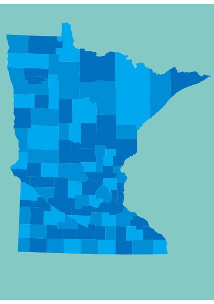
Groundwater quality

July 2019

The Condition of Minnesota's Groundwater Quality, 2013-2017

MINNESOTA POLLUTION
CONTROL AGENCY



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Executive summary

This report describes the condition and trends in the quality Minnesota's ambient groundwater. State agency data collected from 2013-2017 were used to describe the condition of the state's groundwater resources, focusing on the sand and gravel aquifers which occur throughout the state and the bedrock aquifers in southeastern Minnesota. Trends were evaluated using data from 2005-2017.

This assessment of groundwater quality conditions includes familiar pollutants that adversely affect the drinkability of water, such as nitrate, chloride, arsenic, volatile organic chemicals (VOCs), and pesticides. It also includes more recently recognized pollutants including contaminants of emerging concern (CECs) such as medications, insect repellents, and flame retardants and fluorinated compounds known as per- and polyfluorinated alkyl substances (PFAS). Land use strongly affects the occurrence and distribution of most of these pollutants since some of these substances are predominantly used in urban areas while others are used more in agricultural settings. A few of the pollutants discussed in this report are naturally occurring in the groundwater, namely trace elements like arsenic and manganese, and only are detected at high levels when wells are installed in particular parts of the state or at a particular depth in an aquifer.

Chloride, VOCs, and CECs primarily affected the groundwater quality in urban areas. High chloride concentrations were an issue near the water table in the Twin Cities Metropolitan Area (TCMA), where most of the wells that had concentrations over the state class 1 domestic consumption use standard of 250 mg/L (Minn. Rules ch. 7050, 7060) were located. In addition, chloride concentrations in the buried sand and gravel and Prairie du Chien-Jordan aquifers generally were greater in the counties within or near the TCMA compared to those outstate. The few detections of VOCs in the ambient groundwater also occurred in urban areas. New wells installed for the Minnesota Pollution Control Agency's (MPCA) monitoring network showed that commercial/industrial land use affected chloride concentrations in the shallow groundwater the most; the median concentrations in these areas were over 30 mg/L greater than those in residential areas. The high chloride concentrations near the water table also appeared to be migrating downward into the aquifers used for drinking water supplies. The trend analysis conducted for this investigation showed the majority of wells with increasing chloride concentrations were installed in bedrock aquifers in the TCMA and southeastern Minnesota; some of these wells were as deep as 340 feet. Chloroform, the most-frequently detected VOC, appeared to occur where water supplies undergo chlorine disinfection. The detections of VOCs associated with solvents, such as trichloroethylene, typically occurred near the water table in commercial/industrial areas where they may be used to degrease metals and in other applications. The most commonly detected CECs were the antibiotic sulfamethoxazole, the flame retardant tris (1,3-dichloro-2-propyl) phosphate, the x-ray contrast agent iopamadol, and the non-anionic surfactant mixture branch p-nonylphenols. These chemicals all are known to be widely used, resistant to degradation, and persist in the environment.

Perfluorobutanoic acid (PFBA) was the most commonly detected PFAS in the ambient groundwater. Most of the PFAS monitoring in the ambient groundwater from 2013-2017, however, was for the perfluoroalkyl carboxylates and sulfonates, many of which are no longer in use, and the replacement products for these chemicals were not monitored. The data collected also indicated that PFAS detections in the groundwater were related to urban land use. PFBA was detected in almost 70% of the sampled ambient network wells in 2013. The highest measured concentration was 1,680 ng/L, which was well below the 7,000 ng/L human health limit set by the Minnesota Department of Health (MDH) for drinking water. Perfluorooctanoic sulfate (PFOS) was detected in about 12% of the sampled wells in 2013, and concentrations in seven wells had concentrations exceeding the 15 ng/L health based value set by the MDH in 2019. The limited follow-up sampling of 12 wells in 2017 showed that PFAS detections and concentrations did not remain the same in many of the resampled wells. This result was not unexpected since most of the wells contained very young groundwater, and there have been changes in the types of PFAS used in products. In the wells sampled outside of Washington County, which has known industrial contamination, perfluorohexanoic sulfate, perfluorooctanoic acid, and PFOS concentrations decreased by more than one-half compared to what was measured in 2013.

Nitrate primarily was an issue in the agricultural parts of the state. In these areas, 49% of the tested monitoring wells installed near the water table exceeded the state class 1 domestic consumption use standard of 10 mg/L. The Minnesota Department of Agriculture's (MDA's) Township Testing Program identified where domestic water supplies in agricultural areas were most impacted by high nitrate concentrations, which was defined as at least 10% of the tested wells having concentrations of 10 mg/L or greater. The majority of these townships were located in southeastern Minnesota, often in places where the shallow aquifer was naturally vulnerable to contamination from the land surface. Monitoring data collected by the MDA and MPCA shows that nitrate concentrations near the water table in urban areas generally were much lower than those in agricultural areas, with median concentrations ranging from 1.1 to 1.8 mg/L in urban areas and 10 mg/L in agricultural areas.

Herbicides were the most common type of pesticide detected as part of ambient monitoring by the MDA in 2017. No pesticide concentrations exceeded any applicable human health guidance set by the MDH. Degradation products of acetochlor, alachlor, atrazine, and metolachlor were among the most-frequently detected chemicals in the shallow groundwater. All of these pesticides are in "common detection" status by the MDA, which triggers activities such as the development of best management practices. Three neonicotinoid insecticides, clothiadin, imidacloprid, and thiamethoxam, were among the most-commonly detected pesticides in the shallow groundwater. These chemicals were detected in eight to 16% of the groundwater samples.

Introduction

Sufficient amounts of clean groundwater are 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.

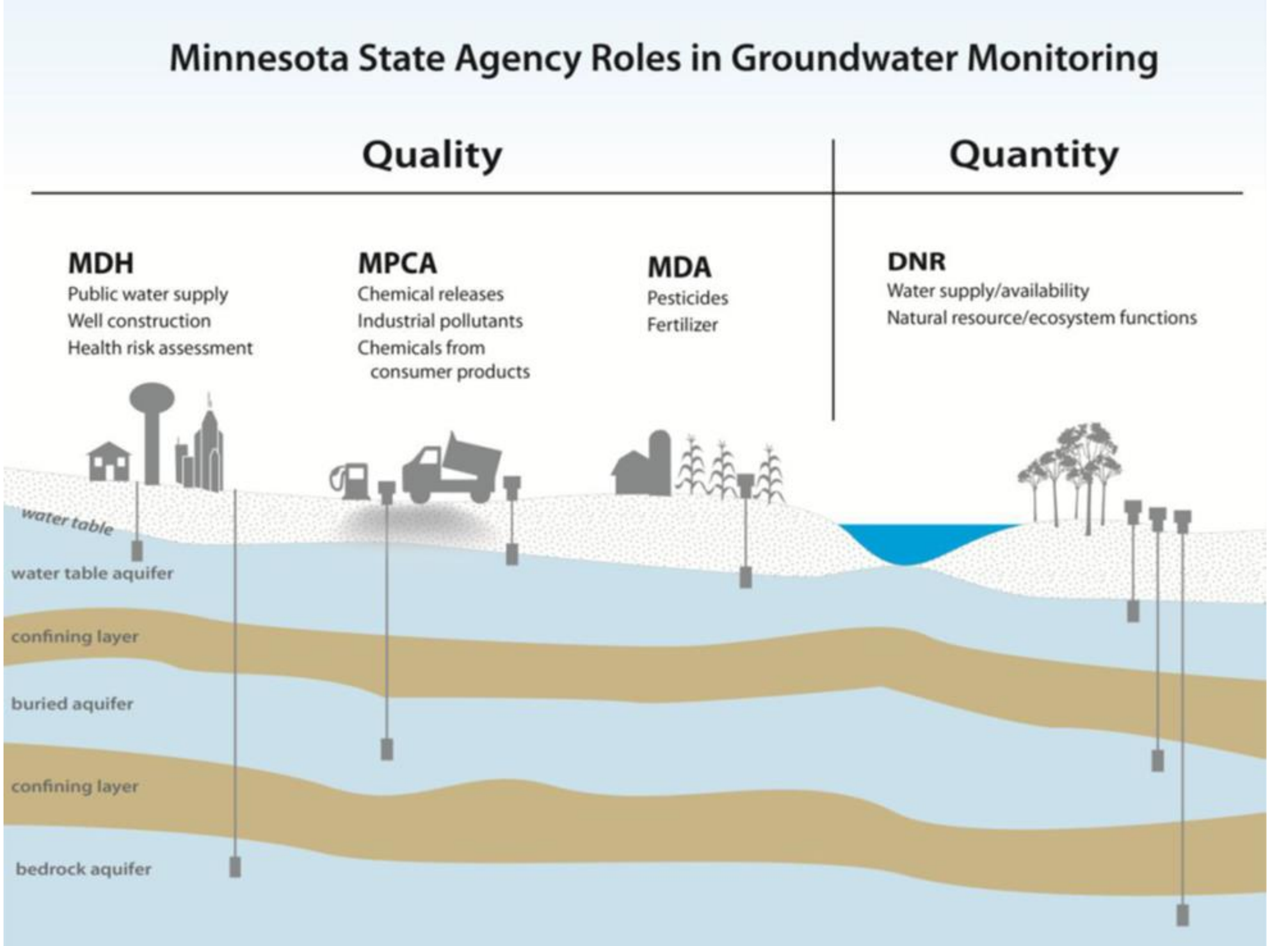
To meet Minnesotans' needs, groundwater must be clean. The Minnesota Pollution Control Agency (MPCA) considers all groundwater as potential drinking water sources, and the agency's policy is to maintain it in its natural condition as nearly as possible (Minn. R. ch. 7060). Polluted groundwater often 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 MDA conduct statewide ambient groundwater quality monitoring for non-agricultural chemicals and agricultural chemicals, respectively. These two 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. The 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.

In the last five years, much more was learned about the quality of Minnesota's groundwater due to enhanced monitoring that was made possible by the Clean Water Legacy Amendment. This funding allowed the MPCA to install shallow monitoring wells in key areas where existing wells were not available, such as residential areas that use subsurface sewage treatment systems (SSTS) for wastewater disposal, and commercial/industrial areas. It also allowed the MPCA to expand the list of chemicals it routinely analyzed in water samples to include contaminants of emerging concern (CECs), such as prescription and non-prescription medicines, and poly- and perfluoroalkyl substances (PFAS). By committing to annual monitoring, particularly in bedrock aquifers, MPCA increased the number of monitored sites with data sufficient to calculate groundwater quality changes over time. This same source of funding also allowed the MDA to better understand the groundwater quality in the aquifers that underlie the agricultural lands of the state. During this same timeframe, the MDA expanded its groundwater monitoring to include domestic wells in selected townships across the state that are naturally vulnerable to contamination due to regional geology.

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



Purpose and Scope

This report describes the recent quality of Minnesota's ambient groundwater 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 2013-2017 were used to determine the condition of the state's groundwater, and information from the last 12 years (2005-2017) 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 Ferrey 2013), 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.

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, and Township Testing Program; the Southeast Volunteer Nitrate Monitoring Network; and the DNR's County Geologic Atlas Program.

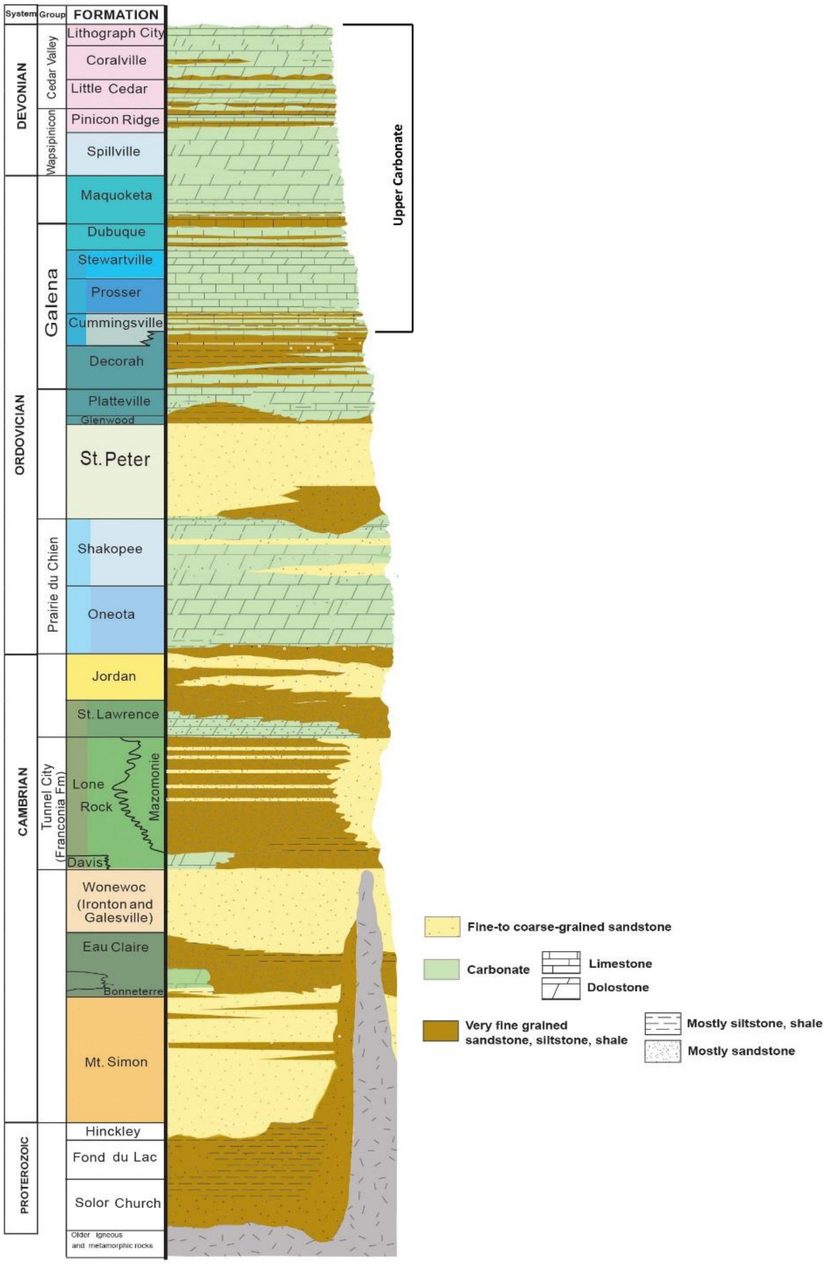
This assessment includes traditional pollutants known to adversely affect the potability of groundwater, such as nitrate, chloride, trace elements like arsenic, and volatile organic compounds (VOCs). In addition, it also includes some more recently recognized pollutants, including CECs and PFAS.

Minnesota's Groundwater Resources

The state's oldest aquifers are composed of crystalline bedrock and are important sources of groundwater in northern and southwestern Minnesota. These aquifers generally were formed from sands and silts that weathered and eroded from ancient volcanic rocks. Over time, these weathered materials were cemented together and transformed into crystalline rocks by the heat from now long-extinct volcanoes. The rocks that form these aquifers are the oldest in the state, at least 600 million to several billion years old. Crystalline bedrock aquifers underlie the entire state, but in most areas, these are deeply buried by other productive aquifers, so they usually are not an important source of water. Important crystalline bedrock aquifers in northeastern Minnesota include the North Shore Volcanic, Proterozoic metasedimentary, and Biwabik iron formation. The Sioux quartzite aquifer is important for some water supplies in Southwestern Minnesota.

Bedrock aquifers composed of sandstone and carbonate rock are important sources of water supply in southeastern Minnesota. These aquifers were formed when seas covered Minnesota about 500 million years ago. These aquifers include (in order from youngest to oldest) the Upper Carbonate, Red River-Winnipeg, St. Peter, Prairie du Chien, Jordan, Tunnel City/Wonewoc, and the Mount Simon-Hinckley. All of these aquifers, except the Red River-Winnipeg, form a vertical sequence of aquifers in southeastern Minnesota, including the Twin Cities Metropolitan Area (TCMA) (Figure 2). The Red River-Winnipeg aquifer only is present in northwestern Minnesota and typically is not used for water supply because it contains naturally salty water.

Figure 2. Stratigraphic column of the bedrock aquifers in the southeastern Minnesota (Figure modified from Runkel et al. 2013)



The Upper Carbonate is the uppermost and youngest in this sequence of bedrock aquifers. The U.S. Geological Survey (USGS) defines the Upper Carbonate Aquifer system as all of the aquifer groups from the Cedar Valley to the Galena (Olcott 1992). This aquifer system is located in extreme southeastern Minnesota and extends only about 80 miles north into Minnesota from the Iowa border. The Upper Carbonate, as its name suggests, primarily is composed of limestone and dolomite, and most of the water from this aquifer is obtained from solution channels, joints, and fissures.

The St. Peter aquifer underlies the Upper Carbonate and extends as far north as the 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 St. Peter typically is not used for public water supplies in the TCMA because it does not occur continuously in this area and the underlying bedrock aquifers are much more productive.

The Prairie du Chien-Jordan is the third in this sequence of bedrock aquifers and is a major source of water supplies. This aquifer is present throughout southeastern Minnesota and extends to the TCMA. Some wells in this aquifer yield as much as 2,700 gallons per minutes (Adolphson, Ruhl, and Wolf 1981). The Prairie du Chien-Jordan aquifer consists of two different units. The first is the Prairie du Chien Group, which is a sandy dolomite. The second is the Jordan sandstone. Since the Prairie du Chien and Jordan aquifers many times have a hydraulic connection, these often are considered together as a single aquifer in many groundwater investigations, usually called the Prairie du Chien-Jordan. However, the lower part of the Prairie du Chien Group can serve locally as a confining unit for the Jordan sandstone.

The Tunnel City/Wonewoc is the fourth in the series of bedrock aquifers in southeastern Minnesota. Like the others, this aquifer is present throughout southeastern Minnesota and extends slightly beyond the TCMA. This aquifer consists of very fine to coarse sandstone that is interbedded with shale, dolomitic sandstone, and dolomitic siltstone. The upper and lower parts of the Tunnel City/Wonewoc aquifer are separated by a confining unit. Flow in the upper part of the aquifer primarily is through bedding plane features, and flow in the lower part of the aquifer is primarily intergranular. Despite having these two parts, the aquifer traditionally is considered as one unit in groundwater investigations.

The Mount Simon-Hinckley is the fifth and lowermost in this aquifer series. This aquifer has the widest extent of all of the state’s limestone and sandstone aquifers and extends almost as far north as the City of Duluth. This aquifer overlies the crystalline basement rocks and consists of two sandstone formations, the Mount Simon and Hinckley. Both of these sandstones have similar hydraulic characteristics (Schoenberg 1984) and usually are grouped together in groundwater investigations. The Mount Simon-Hinckley is overlain by other Paleozoic-age bedrock aquifers south of the TCMA. However, north of the TCMA, these other aquifers are not present and the Mount Simon-Hinckley is the uppermost bedrock aquifer.

In southeastern Minnesota, the rocks that form the Upper Carbonate and Prairie du Chien-Jordan aquifers form flat plateaus and mesas that are important recharge points. The Upper Carbonate Plateau is the highest of the two and is separated from the Prairie du Chien Plateau, which lies to the east, by escarpments and valleys. These two plateaus are important points for recharge water to enter these aquifers because they are 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.

