[1]	
Perfluorododecanoic acid	Per- and polyfluoro ethers
Perfluorotridecanoic acid[1]	Hexafluoropropylene oxide dimer acid (HFPO-DA)[1]
Perfluorotetradecanoic acid[1]	Perfluoro-3,6-dioxaheptanoic acid[2]
	Perfluoro-3-methoxypropanoic acid[2]
	Perfluoro-4-methoxybutanoic acid[2]
	Ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA)[1]
	Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA)[2]
	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (8:2 Cl-PFEESA)[1]
	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (6:2 Cl-PFEESA)[1]

1. Added in 2019
2. Added in 2021

Twenty additional PFAS were added to the analytical suite beginning in 2019 due to improvements in the laboratory analytical methods (table 4). HFPO-DA (used in the GenX technology platform), ADONA, and 6:2 Cl-PFEESA (major constituent of F-53B) were some of the additional PFAS included in the updated analytical method. These chemicals are all part of a class of PFAS called per- and polyfluoro ethers. HFPO-DA and ADONA are relatively new PFAS that replaced PFOA in fluoropolymer manufacturing, and the F-53B has been used since the 1970s and as a replacement for PFOS in mist suppression and as a wetting agent. Other classes of PFAS that were in the improved laboratory method perfluoroalkane sulfamido substances, fluorotelomer-based substances, and seven additional perfluoroalkyl acids.

Perfluoroalkane sulfamido substances are a group of legacy PFAS that are no longer in use in the U.S. These types of PFAS historically were used to make products to protect carpet and upholstery, paper coatings, and other specialty applications and includes the chemicals N-MeFOSE, N-EtFOSE, N-MeFOSA, and N-EtFOSA. This class of PFAS consist of a fluorinated chain of carbon atoms attached to a sulfamido group, which is a sulfur atom that has both an amine group and two doubly bonded oxygen atoms attached to it. The production of these chemicals was phased out in the U.S. by the 3M Company in 2002 (Buck, et al., 2011) since the chemicals were based on an eight-carbon chemistry and degrade to form PFOS.

Fluorotelomer-based substances are another type of PFAS that are used as part of fabric and paper coatings, AFFF foams, and fluoropolymers. These chemicals have been manufactured since the 1960s and 1970s using a process called telomerization (Buck, et al., 2011) and are used as replacements for legacy PFAS like PFOA, PFOS, and the perfluoroalkane sulfamido substances. For example, fluorotelomer sulfonates which are marketed under names like Capstone FS-17, Zonyl FS-62, and Zonyl TBS are used in paints, coatings, adhesives, waxes, polishes, industrial cleaning chemicals, and as mist suppressants in chrome platings (Field & Seow, 2017).

The perfluoroalkane sulfomido and fluorotelomer-based substances are precursors to perfluoroalkyl acids like PFOA and PFOS. Both of these groups of chemicals ultimately degrade, microbially or abiotically to the extremely stable perfluoroalkyl acids (Plumlee, McNeill, & Reinhard, 2009; Styler, Myers, & Donaldson, 2013; Butt, Muir, & Mabury, 2014; Avendano & Liu, 2016; Lv, et al., 2020; Grgas, Petrina, Stefanac, Beslo, & Dragocevic, 2023). A few of the degradation products from these reactions, such as N-MeFOSAA, N-EtFOSAA, and the fluorotelomer carboxylic acids, also were measured as part of the PCA's ambient monitoring.

Perfluoroalkyl acids were the type of PFAS that were detected most frequently in the ambient groundwater. Sixteen different PFAS chemicals were detected in the ambient groundwater samples collected from 2019-2023 (Figure 11, table 5). Perfluorobutanoic acid (PFBA), which contains a 4-carbon long perfluorinated chain, was detected most frequently and typically at the highest concentrations (Figure 11). The highest PFBA concentrations typically were measured in the southeastern TCMA, which is in the vicinity of the known contamination emanating from the historic disposal sites for 3M manufacturing waste. Most of the other PFAS detected in the ambient groundwater generally were detected at concentrations less than 20 ng/L. One exception was that perfluorohexane sulfonate (PFHxS) and PFOS were measured in one shallow monitoring well in Anoka County in 2019 at concentrations of 1,460 and 463 ng/L, respectively.

Very few perfluoroalkane sulfamido substances, fluorotelomer-based substances, or per and polyfluoro ethers were detected in the ambient groundwater samples. Over 300 groundwater samples were collected from the PCA's ambient monitoring network from 2019-2023. Only one per- and poly-fluoro ether, one perfluoroalkane sulfonamide, and one fluorotelomer sulfonate were detected. HFPO-DA, ADONA, and F-53B were not detected in any of the samples collected.

Figure 11. PFAS detections in Minnesota's ambient groundwater, 2019-2023.

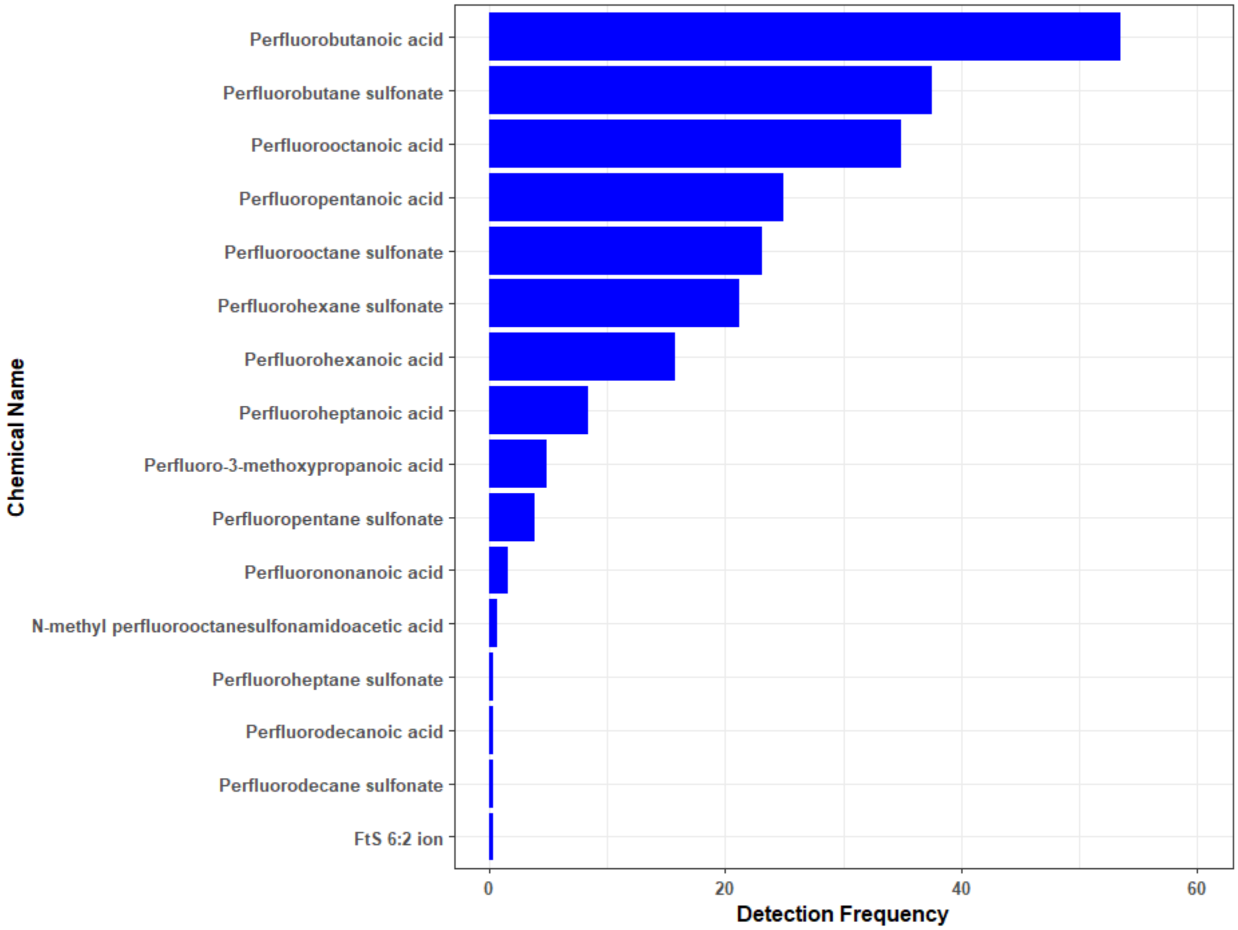


Table 5. Summary statistics of the detected PFAS in the ambient groundwater, 2019-2023 [NC, not calculated due to insufficient data].