In most parts of the state, unconsolidated clay, silt, sand, or gravel deposits overlie all of the bedrock aquifers. These sediments have not yet been cemented together to form rock, and they 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. These sediments form aquifers (called sand and gravel aquifers in this report) in places where the glacial meltwater left sandy and/or gravelly deposits.

The sand and gravel aquifers are the youngest in the state and important sources of groundwater throughout Minnesota. These aquifers are concentrated in the central part of the state, where they may either be near the land surface or buried within clays.

The composition of the state’s 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 distinctive bedrock (Meyer and Knaeble 1996). The glaciers that traversed into Minnesota from source areas northwest of the state 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 up to 118 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).

A large part of the MPCA and MDA's monitoring is not on the ambient environment but instead focuses on sites where pollutants are known to be present from chemical spills and inadvertent releases. Over the years, the MPCA has monitored over 21,000 polluted sites as part of its cleanup activities. These include old landfills, tank releases, gasoline spills, and Superfund sites. The MDA monitors all fertilizer and pesticide spills in the state. Since the contamination associated with most of these spill sites is very localized, the assessments of groundwater quality in this report will be based on the information collected as part of the MPCA and MDA's ambient groundwater monitoring since this best characterizes general groundwater quality conditions across the state.

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 requirements under the Minnesota Groundwater Protection Act 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, to quickly see what non-agricultural chemicals were present and determine whether groundwater conditions improved, got worse, or stayed the same, all of the wells sampled by the MPCA 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.

Since the publication of the last Groundwater Condition Report in 2013 (Kroening and Ferrey 2013), the MPCA upgraded its Ambient Groundwater Monitoring Network, adding approximately 150 new wells. These new wells filled gaps that existed in the network. This included replacing wells sampled in commercial areas that were installed to inform the agency’s groundwater remediation work with others that better represented ambient conditions and improving the network’s coverage in residential areas that rely on SSTS for wastewater disposal and treatment. This network was initially designed using existing wells to minimize the start-up costs associated with groundwater monitoring, but this approach resulted in some monitoring gaps. For example, most of the early warning system wells that represented commercial/industrial settings did not really represent ambient conditions because they were originally installed to inform the agency’s pollution clean-up efforts, mainly petroleum spills. The reliance on these wells for monitoring, even the ones upgradient of the known chemical release, resulted in a greater number of volatile organic compound (VOC) detections as well as a bias towards the VOCs associated with gasoline (Kroening and Ferrey 2013). There also were few shallow wells available in residential areas that relied on SSTS for wastewater treatment and disposal. In 2011, only 14 wells in this land use setting were available for sampling. To address these and other monitoring gaps, the MPCA installed about 150 wells across the state specifically for its network, primarily from 2010-2015. This greatly improved the representation of urban land use in the MPCA’s “early warning system” by adding 34 additional monitoring wells in commercial/industrial areas and 37 new wells in residential areas that use SSTS.

Age dating of select wells sampled by the MPCA’s network confirmed that the water in them was very young which indicates they are very vulnerable to contamination from the land surface. The age of the young part of the groundwater in 51 of the MPCA’s network wells was determined using the tritium-helium method (Cook and Herczeg 2000). Scientists often refer to the tritium-helium method as measuring the “young fraction of the groundwater” because in some situations, the water in the well is a mixture of young and old groundwaters, and this method only determines the age of the young component. The young fraction of the groundwater was less than five years old in 86% of the tested wells.

MDA’s Ambient Groundwater Monitoring Network

The MDA monitors aquifers that are likely impacted by agricultural chemicals. The MDA’s ambient monitoring network is similar to the MPCA’s in that it primarily targets shallow sand and gravel aquifers; except MDA monitors these that underlie the agricultural parts of the state. The network’s monitoring design 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 thirteen springs and twelve 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 twenty 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.

Water samples generally are collected at least annually from all network-monitoring sites. The sampling frequency varies among the sites. Some are sampled as frequently as four times each year. All water samples are analyzed at the MDA Laboratory in St. Paul for nitrate and a suite of 150 pesticides and degradates.

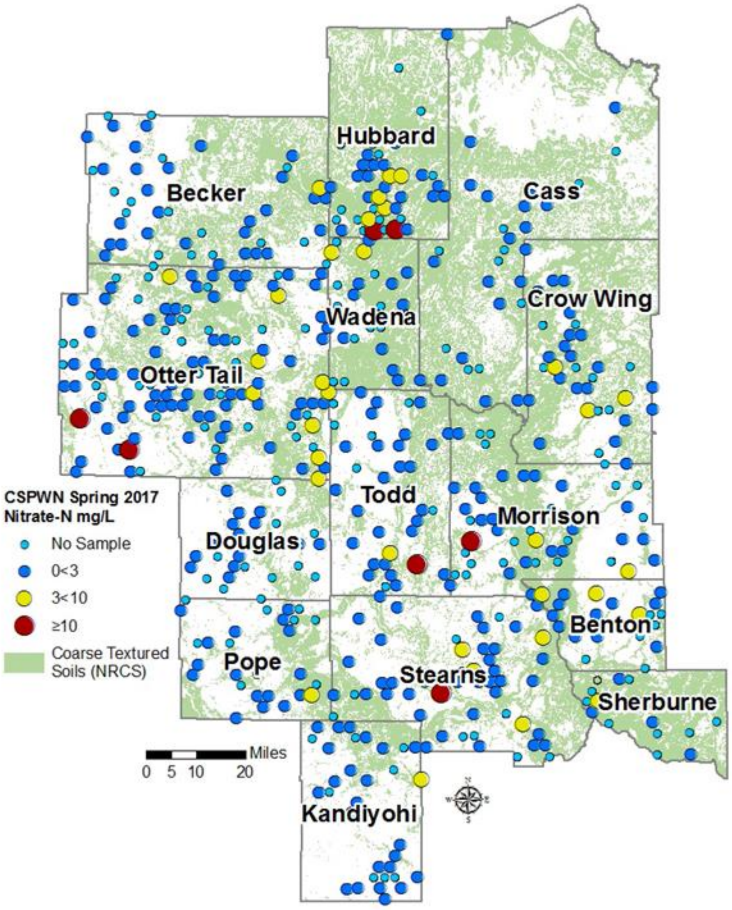
The MDA expanded its assessments of nitrate concentrations in private drinking water wells in vulnerable aquifers throughout the state. These activities included operating the Central Sands Private Well Monitoring Network (CSPWM), Southeast Volunteer Nitrate Monitoring Network (SEVMN), and the Township Testing Program. Goals for all of these activities were to determine whether nitrate concentrations in the groundwater varied with depth and if it affected the aquifers accessed by private domestic wells, which 4 million Minnesotans use (Minnesota Department of Agriculture 2015). The MDA worked closely with other agencies to develop each of these regional private well nitrate networks. Homeowner volunteers are the cornerstone of each of them. For all of the networks, the homeowners collected their own water sample and sent it by mail to be tested by a laboratory at no cost. 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.

The MDA continued to operate the CSPWN, which was started in 2011. For this network, about 500 citizen volunteers in 14 counties in Central Minnesota (Figure 3) were recruited to participate in annual sampling of their private domestic drinking water wells. In 2017, 367 private drinking water wells were sampled for nitrate.

The agency also began coordinating the SEVMN in 2014 (Figure 4). This private well network initially was started in 2008 as part of a project funded by the EPA 319 and the MPCA Clean Water Partnership Programs. In 2017, 341 homeowners from the network collected samples.

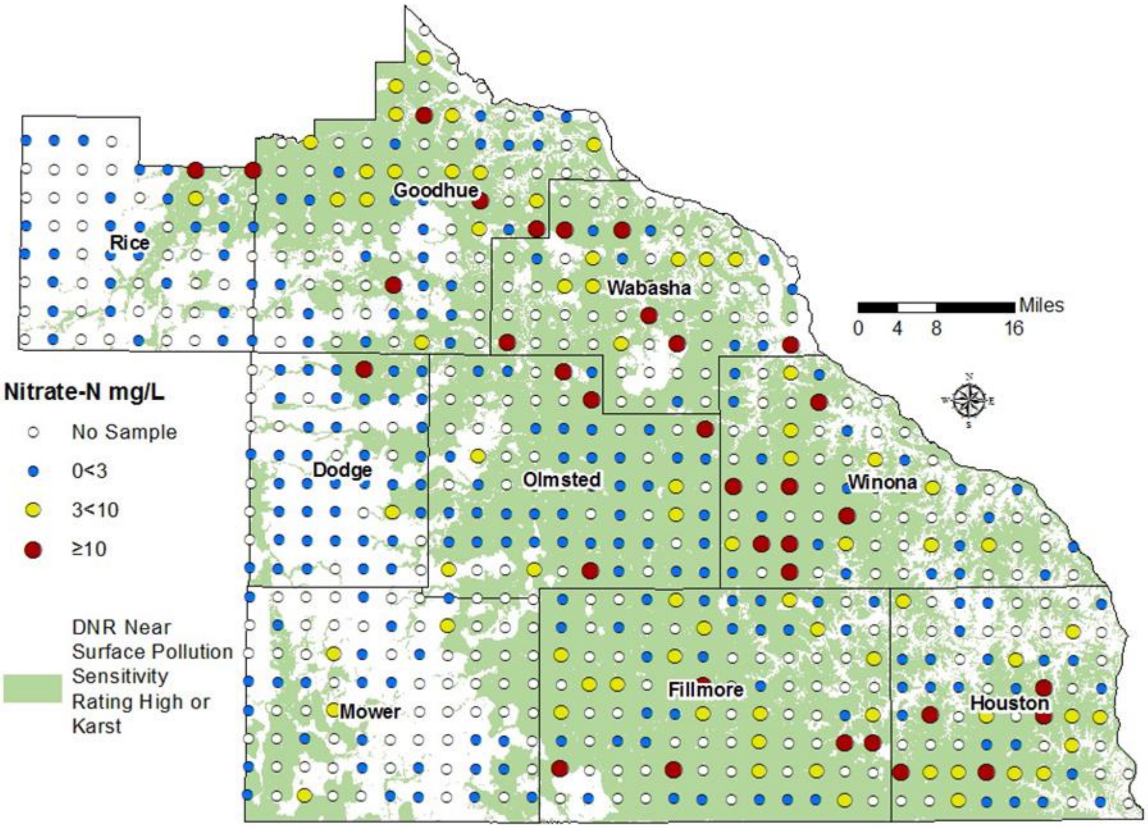
In 2013, the MDA started the Township Testing Program as required by its revised nitrogen fertilizer management plan (Minnesota Department of Agriculture 2015). This program, conducted in partnership with counties and soil and water conservation districts, will run through 2020 and is similar to the other private well networks in that it targets privately owned drinking water wells for sampling but focuses on a finer, township scale compared to the regional networks. The townships selected for sampling in this network 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. It is anticipated that nitrate testing will be offered to over 70,000 domestic wells as part of this effort. The initial water sampling in this program was performed by the property owner, who collected and mailed a water sample to a certified laboratory. If nitrate was detected in the sample, a trained professional collected a second follow-up sample and conducted a site assessment. As of March 2018, nitrate testing was conducted in 242 townships in 24 counties across the state. From 2013-2017, 25,652 wells were tested by this program.

Figure 3. Nitrate concentrations in wells tested as part of the MDA's Central Sands Private Well Monitoring Network in 2017 [Figure courtesy of the Minnesota Department of Agriculture].



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 seven-year effort 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. From 2014-2017, this project sampled about 4,100 private wells, and it is expected that about 3,800 more wells will be sampled by the time this project ends in 2020 (Minnesota Department of Agriculture 2018).

Figure 4. Nitrate concentrations in wells tested as part of the MDA's Southeast Volunteer Nitrate Monitoring Network in 2017 [Figure courtesy of the Minnesota Department of Agriculture].



Groundwater Quality

Both human-caused and natural sources of pollution contaminate the groundwater. Most human-caused pollution results from substances that are deliberately applied or accidently spilled on the land surface, such as fertilizers and pesticides distributed on agricultural fields or garden plots, deicing chemicals applied to pavement or petroleum chemicals that unintentionally leaked from their storage tank. Naturally occurring pollutants often are elements present in the sediments and rocks that form the state's aquifers such as arsenic or manganese. In some instances, the geochemical conditions of the aquifer dictate whether these natural contaminants will be released into the groundwater, like the water's pH or amount of oxygen dissolved in it.

Geology strongly affects how far and fast any pollution will spread in the groundwater, especially for very soluble contaminants such as nitrate and chloride. The physical properties of the soils, unconsolidated sediments, and bedrock determine the speed at which water and any associated pollution move. Coarse-grained sediments, such as sands and gravels, have a high hydraulic conductivity, and water and any associated pollution will very quickly move through them. Surficial aquifers with these types of sediments are classified as "highly sensitive" to groundwater contamination in Minnesota (Adams 2016). In contrast, it may take many decades to hundreds of years for water and any associated pollution to move through sediments with low permeability, such as clays. Several characteristics affect how quickly water and its associated contamination reaches the state's bedrock aquifers. The first of these is the thickness and types of unconsolidated materials covering the bedrock. Water will take a long time to travel through these materials, especially in the parts of the state where they are several hundred feet thick and contain fine-grained material. Secondly, the type of bedrock itself affects the speed at which water flows. Some rocks, such as poorly cemented sandstones, have a high vertical permeability and water easily moves through it. Others, like shale, are very impermeable and readily retard the movement of water and any associated contamination; however, the presence of fractures or sinkholes in these rocks allows movement of water and any associated contaminants.

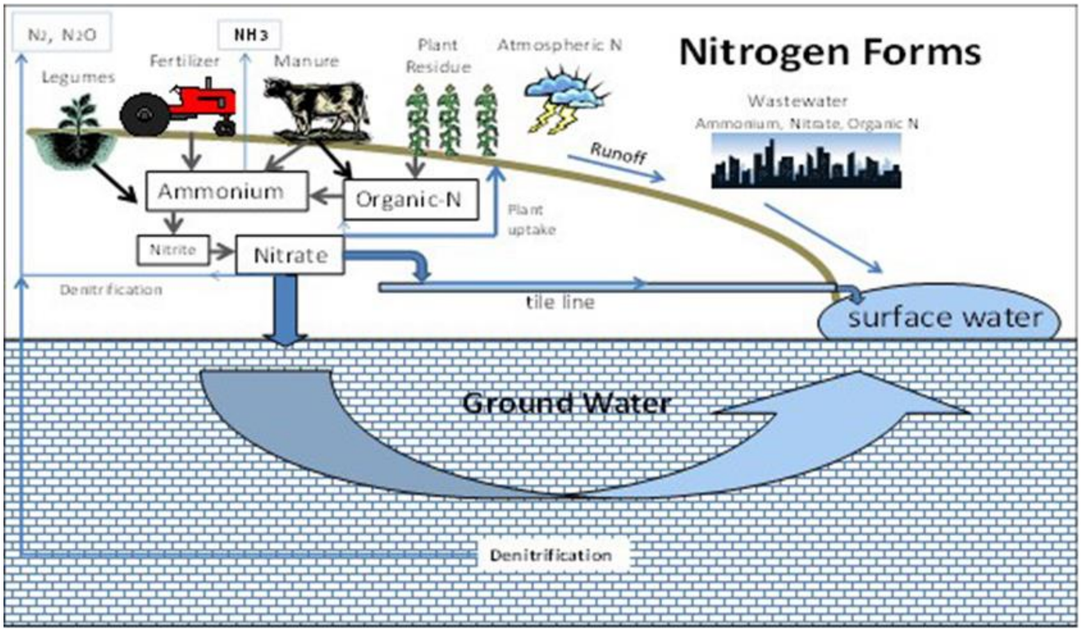
Nitrate

Nitrate is a common human-caused source of pollution to the groundwater. The most recent national assessment of nitrate (Dubrovsky et al. 2010) found that concentrations usually were much greater in the groundwater underlying urban and agricultural lands compared to those, which occur naturally. Very high concentrations tended to be measured in the groundwater in agricultural areas. Nationally, more than 20% of the shallow wells (less than 100 feet deep) sampled in agricultural areas throughout the nation had concentrations greater than 10 mg/L as nitrogen.

Nitrogen-containing compounds are needed for all life to survive, but too much, especially in the form of nitrate, harms human and aquatic health. Nitrogen is an integral part of all proteins, which are the basic building blocks of all plants and animals. In addition, it forms the enzymes involved in life-sustaining reactions and the chemicals involved in plant photosynthesis. Too much nitrate in water, on the other hand, harms human health, especially young babies. 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 (EPA) established a Maximum Contaminant Level (MCL) of 10 mg/L for nitrate. 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 activities like swimming and boating. Foul odors also can occur when this algae decays, and the decomposition process can deplete all of the oxygen from the water resulting in fish kills.

When assessing the groundwater, it is important to consider all of the forms of nitrogen that may be present because these can changed into nitrate by a variety of natural processes. These include assimilation, mineralization, nitrification, denitrification, and volatilization. The combination of all of these is called the Nitrogen Cycle (Figure 5).

Figure 5. Nitrogen cycle, showing primary sources, forms, and routes to surface and groundwater [Minnesota Pollution Control Agency (2013)].



The form nitrogen takes also dictates how quickly it will be transported to the groundwater. The very soluble forms, such as nitrate, may be directly transported to the soils and groundwater with rainfall. Other forms of nitrogen are not very soluble and do not readily move to the groundwater. For example, ammonium (NH_4^+) is a positively charged compound and readily sorbs onto most soils, organic matter, and aquifer materials and does not move quickly in the groundwater.

Sources to the Environment

High nitrate concentrations in groundwater usually are the result of human-caused pollution, such as fertilizers, animal and human waste, and contaminated rainfall. Nitrogen fertilizers commonly are applied to the state's agricultural crops and urban landscapes to enhance crop yields and maintain optimal turfgrass, garden, and landscape plant growth. It is estimated that 1,359 million pounds of nitrogen fertilizer are applied to the state's crops each year and about 12 million pounds are applied to urban lawns (Mulla et al. 2013). Most of these are in the form of ammonia, ammonium nitrate, and ammonium sulfate. Animal and human wastes are another nitrogen source that can reach both surface and groundwater if not properly managed. Mulla et al. (2013) estimated that 446 million pounds of livestock manure are spread on the state's agricultural lands each year. Another important source of nitrogen to Minnesota's landscape is atmospheric deposition. This contributes almost as much nitrogen to Minnesota as livestock manure, contributing about 427 tons of nitrogen to the state each year. Human activities contribute most of this nitrogen to the atmosphere. The EPA (2011) estimates that fossil fuel combustion and ammonia volatilization from livestock manure and commercial fertilizers are the largest sources of nitrogen to the atmosphere in the United States.

Undisturbed landscapes typically contribute small amounts of nitrogen to the environment. Only a few natural, undisturbed settings are known to contain high nitrate concentrations, and none of these occur in Minnesota. Data collected across the Nation by the USGS indicates the background nitrate concentration in the groundwater is low, about 1 mg/L (Dubrovsky et al. 2010). The MPCA's last statewide groundwater quality assessment indicates that the shallow groundwater underlying forested settings in Minnesota is even lower than this, with a median concentration of 0.05 mg/L (Kroening and Ferrey 2013).

Nitrate in the Groundwater

Monitoring conducted in Minnesota from 2013-2017 showed the highest nitrate concentrations usually occur near the water table in agricultural areas (Figure 6, Table 1). High concentrations near the water table generally are not a human health issue because this groundwater typically is not a drinking water supply. However, these may migrate downward to the deep aquifers used for potable water supplies or be transported to surface waters as groundwater inflow. Monitoring data compiled from the "early warning" component of the MPCA's monitoring network and the MDA's ambient network were used to assess the effect of land use on nitrate concentrations. In the agricultural parts of the state, the median nitrate concentration reported from 2013-2017 was at the state class 1 domestic consumption use standard of 10 mg/L, and 49% of the wells had concentrations that exceeded the state class 1 standard. Concentrations were much lower in the groundwater underlying urban areas, with median concentrations ranging from about 1-2 mg/L, and in forested areas the median concentration was just slightly above the analytical method reporting limit. These results were similar to the results from the last MPCA Groundwater Condition Report (Kroening and Ferrey 2013) and other groundwater quality assessments conducted in Minnesota (Anderson 1993, Fong 2000, Trojan et al. 2003) In contrast to the results from the agricultural parts of the state, few shallow wells in the urban settings had concentrations that exceeded 10 mg/L. Six of the 144 sampled shallow wells in the urban settings had nitrate concentrations which exceeded 10 mg/L.

Table 1. Summary statistics of nitrate nitrogen concentrations in the groundwater with land use, 2013-2017 [statistics based upon the most recent sampling event during this period at each well].

Land Use	Number of Wells Sampled	Median Well Depth	Median Concentration	Range in Concentrations
Agricultural	113	20.0 feet	10.0 mg/L	<0.2 – 71.5 mg/L
Sewered Residential	50	18.8 feet	1.8 mg/L	<0.05 – 24.0 mg/L
Residential SSTS	51	25.0 feet	1.1 mg/L	<0.05 – 20.0 mg/L
Commercial/Industrial	44	19.0 feet	1.2 mg/L	<0.05 – 12.0 mg/L
Undeveloped	50	18.0 feet	0.1 mg/L	<0.05 – 2.9 mg/L

Figure 6. Nitrate concentrations in the surficial sand and gravel aquifers, 2013-2017 [concentrations are expressed as nitrogen].

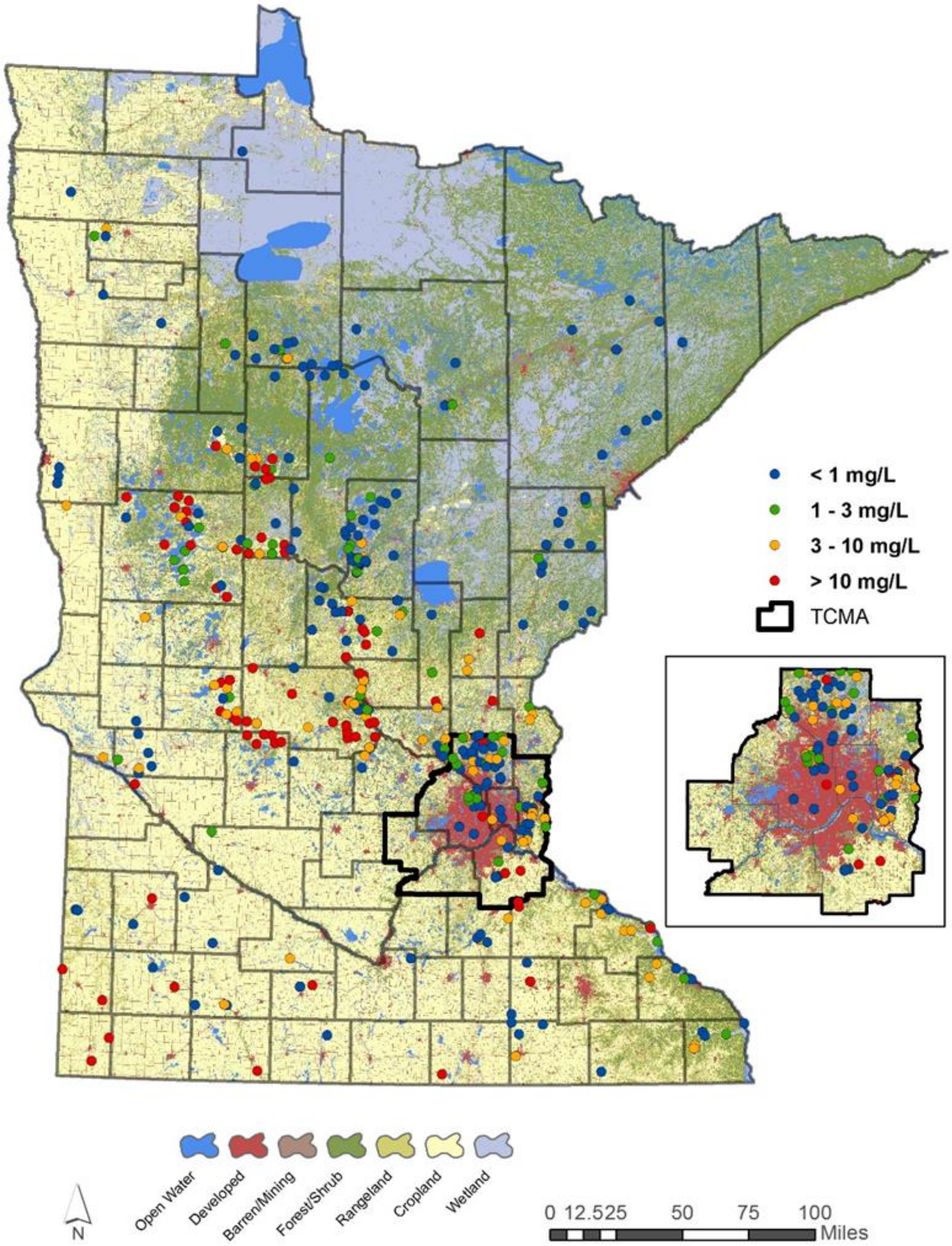


Table 2. Summary statistics (based on the most recent sampling event from the well) for nitrate nitrogen concentrations in Minnesota's groundwater, 2013-2017, by aquifer.

Aquifer	Number of Wells	Median Depth of Wells	Median Concentration	Minimum Concentration	Maximum Concentration
Surficial sand and gravel	446	22 feet	1.7 mg/L	<0.003 mg/L	71.5 mg/L
Buried sand and gravel	810	102 feet	0.01 mg/L	<0.0030 mg/L	26.4 mg/L
Cretaceous	44	187 feet	0.01 mg/L	0.002 mg/L	0.4 mg/L
Galena	47	136 feet	0.05 mg/L	<0.05 mg/L	13.0 mg/L
St. Peter	43	253 feet	0.05 mg/L	0.02 mg/L	15.2 mg/L
Prairie du Chien	161	240 feet	2.0 mg/L	<0.01 mg/L	26.0 mg/L
Jordan	124	340 feet	0.66 mg/L	<0.003 mg/L	32.0 mg/L
Tunnel City	118	318 feet	0.021 mg/L	<0.003 mg/L	12.0 mg/L
Wonewoc	69	268 feet	0.026 mg/L	<0.003 mg/L	4.7 mg/L

High nitrate concentrations occasionally were reported in the parts of the sand and gravel aquifers that are tapped for water supplies. MPCA and DNR staff measured concentrations exceeding the state class 1 standard of 10 mg/L in 18 water-supply wells in these aquifers from 2013-2017. Most of these wells were located outside of the 7-county TCMA and ranged from 40 to 111 feet deep.

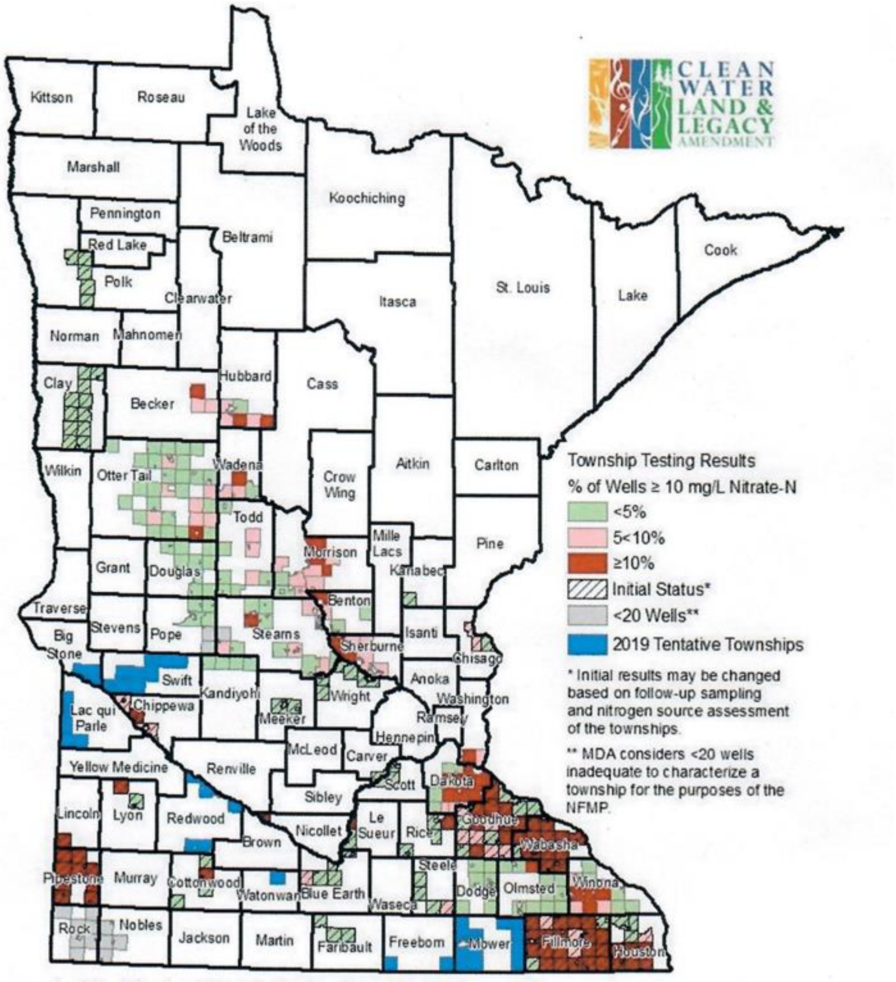
Concentrations in the buried sand and gravel and bedrock aquifers typically were much lower compared to those in the surficial sand and gravel (Table 2). The high median nitrate concentration reported in the Prairie du Chien aquifer likely reflects that the data compiled from 2013-2017 represent the parts of this aquifer that are very vulnerable to contamination from the land surface. Twenty wells installed in the Prairie du Chien had concentrations exceeding the state class 1 standard of 10 mg/L. Three of these 20 wells were located in the southeastern TCMA, and the remainder were located in southeastern Minnesota. The wells in southeastern Minnesota that exceeded the nitrate state class 1 standard were located on the Prairie du Chien Plateau, where large amounts of recharge water and any associated contamination, like nitrate, enter it.

The available monitoring data suggested that nitrate concentrations generally decreased with depth in the surficial sand and gravel aquifers. For this report, data were compiled from 375 shallow monitoring wells and 71 water-supply wells installed in these aquifers. The monitoring wells had a median depth of 21 feet, and the water-supply wells, which mainly supplied water to individual residences, had a median depth of 64 feet. Nitrate concentrations were typically higher in the shallow wells than in the deeper ones. The median concentration in the shallow monitoring wells was 2.0 mg/L compared to 0.7 mg/L in the deeper water-supply wells. The results from MDA's monitoring near the water table and the CSPWN also suggested that concentrations decreased with depth. In 2017, 2.2% of the tested wells in the CSPWM had concentrations equal to or exceeding 10 mg/L compared to 49% of the water table wells. There are a couple of reasons that may explain the low concentrations in the deep wells. First, the nitrate in the shallow parts of these aquifers may not yet have migrated down into the deep parts of the sand and gravel aquifers. Second, nitrate also may have been removed naturally in the deeper parts of the aquifer by denitrification.

Some wells in the bedrock aquifers tapped for water supplies in southeastern Minnesota also were impacted by high nitrate concentrations. MPCA and DNR staff measured nitrate concentrations exceeding state class 1 standard of 10 mg/L in 43 wells accessing these aquifers. These wells were deeper compared to the sand and gravel aquifer wells with high concentrations and had a median depth of 151 feet. The MDA also found that concentrations were equal to or greater than 10 mg/L in 10% of the samples collected for the SEVMN in 2017, which primarily targets bedrock aquifer wells (Minnesota Department of Agriculture 2017).

Expanded testing by the MDA showed the townships with the largest percentages of drinking water supply wells with nitrate concentrations exceeding 10 mg/L tend to be located in southeastern Minnesota (Figure 7). Since the beginning of the Township Testing Program in 2017, 10% of the 25,652 wells tested contained nitrate concentrations greater than or equal to 10 mg/L. The MDA produced result maps from this program at both the county and statewide scale and classified the townships most-impacted by nitrate as having at least 10% of the tested wells with concentrations equal to or exceeding the state class 1 standard of 10 mg/L. The majority of townships most impacted by nitrate contamination (shown in red in Figure 7) were located in southeastern Minnesota.

Figure 7. Percentage of wells exceeding 10 mg/L in townships tested in Minnesota [Figure courtesy of the Minnesota Department of Agriculture].



* Initial results may be changed based on follow-up sampling and nitrogen source assessment of the townships.

** MDA considers <20 wells inadequate to characterize a township for the purposes of the NFMP.

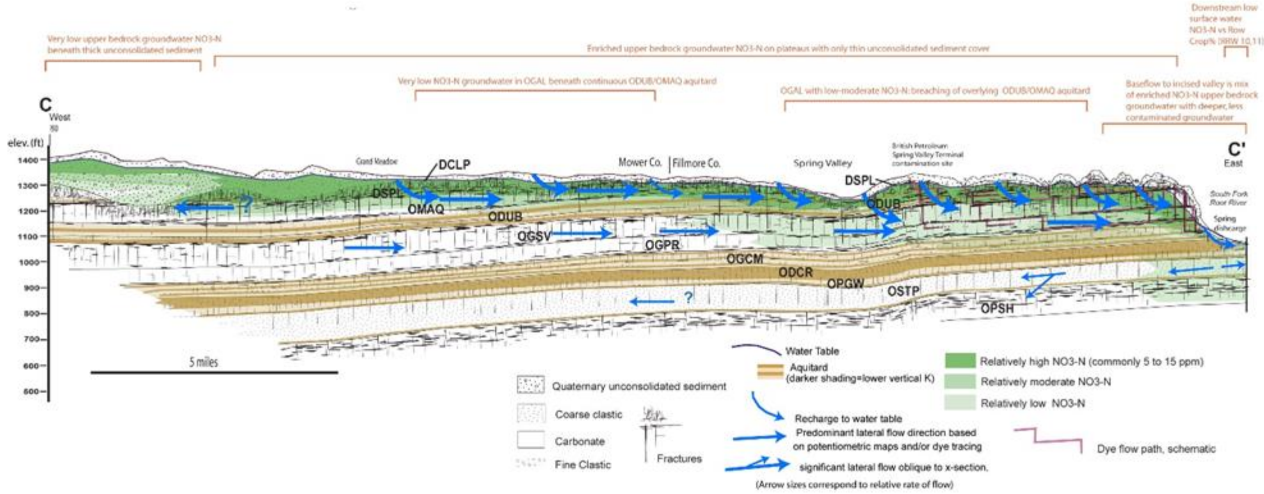
Combined Final and Initial Testing Results, updated February 2019.

Over 40% of the tested wells in a few townships exceeded the state class 1 standard. The limited initial sampling data from Nobles and Rock Counties in southwestern Minnesota showed that 41 to 93% of the tested wells in each township contained nitrate concentrations that exceeded the state class 1 standard. Four other townships in the state had 40% or more of the tested wells exceeding the state class 1 standard. These included Marshan Township in eastern Dakota County, Agram Township in central Morrison County, and Fremont and Utica Townships in western Winona County. In each of these four townships, 43 to 55% of the tested wells had nitrate concentrations of 10 mg/L or greater.

Geology had a large influence on whether high nitrate concentrations were transported to the state's bedrock aquifers. The geologic controls on nitrate transport to the bedrock aquifers in southeastern Minnesota was recently assessed by the MGS (Runkel et al. 2013) as part of an investigation conducted for the MPCA to assist with watershed planning efforts. For this study, the MGS researchers compiled existing nitrate data along with geologic maps and other databases in order to evaluate how the concentrations varied with respect to this region's hydrogeology. This work, along with a few other studies (Falteisek et al. 1996, Falteisek 1997, Minnesota Department of Natural 2002, Minnesota Department of Natural Resources 2003, 2001), found that recharge water along with any associated contamination like nitrate quickly enters the bedrock aquifers on the Upper Carbonate and Prairie du Chien Plateaus.

The influence of the thickness of the unconsolidated materials covering the bedrock aquifers on nitrate transport to the groundwater can be seen in a cross section in Mower County that was published by Runkel et al. (2013) (Figure 8). In the western part of the cross section, the bedrock aquifers are covered by about 100 feet or more of unconsolidated deposits (identified as quaternary unconsolidated sediment or coarse clastic). These thick deposits sufficiently retard the flow of water and any associated contamination, resulting in low nitrate concentrations in the underlying bedrock aquifers. In contrast, the uppermost bedrock aquifer is covered by a thin layer (less than 50 feet) of unconsolidated deposits in the eastern part of the cross section. These thin deposits readily allow water and associated nitrate to flow through them, and as a result, concentrations in the uppermost bedrock aquifers commonly range between 5-15 mg/L.

Figure 8. Cross section showing nitrate transport in the bedrock aquifers in Mower and Fillmore Counties [Figure from Runkel et al 2013].



The investigation by Runkel et al. (2013) also showed that nitrate concentrations in the bedrock aquifers in southeastern Minnesota are strongly influenced by the aquitards that separate them, such as the Dubuque, Decorah, or Glenwood shales. These aquitards generally limit the vertical transport of water and any associated nitrate contamination, resulting in low nitrate concentrations in the deep, underlying aquifers, which generally is related to the age of the groundwater. This also can be seen in the cross section shown in Figure 8. In the middle part of the cross section, the recharge water and nitrate contamination in the uppermost bedrock aquifer flows laterally along the underlying thick aquitard that lacks vertical fractures (identified as ODUB and OGCM). In the eastern part of the cross section, the upper aquitard is thin and breached by vertical fractures in many places, and this allows the nitrate contamination to be transported to another underlying bedrock aquifer. These vertical fractures are especially common where the uppermost bedrock is within about 50 feet of the land surface. Eventually, the groundwater and its associated nitrate contamination reaches the incised river valleys in southeastern Minnesota, and is discharged as baseflow to these streams.

Temporal Trends

Trends in nitrate concentrations from 2005-2017 generally showed no consistency statewide, at the watershed scale, or within any particular land use setting. Trends could be examined at all of these levels due to the wealth of available nitrate data. Over 100 wells and springs sampled by the MPCA and MDA's ambient monitoring networks had sufficient data to determine whether nitrate concentrations changed from 2005-2017. These sites were fairly evenly split between the MPCA's and MDA's ambient monitoring networks. Fifty of the wells used for trend analysis were part of the MPCA's Ambient Groundwater Monitoring Network, and the remaining sixty-four wells and three springs were from the MDA's monitoring network.