Chemical	Number detected values	Range in detected concentration (ng/L)	Mean (ng/L)	Median (ng/L)	Standard deviation (ng/L)	Interquartile range (ng/L)
PFBA	170	6.67-1460	49.0	9.5	117.9	43.9
PFBS	118	1.79-151	3.4	0.7	11.6	2.4
PFOA	110	1.84-143	4.5	0.6	14.2	2.7
PFPeA	79	3.67-82.3	3.9	0.9 ng/L	8.0	2.2
PFOS	72	1.62-463	4.2	0.3 ng/L	27.1	1.04
PFHxS	66	1.7-1460	6.5	0.3	82.1	0.93
PFHxA	49	1.87-52.3	NC	NC	NC	NC
PFHpA	26	1.84-18.4	NC	NC	NC	NC
PFPeS	12	1.65-202	NC	NC	NC	NC
PFNA	5	1.98-4.16	NC	NC	NC	NC
Perfluoro-3-methoxypropanoic acid	3	3.7-13.2	NC	NC	NC	NC
N-MeFOSAA	2	2.08-2.1	NC	NC	NC	NC
PFDS	1	3.08	NC	NC	NC	NC
PFDA	1	2.54	NC	NC	NC	NC
PFHpS	1	30.7	NC	NC	NC	NC
6:2 FtS	1	107	NC	NC	NC	NC

All detected PFOA concentrations were greater than the health-based value of 0.24 ng/L set by the MDH for drinking water in 2024 since the method reporting limit for this chemical was greater than this value. PFOA was detected in 110 wells. Eleven of these wells supplied drinking water, primarily to individual residences in the TCMA. Fifty-three wells had PFOA concentrations that were greater than the MCL of 4 ng/L set by the EPA. Six of the wells with concentrations exceeding the MCL supplied drinking water to private residences in Washington County. These wells ranged from 126-278 feet deep. The remainder of the wells that had PFOA concentrations exceeding the MCL were shallow monitoring wells located throughout the TCMA, and in the Bemidji and Brainerd urban areas.

Some PFOS, perfluorobutane sulfonate (PFBS), and PFHxS concentrations were measured that exceeded the human health criteria set for drinking water by the MDH or EPA. Forty-six wells, which primarily were shallow monitoring wells less than 25 feet deep, had PFOS concentrations exceeding the human health criteria of 2.3 ng/L set by the MDH in 2024, and thirty-one wells had concentrations exceeding the EPA's PFOS MCL of 4 ng/L. Five of the wells exceeding the EPA's PFOS MCL supplied drinking water. Three of the water-supply wells with PFOS MCL exceedances were in Hennepin and Washington Counties and ranged from 133-278 feet deep. The remaining two water-supply wells with PFOS MCL exceedances were located in Stearns and Wabasha Counties; these wells were shallower than the ones with exceedances in the TCMA and were both about 60 feet deep. PFBS and PFHxS concentrations exceeding the MDH's human health criteria only were measured in monitoring wells. PFBS concentrations in two shallow monitoring wells in the TCMA exceeded the health risk limit of 100 ng/L set by the MDH in 2023, and one monitoring well in Anoka County had a PFHxS concentration exceeding the health risk limit of 47 ng/L set by MDH in 2023.

Very few sites had sufficient data to determine trends. Six sites have records extending back to 2006. These primarily are monitoring wells located in the northwest TCMA and the St. Cloud area. The monitoring wells with the longest records are in Hennepin County (unique well number 560425, sampled for PFAS from 2006-2022) and Anoka County (unique well number 560381, sampled for PFAS from 2006-2021).

Contaminants of emerging concern

Contaminants of Emerging Concern (CECs) are synthetic or naturally occurring chemicals that have not been commonly monitored or regulated in the environment. Common classes of these chemicals include antibiotics, detergents, fire retardants, hormones, personal care products, and pharmaceuticals. CECs are not necessarily newly manufactured chemicals. In some cases, the release of these chemicals into the environment has occurred for a long time, but laboratory techniques sensitive enough to detect them in the environment only were developed within the last decade.

The release of CECs into the environment is of a particular concern because they may affect ecological or human health. The effect of chronic exposure to low levels of most of these chemicals to human or aquatic life often is not known. In addition, some of these chemicals function as endocrine active chemicals (EACs) , which are natural or synthetic chemicals that mimic or block the function of the natural hormone systems in humans and animals. EACs also are referred to as endocrine disrupting chemicals or EDCs in the scientific literature; however, scientists are increasingly adopting the usage of the term EAC as a more accurate description for contaminants that affect the endocrine system.

The MPCA has analyzed water samples collected from its Ambient Groundwater Monitoring Network for CECs since 2009. Due to the high cost of these chemical analyses, only a subset of the network wells (about 40) was sampled each year for this suite of chemicals. From 2009-2014, US Geological Survey laboratories in Denver, Colorado and Lawrence, Kansas analyzed the MPCA’s groundwater samples for a suite of over 200 CECs. Since 2015, the groundwater samples have been analyzed for CECs by SGS

AXYS Analytical Services in British Columbia. The CEC data collected through 2017 was summarized in the last MPCA Groundwater Condition Report (Kroening & Vaughan, 2019). This report focuses on the data collected from 2018-2023.

Pharmaceuticals and personal care products

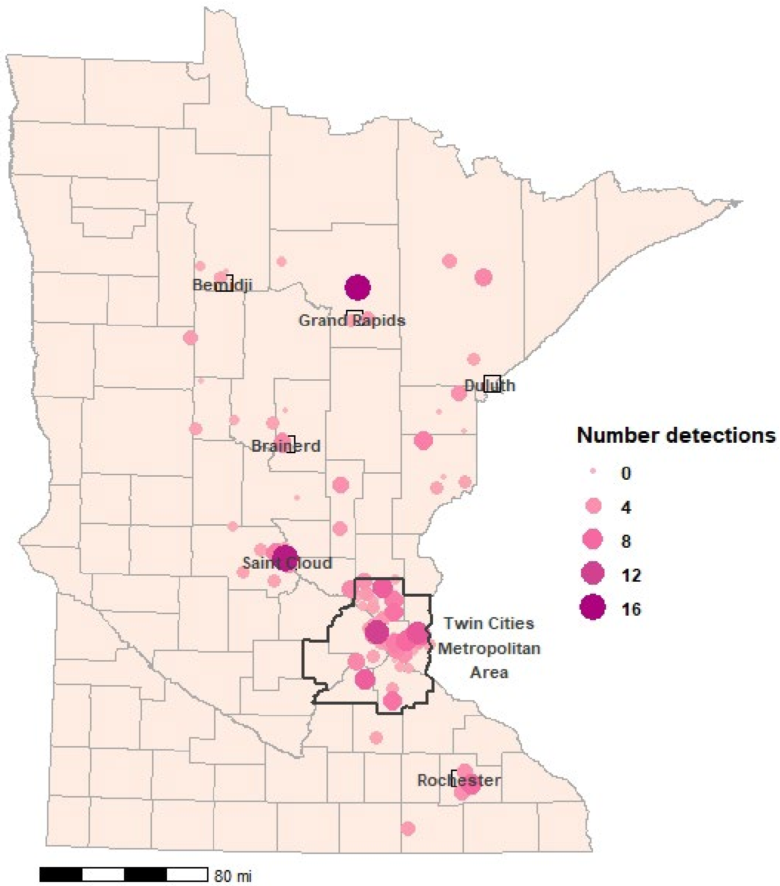
The MPCA monitored 108 ambient network wells for CECs from 2018-2023. Like past sampling campaigns for CECs in Minnesota’s ambient groundwater, about 40 wells were sampled each year. No sampling, however, was conducted during the height of the COVID-19 pandemic in 2020 and 2021. Most of the wells sampled from 2018-2023 had previously been sampled for CECs in past monitoring campaigns and were selected for continued sampling because at least one CEC was detected in the well water. Most of the sampled wells were shallow monitoring wells that primarily were in urban areas. The average depth of these wells was about 27 feet, and the deepest monitoring well sampled was 133 feet. Twelve domestic water-supply wells also were sampled for CECs. The sampled domestic wells were much deeper than the monitoring wells, with an average depth of 113 feet and a maximum depth of 240 feet. An outside tap was used to collect all water samples from the domestic wells; this water typically is not consumed and is not treated by any devices such as water softeners that may be installed in the residence.

All well water samples were analyzed at SGS AXYS laboratories in British Columbia, Canada for over 130 pharmaceutical and personal care products, bisphenol A and/or its analogs, and triclosan. Antibiotics were the largest class of pharmaceuticals analyzed in the water samples. A complete list of the CECs analyzed along with the analytical methods are included in Appendix A. The analytical procedure entailed analyzing a few different types of QA samples along with each batch of water samples, including lab blank and matrix spike samples.

Some CECs were detected in a substantial number of the laboratory blank samples. DEET, bisphenol A, and branched p-nonylphenols were detected in 96, 52, and 23 percent of the laboratory blank samples, respectively. Several other studies have reported detections of these chemicals in laboratory and field blank samples (Salgueiro-Gonzalez, et al., 2012; Merel & Snyder, 2016; Churchill, Baldys, Gunn, Mobley, & Quigley, 2020). Sources of contamination for alkylphenols and bisphenol A include using detergents for cleaning laboratory equipment and the plastic parts in the analytical instrument or sampling equipment (both bisphenol A and alkylphenols are used in the manufacture of plastics). Due to the large number of blank detections, the 90% upper confidence limit (80 percent confidence) was calculated for the DEET, bisphenol A, and branched p-nonylphenol concentrations in the laboratory blank samples, and the groundwater data were censored at these limits. In addition, any CEC was not considered detected if the laboratory flagged the result as being affected by blank contamination; this occurred when the reported concentration was within 10 times that reported in the lab blank sample associated with the batch of samples analyzed at the laboratory.