The majority of the tested sites had no significant temporal trend in nitrate concentrations. All of the wells and springs were tested individually for temporal trends in nitrate using the nonparametric Mann-Kendall test, which accounted for both censored and tied data. Seventy-four of the sites had no statistically significant change in concentrations from 2005-2017. A much smaller number of sites had significant increases or decreases in nitrate concentrations. Nineteen sites had statistically significant upward trends in nitrate from 2005-2017, and twenty-four sites had statistically significant decreases. The sites with significant upward or downward trends were scattered throughout the state and generally did not appear to be located within any particular region or land use setting.

Further statistical testing confirmed the informal finding that there was no statewide trend in nitrate concentrations in the state's shallow groundwater. A variation of the Mann-Kendall trend test called the Regional Kendall test (Helsel and Frans 2006) was used for this analysis and confirmed that there was no consistent trend at the statewide scale in nitrate concentrations in the shallow groundwater (slope=0, tau=-0.0409, p-value=0.0156). Even though the result from this statistical test was statistically significant, the Theil-Sen's slope of zero and low Kendall's tau value indicated that the nitrate concentrations in the groundwater have not changed.

No trends in nitrate concentrations generally were found in the groundwater in each of the state's major watersheds or the TCMA from 2005-2017 (Appendix A). For this analysis, only major watersheds that had at least five wells with sufficient data to compute temporal trends were considered. There was a statistically significant upward trend in nitrate concentrations in the Lower Mississippi River Basin. In this watershed, five of the nine sites had statistically significant increasing trends. Three of these sites were springs, and the other two were domestic water-supply wells.

In this report, the major watersheds used for the trend analysis generally were considered to be the subregions defined by the USGS's Hydrologic Unit Maps (Seaber, Kapinos, and G.L. 1987). In the instance where a major watershed overlapped the TCMA, the watershed boundary was truncated so it did not include the TCMA. There were at least five wells with sufficient data for trend analysis in the TCMA and 4 of the 12 major watersheds. There were no or insufficient data to calculate temporal trends in these watersheds: 1) Big Sioux and Rock River Basins, 2) Des Moines River Basin, 3) Little Sioux River Basin, 4) Rainy River Basin, 4) St. Croix River Basin, 5) Western Lake Superior Basin, 6) Upper Iowa River Basin, 7) Wapsipnicon River Basin, and 8) Western Lake Superior Basin.

There also were no statistically significant trends in nitrate concentrations from 2005-2017 when the analysis was performed by land use setting (Appendix A). Similar to the trend testing by watershed, this testing only included land use settings that had at least five wells with sufficient data to compute temporal trends. For the urban settings, there only were sufficient nitrate data collected from the wells located in sewered residential areas to compute trends.

MDA's analysis of the private well networks also showed nitrate concentrations have not changed recently. Kaiser, Schaefer, and VanRysWyk (2017) analyzed the SEVMN and CSPWN data for trends. No temporal trends were found in the SEVMN data from 2008-2015 or the CSPWN data from 2011-2015.

Chloride

Chloride transported to the groundwater is considered a "permanent" pollutant because it is not broken down by typical environmental processes. Once in the groundwater, 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.

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 affects 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, and Dodrill 1999, Nguyen et al. 2010, Nguyen, Stone, and Edwards 2011). To minimize taste problems with public drinking water supplies, the 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).

Additional monitoring conducted over the last several years filled some of the gaps in our knowledge of human-caused chloride contamination in Minnesota's groundwater. This included chloride data collected from the: 1) MPCA's newly-installed ambient network monitoring wells, 2) MDA's ambient monitoring network, 3) the SEVMN, and 4) DNR's County Geologic Atlas projects.

The MPCA's monitoring network enhancements allowed the agency to better assess how land use affects chloride concentrations in the groundwater. The assessment of chloride concentrations in the last MPCA Groundwater Condition Report (Kroening and Ferrey 2013) was based on limited data from commercial/industrial areas and residential areas using SSTS for wastewater disposal and treatment. For the 2013 assessment, chloride data were available only from nine shallow wells representing ambient conditions commercial/industrial areas and thirteen wells in residential areas that rely on SSTS for wastewater treatment.

The most complete picture to date of chloride concentrations in the shallow groundwater underlying the state's agricultural areas was provided by the sampling of the MDA's ambient monitoring network in 2014. For this collaborative monitoring effort, the MDA drew groundwater samples from their network of over 100 wells in agricultural areas, and MPCA analyzed the samples for chloride, bromide, and sulfate. Prior to this sample collection, the only available chloride data in the agricultural parts of the state were collected about 20-25 years ago by the MPCA and USGS (Cowdery 1998, Fong 2000, Trojan et al. 2003). These studies were not conducted statewide but focused on the shallow groundwater underlying agricultural areas in western Minnesota, the Anoka Sand Plain in central Minnesota, and agricultural land near the City of St. Cloud.

Chloride information from the SEVMN and the DNR's County Geologic Atlas Program expanded coverage in the bedrock aquifers in southeastern Minnesota and the buried sand and gravel aquifers. The main goal of the SEVMN is to track nitrate concentrations in drinking water from private wells; however, chloride samples were collected from 416 network wells during 2013-14. Data from the buried sand and gravel aquifers included the information 365 wells, primarily private drinking water wells, in Anoka, Renville, Sherburne, and Wright Counties.

The trend analyses in this report also represented a broader distribution of wells compared to the last analysis (Kroening and Ferrey 2013). The last temporal trend analysis of chloride in groundwater primarily focused on wells located in the northern TCMA, Washington County, and near the cities of Bemidji and St. Cloud because at this time these were the only ones available that had long-term information. Since this time, enough data has been collected from the MPCA's Ambient Groundwater Monitoring Network to compute trends in other locations, including near the cities of Austin, Rochester, and Wabasha. The updated trend analysis in this report also included more wells installed in the state's bedrock aquifers. Fifteen of the 35 wells used for chloride trend analysis were installed in bedrock aquifers, primarily the Prairie du Chien-Jordan.

The wells used in this temporal trend analysis also were installed at a variety of depths. The sand and gravel aquifer wells ranged from 9 to 73 feet deep. These primarily were monitoring wells screened at the water table, and the majority of these wells were located in the TCMA and near the City of St. Cloud. The bedrock aquifer wells analyzed for trends were 52 to 340 feet deep. These primarily were domestic water-supply wells installed in the Prairie du Chien-Jordan aquifer in the TCMA; however, five wells tapping the Galena aquifer and one well tapping the St. Peter aquifer in southeastern Minnesota were included in the analysis.

Sources and Fate of Chloride in Groundwater

Chloride is present naturally to some degree in Minnesota's groundwater. Many of the minerals that comprise the state's bedrock and sand and gravel aquifers contain a little chloride, and rock weathering releases some of this into the groundwater. Sedimentary rocks, especially those containing the mineral halite (commonly known as rock salt), usually contain more chloride compared to igneous rocks. In aquifers with very old water, chloride also may be naturally present if these still contain connate water, which is the water that was initially trapped in the rock when it was formed in a marine environment. In Minnesota, the aquifers composed of sedimentary rocks, like the Prairie du Chien-Jordan, likely contained high chloride concentrations when they were formed. Some aquifers also may naturally contain chloride if it is transported from saline to fresh aquifers through contacts between the aquifers, faults, or fractures.

Scientists at the University of Minnesota estimate that the largest sources of chloride to Minnesota's environment are de-icing chemical application, agriculture, and household water softening (Overbo and Heger 2018). The use of salt for pavement de-icing is the largest anthropogenic source, contributing over 400,000 tons each year. Agricultural activities also contribute about this same amount of chloride to Minnesota's environment. Overbo and Heger (2018) estimate that almost 200,000 metric tons of chloride are applied each year in Minnesota to fertilize crops and over 150,000 metric tons of chloride were excreted by livestock. Household water softening is estimated to contribute almost 150,000 tons of chloride each year to Minnesota's environment.

Monitoring conducted in Minnesota and other northern climates found that these anthropogenic sources of chloride have migrated down into the groundwater. The last statewide MPCA assessment of chloride in the groundwater (Kroening and Ferrey 2013), which focused on aquifers that are vulnerable to contamination in urban areas, found human-caused chloride contamination in a substantial number of the tested wells, especially those installed near the water table in the TCMA. Similar contamination of the groundwater has been found in studies conducted in other states in the northern U.S. and Canada (Cassanelli and Robbins 2013, Howard and Taylor 1998, Kelly 2008, Williams, Williams, and Cao 2000) and in a national-scale assessment of the glacial aquifer system (Mullvaney, Lorenz, and Arntson 2009). Other studies have characterized chloride concentrations in the groundwater in agricultural areas. Pionke and Urban (1985) measured the chloride concentrations in groundwater in Pennsylvania, and Fong (2000) assessed the shallow groundwater beneath agricultural land in the Anoka Sand Plain in Minnesota. Both of these studies found that agricultural land use resulted in increased chloride concentrations in the shallow groundwater. The average measured concentrations reported in the groundwater underlying agricultural areas were around 15 mg/L, which was considerably lower compared to those reported in urban areas. The low concentrations likely resulted from fertilizers and manure being typically distributed among much larger areas compared to de-icing chemicals.

Distribution and Sources in the Groundwater

The highest chloride concentrations in the groundwater typically occurred near the water table in sand and gravel aquifers, especially within the TCMA (Figure 9). Similar to nitrate, high chloride concentrations near the water table typically are not a drinking water concern, but they do signal contaminated water may slowly be seeping downward to the aquifers tapped for drinking water or, alternatively, could adversely affect aquatic life if they are transported to surface waters. Concentrations varied widely throughout the surficial sand and gravel aquifers, ranging from less than the reporting limit of 0.5 to 815 mg/L (Table 3). The lowest concentrations typically were measured in northern Minnesota, and the highest were in the TCMA.

The state class 1 domestic consumption use standard of 250 mg/L was exceeded mainly in shallow monitoring wells located in the TCMA and other urban areas in the state. Twenty-four of the sampled wells contained water with chloride concentrations that exceeded the state class 1 standard in the most recent samples collected from the wells from 2013-2017 (Figures 9-10, table 3). All but two of these were monitoring wells, and they typically were very shallow, with a median depth of 26 feet. The deepest well with a chloride concentration exceeding the state class 1 standard had a depth of 72 feet. Two-thirds of the wells that exceeded the state class 1 standard were located in the 11-county TCMA, and the remaining wells typically were located in other urban areas, such as Cloquet or Moose Lake.

Fewer wells in the TCMA exceeded the state class 1 standard compared to the last MPCA Groundwater Condition Report (Kroening and Ferrey 2013), but this should not be inferred as declining concentrations. The prior assessment included chloride data collected from wells that were originally installed to inform the agency's remediation efforts, primarily investigations of petroleum spills at gas stations. The sampling of these wells was discontinued by the agency's Ambient Groundwater Monitoring Network in 2008 after a review of the data indicated that these wells biased the statewide assessment of VOCs in the groundwater. A reanalysis of the chloride data compiled for the MPCA's 2013 statewide assessment of groundwater quality (Kroening and Ferrey 2013) showed that the median concentration in the remediation wells (330 mg/L) was over ten times greater compared to those in wells installed outside of contaminated areas (22 mg/L). The shallow groundwater near the petroleum spill sites probably contained high chloride concentrations because places such as gas stations likely received large applications of de-icing chemicals during the winter months.

Table 3. Summary statistics (based on the most recent sampling event from the well) for chloride concentrations in Minnesota's groundwater, 2013-2017, by aquifer.

Aquifer	Number of Wells	Median Depth of Wells	Median Concentration	Minimum Concentration	Maximum Concentration
Surficial sand and gravel	373	21 feet	17.7 mg/L	<0.5 mg/L	815 mg/L
Buried sand and gravel	306	108 feet	3.5 mg/L	<0.5 mg/L	184 mg/L
Galena	47	136 feet	13.2 mg/L	<0.5 mg/L	89.3 mg/L
St. Peter	40	270 feet	1.5 mg/L	<0.5 mg/L	30.1 mg/L
Prairie du Chien	129	285 feet	6.8 mg/L	<0.5 mg/L	443 mg/L
Jordan	66	350 feet	2.4 mg/L	<0.5 mg/L	145 mg/L
Tunnel City	50	207 feet	1.4 mg/L	0.367 mg/L	112 mg/L

Figure 9. Chloride concentrations in the surficial sand and gravel aquifers, 2013-2017.

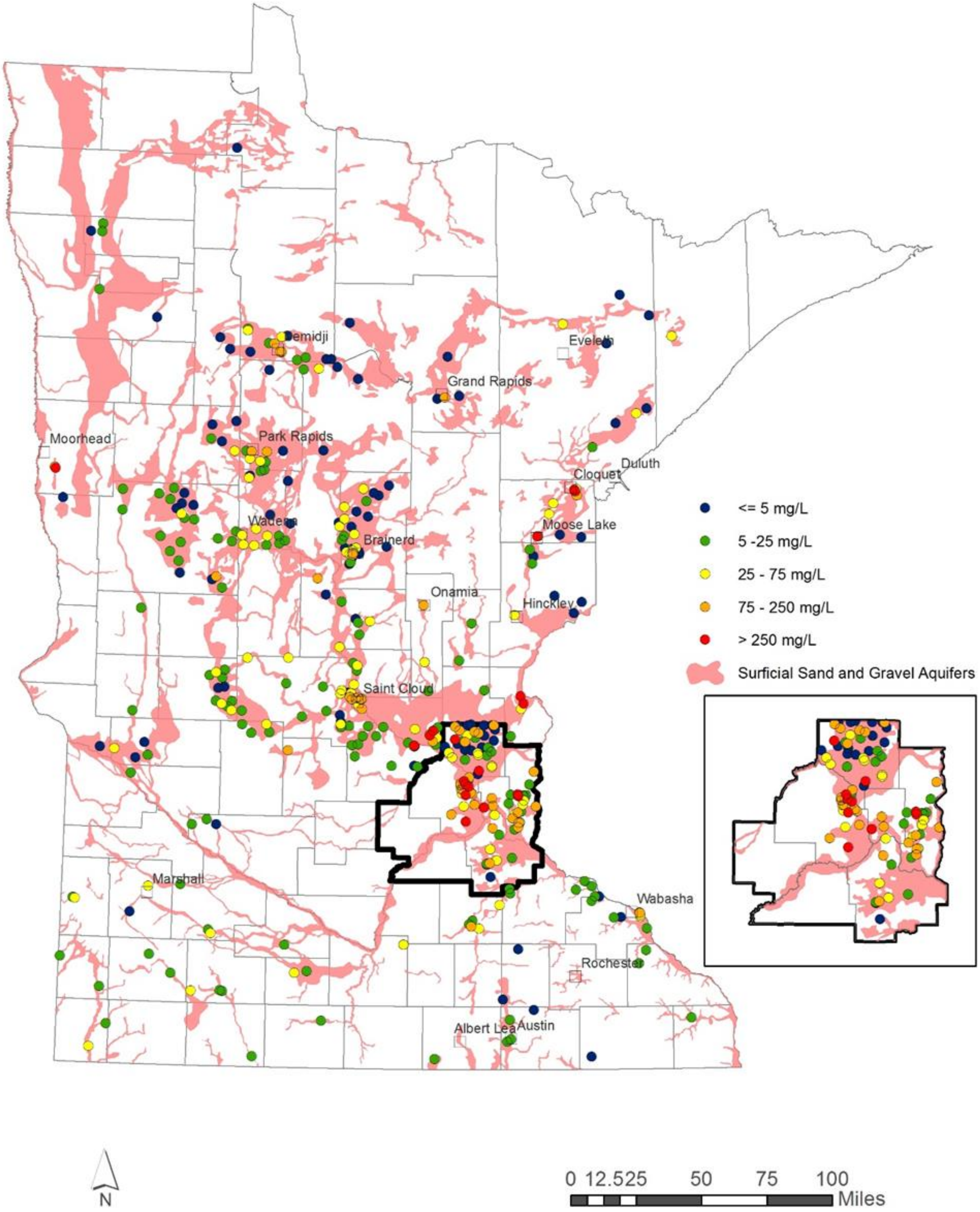
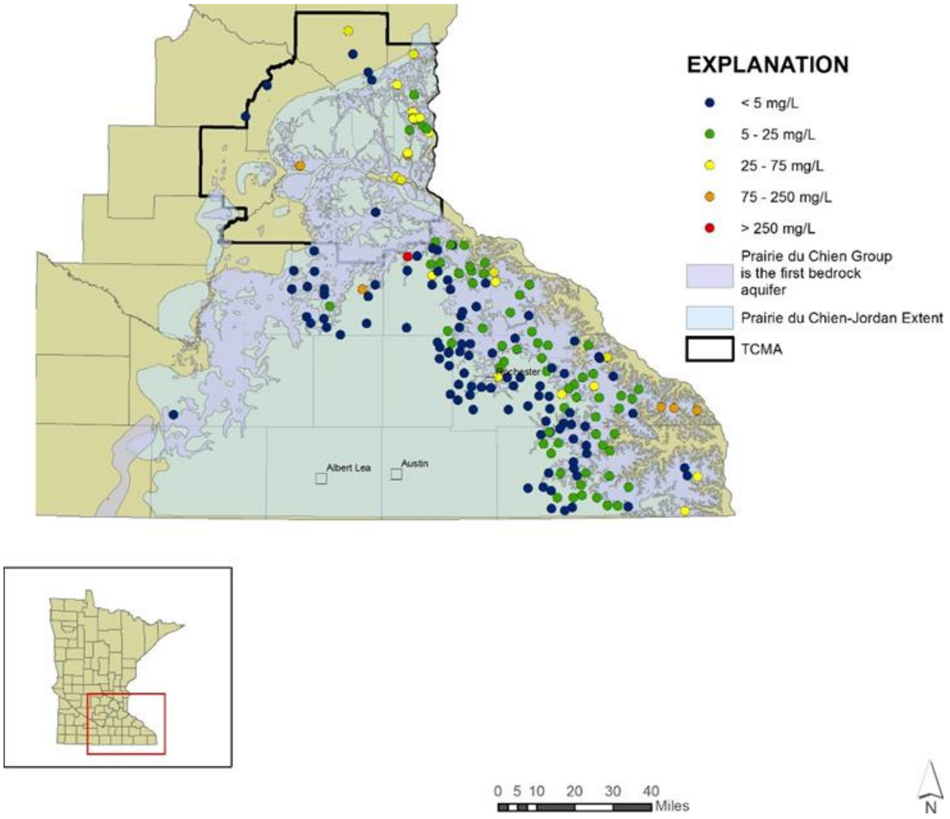


Figure 10. Chloride concentrations in the Prairie du Chien-Jordan Aquifer, 2013-2017



Two of the sampled domestic wells had chloride concentrations exceeding the state class 1 standard. One of these wells tapped the Prairie du Chien aquifer in Goodhue County (Figure 10). This well was installed in 1955, almost two decades before the state well code was enacted in 1974, and was 60 feet deep. The other domestic well that contained water with a chloride concentration exceeding the SMCL was 72-feet deep and installed in the Buffalo Aquifer in Clay County (Figure 9); this is an area which is known to contain recently recharged groundwater and human-caused chloride contamination (Berg 2018).

Land Use Influences

The MPCA's monitoring network improvements found that commercial/industrial land use affects chloride in groundwater more than what was previously known. The expanded monitoring in this setting showed the median chloride concentration in the shallow groundwater underlying the state's commercial/industrial areas was 81.9 mg/L (Table 4). This is about 25 mg/L higher than the median value reported in 2013 (Kroening and Ferrey 2013). In addition, the data from the expanded monitoring showed that concentrations were almost twice as high in the shallow groundwater underneath commercial/industrial areas compared to residential. The wells in commercial/industrial areas with the highest chloride concentrations generally were located near heavily travelled roadways, such as interstate freeways or U.S. highways, or were near parking lots.

Table 4. Summary statistics of chloride concentrations in the groundwater with land use, 2013-2017 [statistics based upon the most recent sampling event during this period at each well].

Land Use	Number of Wells Sampled	Median Well Depth	Median Concentration	Range in Concentrations
Commercial/Industrial	43	19 feet	81.9	1.4 – 790 mg/L
Sewered Residential	50	9 feet	44.6 mg/L	<0.5 – 463 mg/L
Residential SSTS	51	25 feet	16.1 mg/L	<0.5 – 429 mg/L
Agricultural	113	20 feet	14.1 mg/L	<0.5 – 308 mg/L
Undeveloped	50	13 feet	1.1 mg/L	<0.5 – 97 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, and 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 source of most of the high chloride concentrations in the shallow wells in commercial/industrial areas likely was related to the use of salt as a de-icing chemical or possibly for water softening. This study did not determine the extent of chloride-contaminated water at each of the sampled wells. Bromide, however, was analyzed in addition to chloride in most of the studies compiled for this report, and chloride/bromide (Cl/Br) ratios were computed (Davis, Whittemore, and Fabryka-Martin 1998) to determine the potential sources that were contributing the chloride to the groundwater. Almost three-quarters of the shallow wells sampled in commercial/industrial areas had a Cl/Br ratio greater than 1,000, which indicated that the chloride source was halite, which usually is applied as a deicing chemical to pavement, sidewalks, and parking lots in these areas. Salt in the form of halite also may be used in water softening to regenerate the resins in water softeners that remove the calcium and magnesium from the water. It is less likely that water softening was the source of the high chloride concentrations in commercial/industrial areas since most of the sampled wells were located in places where any wastewater from these systems would be discharged to a centralized sewage treatment system rather than the land in the immediate vicinity of the sampled monitoring wells.

The expanded monitoring showed that chloride concentrations in the shallow groundwater underlying residential areas that use SSTS and agricultural areas were similar, with median concentrations ranging from 14.1 to 16.1 mg/L. The median chloride concentration underlying residential areas that use SSTS for wastewater treatment was almost 30 mg/L lower compared to those underlying sewered residential areas. One reason that concentrations may be lower in the shallow groundwater underlying residential areas using SSTS compared to those using centralized sewage treatment systems is the low housing and road density in these areas. This would tend to spread out the chloride sources to the groundwater over a larger area compared to sewered residential areas, resulting in lower concentrations in the groundwater.

The calculated Cl/Br ratios also indicated that de-icing chemicals or water softener salt still were important chloride sources in both types of residential settings. Sixty-two percent of the shallow wells in sewered residential areas had a Cl/Br ratio that exceeded 1,000, indicating a halite source, whereas

51% of the shallow wells in the residential SSTS areas had a Cl/Br ratio suggesting that the chloride source was either a de-icing chemical or water softener salt.

De-icing chemicals or water softener salt generally did not appear to be the sources of the chloride in the groundwater underlying agricultural areas. The majority of the shallow wells contained water with Cl/Br ratios ranging from 300 to 1,000, which indicated the source of chloride was a mixture of water with different Cl/Br ratios or wastewater. Seventeen percent of the wells in agricultural areas had a Cl/Br ratio that indicated the source was either a de-icing chemical or water softener salt.

Similar to the results from the 2013 statewide groundwater quality assessment, chloride concentrations remained lowest in the shallow groundwater underlying the undeveloped, forested parts of the state. Concentrations in this setting ranged from <0.5 to 97 mg/L, with a very low median concentration of 1.1 mg/L. Most of the chloride present in these wells was contributed by natural sources. Twenty-nine of the 50 sampled wells in this setting had a Cl/Br ratio that was less than 200, which indicated a natural source.

Buried Sand and Gravel Aquifers

The available data suggested that high chloride concentrations in the buried sand and gravel aquifers within or near the TCMA were related to de-icing chemical or water softener salt use. The chloride information compiled for this report was not evenly distributed throughout the state. Ninety-four percent of the chloride data in these aquifers were from four counties (Anoka, Renville, Sherburne, and Wright) because they originally were collected by the DNR to produce county-scale maps showing the pollution sensitivity of the state's aquifers. The median chloride concentrations in the buried sand and gravel aquifers in each of these four counties were similar, ranging from 2.2 mg/L in Wright County to 4.9 mg/L in Sherburne County. Concentrations, however, were more variable in the three counties closest to the TCMA compared to Renville County. The interquartile range (IQR), a statistic that describes the variation in the data, in the wells in Anoka, Sherburne, and Wright Counties ranged from 9.1 to 14.1 mg/L. The variation in concentrations was much lower in the aquifers in Renville County, with an IQR of 4.1 mg/L. Many of highest concentrations in Anoka County appeared to be related de-icing chemical or water softener salt use. In this county, almost three-quarters of the wells with chloride concentrations greater than 14.1 mg/L had a Cl/Br ratio that was greater than 1,000, which suggested a de-icing chemical or water softener source. In contrast, none of the wells sampled in Renville County had a Cl/Br ratio that suggested it was contaminated from these two sources.

Bedrock Aquifers

The median chloride concentration in the Prairie du Chien-Jordan aquifer was substantially higher in the available 11-county TCMA wells compared to the rest of southeastern Minnesota. The median concentration in the 11-county TCMA was 28.3 mg/L, which was calculated from 28 wells. In contrast, the median concentration in this aquifer outside of the TCMA was almost 10 times lower; 3.0 mg/L (calculated using 167 wells).

More wells in the TCMA also had a chemical signature consistent with a de-icing chemical or water softener salt compared to those located outside of this area. In the TCMA, 77% of the Prairie du Chien-Jordan wells had a Cl/Br ratio greater than 1,000. In contrast, only 5.1% of the wells outside of the TCMA had a Cl/Br ratio greater than 1,000.

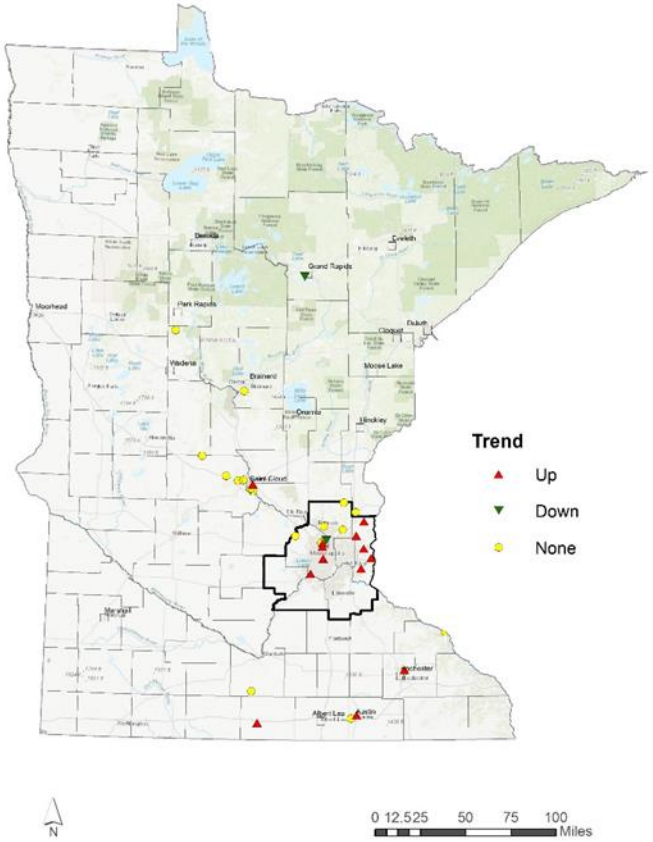
There were no distinctive geographic variations in chloride concentrations in the Galena or St. Peter aquifers (Appendix B). The chloride sources in these wells generally were not related to the use of deicing chemicals or water softener salt. About 20% of the Galena wells and 9% of the St. Peter wells had a Cl/Br ratio consistent with a de-icing chemical or water softener salt.

Temporal Trends

All wells with significantly increasing chloride trends had a chemical signature that was consistent with a human-caused source. Recent changes (2005-2017) in chloride concentrations were calculated at 35 sites that had sufficient data for analysis using the Mann-Kendall test, similar to the methods used for nitrate trends. Overall, 14 of the 35 wells (40%) tested across the state had a statistically significant upward trend in chloride concentrations from 2005-2017 (Figure 11). Eleven of these 14 wells had a Cl/Br ratio greater than 1,000, which is consistent with a de-icing chemical or water softener source. The remaining three wells with a significant upward trend had slightly lower Cl/Br ratios, ranging from 447 to 983, which are consistent with either a municipal wastewater source or a mixture of waters with different ratios.

Increasing chloride concentrations were not just restricted to the water table, but also occurred in the state's bedrock aquifers. Chloride trends in the bedrock aquifers were largely untested in the last MPCA statewide groundwater quality assessment (Kroening and Ferrey 2013) because most of the wells in the agency's monitoring network had insufficient data for this analysis. The recent analysis found that 10 of the 14 wells with increasing chloride trends were in bedrock aquifers, ranging from 90 to 340 feet deep. Seven of the 10 bedrock aquifer wells with increasing trends were installed in the Prairie du Chien aquifer. The remaining three wells were installed in the Galena and St. Peter aquifers. All except one of the 10 wells were used to provide water supplies to individual residences.

Figure 11. Temporal trends in chloride concentrations in Minnesota's groundwater, 2005-2017.



In the wells with upward trends, the changes in chloride concentrations from 2005-2017 varied considerably. In the deepest well with an upward trend, a 340-foot deep Galena well in Mower County, the change in chloride concentrations were very slight (Figure 12). In comparison, greater increases in chloride concentrations were seen in the shallower bedrock aquifer wells with upward trends, such as a 169-foot deep Galena well near the City of Austin (Figure 13).

Figure 12. Chloride concentrations in well 562727 in Mower County, Minnesota

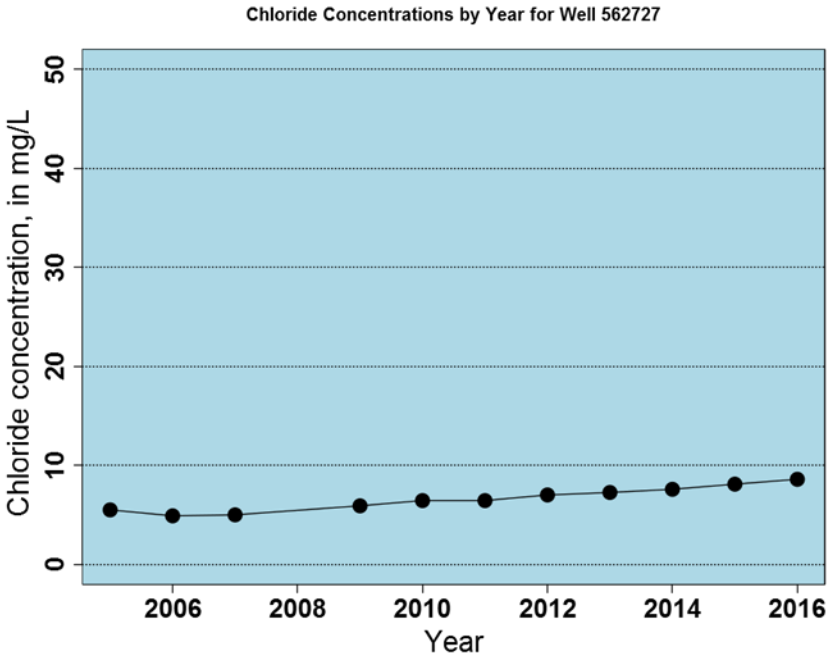
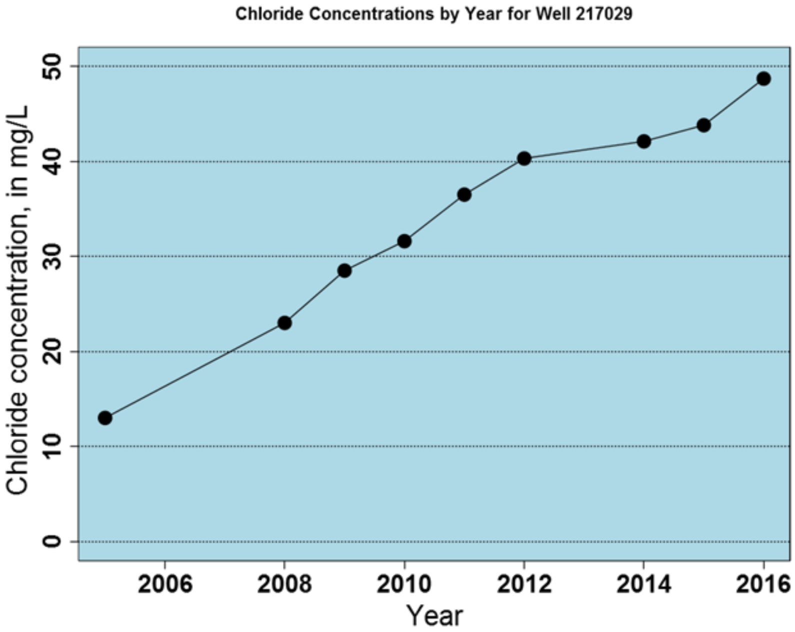


Figure 13. Chloride concentrations in well 217029 in Austin, Minnesota.



Increasing chloride trends continued to occur in some shallow sand and gravel aquifer wells in the TCMA and the City of St. Cloud. The last assessment of groundwater quality conditions, using all of the available data up to 2011, found that chloride concentrations had increased in about 30% of the wells in these aquifers. Overall, four of the 20 shallow sand and gravel aquifer wells tested for chloride trends from 2005-2017 had a statistically significant increasing trend. These four wells were located in heavily urbanized areas; three were near the urban core of the TCMA in Hennepin County, and the remaining well was located in a commercial/industrial area in the City of St. Cloud. Chloride concentrations increased at a much greater rate, with a median increase of 3.7 mg/L per year, in the shallow sand and gravel aquifer wells than the ones installed in bedrock aquifers, where the median increase was 1.38 mg/L per year.

Trace Elements

Trace elements are metals and semi-metals (e.g. arsenic) that usually are present at low concentrations in water. Both natural and human-caused sources contribute trace elements to the environment. Trace elements are different from most of the other contaminants discussed in this report because they naturally are present in rocks and soils. However, human activities also may release substantial amounts of them to the environment since these are present in many commonly used products such as steel and metal alloys, pigments, batteries, and electronic equipment. Under natural conditions, many of the compounds trace elements form are usually not very soluble and are not detected or measured at any appreciable concentrations in the groundwater. In water, trace elements typically are measured at concentrations less than 1 ug/L. However, under certain natural or human-caused geochemical conditions, such as low pH or low oxygen concentrations, some trace elements can be mobilized into the water and can occur at high concentrations.

The presence of trace elements in groundwater used for drinking is a concern because some may adversely affect human health or cause aesthetic problems. Some trace elements, such as arsenic, are known to be toxic. Others, like iron, are not known to cause adverse health effects but often form compounds that cause the water to be rust or black colored and stain plumbing fixtures and laundry.

Arsenic

Arsenic commonly is present in the groundwater throughout the upper Midwest. Several studies have reported high concentrations in the sand and gravel aquifers. Warner and Ayotte (2014) assessed arsenic in all of the sand and gravel aquifers formed by glacial processes across the nation from Washington State to Maine. Their investigation found that overall about 7% of the tested wells had arsenic concentrations that exceeded the Minnesota class 1 domestic consumption use standard of 10 ug/L. Concentrations, however, varied with region and depth. More than 20% of the wells sampled in the central part of the aquifer system, which includes the state of Minnesota, had concentrations that exceeded the Minnesota class 1 standard.

High concentrations of arsenic in groundwater used for drinking are a concern because this element is toxic. Inorganic arsenic is classified by the EPA as a known human carcinogen and has been linked to bladder, lung, skin, kidney, nasal passage, liver, and prostate cancer. The ingestion or skin exposure to water with high arsenic concentrations also may cause skin discoloration and lesions.

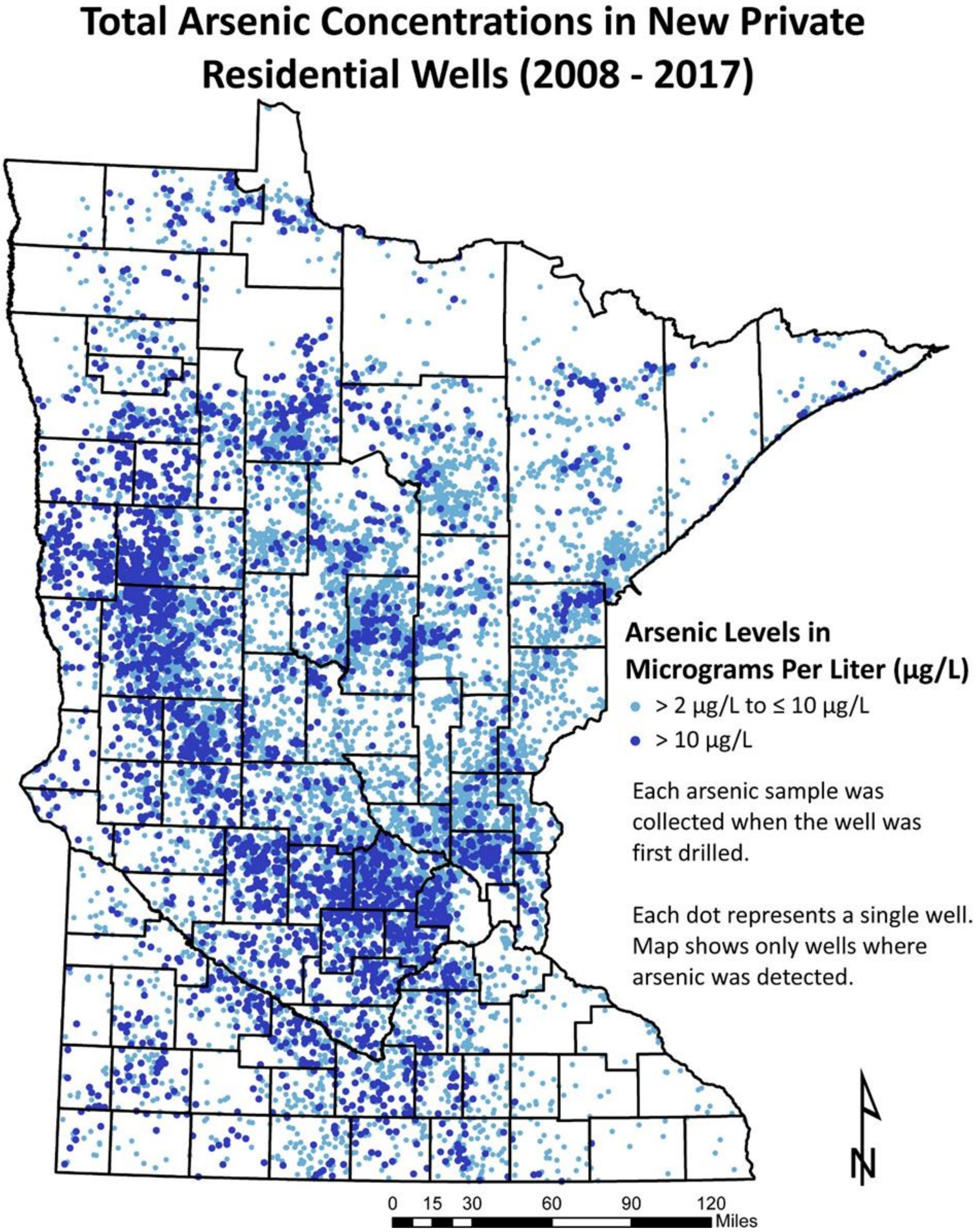
Arsenic found in Minnesota’s groundwater, as well as that found elsewhere, generally is naturally occurring. In Minnesota, arsenic sorbed or “stuck” to the aquifer sediments, especially to any iron and manganese oxides that coat them, is the most important source of this element to the groundwater. Only a very small percentage of the arsenic sorbed to aquifer sediment needs to be mobilized to make water unsafe for drinking, and research in Minnesota has shown that substantial amounts of sorbed or coprecipitated arsenic can be readily released from Minnesota's aquifer sediments (Erickson and Barnes 2005a). The weathering of minerals also may naturally contribute arsenic to the groundwater. Sulfide minerals, such as arsenopyrite (FeAsS) or pyrite (FeS_2), generally are the most important sources of arsenic (Smedley and Kinniburgh 2002). Pyrite can originate from ore bodies or may be formed in aquifers and sediments when little oxygen is present.