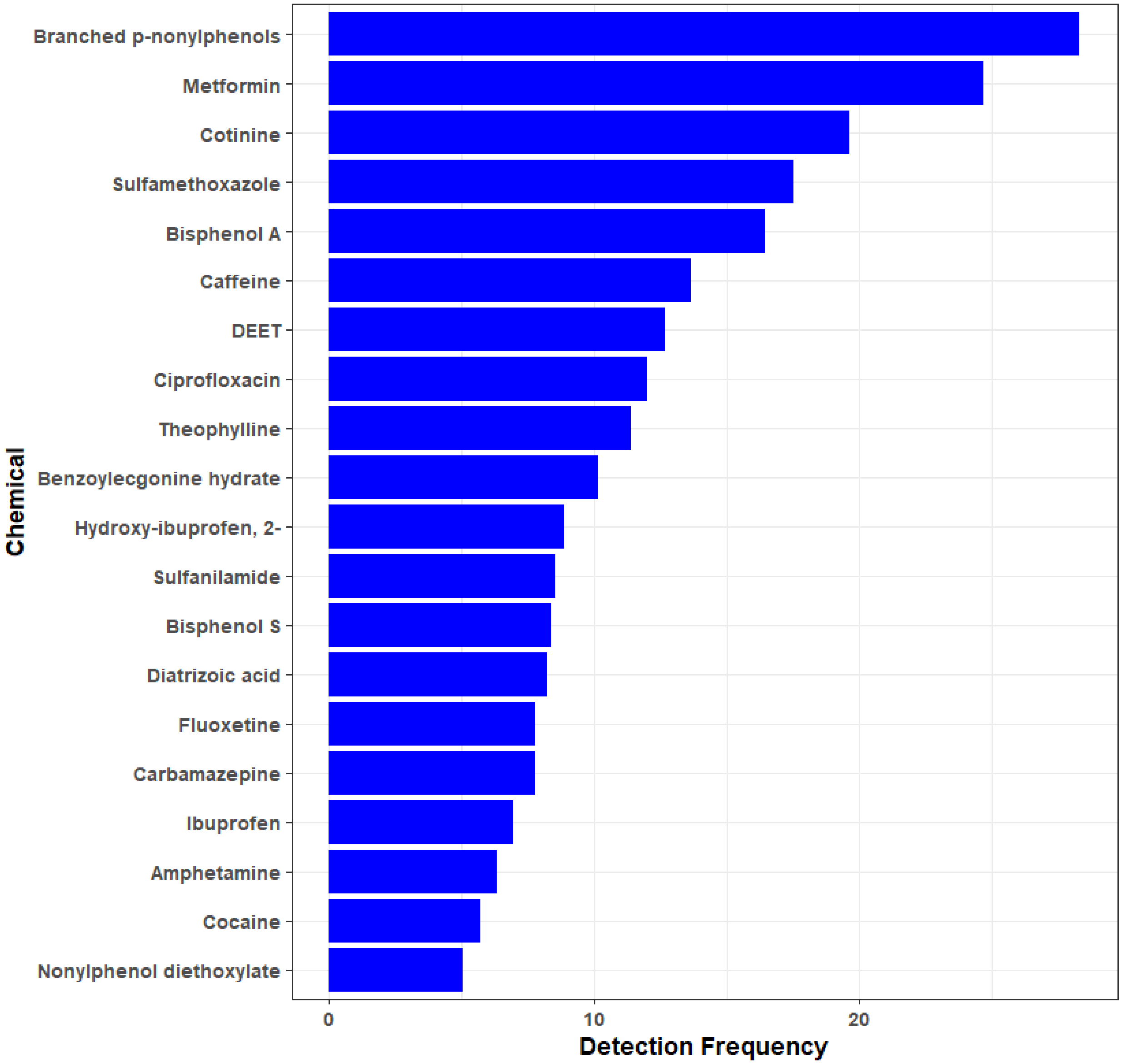
CECs were detected in almost 90 percent of the sampled wells (Figure 12). Most of the wells with detections were shallow (on average about 25 feet deep) and intersected the water table. Up to as many as 16 CECs were found in an individual well. The wells with the greatest number of CEC detections generally were in urban areas, such as the TCMA, St. Cloud, and Rochester. The well with the greatest number of CEC detections was a shallow (30 feet deep) monitoring well located in Itasca County. The most recent water sample from this well contained 16 individual CECs, including caffeine, clotrimazole, diphenhydramine, and almost ten different antibiotics. It was unexpected that so many CECs found in this particular well because it was located off of a forest road in the Chippewa National Forest, and the surrounding landscape was undeveloped. The detection of caffeine in the groundwater suggested that the source of this chemical and the other CECs may have resulted from a localized wastewater discharge. Caffeine is frequently detected in groundwater impacted by wastewater effluent (Godfrey, Woessner, & Benotti, 2007; Seiler, Zaugg, Thomas, & Howcraft, 1999; Teijon, Candela, Tamoh, Molina-Diaz, & Fernandez-Alba, 2010) and is rapidly degraded in the environment (Korosa, Brencic, & Mali, 2020; Hillebrand, Nodler, Sauter, & Licha, 2015; Hillebrand, Nodler, Licha, Sauter, & Geyer, 2012), which suggested any wastewater discharge near this site was fairly recent. The area surrounding the well in the Chippewa National Forest is forested and not served by any centralized sewer system, but there is some development near the lakes in the area that likely used SSTS for wastewater treatment and disposal. Additionally, camping was permitted anywhere within the National Forest, and the wastewater impacting the groundwater may have been generated from this activity.

Figure 12. CEC detections in ambient groundwater monitoring network wells, 2018-2023 [Plot shows the most recent detection in the sampled wells].



Sixty-eight of the 135 CECs analyzed were detected in the groundwater samples. Antibiotics were the type of CEC that was detected most often, which is consistent with this group of medications dominating the list of pharmaceuticals that were analyzed in the water samples. The twenty most-frequently detected CECs are shown in Figure 13, and all the chemicals detected are listed in Appendix table A-4. Some of the most-commonly detected CECs in the groundwater, such as the branched p-nonylphenols, metformin, cotinine, and bisphenol A, also were frequently detected in Minnesota's stream and rivers (Ferrey, Martinovic, Backe, & Andrews, 2017) and lakes (Ferrey & Backe, 2021).

Figure 13. Contaminant of emerging concern (CEC) detection frequency in the ambient groundwater, 2018-2023 [Chart shows top 20 detected CECs].



The CEC's physical-chemical properties as well as their use and subsequent release into the environment determines whether they are transported to the groundwater. Some key properties that affect the transport of chemicals to groundwater include its water solubility, organic carbon partition coefficient (Koc), and the octanol/water partition coefficient (Kow). Koc also is referred to as the adsorption coefficient, and this property affects the ability of a chemical to bind or sorb to organic matter in soils and sediments. A high Koc value indicates that the substance binds tightly to soils and is less likely to be present in the water. The Kow value is a measure of how a chemical is distributed between octanol and water, and this represents the chemical's potential to accumulate in animal fat. A chemical with a high Kow value is more likely to bioaccumulate in animal fat.

The water solubility, Kow, and Koc values were estimated for most of the CECs analyzed in this study using the EPA's EPI (Estimation Programs Interface) suite (U.S. Environmental Protection Agency, n.d.).

Water solubility was estimated using the fragment constant method, and the Koc was estimated using the Sabljic molecular connectivity method with improved correction factors. Water solubility, Kow, and Koc estimates could not be made for the following thirteen chemicals: 2-hydroxy ibuprofen, nonylphenol diethoxylate, nonylphenol monoethoxylate, p-octylphenol, erythromycin-H20, norfluoxetine, 10-hydroxy amitriptyline, norverapamil, triclosan, desmethyldiltriazem, drospirenone, and fluticasone propionate. Since water solubility, Kow, and Koc values were estimated using the EPA computer program and not directly measured, the CECs were categorized by high or low solubility, Kow, and Koc. The threshold for these categories were based on the classifications used by Bexfield et al (2019) who assigned classes for water solubility based on a threshold of 100 mg/L, Kow values based on a threshold of 2.7, and Koc values based on a threshold of 2.4 L/kg.

The CECs detected in Minnesota's ambient groundwater generally had a high water solubility as well as low log Kow and log Koc values. Contingency tables were used to quantify whether the detection of the CECs in the groundwater was related to its water solubility, Kow or Koc values. This statistical analysis showed the CECs detected in the groundwater tend to have high water solubilities along with low Kow and Koc values compared to the other detected CECs. Most of the most-frequently detected CECs in the ambient groundwater (Figure 13) had high water solubilities and low log Koc and log Kow values. This result is consistent with the findings from other groundwater studies (Bexfield, Toccalino, Belitz, Foreman, & Furlong, 2019) that typically find chemicals in the groundwater that are water soluble and typically do not sorb to soils or sediments or accumulate in biota.

Chemical use also affected whether some of the measured CECs were found in the groundwater. For example, a chemical may have a very high water solubility, but it will not be found in the groundwater if it is not used. CEC use information was not available for all the chemicals analyzed in this study, but there was information available for about one-half of them. Chemical production volume data were available for the eight of the CECs that were required to be reported under the Federal Toxic Substances Control Act (TSCA): 1) branched p-nonylphenols, 2) bisphenol A, 3) caffeine, 4) DEET, 5) bisphenol S, 6) triclocarbon, 7) bisphenol AF, and 8) triclosan. Chemical use information is collected by TSCA every four years from manufacturers of certain chemicals whose production volumes are greater than 25,000 pounds each year. Medication prescription information was available for 59 of the analyzed CECs from the Medical Expenditure Panel Survey (MEPS), which is sponsored by the U.S. Agency for Healthcare Research and Quality. MEPS is a survey of households in the U.S. and collects data on the number of times members in the surveyed households obtained prescribed medications. This survey does not include medications administered in hospitals or other institutional settings, medications administered to animals, or non-prescription medications.