Human activities also may occasionally contribute arsenic to the groundwater. Arsenic was used in the past to produce semiconductors and as a wood preservative (chromated copper arsenate). Arsenic also was historically applied as a pesticide, but this use has decreased over time. The EPA banned the use of lead arsenate as a pesticide in 1988 (53 Fed. Reg. 24787), and most organic arsenic pesticide uses were cancelled by the EPA in 2009 (74 Fed. Reg. 50187) (FRL-8437-7).

Some of Minnesota's groundwater contains high enough arsenic concentrations to render the water unsafe for drinking. Erickson and Barnes (2005b) found that about 14% of the sampled wells in the State have arsenic concentrations that exceed the state class 1 domestic consumption use standard of 10 ug/L. This analysis primarily was based on databases of arsenic concentrations in the groundwater that were compiled during the 1990s. A substantial number of new wells constructed in the State also are affected by high arsenic concentrations. Since 2008, the State of Minnesota has required the water from new potable water-supply wells to be tested for arsenic. The data collected from this well testing have shown that 10% of the over 20,000 new wells drilled since about 2008 have concentrations that exceeded the state class 1 standard (Minnesota Department of Health 2019a). Domestic drinking water wells, which typically supply water to a single residence, usually have higher concentrations than public water supply wells (Erickson and Barnes 2005b).

Wells with exceedances of the arsenic class 1 standard are scattered across Minnesota (Figure 14); however, some parts of the state have a high percentage of wells with water with arsenic concentrations in excess of 10 ug/L. West-Central and South-Central Minnesota are two of these regions (Minnesota Department of Health 2008, Toner et al. 2011). In West-Central Minnesota, approximately 50% of the 869 domestic drinking water wells sampled as part of MDH's Minnesota Arsenic Study had arsenic concentrations of 10 ug/L or greater (Minnesota Department of Health and United States Agency for Toxic Substances Disease Registry 2001).

Figure 14. Arsenic concentrations in new private wells in Minnesota constructed from 2008-2017 [Figure courtesy of the Minnesota Department of Health].



Total Arsenic Concentrations in New Private Residential Wells (2008 - 2017)

Each arsenic sample was collected when the well was first drilled.

Each dot represents a single well. Map shows only wells where arsenic was detected.

Research continued to identify how arsenic is naturally released from the aquifer sediments into the state's groundwater. Nicholas et al. (2017) used a novel combination of identifying the solid-phase forms of arsenic on the aquifer and confining unit sediments along with historical well water chemistry data to propose the mechanisms associated with arsenic release in the groundwater. This research confirmed that the aquitard was the source of arsenic to the groundwater at two of the three assessed sites and that arsenic was released from the aquifer sediments into the groundwater by three different mechanisms, including desorption from the sediments, reductive dissolution of iron oxides, and oxidative dissolution of iron sulfides.

Manganese

Manganese is one of the most abundant elements in rocks and soils and naturally occurs in the groundwater under the appropriate geochemical conditions. Manganese is the fifth most abundant element in the earth's crust (United States Agency for Toxic Substances Disease Registry 2008). It is found in over 100 different minerals including sulfides, oxides, carbonates, and silicates (Minnesota Ground Water Association 2015), and many of these types of minerals are present in the state's aquifers. The amount of manganese dissolved in the groundwater depends on how many manganese-bearing minerals are present in the aquifer matrix as well as its geochemical conditions.

All organisms, such as plants and animals, require some manganese to live. Manganese is an essential trace element that is needed by several enzyme systems in the human body to function properly (Kies 1987). It also is an essential nutrient needed to make carbohydrates, amino acids, and cholesterol, and it is critical for cartilage, collagen, and bone synthesis. The MDH states that children over 8 years old and adults require 1,900 to 2,600 micrograms (ug) of manganese each day and infants need 600 ug each day (Minnesota Department of Health 2019b).

Exceeding the recommended amounts of manganese is harmful to human health, especially to infants. High doses of manganese cause neurological problems similar to Parkinson's disease, such as lethargy, tremors, and slow speech (U.S. Environmental Protection Agency 2004, Minnesota Ground Water Association 2015). This myriad of health effects is referred to as "manganism" and has been found in occupationally exposed adults, such as welders and workers at dry-cell battery factories and smelters (Huang 2007). Since the early 2000s, several studies have shown the exposure of infants and young children to manganese concentrations as low as 100 ug/L in water or infant formula causes problems with learning, motor skills, as well as problems with learning, behavior, and attention (Minnesota Ground Water Association 2015).

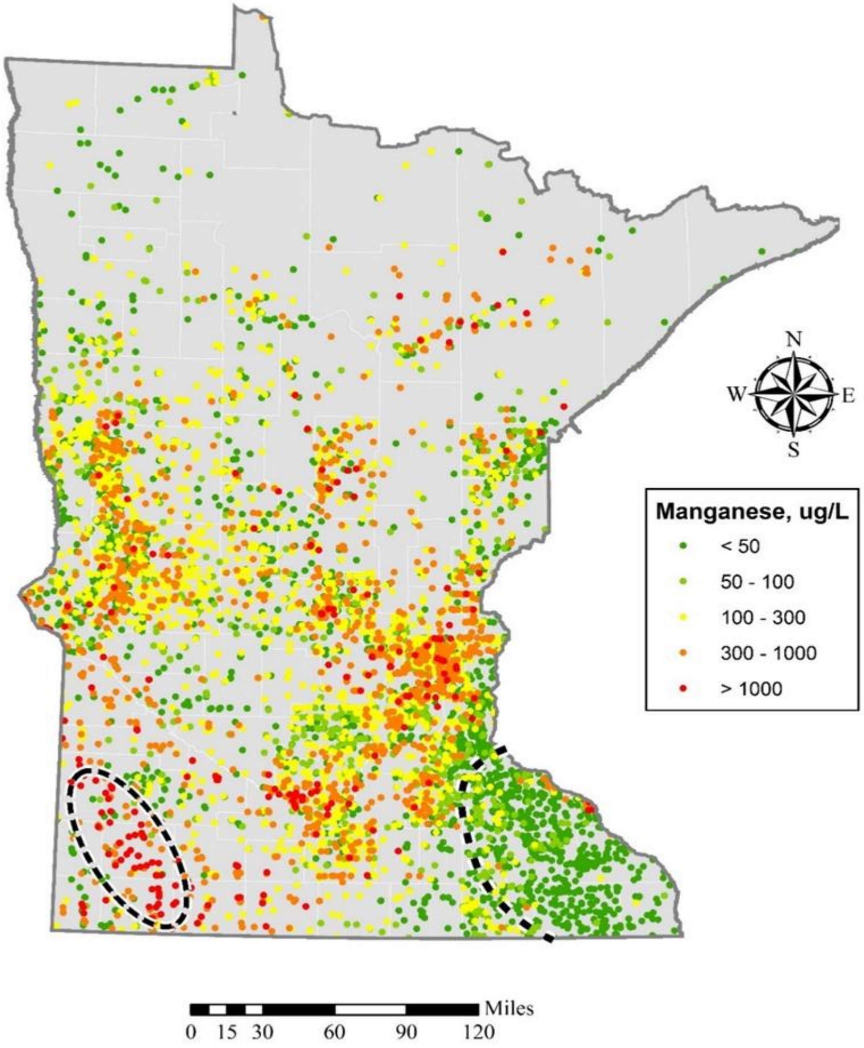
To prevent these health effects, the MDH set human health guidance for manganese in drinking water. The agency revised its human health guidance for this element in 2018 and set a health-based value (HBV) of 100 ug/L to protect children less than one year old who drink tap water or formula prepared from tap water. For households that do not include children less than one year old, the MDH states that the manganese concentration in the drinking water should be less than 300 ug/L (Minnesota Department of Health 2019b). The agency also found that water softeners may be effective at removing manganese from drinking water.

The distribution of manganese in the state's groundwater was recently assessed by the Minnesota Ground Water Association (2015) using over 8,000 records. This includes data collected by local units of government, the MPCA's ambient monitoring, the MDH's drinking water compliance and source water protection data, the DNR's County Geologic Atlas program, and the USGS's National Water-Quality Assessment. These data represent a range of aquifers that contain very young oxygenated water to those that have water that is thousands of years old.

This assessment showed that the manganese concentration in the state's groundwater is quite variable by location and aquifer. The reported concentrations ranged from less than 1 to 5,000 ug/L, and the median value was 101 ug/L. About 50% of the samples had manganese concentrations greater than 100 ug/L, and 22% had concentrations above 300 ug/L.

Concentrations in southeastern Minnesota typically were less than 50 ug/L (Figure 15). In contrast, in the southwestern part of the state concentrations typically were greater than 1,000 ug/L. An initial investigation of manganese in the state's groundwater conducted by the MDH, which used most of the same data sources as the Minnesota Ground Water Association investigation, found that manganese concentrations were higher in the state's sand and gravel aquifers compared to the Cretaceous and Paleozoic bedrock aquifers (Minnesota Department of Health 2012). The median concentrations in the state's surficial and buried artesian sand and gravel aquifers were 155 and 160 ug/L, respectively. Concentrations were lower in the Cretaceous and the bedrock aquifers composed of sandstone and carbonate rock, which had median concentrations ranging from 32 to 53 ug/L.

Figure 15. Manganese concentrations in Minnesota's groundwater [Figure from Minnesota Ground Water Association 2015].



Other Trace Elements

Many other trace elements are present to varying degrees in Minnesota's groundwater. The other trace elements routinely measured in the groundwater as part of the MPCA's Ambient Groundwater Monitoring Network, besides arsenic, iron, and manganese, are listed in table 5 along with summary statistics based on the most recent sampling of each well from 2013-2017. Similar to the results from an assessment of trace elements in all of the sand and gravel aquifers of glacial origin in the U.S. (Groschen et al. 2008), strontium and barium were the most frequently detected trace elements in the groundwater samples and lead, silver, and beryllium were detected the least, if at all.

The concentration of most of these trace elements did not exceed any applicable health guidance set by either the MDH or EPA. The MDH's 2017 risk assessment advice for boron was exceeded in water samples collected from two wells. One of these was a private drinking water well in Lyon County, and the other a monitoring well in Hennepin County. The MDH's 1994 HRL for zinc was exceeded in one shallow monitoring well in Beltrami County. This same well contained water with a cadmium concentration that approached the 2015 MDH HRL set for drinking water.

Table 5. Summary statistics of selected trace elements measured as part of the MPCA's Ambient Groundwater Monitoring Network, 2013-2017 [Summary statistics are based on the most recent sample collected from the well during this period; NA, not applicable; ND, not detected].

Element	Number of Wells with Detections	Detection Frequency	Reporting Limit	Median Concentration	Minimum Concentration	Maximum Concentration	Human health guidance
Strontium	296	98.6%	2-10 ug/L	96.8 ug/L	<2 ug/L	2,700 ug/L	3,000 ug/L[6]
Barium	266	89.9%	5-20 ug/L	46.5 ug/L	<5 ug/L	1,600 ug/L	2,000 ug/L[1,5]
Nickel	190	64.1%	1-50 ug/L	1.98 ug/L	<1 ug/L	30.1 ug/L	100 ug/L[1]
Boron	109	36.8%	20-200 ug/L	37.7 ug/L	<20 ug/L	791 ug/L	500 ug/L[2]
Chromium	81	27.5%	1-50 ug/L	1.5 ug/L	<1 ug/L	5.4 ug/L	100 ug/L[8]
Molybdenum	45	15.2%	1-5 ug/L	1.6 ug/L	<1 ug/L	8.06 ug/L	NA
Copper	43	14.5%	10-50 ug/L	21.9 ug/L	<10 ug/L	524 ug/L	1,300 ug/L[5]
Zinc	42	14.2%	10-100 ug/L	62.9 ug/L	<10 ug/L	2,060 ug/L	2000 ug/L[3]
Aluminum	32	10.8%	5-40 ug/L	46.4 ug/L	<5 ug/L	446 ug/L	NA
Cobalt	24	8.1%	1-5 ug/L	2.0 ug/L	<1 ug/L	6.6 ug/L	NA
Vanadium	19	6.4%	2-10 ug/L	3.2 ug/L	<2 ug/L	25.3 ug/L	50 ug/L[3]
Lithium	15	5.1%	20-100 ug/L	42.5 ug/L	<20 ug/L	129 ug/L	NA
Cadmium	8	2.7%	0.1-0.5 ug/L	0.18 ug/L	<0.1 ug/L	0.35 ug/L	0.5 ug/L[4] – 5 ug/L[8]
Titanium	5	1.7%	5-25 ug/L	8.0 ug/L	<5 ug/L	9.8 ug/L	NA
Lead	3	1.0%	1 ug/L	6.3 ug/L	<1 ug/L	10.8 ug/L	15 ug/L[7]
Silver	0	0.0%	0.2 – 5 ug/L	ND	<0.2 ug/L	ND	30 ug/L[1]
Beryllium	0	0%	0.4-2.0 ug/L	ND	<0.4 ug/L	ND	80 ng/L[1]-4,000 ng/L[8]

1. MDH 1993 health risk limit
2. MDH 2017 risk assessment advice
3. MDH 1994 health risk limit
4. MDH 2015 chronic health risk limit
5. EPA primary drinking water standard
6. MDH 2019 risk assessment advice
7. EPA action level
8. Minnesota state class 1 domestic consumption use standard

The highest concentrations of barium and strontium, the two most commonly detected trace elements in the groundwater, generally occurred in parts of the state where calcareous glacial deposits were present. The concentrations of both of these trace elements had a similar pattern in the groundwater. The highest concentrations typically were measured in groundwater in the TCMA, especially Anoka and Hennepin Counties, and south central, southeastern, and western Minnesota. In these areas, barium concentrations ranged from 5.4 to 1,600 ug/L, and strontium concentrations ranged from 9.7 to 2,700 ug/L. There was a moderately strong correlation between barium and strontium concentrations (Kendall's tau-b=0.4687, p=0.0000) which suggested a common source for both elements. Data from the shallow monitoring wells in the MPCA's network found that concentrations of both elements were significantly greater in parts of the state where the sand and gravel aquifers were composed of calcareous sediments compared to those made up of siliceous materials (Table 6).

This information, combined with the general statewide distribution of both elements in the groundwater, suggested that the presence of barium and strontium in the groundwater likely was related to naturally occurring minerals in the aquifer matrix. Both elements occur in many different types of rocks. The highest barium concentrations typically occur in shale, and barium sulfate ($BaSO_4$) is the principal mineral containing this element (Salminen et al. 2006). Strontium also is known to substitute for barium in $BaSO_4$ (Salminen et al. 2006) and also is present in calcareous rocks since it readily substitutes for calcium in the component minerals. A significant correlation between sulfate concentrations and barium (tau=0.3898, p=0.0000) and strontium (tau=0.3655, p=0.0000) was found which suggested that the distributions of both of these elements may be related to the presence of sulfate minerals in the aquifer matrix.

Table 6. Median concentrations of barium and strontium in the shallow sand and gravel aquifers, 2013-2017 by glacial lobe provenance.

Element	Median Concentration in Areas with Calcareous Glacial Sediments	Median Concentration in Areas with Siliceous Glacial Sediments
Barium[1]	**51.9 ug/L**	**25.5 ug/L**
Strontium[2]	**106 ug/L**	**85.4 ug/L**

1) Barium concentrations were significantly greater in the aquifers composed of calcareous sediments compared to those with siliceous sediments (p=0.0000).
2) Strontium concentrations were significantly greater in the aquifers composed of calcareous sediments compared to those with siliceous sediments (p=0.0115).

The presence and distribution of some trace elements in the groundwater, such as nickel and chromium, may have been the result of both natural and anthropogenic factors. The analysis of the data collected from the early warning component of the MPCA's ambient monitoring network showed that concentrations of these two elements were significantly higher in the shallow groundwater underlying commercial/industrial and sewered residential areas compared to the other assessed settings. This result suggested that the increased nickel and chromium concentrations may have resulted from human uses of these metals such as in alloys, batteries, coins, and plating. These land use associations only were statistically significant for the shallow sand and gravel aquifers formed from calcareous materials. The lack of a similar statistically significant relation between these metal concentrations and land use for the aquifers composed of siliceous glacial deposits might have been related to the naturally high nickel and chromium concentrations in the soils that occur in this part of the state. In northeastern Minnesota, the high concentrations in the groundwater were consistent with soils data collected by the USGS (Smith et al. 2014) that showed the highest nickel and chromium concentrations occurred in this area.

Boron concentrations in the groundwater typically were highest in southern and western Minnesota as well as in urban areas, especially the TCMA and St. Cloud. Like nickel and chromium, human and natural sources both contribute boron to the groundwater. Chemicals containing boron have many anthropogenic uses, including cleaning aids in detergents and the manufacturing of fiberglass insulation and borosilicate glass. Boron also occurs naturally in rocks and minerals, especially evaporite minerals and sedimentary rocks formed in marine environments. Information from the early warning component of the MPCA's monitoring network found that boron concentrations varied by both the source of the glacial deposits that form the sand and gravel aquifers and land use. Concentrations were significantly greater in the shallow aquifers formed by calcareous sediments compared to those formed by siliceous sediments. This was consistent with the composition of the rocks that are the source of the state's calcareous glacial deposits, which are located to the north and west of Minnesota and contain both sedimentary rocks and evaporite deposits. Boron concentrations also varied by land use setting in the shallow groundwater. Regardless of whether the sand and gravel aquifers were composed of siliceous or calcareous materials, the boron concentrations in the shallow groundwater underlying commercial/industrial and sewered residential areas were significantly greater than those in residential areas that use SSTS and undeveloped areas, which suggested human-caused contamination.