Many of the most-frequently detected CECs in the groundwater had a high water solubility combined with a high use. These CECs included metformin, cotinine, sulfamethoxazole, bisphenol A, bisphenol S, caffeine, DEET, ciprofloxacin, amphetamine, cocaine and its metabolite, benzoylecgonine hydrate. Metformin, the second most-commonly detected CEC in the groundwater and anti-diabetic medication, was the 5th most-prescribed medication in the U.S. according to the 2021 MEPS data. Sulfamethoxazole and ciprofloxacin are among the top 100 medications prescribed in the U.S. in 2019. Cotinine, which is present in tobacco products and is the primary degradation product of nicotine, was estimated to be used by almost 140 million people in the U.S. at least once a month in 2019 (Substance Abuse and Mental Health Services Administration, 2019). Sulfamethoxazole, the third most detected CEC and an antibiotic, was the 52nd most-prescribed medication in the nation. Bisphenol A, bisphenol S, and DEET are all high production volume chemicals and are estimated to have a nationwide production volumes ranging from one million up to five billion pounds each year in 2019. Cocaine, along with its degradation product benzoylecgonine hydrate, is an illicit drug which was estimated to be used by 5.5 million people in the U.S. in 2019 (SAMHSA, 2020). Caffeine, the sixth most-frequently detected CEC in the groundwater, is well-known to be a frequently consumed product in the U.S. and has a global market size valued at $715.2 billion dollars in 2021 (Allied Market Research, 2024), and eighty-five percent of the U.S. population consumes at least one caffeinated beverage each day (Mitchell, Knight, Hockenberry, Teplansky, & Hartman, 2014).

Other CECs were detected in the groundwater that were less soluble compared to the substances discussed in the previous paragraph, but their detection likely was due to their high use. These chemicals included branched p-nonylphenols, diatrizoic acid, fluoxetine, carbamazepine, and ibuprofen. Branched p-nonylphenols, the most-frequently detected CEC in the groundwater, is a high-volume production chemical. These are part of the nonionic surfactants used in laundry detergents, personal hygiene, automotive, latex paints, and lawn care products. This chemical has a low water solubility and high log Kow and log Koc value, which suggests it is not particularly mobile in water, but it had estimated use (based on the TSCA information) between 100 and 250 million pounds per year in 2019. Diatrizoic acid is a contrast agent. Iodinated contrast agents like this are a commonly used drug in radiology, and it is estimated that 120 million doses of contrast agent are administered each year in the U.S (Koeppel & Boehm, 2023). Finally, fluoxetine, carbamazepine, and ibuprofen are pharmaceuticals that have a low water solubility but have a high use. Fluoxetine and ibuprofen are among the top 50 prescribed medications prescribed in 2019, and ibuprofen also is a commonly used non-prescription medication. Carbamazepine also is among the top 300 most prescribed medications in the U.S according to the 2021 MEPS data.

The concentrations of the CECs measured in the ambient groundwater did not exceed any applicable human health guidance values. The MDH has issued human health guidance for 10 of the CECs measured in this study (table 6), and no concentrations were even within 10 percent of the human health guidance.

Table 6. Maximum concentrations of selected CECs detected in Minnesota's ambient groundwater with the state human health guidance for drinking water [Data from the Minnesota Pollution Control Agency from 2018-2023].

Chemical name	CAS registry number	Maximum concentration detected	Human health guidance for drinking water	
Acetaminophen	103-90-2	31.7 ng/L	200,000 ng/L	HRL (2015)
Bisphenol A	80-05-7	246 ng/L	20,000 ng/L	HRL (2015)
Branched p-nonylphenols	84852-15-3	260 ng/L	20,000 ng/L	HRL (2023)
Carbamazepine	298-46-4	79.2 ng/L	40,000 ng/L	HRL (2013)
DEET	134-62-3	417 ng/L	200,000 ng/L	HRL (2013)
Sulfamethazine	57-68-1	1.19 ng/L	100,000 ng/L	HRL (2015)
Sulfamethoxazole	723-46-6	56.6 ng/L	100,000 ng/L	RAA (2013)
Triclocarban	101-20-2	1.69 ng/L	100,000 ng/L	RAA (2013)
Triclosan	3380-34-5	Not detected	50,000 ng/L	HRL (2015)
Venlafaxine	93413-69-5	Not detected	10,000 ng/L	HRL (2023)

Organophosphate flame retardants

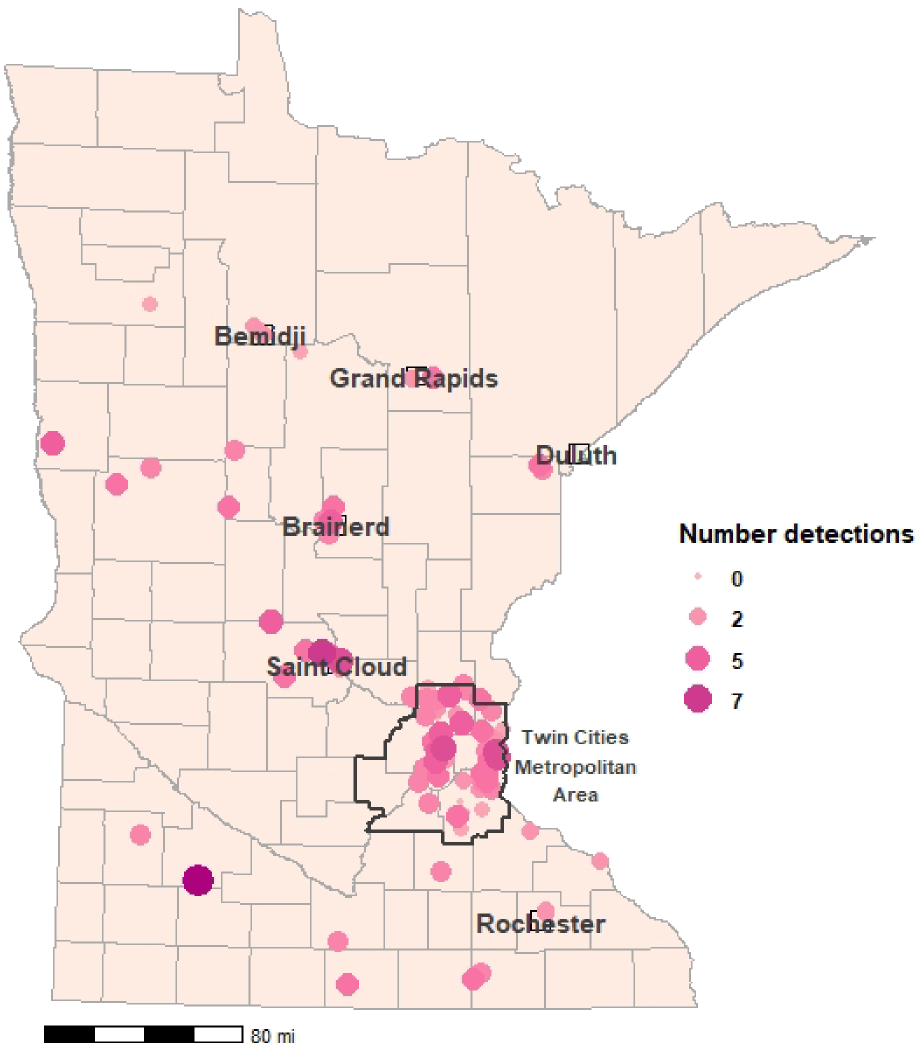
Organophosphate flame retardants are a class of chemicals whose use has increased over the last 10-15 years (Blum, et al., 2019; Schreder & La Guardia, 2014). As the name suggests, flame retardants are chemicals that have been added or applied to materials since the 1960s to slow or prevent the start of growth of a fire. These substances commonly are added to many products including home furnishings, electronics, building materials, and transportation products. In the past, several different types of brominated chemicals commonly were used as fire retardants, including polybrominated diphenyl ethers or PBDEs, but the use of these chemicals has been phased out by regulatory action and manufacturer's voluntary actions because of they persist in the environment, bioaccumulate, and some are known to be toxic. Flame retardants based on an organophosphate ester chemistry, which was the focus of this sampling effort, are a group of chemicals that have replaced the PBDEs because they are expected to be less environmentally persistent (Blum et al, 2019). This group of chemicals are used as plasticizers as well.

The presence of organophosphate flame retardants in the environment is a concern due to their mobility in water and toxicity. Organophosphate flame retardants, especially the ones that are chlorinated, are more soluble in water compared to the PBDEs, and persistent, which can permit organophosphate flame retardants to be transported long distances which make them appear to be persistent mobile organic compounds (Blum, et al., 2019). Some of these chemicals also are known to be toxic (National Institute of Health, 2023), and the MDH has set human health limits for three chemicals in this class for drinking water: tris(2-butoxy) phosphate, tris(2-chloroethyl) phosphate, and tris(1,3-dichloroisopropyl) phosphate. Eight organophosphate flame retardants were identified by the MDH's Toxic Free Kids Program as chemicals of high concern, which are chemicals that have a high probability to cause adverse impacts, including harming the normal development of children and fetuses, causing cancer, damaging the nervous or immune system, and having persistent and bioaccumulative properties (Minnesota Department of Health, n.d.).

In 2021, groundwater samples were collected from 116 ambient network wells and analyzed for a suite of 13 organophosphate flame retardants and plasticizers (Appendix A, table A-5). All water samples were analyzed at the SGS Analytical Laboratory in Sydney, British Columbia using their analytical method MLA-098. Most of the sampled wells were in urban areas, including the TCMA, Brainerd, and St. Cloud. Like the sampling effort for CECs in the groundwater, a combination of both monitoring and drinking water supply wells was sampled. About 65 percent of the sampled wells were installed specifically to monitor the groundwater quality, and the water in these wells is not consumed. The remaining 35 percent of the sampled wells were installed to provide drinking water primarily to individual residences although one water supply well in a park was sampled. The sampled monitoring wells were shallow, with depths ranging from 9 to 90 feet and an average depth of about 26 feet. The sampled domestic and public water supply well were deeper compared to these, with depths ranging from 24 to 340 feet and an average depth of 136 feet.

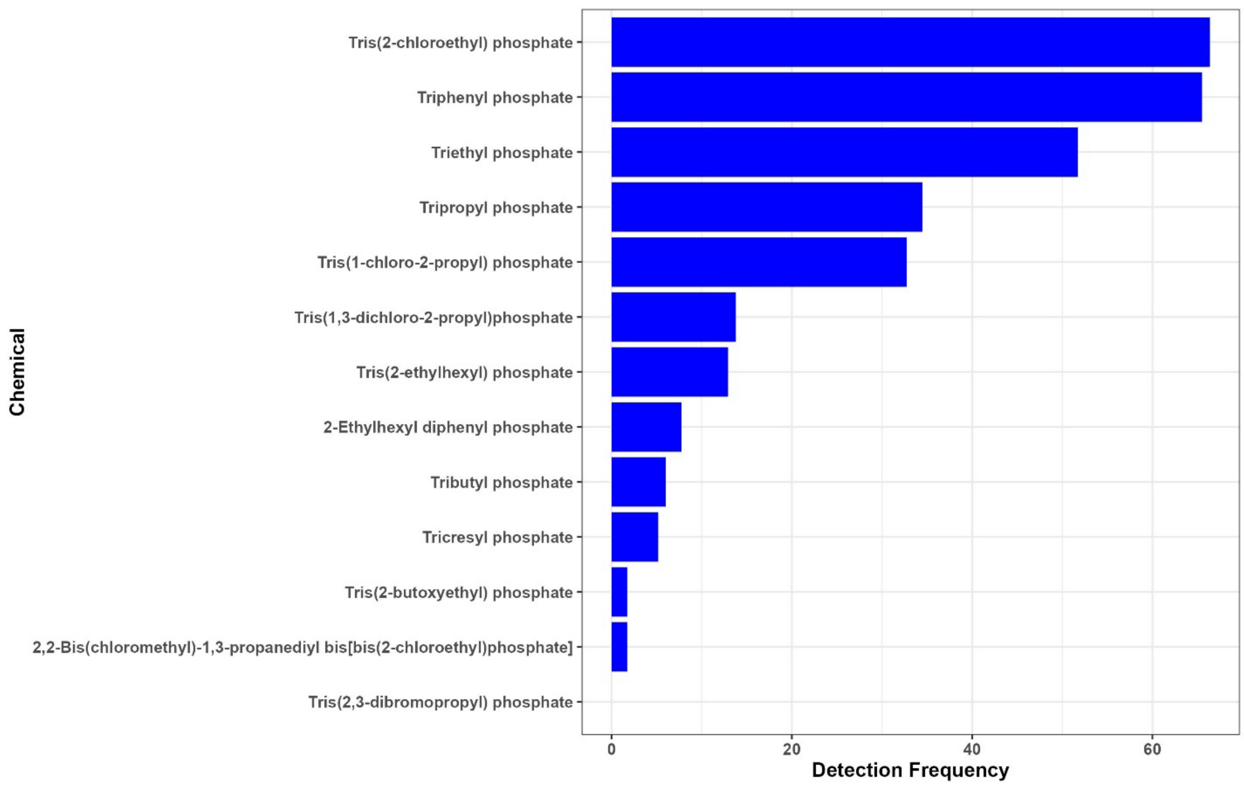
Flame retardants and plasticizers were detected in almost 95 percent of the sampled wells. Up to 9 organophosphate flame retardants were detected in an individual wells, and the average number of chemicals detected was three. The well with the greatest number of organophosphate flame retardant detections was a 57-foot deep domestic well in Redwood County (Figure 14). The large number of detections likely results from a couple of factors. First, most of the sampled wells sampled were in places where these chemicals would be most likely be detected. As mentioned previously, most of the sampled wells were located in urban areas, where the use products containing organophosphate flame retardants would be concentrated. In addition, the sampled wells were installed in aquifers that had little natural geologic protection against contamination. Many of them intersected the water table and were overlain by permeable sandy sediments, which would allow water and any associated contamination to percolate through it. Secondly, most of the flame retardants targeted in this analysis were high production volume chemicals. Production volume information was reported for 9 of the 13 analyzed OPFRs in the 2019 CDR. Most of these were high production volume chemicals, with production volumes as high as 100,000,000 million pounds per year in 2019, with the exception of V6.

Figure 14. Organophosphate flame retardant detections in Minnesota's ambient groundwater, 2021 [Data from the Minnesota Pollution Control Agency].



The most-frequently detected organophosphate flame retardants in the groundwater were tris(2-chloroethyl) phosphate, triphenyl phosphate, and triethyl phosphate. These three chemicals were detected in over one-half of the sampled wells (Figure 15). Tris(2,3-dibromylpropyl) phosphate or TBPP was not detected in any water samples. In the past, this chemical was used as a flame retardant in children's sleepwear, but this use was banned in 1977 in the U.S.

Figure 15. Organophosphate flame retardant detection frequency in Minnesota's ambient groundwater, 2021 [Data from the Minnesota Pollution Control Agency].



The detected organophosphate flame retardant concentrations generally were less than 25 ng/L, on average. MDH has set human health guidance for three of the analyzed chemicals in drinking water: TCEP, tris(1,3-dichloro-2-propyl) phosphate, and tris(2-butoxyethyl) phosphate. No concentrations measured in the ambient groundwater in 2021 exceeded these values (table 7). One measured tris(1,3-dichloro-2-propyl) phosphate value was within about 25% of the health risk limit set in 2023. The highest concentration, a tris(2-butoxyethyl) phosphate value of 1,720 ng/L, was measured in a 48-foot-deep monitoring well in Sherburne County.

Table 7. Maximum concentrations of selected organophosphate flame retardants detected in Minnesota's ambient groundwater with the state human health guidance for drinking water [Data from the Minnesota Pollution Control Agency from 2021; NA, not available].

Chemical Name	CAS Registry Number	Maximum concentration detected	Human health guidance for drinking water	
Tris(2-chloroethyl) phosphate	115-96-8	39.2 ng/L	5,000 ng/L	HRL (2013)
Triphenyl phosphate	115-86-6	208 ng/L	NA	NA
Triethyl phosphate	78-40-0	140 ng/L	NA	NA

Chemical Name	CAS Registry Number	Maximum concentration detected	Human health guidance for drinking water	
Tripropyl phosphate	513-08-6	0.848 ng/L	NA	NA
Tris(1-chloro-2-propyl) phosphate	13674-84-5	548 ng/L	NA	NA
Tris(1,3-dichloro-2-propyl) phosphate	101-20-2	182 ng/L	800 ng/L	HRL (2023)
Tris(2-ethylhexyl) phosphate	78-42-2	0.403	NA	NA
2-ethylhexyl diphenyl phosphate	1241-94-7	11.7 ng/L	NA	NA
Tributyl phosphate	126-73-8	19.2 ng/L	NA	NA
Tricresyl phosphate	1330-78-5	2.05 ng/L	NA	NA
Tris(2-butoxyethyl) phosphate	78-51-3	1,720 ng/L	30,000 ng/L	HRL (2023)
V6	38051-10-4	1.02 ng/L	NA	NA
Tris(2,3-dibromopropyl) phosphate	126-42-7	NA	NA	NA