Zinc detections in the MPCA's groundwater samples were not due to natural or human-caused contamination, but primarily were an artifact of sampling some wells with metal casings, especially galvanized steel. The high zinc concentrations in these wells likely resulted from the corrosion of the galvanized coating on the well casing, which released zinc into the well water. Zinc was detected in 42 wells from 2013-2017. The majority of these wells (35) were constructed using metal well casings, and the remainder were either constructed using plastic well casing or there was no record regarding the type of casing used. The differences in zinc concentrations among wells constructed using galvanized steel, steel, or plastic well casings were statistically significant (p=0.000).

The highest zinc concentrations were measured in the 13 monitoring wells that were constructed using galvanized steel casing. The median concentration in these wells was 167 ug/L, and the maximum zinc concentration reported was 2,060 ug/L.

Wells constructed using steel casing also had significantly higher zinc concentrations compared to those constructed with PVC casing. The median concentration estimated using regression on order statistics (Helsel 2005) in the steel-cased wells was 10.5 ug/L, compared to 0.02 ug/L in the wells constructed with PVC casing. Zinc only was detected in a minute number of PVC-cased wells from 2013-2017. Only five of the 206 wells tested during this period had detectable zinc concentrations in the water, and one of these wells was constructed using a steel well screen. The higher concentrations in the steel-cased wells was consistent with research showing that the water in these wells is enriched in zinc and other trace metals including cadmium, chromium, and copper (Llopis 1991).

Volatile Organic Compounds (VOCs)

VOCs comprise a wide variety of chemicals that are emitted as gases from some liquids and solids. The chemical properties of VOCs allow them to readily move between the atmosphere, soil, surface water, and groundwater. Some of these chemicals readily degrade in the environment, while others persist for decades. Most VOCs are refined from petroleum, or are otherwise synthesized, and have many industrial, commercial, and household applications. These chemicals are found in gasoline, solvents, refrigerants, and many commonly used household products such as paints, spot cleaners, and glue (McDonald et al. 2018, Nazaroff and Weschler 2004). Some VOCs also are produced when drinking water is treated with chlorine to kill organisms in the water that may cause illness.

The presence of VOCs in drinking water or indoor air is a cause for concern because many of these chemicals are toxic and can persist for long periods of time once they reach the groundwater. Some VOCs, such as trichloroethylene (TCE), are known carcinogens. Others may harm the nervous system, liver, or kidneys or cause lung and skin irritation (Minnesota Department of Health 2019c). VOCs are not naturally occurring in the groundwater, so the detection of any of these chemicals indicates human impact.

Sources and Fate of VOCs in Groundwater

VOCs readily leach into the underlying groundwater once released into the soil and degrade over time, depending on aquifer conditions. The VOCs that contain more than two chlorine atoms, such as tetrachloroethylene (PERC) or TCE, slowly degrade only when the groundwater contains no oxygen. If the groundwater is oxygenated, these chemicals typically persist for many years.

Groundwater can become contaminated by VOCs when solvents are disposed of improperly, chemical or gasoline storage tanks leak, or chemicals are spilled on soil. Prior to our understanding that VOCs could easily contaminate groundwater, these chemicals were typically disposed by burying in landfills or simply dumping them on the ground. In the 1970s, passage of the federal Resource Conservation and Recovery Act (RCRA) and its amendments made it illegal to dispose of VOCs in this manner. Waste products containing VOCs are now collected and handled as hazardous waste.

In some circumstances, VOCs present in the groundwater may migrate upward through the soil and into the basements of buildings. This phenomenon is known as vapor intrusion, and people’s health can be adversely affected by inhaling these chemical vapors. Vapor intrusion can result from spills of chlorinated solvents like TCE or petroleum-related chemicals. However, chlorinated solvents typically are the most common sources (Minnesota Pollution Control Agency 2019) because the relatively rapid degradation of petroleum-related chemicals often limits their potential for vapor intrusion (U.S. Environmental Protection Agency 2012).

Sites where large quantities of VOCs were disposed of in the past are the major focus of groundwater remediation. Over the past 20 years, state or federal programs have addressed contamination from VOCs at thousands of chemical release sites across Minnesota. The remediation efforts at these sites are managed by either federal environmental cleanup programs such as the hazardous waste (RCRA) and Superfund programs, or Minnesota state cleanup programs such as the state Superfund Program, the Voluntary Cleanup and Investigation program, and the Petroleum Remediation Program. Over the years, these remediation programs have worked on almost 21,000 sites across Minnesota. The majority of these sites no longer require active remediation and monitoring. There are about 1,700 active remediation sites in Minnesota. These sites mostly are relatively small, and most of them have a less than one acre of land where the underlying groundwater is contaminated.

The atmosphere is another source of VOCs to the groundwater. Emissions of non-combusted and partially-combusted fuels from vehicles are a major source of VOCs to the air. Non-vehicular VOC sources, however, are becoming increasingly important VOC sources as vehicle emissions have decreased over time due to pollution prevention efforts (McDonald et al. 2018). Once emitted into the air, the VOCs are quickly scavenged by raindrops (Slinn et al. 1978) and can enter the groundwater by infiltrating precipitation (Pankow et al. 1997, Yu et al. 2017). The incomplete combustion of fuels results in VOCs being deposited on surfaces (Revitt et al. 2014), which can be transported to the groundwater by infiltrating water.

Occurrence and Distribution in Minnesota's Groundwater

From 2013-2017, the MPCA sampled its ambient groundwater monitoring network for 68 different VOCs. The measured chemicals, along with common sources and the laboratory reporting limits, are listed in Appendix C.

VOCs were not detected very frequently. From 2013-2017, the MPCA tested 275 ambient network wells for these chemicals. The percentage of the sampled wells with detectable VOC concentrations ranged from 5% in 2015 to 8% in 2013 and 2014.

Detected concentrations of VOCs in ambient groundwater were typically low (less than 1 ug/L). Seventy-five percent of the VOCs detected in Minnesota's ambient groundwater were at this concentration or less. This was very similar to the results from a national-scale assessment. Zogorski et al. (2006) reported that 90% of the VOC concentrations measured throughout the U.S. were less than 1 ug/L.

Most of the VOCs detected in Minnesota's ambient groundwater were found in shallow wells. VOCs were detected at least once in 51 ambient monitoring network wells from 2013-2017, and 88% of these were monitoring wells that were screened near the water table. The median well depth was 20 feet. The water in these wells was not used for drinking. VOCs were detected in a few of the sampled bedrock aquifer wells. Six of the 39 sampled bedrock aquifer wells had VOCs detected in them. One of these wells was shallow (52 feet deep), and another one was near a known contaminant plume in the eastern TCMA.

Very few of the VOCs that were on the extensive list analyzed by the MPCA were detected in the ambient groundwater. From 2013-2017, 22 of the 68 analyzed VOCs (32%) were detected at least once during this period, and only 13 of the 68 analyzed VOCs (19%) were detected more than once (Table 7). The more frequently detected VOCs (excluding the xylenes and chloromethane) were the disinfection byproduct, chloroform; the solvents PERC, TCE, and their degradation product cis-1,2-dichloroethylene. The occurrence and distribution of these chemicals in the groundwater will be discussed more in the subsequent sections of this report.

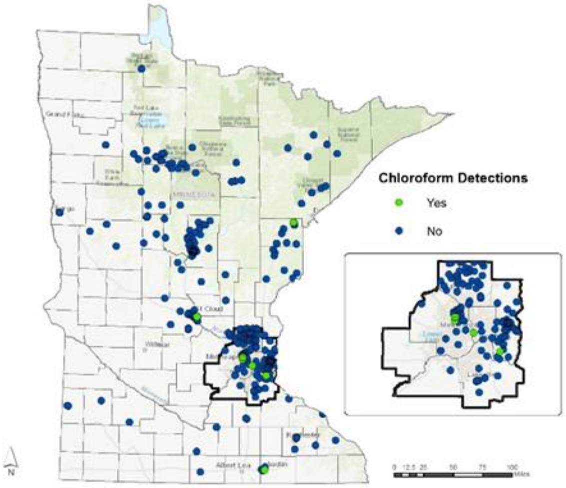
Table 7. Detection frequencies and concentration ranges for volatile organic compounds detected in the ambient groundwater, 2013-2017 [statistics are based on the most recent sampling of the well during this period].

Chemical Name	CAS Number	Median Concentration	Detection Frequency	Range in Detected Concentrations	Method Reporting Limit
Chloroform	67-66-3	0.23 ug/L	2.1 %	0.10 – 11.0 ug/L	0.1 – 0.2 ug/L
Tetrachloroethylene	127-18-4	0.55 ug/L	1.3 %	0.21 – 3.9 ug/L	0.2 – 0.4 ug/L
Trichloroethylene	79-01-6	1.0 ug/L	1.0 %	0.10 – 46.0 ug/L	0.1 – 0.2 ug/L
Cis-1,2-Dichloroethylene	156-59-2	0.64 ug/L	0.9 %	0.23 – 1.5 ug/L	0.2 – 0.4 ug/L
Toluene	108-88-3	0.62 ug/L	0.9 %	0.21 – 8.3 ug/L	0.2 – 0.4 ug/L
m-Dichlorobenzene	541-73-1	0.27 ug/L	0.5 %	0.21 – 1.3 ug/L	0.2 – 0.4 ug/L
Ethylbenzene	100-41-4	0.68 ug/L	0.4 %	0.51 – 3.2 ug/L	0.5 – 1.0 ug/L
Benzene	71-43-2	0.59 ug/L	0.3 %	0.35 – 0.91 ug/L	0.2 – 0.4 ug/L
1,1-Dichloroethane	75-34-3	0.32 ug/L	0.2 %	0.28 – 0.37 ug/L	0.2 – 0.4 ug/L
Dichlorobromomethane	75-27-4	0.99 ug/L	0.2%	0.24 – 1.0 ug/L	0.2 – 0.4 ug/L
Dichlorodifluoromethane	75-71-8	1.5 ug/L	0.2 %	1.3 – 2.1 ug/L	1.0 – 2.0 ug/L
p-Isopropyltoluene	99-87-6	0.85 ug/L	0.2 %	0.81 – 1.2 ug/L	0.5 – 1.0 ug/L
Trans-1,2-Dichloroethylene	156-60-5	0.12 ug/L	0.2 %	0.12 – 0.13 ug/L	0.1 – 0.2 ug/L
1,2,4-Trimethylbenzene	95-63-6	6.9 ug/L	0.07 %	6.90 ug/L	0.5 – 1.0 ug/L
1,3,5-Trimethylbenzene	108-67-8	1.4 ug/L	0.07 %	1.40 ug/L	0.5 – 1.0 ug/L
Acetone	67-64-1	25 ug/L	0.07 %	25 ug/L	20 – 40 ug/L
Cumene	98-82-8	1.1 ug/L	0.07 %	1.10 ug/L	0.5 – 1.0 ug/L
Methyl ethyl ketone	78-93-3	23 ug/L	0.07 %	23 ug/L	10 – 20 ug/L
n-Propylbenzene	103-65-1	2.0 ug/L	0.07 %	2.0 ug/L	0.5 – 1.0 ug/L
Naphthalene	91-20-3	1.6 ug/L	0.07 %	1.6 ug/L	1.0 – 2.0 ug/L
Sec-Butylbenzene	135-98-8	1.6 ug/L	0.07 %	1.6 ug/L	0.5 – 1.0 ug/L
Tetrahydrofuran	109-99-9	14 ug/L	0.07 %	14 ug/L	10 – 20 ug/L

Chloroform

Chloroform was the most-frequently detected VOC in Minnesota's ambient groundwater. This chemical is formed by the chlorination of drinking water, wastewater, and swimming and whirlpool water (Research Triangle Institute and United States Agency for Toxic Substances Disease Registry 1997). It also can be released into the environment during its manufacture and use. Detections of this chemical generally were sporadic. In the majority of the wells with detections, chloroform was only detected once in all of the samples collected from 2013-2017. The wells with chloroform detections also were shallow and ranged from 14 to 72 feet deep. Most of them also were constructed specifically for monitoring the groundwater. The wells with chloroform detections were mainly located in urban areas including the TCMA, St. Cloud, and a few smaller cities (Figure 16).

Figure 16. Chloroform detections in the ambient groundwater, 2013-2017 [Map shows the most recent chloroform detection at each sampled well].



Service Layer Credits: Sources: Esri, HERE, Garmin, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, © OpenStreetMap contributors, and the GIS User Community

The measured chloroform concentrations were all lower than the 20 ug/L HRL set by the MDH in 2018 to prevent against liver damage, developmental problems, and suppression of the immune system. Eighty-nine percent of the detected concentrations were less than 1 ug/L, and the highest concentration measured was 11 ug/L.

The use of disinfected public water and its eventual recharge into the groundwater was the likely source of the chloroform found in the ambient groundwater. The one common feature among all of the wells with any chloroform detections from 2013-2017 was that they were located in areas served by municipal water-supply systems that disinfect their water using chlorine or chloramines (Austin Utilities 2016, City of Brooklyn Center 2018, City of Baxter 2019, City of Cloquet 2018, City of St. Cloud 2018, City of Saint Paul 2018, City of Sturgeon Lake 2011, Lincoln-Pipestone Rural Water 2017, Rochester Public Utilities 2017). It is likely that some of the disinfected drinking water recharged the groundwater after it was used for activities like lawn, golf course, athletic field, and garden irrigation. Disinfected waters also may have entered the groundwater through leaking water distribution or sewer pipes.

Tetrachloroethylene

PERC was the second most-commonly detected VOC in the ambient groundwater. This chemical is a solvent whose major uses are dry cleaning and metal parts degreasing (World Health Organization 2006). The MPCA detected PERC in six wells from 2013-2017. Five of these were shallow monitoring wells (19.5 to 48 feet deep) that were located within or less than one-half mile from commercial/industrial areas. Four of these wells were located within the TCMA, and the other was located in southern Minnesota. The only other well where PERC was detected was a 133-foot deep water supply well in the eastern part of the TCMA.

None of the measured concentrations exceeded the 4 ug/L HBV set by the MDH in 2014 to prevent cancer. However, the concentration measured in one shallow monitoring well in St. Paul (3.9 ug/L) was very close to the HBV.

Only one of the tested wells had sufficient data to determine trends in PERC concentrations. This was the 133-foot deep water supply well in the eastern TCMA. The MPCA sampled this well from 2004-2017 and the concentrations did not significantly change during this period ($p=0.1177$).

Trichloroethylene

TCE, a solvent whose major use is to degrease metal parts, was detected in five wells from 2013-2017. Similar to the results for PERC, TCE mostly was detected in shallow monitoring wells, ranging from 16 to 48 feet deep that were located near or within commercial/industrial areas. Two of these wells also had PERC detected in them; these two wells were located a few hundred feet apart and were approximately one-half mile south of a commercial/industrial area in St. Paul. The two other monitoring wells with TCE detections were located in commercial/industrial areas in Wadena and Sherburne Counties.

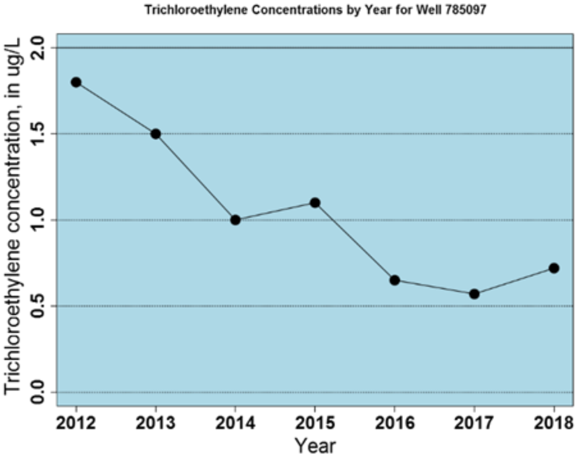
The highest TCE concentrations were measured in the two monitoring wells in St. Paul. In these wells, concentrations as high as 46 ug/L were reported.

TCE was detected in one of the sampled domestic wells. This well was 285 feet deep and was located within the TCE contamination plume that emanates from the Baytown Township Groundwater Contamination site. This well-known source of groundwater contamination in the TCMA encompasses 12.5 square miles in Washington County (Minnesota Pollution Control Agency 2007). The TCE in this well water likely was not consumed because the water samples for this study were drawn from the untreated outside water spigot, and the residence's drinking water-supply has had a carbon filter installed on it since 2004 to remove any TCE from it (K. Schroeder, Minnesota Pollution Control Agency, personal communication, 2016).

Most of the measured TCE concentrations exceeded the MDH's recently updated human health guidance. Since the MPCA published its last Groundwater Condition Report in 2013, the MDH lowered its human health guidance for TCE by more than 10 times due to new toxicity and health effects data (Minnesota Department of Health 2013). These new human health guidance values were promulgated as HRLs in 2015. The updated chronic value was lowered to 0.4 ug/L to prevent against developmental and immune system effects, such as heart defects in a developing fetus during the first trimester, hypersensitivity, or developing an autoimmune disease. The cancer value was lowered to 2 ug/L. All five of the wells with TCE detections had concentrations that exceeded the 0.4 ug/L HRL set for chronic exposure at least once from 2013-2017. In three of the five sampled wells, TCE concentrations exceeded the 2 ug/L cancer HRL set by the MDH in 2015. One of these three wells was the previously discussed well near the Baytown Township Groundwater Contamination site, and the other two were monitoring wells located south of a commercial/industrial area in St. Paul.

One of the wells had sufficient data to determine whether TCE concentrations changed over time. This was a monitoring well in Elk River, which was sampled from 2012-2017. TCE concentrations in this well have steadily decreased from 1.8 ug/L in 2012 to 0.57 ug/L in 2017, which was statistically significant ($p=0.0355$) (Figure 17).

Figure 17. Trichloroethlyene concentration declines at monitoring well 785097 in Sherburne County, Minnesota.



Cis-1,2-Dichloroethylene

Many of the same wells with TCE detections also had cis-1,2-dichloroethylene detected in the water. The measured concentrations all were less than the chronic HRL of 6 ug/L set by the MDH in 2018. This chemical was the fourth most-commonly detected VOC in the groundwater and is produced when TCE or PERC is degraded in the environment (World Health Organization 2006). This chemical also is used to manufacture solvents and chemical mixtures (United States Agency for Toxic Substances Disease Registry 1997). The MPCA detected cis-1,2-dichloroethylene in four monitoring wells that ranged from 15 to 48 feet deep. All of these wells were located near or within commercial/industrial areas in the City of St. Paul, Sherburne County, and Wadena County. Three of the four wells with cis-1,2-dichloroethylene detections also had TCE in them, which suggested that the cis-1,2-dichloroethylene present in these three wells may have resulted from TCE degradation.

Per - and Polyfluorinated Alkyl Substances (PFAS)

PFAS are a class of over 6,000 manmade chemicals used worldwide to manufacture products that are heat and stain resistant and repel water. These chemicals are in a wide variety of products including water- and stain-resistant fabric; carpet; coatings on paper products such as popcorn bags, chip bags, or fast-food wrappers; floor polish; personal care products; non-stick cookware; fire-fighting foam; and certain insecticides.