Pesticides

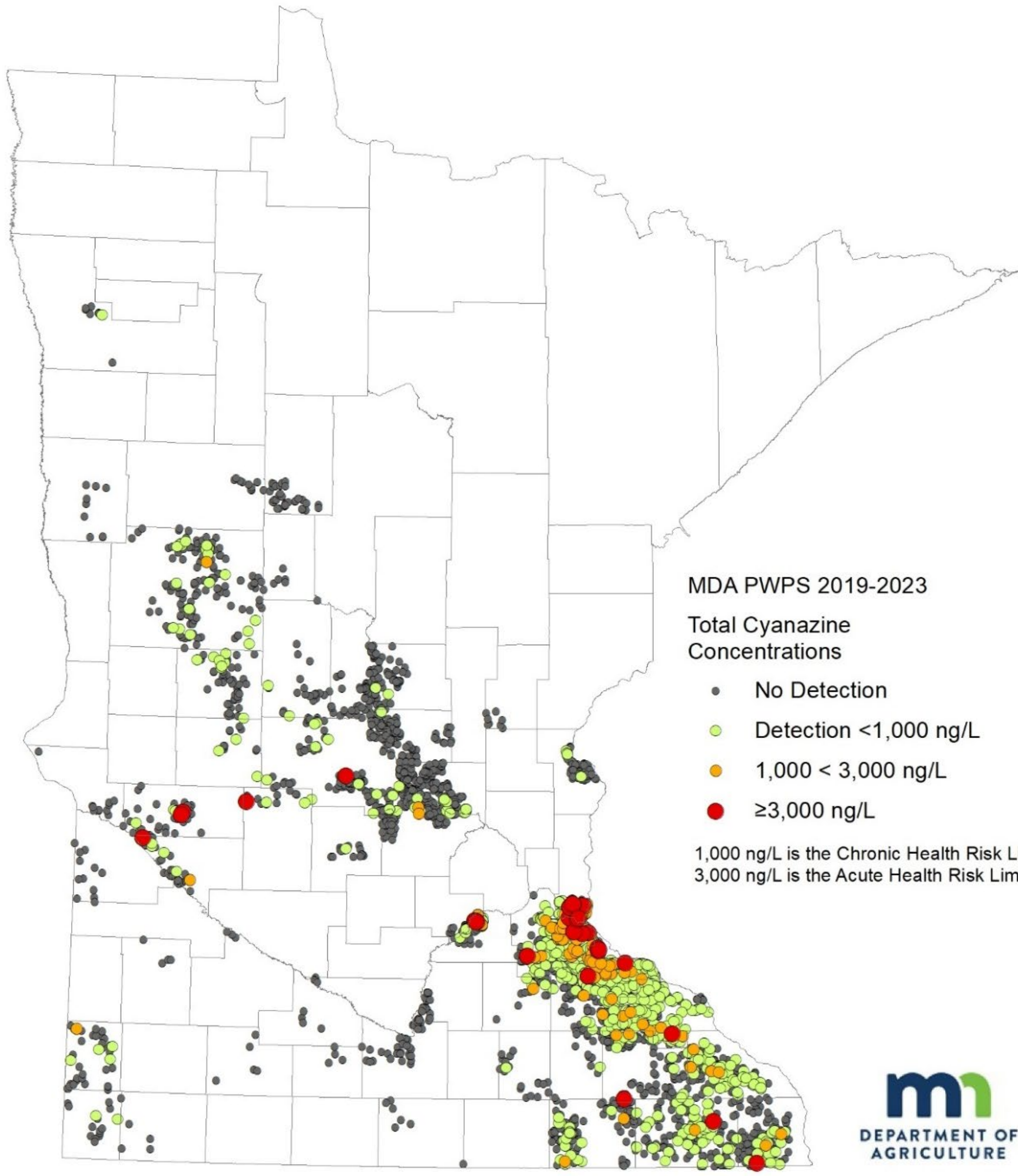
Private well pesticide sampling

The MDA began the second phase of the Private Well Pesticide Sampling (PWPS) Project in 2021. Phase two focused on characterizing the presence of the pesticides cyanazine and atrazine, and their degradates, in areas of the state with vulnerable groundwater. The main purpose of this sampling effort was to provide information to homeowners on the presence of these chemicals in their drinking water. The information is also used to inform pesticide management decision making. The degradates of the herbicide cyanazine were identified as posing the greatest pesticide related risk to drinking water based on the first phase of PWPS (Minnesota Department of Agriculture, 2022). Cyanazine has not been registered for use in Minnesota since 2002 and its degradates are considered legacy contaminants.

Beginning in the summer of 2021, the PWPS resampled wells that had a previous detection of didealkylatrazine. The presence of didealkylatrazine was used to target wells for sampling because it is a degradate of both atrazine and cyanazine. In southeastern Minnesota, the presence of didealkylatrazine is a strong indicator that some of the other cyanazine degradates may be present. Sampling has also been expanded to areas of similar geologic settings in the metro area.

From 2019-2023, the MDA collected 3,929 private well pesticide samples across 51 counties in Minnesota (Figure 16). Samples were analyzed for nitrate and several pesticides including atrazine, cyanazine and their degradates. Total cyanazine, which is the summation of cyanazine parent plus its applicable degradates, was detected in approximately 30% of the targeted wells. During this period 174 private drinking water wells were identified with total cyanazine concentrations above the health risk limit of 1,000 ng/L, while 35 were above the acute health risk limit of 3,000 ng/L. Most of the detections identified to date occurred in Dakota, Goodhue, Scott and Washington Counties (Figure 16).

Figure 16. Total cyanazine concentrations in wells sampled by the Minnesota Department of Agriculture Phase 2 Private Well Sampling Project.



Ambient groundwater pesticide monitoring network

MDA's groundwater monitoring network provides information on impacts to the state's groundwater from the routine use of agricultural chemicals. Minnesota was divided into 10 Pesticide Monitoring Regions (PMRs) intended to represent areas of different agricultural land use as well as differing geologic and hydrogeologic regions in the state.

Samples were collected from 168 groundwater monitoring sites in 2023 (**Figure 17**). Of these sites, 142 consisted of one or more specifically designed and installed monitoring or observation wells, 13 were private drinking water wells, and 13 consisted of naturally occurring springs emerging from bedrock formations of interest in the southeastern area of the state. All of the locations are considered sensitive to contamination from activities at the surface. Network design and sampling protocols are available in the program's groundwater design document on the MDA website at: [https://www.mda.state.mn.us/monitoring.](https://www.mda.state.mn.us/monitoring)

The MDA Laboratory has continued to expand their analytical capabilities, resulting in an increase in the number of compounds evaluated. In 2014, 133 different pesticide compounds were evaluated; by 2023, that number increased to 186. The MDA laboratory has also been able to lower the detection limit for some pesticides, meaning lower concentrations can be detected and quantified. Forty-nine different pesticides or pesticide degradates were detected in groundwater in 2023. Although exceedances of established human health guidance values (which denote levels of pesticides that could possibly have adverse effects) have historically been very rare, in 2023, twelve samples collected from monitoring wells in PMR 4 (Central Sands Region) had concentrations of 4-hydroxychlorothalonil, a degradate of the fungicide chlorothalonil, greater than the drinking water Risk Assessment Advice (RAA) of 2,000 ng/L.

In accordance with statutory requirements in the Groundwater Protection Act (Minn. Stat. chapter 103H) and the Pesticide Management Plan, the MDA has determined that five pesticides are commonly detected in groundwater, leading to the development of Best Management Practices to prevent or reduce ongoing degradation of groundwater resources. The five common detection pesticides are agricultural herbicides including: acetochlor, alachlor, atrazine, metolachlor and metribuzin.

Figure 17 presents the number of common detection pesticides detected at each sampling site in 2023. The locations showing the greatest number of pesticides per site are concentrated in the central sand plains (PMR-4), east central (Pesticide Monitoring Region 5), and in southeastern Minnesota (Pesticide Monitoring Region 9).

Metolachlor ESA (a degradate of the herbicide metolachlor) was the most commonly detected pesticide compound within the MDA dataset in 2023. The most extensive dataset for assessing changes in metolachlor ESA impacts to groundwater over time is the concentration data from PMR-4. The median values on the most recent 10-year period (2014-2023) indicate a statistically significant increasing trend in concentrations for this period in PMR 4. The detection frequency trend for metolachlor ESA in PMR 4 has also risen in a statistically significant fashion for this period. In 2023, the highest concentration measured for metolachlor ESA was 11,200 ng/L in PMR 4, which is substantially lower than the Health Risk Limit of 1,000,000 ng/L.

Statewide detection frequency for the common detection pesticides and their degradates is presented in Figure 18. The graphic indicates that detections for these pesticides are generally stable or declining when evaluated on a statewide basis. However, when evaluated on a regional basis there are pesticide detection frequencies that indicate a statistically significant increasing trend such as metolachlor ESA in PMR 4, as discussed above. Also presented in Figure 18 is a statewide common detection pesticide 90th

percentile concentration as a percentage of their corresponding reference values. All of the primary degradates presented indicate a 90th percentile concentration that is less than 5% of their respective human health drinking water reference value. The data presented in Figure 18 indicate that detection of certain pesticides or their degradates can occur frequently in sensitive groundwater, the concentrations rarely approach drinking water reference values.

Neonicotinoid insecticides were first analyzed by the MDA in groundwater samples in 2010. Currently, MDA analyzes water samples for six neonicotinoid parent pesticides and two degradates including: acetamiprid, imidacloprid, thiamethoxam, clothianidin (analysis began in mid-2011), dinotefuran (analysis began in 2012), thiacloprid (analysis began in 2014), and the degradates imidacloprid-urea and imidacloprid-olefin (analysis began in 2017). Clothianidin, imidacloprid, and thiamethoxam have been detected in groundwater in agricultural areas. Dinotefuran and imidacloprid are the only neonicotinoid insecticides that have been detected in urban groundwater samples. All detections of neonicotinoids in groundwater were below applicable reference values in 2023. Acetamiprid, the imidacloprid degradates, dinotefuran, and thiacloprid have not been detected in groundwater by MDA.

Additional information about detections, concentrations and time-trend analysis for pesticides can be found in the MDA's annual monitoring reports under "Reports and Resources" at: https://www.mda.state.mn.us/monitoring.

Figure 17. Number of common detection pesticides detected per sample site in 2023.

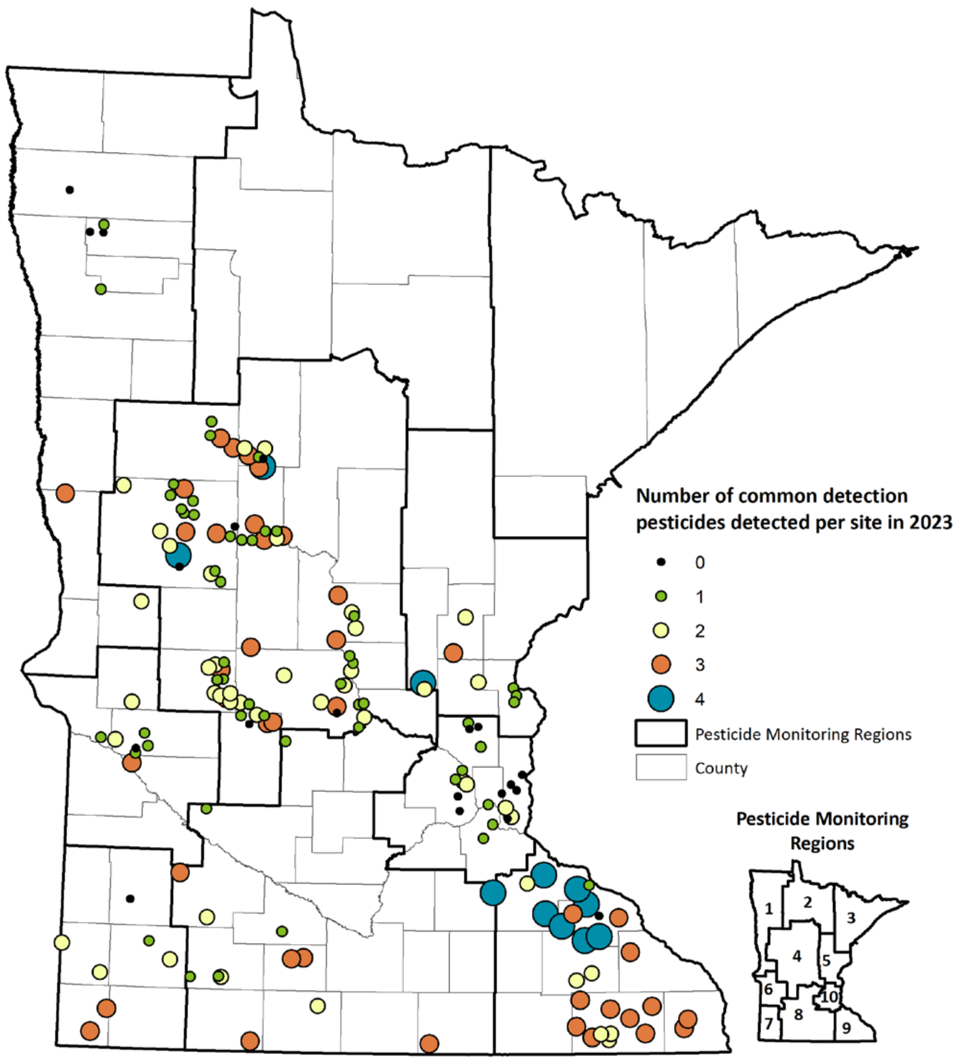
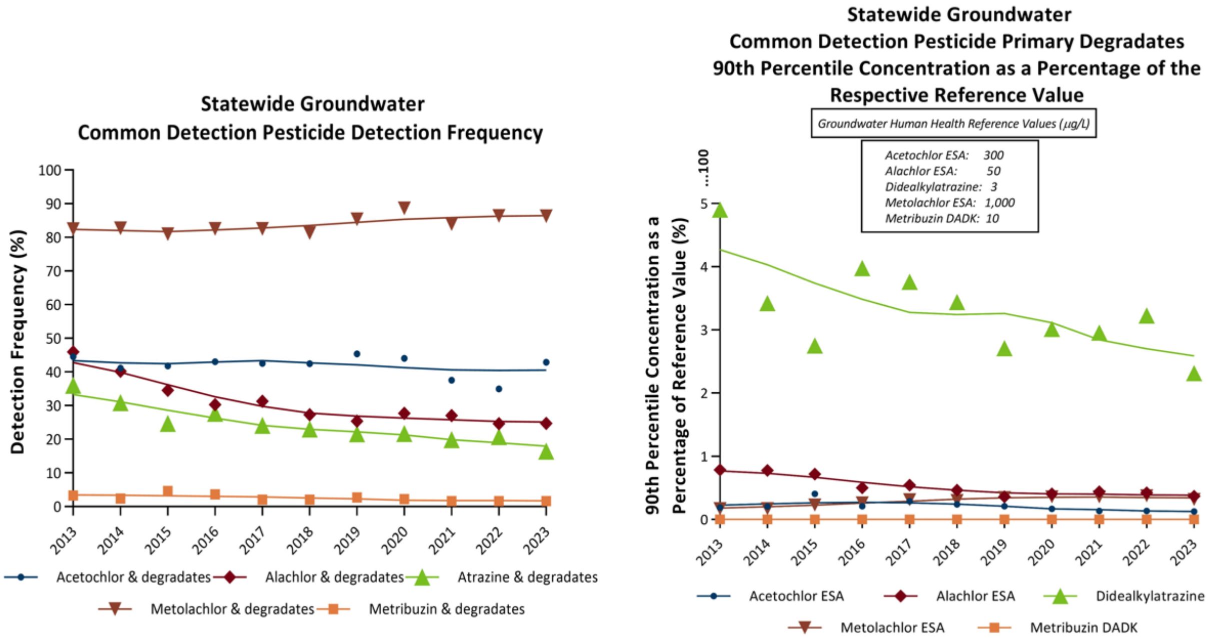


Figure 18. Statewide groundwater common detection pesticides.



Appendix A.

Table A-1. Pharmaceutical and personal care products analyzed in ambient groundwater samples, 2018-2023

Chemical name		
1,7-Dimethylxanthine	611-59-6	Stimulant
Acetaminophen	103-90-2	Analgesic
Albuterol	18559-94-9	Bronchodilator
Alprazolam	28981-97-7	Anti-anxiety
Amitriptyline	50-48-6	Anti-depressant
Amlodipine	88150-42-9	Anti-hypertension
Amphetamine	300-62-9	Stimulant
Amsacrine	51264-14-3	Anti-neoplastic agent
Atenolol	29122-68-7	Anti-hypertension
Atorvastatin	134523-00-5	Lipid regulator
Azathioprine	446-86-6	Immunosuppressant
Azithromycin	83905-01-5	Antibiotic
Benzoylecgonine hydrate	519-09-5	Stimulant
Benztropine	86-13-5	Anti-tremor
Betamethasone	378-44-9	Steroid
Busulfan	55-98-1	Chemotherapy
Caffeine	58-08-2	Stimulant
Carbadox	1791337	Antibiotic
Carbamazepine	298-46-4	Anti-convulsant
Cefotaxime	63527-52-6	Antibiotic

Chemical name		
Cimetidine	51481-61-9	Antacid
Ciprofloxacin	85721-33-1	Antibiotic
Citalopram	59729-33-8	Anti-depressant
Clarithromycin	81103-11-9	Antibiotic
Clinafloxacin	105956-97-6	Antibiotic
Clonidine	4205-90-7	Anti-hypertension
Clotrimazole	23593-75-1	Anti-fungal
Cloxacillin	61-72-3	Antibiotic
Cocaine	50-36-2	Stimulant
Codeine	76-57-3	Analgesic
Colchicine	64-86-8	Anti-gout agent
Cotinine	486-56-6	Nicotine metabolite
Cyclophosphamide	50-18-0	Chemotherapy
Daunomycin	20830-81-3	Anti-neoplastic agent
DEET	134-62-3	Insect repellent
Dehydronifedipine	67035-22-7	Anti-hypertension
Desmethyldiltiazem	84903-78-6	Anti-hypertension
Diatrizoic acid	117-96-4	Contrast agent
Diazepam	439-14-5	Anti-anxiety
Digoxigenin	1672-46-4	Steroid
Digoxin	20830-75-5	Anti-arrhythmic
Diltiazem	42399-41-7	Anti-hypertension
Diphenhydramine	58-73-1	Antihistamine
Doxorubicin	23214-92-8	Chemotherapy
Drospirenone	67392-87-4	Hormonal medication
Enalapril	75847-73-3	Anti-hypertension
Enrofloxacin	93106-60-6	Antibiotic
Erythromycin-H20	114078-H2O	Antibiotic
Etoposide	33419-42-0	Chemotherapy
Flumequine	42835-25-6	Antibiotic
Fluocinonide	356-12-7	Steroid
Fluoxetine	54910-89-3	Anti-depressant
Fluticasone propionate	80474-14-2	Steroid
Furosemide	54-31-9	Diuretic
Gemfibrozil	25812-30-0	Lipid regulator
Glipizide	29094-61-9	Blood sugar control
Glyburide	10238-21-8	Blood sugar control
Hydrochlorothiazide	58-93-5	Anti-hypertension
Hydrocodone	125-29-1	Analgesic
Hydrocortisone	50-23-7	Steroid

Chemical name		
Hydroxy-amitriptyline, 10-	1159-82-6	Anti-depressant
Hydroxy-ibuprofen, 2-	51146-55-5	Anti-inflammatory
Ibuprofen	15687-27-1	Anti-inflammatory
Iopamidol	60166-93-0	Contrast agent
Lincomycin	154-21-2	Antibiotic
Lomefloxacin	98079-51-7	Antibiotic
Medroxyprogesterone acetate	71-58-9	Hormonal medication
Melphalan	148-82-3	Chemotherapy
Meprobamate	57-53-4	Anti-anxiety
Metformin	657-24-9	Anti-diabetic
Methylprednisolone	83-43-2	Steroid
Metoprolol	51384-51-1	Anti-hypertension
Metronidazole	443-48-1	Antibiotic
Miconazole	22916-47-8	Anti-fungal
Moxifloxacin	151096-09-2	Antibiotic
Naproxen	22204-53-1	Anti-inflammatory
Norfloxacin	70458-96-7	Antibiotic
Norfluoxetine	83891-03-6	Anti-depressant
Norgestimate	35189-28-7	Hormonal medication
Norverapamil	67018-85-3	Anti-hypertension
Ofloxacin	82419-36-1	Antibiotic
Ormetoprim	6981-18-6	Antibiotic
Oxacillin	66-79-5	Antibiotic
Oxazepam	604-75-1	Anti-anxiety
Oxolinic acid	14698-29-4	Antibiotic
Oxycodone	76-42-6	Analgesic
Paroxetine	61869-08-7	Anti-depressant
Penicillin G	61-33-6	Antibiotic
Penicillin V	87-08-1	Antibiotic
Prednisolone	50-24-8	Steroid
Prednisone	53-03-2	Steroid
Promethazine	60-87-7	Antihistamine
Propoxyphene	469-62-5	Analgesic
Propranolol	525-66-6	Anti-hypertension
Ranitidine	66357-35-5	Antacid
Rosuvastatin	287714-41-4	Lipid regulator
Roxithromycin	80214-83-1	Antibiotic
Sarafloxacin	98105-99-8	Antibiotic
Sertraline	79617-96-2	Anti-depressant
Simvastatin	79902-63-9	Lipid regulator

Chemical name		
Sulfachloropyridazine	80-32-0	Antibiotic
Sulfadiazine	68-35-9	Antibiotic
Sulfadimethoxine	122-11-2	Antibiotic
Sulfamerazine	127-79-7	Antibiotic
Sulfamethazine	57-68-1	Antibiotic
Sulfamethizole	144-82-1	Antibiotic
Sulfamethoxazole	723-46-6	Antibiotic
Sulfanilamide	63-74-1	Antibiotic
Sulfathiazole	72-14-0	Antibiotic
Tamoxifen	10540-29-1	Anti-estrogen
Teniposide	29767-20-2	Chemotherapy
Theophylline	58-55-9	Bronchodilator
Thiabendazole	148-79-8	Anti-fungal
Trenbolone	10161-33-8	Steroid
Trenbolone acetate	10161-34-9	Steroid
Triamterene	396-01-0	Diuretic
Triclocarban	101-20-2	Anti-bacterial
Trimethoprim	738-70-5	Antibiotic
Tylosin	1401-69-0	Antibiotic
Valsartan	137862-53-4	Anti-hypertension
Venlafaxine	93413-69-5	Anti-depressant
Verapamil	52-53-9	Anti-hypertension
Virginiamycin M1	21411-53-0	Antibiotic
Warfarin	81-81-2	Anti-coagulant
Zidovudine	30516-87-1	Anti-viral

Table A-2 Alkylphenol surfactants analyzed in ambient groundwater samples, 2018-2023

Chemical	CAS Registry number	
p-Octylphenol	1806-2-4	
Branched p-nonylphenols	84852-15-3	
Nonylphenol monoethoxylate	NA	
Nonylphenol diethoxylate	NA	

Table A-3 Bisphenol A analogs analyzed in ambient groundwater samples, 2018-2023

Chemical	CAS Registry number	Analytical method	Years analyzed
Bisphenol A	80-05-7	MLA-082/MLA-113	2018-2023
Bisphenol AF	1478-61-1	MLA-113	2019-2023
Bisphenol B	77-40-7	MLA-113	2019-2023
Bisphenol E	2081-08-5	MLA-113	2019-2023
Bisphenol F	620-92-8	MLA-113	2019-2023
Bisphenol S	80-09-1	MLA-113	2019-2023

Table A-4 Detection frequency and summary statistics for contaminants of emerging concern in the ambient groundwater, 2018-2023.

Chemical name	CAS registry number	Detected concentration, in ng/L		Number of samples		Detection frequency
		Minimum	Maximum	Detected	Total	
Branched p-nonylphenols	84852-15-3	0.913	260	45	159	28.3%
Metformin	657-24-9	0.309	18.8	39	158	24.7%
Cotinine	486-56-6	0.315	18.3	31	158	19.6%
Sulfamethoxazole	723-46-6	0.691	56.6	27	154	17.5%
Bisphenol A	80-05-7	1.98	246	26	158	16.5%
Caffeine	58-08-2	6.57	34.7	21	154	13.6%
DEET	134-62-3	1.56	417	20	158	12.7%
Ciprofloxacin	85721-33-1	1.72	47.8	18	150	12%
Theophylline	58-55-9	6.36	27.1	18	158	11.4%
Benzoylecgonine hydrate	519-09-5	0.169	29.3	16	158	10.1%
Hydroxy-ibuprofen, 2-	51146-55-5	6.43	209	14	158	8.9%
Sulfanilamide	63-74-1	8.02	106	12	140	8.6%
Bisphenol S	80-09-1	1.28	55.4	10	119	8.4%
Diatrizoic acid	117-96-4	12.6	632	13	158	8.2%
Carbamazepine	298-46-4	0.725	79.2	12	154	7.8%
Fluoxetine	54910-89-3	0.243	2.34	12	154	7.8%
Ibuprofen	15687-27-1	4.69	46.4	11	158	7.0%
Amphetamine	300-62-9	0.451	1.74	10	158	6.3%
Cocaine	50-36-2	0.164	1.79	9	158	5.7%
Nonylphenol diethoxylate	NP2EO	2.5	107	8	159	5.0%
Virginiamycin M1	21411-53-0	0.666	3.52	7	154	4.5%
Ofloxacin	82419-36-1	0.688	3.41	6	147	4.1%

Chemical name	CAS registry number	Detected concentration, in ng/L		Number of samples		Detection frequency
		Minimum	Maximum	Detected	Total	
Diphenhydramine	58-73-1	0.647	1.1	6	154	3.9%
Clotrimazole	23593-75-1	0.441	1.01	6	158	3.8%
Nonylphenol monoethoxylate	NP1EO	1.67	15	5	159	3.1%
p-Octylphenol	1806-26-4	0.456	5.88	5	159	3.1%
Erythromycin-H20	114078-H2O	2.35	3.08	4	154	2.6%
Penicillin G	61-33-6	3.16	7.28	4	154	2.6%
Benztropine	86-13-5	0.546	1.11	4	157	2.5%
Hydrochlorothiazide	58-93-5	9.25	22.8	4	158	2.5%
Bisphenol E	2081-08-5	6.19	8.5	3	119	2.5%
Acetaminophen	103-90-2	4.16	31.7	3	154	1.9%
Sulfadiazine	68-35-9	0.717	1.34	3	154	1.9%
Thiabendazole	148-79-8	0.745	15.9	3	154	1.9%
Citalopram	59729-33-8	0.504	1.06	3	156	1.9%
Iopamidol	60166-93-0	140	681	3	158	1.9%
Norfluoxetine	83891-03-6	0.7	0.93	3	158	1.9%
Triclocarban	101-20-2	0.464	1.69	3	158	1.9%
Venlafaxine	93413-69-5	0.531	2.41	3	158	1.9%
Zidovudine	30516-87-1	42.2	80.5	3	158	1.9%
Bisphenol AF	1478-61-1	3.47	78.8	2	119	1.7%
Bisphenol F	620-92-8	13.8	28.7	2	119	1.7%
Enrofloxacin	93106-60-6	0.854	8.94	2	148	1.4%
Norfloxacin	70458-96-7	2.18	3.73	2	150	1.3%
1,7-Dimethylxanthine	611-59-6	10	10.6	2	154	1.3%
Oxolinic acid	14698-29-4	1.05	3.2	2	154	1.3%
Sulfadimethoxine	122-11-2	0.397	0.759	2	154	1.3%
Gemfibrozil	25812-30-0	1.18	1.82	2	158	1.3%
Meprobamate	57-53-4	28.5	29.3	2	158	1.3%
Naproxen	22204-53-1	2.43	5.34	2	158	1.3%
Clinafloxacin	105956-97-6	6.05	6.05	1	145	0.7%
Lomefloxacin	98079-51-7	3.96	3.96	1	145	0.7%
Sarafloxacin	98105-99-8	6.14	6.14	1	151	0.7%
Azithromycin	83905-01-5	1.86	1.86	1	153	0.7%
Moxifloxacin	151096-09-2	5.84	5.84	1	153	0.7%
Sulfamethazine	57-68-1	1.19	1.19	1	154	0.6%
Trimethoprim	738-70-5	0.33	0.33	1	154	0.6%
Amsacrine	51264-14-3	0.069	0.069	1	157	0.6%
Melphalan	148-82-3	29.6	29.6	1	157	0.6%
Cimetidine	51481-61-9	2.06	2.06	1	158	0.6%

Chemical name	CAS registry number	Detected concentration, in ng/L		Number of samples		Detection frequency
		Minimum	Maximum	Detected	Total	
Colchicine	64-86-8	6.59	6.59	1	158	0.6%
Diazepam	439-14-5	0.415	0.415	1	158	0.6%
Hydroxy-amitriptyline, 10-	1159-82-6	0.164	0.164	1	158	0.6%
Norverapamil	67018-85-3	0.476	0.476	1	158	0.6%
Sertraline	79617-96-2	0.409	0.409	1	158	0.6%
Triamterene	396-01-0	0.346	0.346	1	158	0.6%
Triclosan	3380-34-5	7.46	7.46	1	158	0.6%
Verapamil	52-53-9	0.311	0.311	1	158	0.6%

Table A-5 Organophosphate flame retardants analyzed in ambient groundwater samples, 2021

Chemical	CAS Registry Number
Triphenyl phosphate	115-86-6
Tris(2-chloroethyl) phosphate	115-96-8
2-Ethylhexyl diphenyl phosphate	1241-94-7
Tris(2,3-dibromopropyl) phosphate	126-72-7
Tributyl phosphate	126-73-8
Tricresyl phosphate	1330-78-5
Tris(1-chloro-2-propyl) phosphate	13674-84-5
Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8
2,2-Bis(chloromethyl)-1,3-propanediyl bis[bis(2-chloroethyl) phosphate]	38051-10-4
Tripropyl phosphate	513-08-6
Triethyl phosphate	78-40-0
Tris(2-ethylhexyl) phosphate	78-42-2
Tris(2-butoxyethyl) phosphate	78-51-3

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