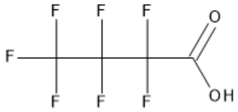
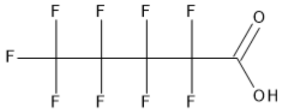
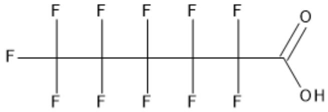
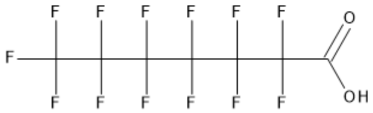
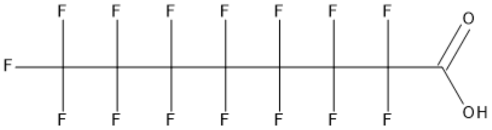
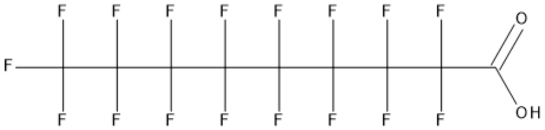
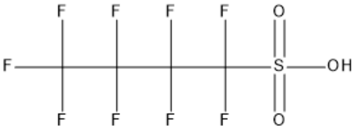
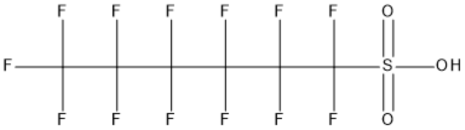
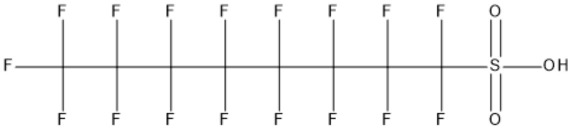
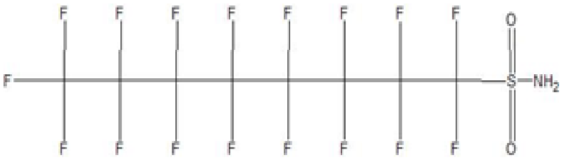
The presence of PFAS in the environment and the resulting exposure is a concern because these chemicals accumulate in humans and animals and several of them are known to be toxic. PFAS have been found in fish, reptiles, and mammals all over the globe, and these chemicals biomagnify in birds and marine mammals (Houde et al. 2011). In addition, PFAS are persistent in the environment and do not readily break down. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are the two most studied PFAS. Toxicity studies indicate these cause developmental problems to fetuses, cancer, liver damage, and immune and thyroid effects. The EPA set lifetime health advisories for PFOA and PFOS at 70 ng/L in drinking water in May 2016. In Minnesota, the MDH has established human health guidance for PFAS in drinking water since 2002, which are periodically updated after new toxicological information are published. In May 2017, the MDH revised its human health guidance for PFOA, setting a HRL of 35 ng/L. In 2019, the agency lowered its guidance for PFOS, setting a HBV of 15 ng/L. These values, much lower than EPA's, are meant to protect the health of breastfeeding infants. The MDH also has set human health guidance for three other PFAS, perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS), and perfluorohexane sulfonate (PFHxS). In 2017, the MDH lowered its human health guidance for PFBS, setting a HBV of 2,000 ng/L. The agency also reevaluated its human health guidance for PFBA at the same time; however, the HRL set in 2018 remained at 7,000 ng/L. In 2019, the MDH set a HBV of 47 ng/L for PFHxS.

In Minnesota, PFAS are of particular interest because this is one of the few places in the nation where these chemicals are made. Two well-known PFAS, PFOS and PFOA, were manufactured at a 3M facility in the city of Cottage Grove from the late 1940s until 2002 when the company voluntarily phased out the production of these chemicals. The disposal of fluorochemical manufacturing wastes from this facility prior to the enactment of hazardous waste laws several decades ago caused contamination of the area's aquifers as well as surface waters and fish.

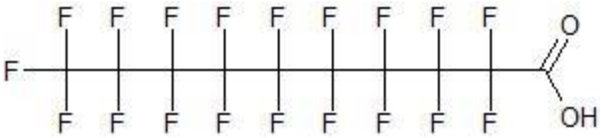
The MPCA periodically sampled the groundwater for PFAS outside of this known area with industrial contamination to determine the occurrence and distribution of these chemicals in the ambient environment. The agency sampled the ambient groundwater twice for PFAS between 2013 and 2017. The first sampling event was the largest and was conducted in 2013. During this time, the MPCA still was actively installing new wells to its monitoring network, so the PFAS investigation only included the network wells that were in existence at that time, which was almost 200. A more limited follow-up PFAS sampling was conducted in 2017. This event focused on 12 wells that had the highest concentrations in 2013 primarily to determine whether concentrations had changed.

Both of these studies measured a small number of the known PFAS. The 2013 and 2017 MPCA ambient groundwater assessments monitored for 13 PFAS; these primarily were perfluoroalkyl acids (Table 8). These PFAS consist mainly of a carboxylate (COOH) or sulfonate (SO_3H) functional group attached to a "perfluorinated chain" of varying length. The perfluoroalkyl acids that contain seven or more carbon atoms in their perfluorinated chain, such as PFOA and PFOS, are termed "long-chain PFAS" and are recognized as bioaccumulative and toxic in the environment (Scheringer et al. 2014).

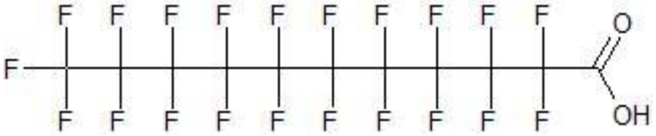
Table 8. Perfluorinated Substances Measured in the 2013 and 2017 MPCA Ambient Groundwater Assessments.

Chemical Name	Structure
Perfluorobutanoic acid (PFBA)	
Perfluoropentanoic acid (PFPeA)	
Perfluorohexanoic acid (PFHxA)	
Perfluoroheptanoic acid (PFHpA)	
Perfluorooctanoic acid (PFOA)	
Perfluorononanoic acid (PFNA)	
Perfluorobutanesulfonate (PFBS)	
Perfluorohexanesulfonate (PFHxS)	
Perfluorooctanesulfonate (PFOS)	
Perfluorooctanesulfonamide (PFOSA)	

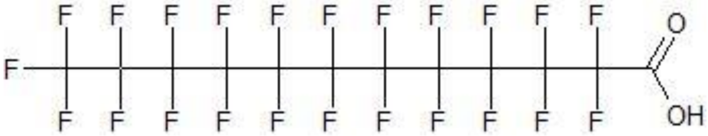
Perfluorodecanoate (PFDA)



Perfluoroundecanoate (PFUnA)



Perfluorododecanoate (PFDoDA)



The use of many of the PFAS analyzed as part of these two investigations has declined or ceased in the U.S. and other countries (Ritter 2010). Since 2006, the EPA worked with the leading companies that produce PFAS to participate in a global stewardship program to achieve the goal of eliminating PFOA and other similar chemicals with long perfluorinated chains by 2015. Long-chain PFAS are considered by the EPA to be perfluoroalkyl carboxylic acids containing eight or more carbon atoms (e.g. PFOA), and perfluoroalkylsulfonates containing six or more carbon atoms (e.g. PFHxS and PFOS). Eight long-chain PFAS were part of the 13 analyzed in the water samples for this investigation. The EPA also regulated 191 PFAS, including the long-chain PFAS, through orders and significant new use rules (U.S. Environmental Protection Agency 2019) under the Toxic Substances Control Act. Despite these changes, it still remains important to assess the presence of these types of PFAS in the environment because of their extreme persistence.

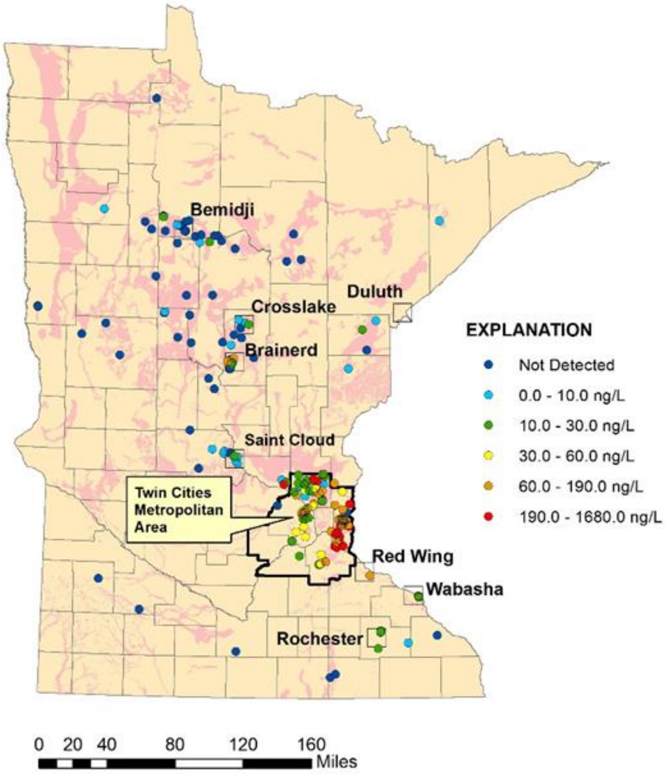
The replacement chemicals for the long-chain PFAS were not monitored in Minnesota's ambient groundwater. A number of new PFAS were developed and marketed since the phase-out of PFOA, PFOS, and their related chemicals. HFPO-DA (the major component of GenX) and ADONA are two perfluoropolyethers that are now used to manufacture fluorinated polymers. Another replacement chemical is F-53B, which is a chlorinated polyfluorinated ether sulfonate used in metal plating. F-53B has been produced for several decades but was first detected in the environment in 2013. Replacement PFAS in AFFF include fluorotelomer sulfonamide alkylbetaines and fluorotelomer sulfonamide aminoxides.

2013 Statewide Investigation

The 2013 investigation (Kroening 2017) found that PFBA was the most commonly detected PFAS in the ambient groundwater, being found in almost 70% of the sampled wells (Figure 18). Again, most of the wells sampled for this study primarily were located in areas susceptible to groundwater contamination from the land surface and contained water that was recently recharged from the land surface. The highest PFBA concentration measured was 1,680 ng/L, which was detected in a domestic water supply well in Washington County. This concentration, however, was well below the 7,000 ng/L human health limit set by the MDH.

PFAS detections and concentrations in the ambient groundwater also were associated with urban land use. The 2013 study found that one or two PFAS typically were detected in the ambient groundwater in urban areas, but these chemicals typically were not detected in the groundwater underlying forested, undeveloped areas. This suggests that most of the PFAS measured in the ambient groundwater originated from the chemicals being disposed to the land surface rather than regional atmospheric deposition.

Figure 18. Perfluorobutanoic acid in Minnesota's ambient groundwater, 2013 [Figure from Kroening (2017)].



PFOA was detected in about 30% of the wells tested in 2013. Eight of these wells contained water with concentrations that exceeded the HBV of 35 ng/L set by the MDH in 2017. Some of the wells with water exceeding the PFOA HBV were located in Washington County, where there was known industrial PFAS contamination. The concentrations in these wells ranged from 38 to 64 ng/L. The other wells with concentrations exceeding the PFOA HBV were located near the cities of Brainerd and Wabasha. The well in Brainerd, a 44-foot deep monitoring well in a residential area, contained water with a PFOA concentration of 61 ng/L. The well in the vicinity of Wabasha was a 58-foot deep domestic water supply well and contained water with a PFOA concentration of 74 ng/L.

PFOS was detected in about 12% of the sampled wells tested in 2013, and seven of these wells contained water with concentrations that exceeded the 15 ng/L HBV set by the MDH in 2019. Four of the wells with concentrations exceeding the HBV were located in the TCMA, and the remaining three were located in the vicinity of the cities of Brainerd and Wabasha. The highest PFOS concentrations (98 – 98.8 ng/L) were measured in two shallow monitoring wells (15-19 feet deep) in Anoka and Hennepin Counties. The two wells in the vicinity of Brainerd with exceedances of the PFOS HBV also were shallow (18-44 feet deep) and intersected the water table. The 44-foot deep well near Brainerd was the same one that contained water with a PFOA concentration that exceeded the MDH HBV. Two of the sampled domestic water supply wells contained water with PFOS concentrations that exceeded the HBV. One of these wells was located near the known industrial contamination in Washington County, and the other was a 66-foot deep domestic water supply well in the vicinity of Wabasha. The well near the City of Wabasha was located in the same neighborhood as the domestic well that had a PFOA concentration that exceeded the HBV.

PFHxS was detected in about 11 percent of the wells sampled in 2013. Three of the sampled wells contained water with concentrations greater than 47 ng/L, the HBV set by MDH in 2019. Two of the wells with concentrations exceeding the HBV were shallow monitoring wells (16-18 feet deep) in the TCMA, and the other was a shallow monitoring well (44 feet deep) located in the vicinity of Brainerd.

A couple of the sampled wells had a notable number of PFAS detections or high concentrations of some of the chemicals. All of the 13 analyzed PFAS were measured in the 44-foot deep monitoring well in the vicinity of Brainerd that also contained the high PFOA, PFOS, and PFHxS concentrations. This well also contained the highest measured PFPeA (87.4 ng/L) and PFHpA (123 ng/L) concentrations. A monitoring well in Anoka County contained water with the highest PFHxS (3,580 ng/L) and PFBS concentrations (555 ng/L) measured in the 2013 investigation. The PFHxS concentration in this well was over 10 times greater than those measured of any other sampled wells.

2017-Limited Follow-up Sampling

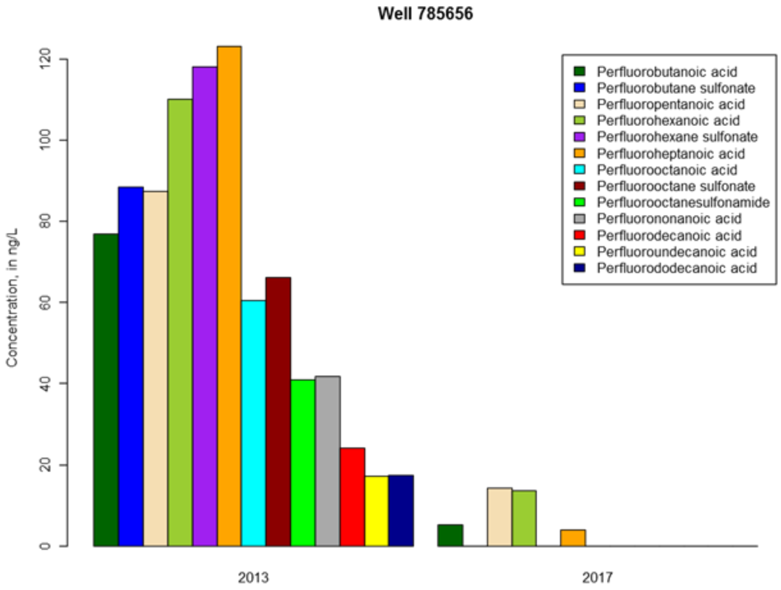
The limited follow-up sampling in 2017 showed that PFAS detections and concentrations did not remain the same in many of the resampled wells. Changes in the occurrence and distribution of these chemicals in the ambient groundwater were not unexpected since the types of PFAS used in products changed over the last 10 years. In addition, most of the sampled wells intersected the water table and contained very young groundwater that would be expected to respond rapidly to changes in pollutant inputs. Even the few deep domestic water-supply wells that were resampled were located in aquifers that are vulnerable to contamination from the land surface.

This sampling showed that the number of PFAS detections drastically declined in the monitoring well located near the City of Brainerd that had all 13 analyzed PFAS were detected in it in 2013. Only four PFAS were detected in this well in 2017, and the measured concentrations were at least five times lower than the concentrations measured in 2013 (Figure 19, Table 9).

Table 9. Concentrations of selected PFAS measured in well 785656 in Crow Wing County in 2013 and 2017.

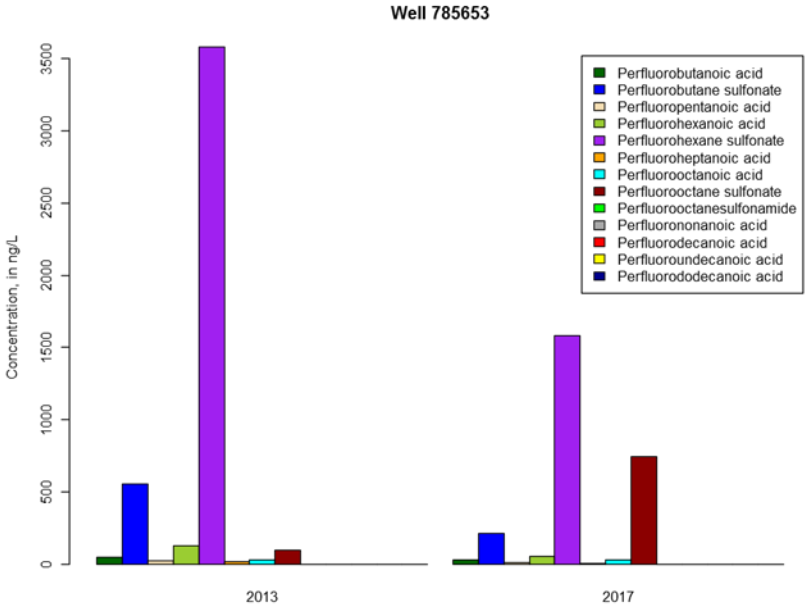
Chemical	2013 Concentration	2017 Concentration
PFBA	76.9 ng/L	5.2 ng/L
PFPeA	87.4 ng/L	14.3 ng/L
PFHxA	110 ng/L	13.5 ng/L
PFHpA	123 ng/L	3.96 ng/L

Figure 19. PFAS concentrations in monitoring well 785656 in Crow Wing County, 2013 and 2017



Large changes in PFAS concentrations also were seen in a shallow monitoring well in Anoka County. In 2013, this well had the highest measured PFHxS concentration (3,580 ng/L); however, the concentration decreased by more than one-half to 1,580 ng/L in 2017 (Figure 20). The concentrations of a few other PFAS in this well also had notable declines from 2013 to 2017. The PFBS concentration in this well decreased from 555 to 215 ng/L, and the PFHxA concentration decreased from 124 to 50.7 ng/L.

Figure 20. PFAS detections in monitoring well 785653 in Anoka County, 2013 and 2017.



This same well, however, showed an increase in the PFOS concentration. In 2017, the concentration in this well increased substantially to 745 ng/L. This was over 25 times greater than the HBV set by MDH in 2017. The exact cause of the increased concentration in this well was not known, but it might have been due to the use of products in which PFOS still is permitted, such as mist suppressants for plating operations, or the use old stocks of PFOS-containing chemicals.

The 2017 resampling also showed that PFHxS, PFOA, or PFOS concentrations decreased by more than one-half in most of the wells sampled outside of Washington County (Table 10). The domestic water-supply wells near Wabasha that contained water with PFOA or PFOS concentrations that exceeded the 2017 HBVs set by the MDH could not be accessed for resampling. Another water supply well in the same vicinity of these two wells was resampled in 2017, and the PFOS concentration in it decreased by more than one-half from 2013-2017.

The concentrations of most of these chemicals largely stayed the same or even increased in the monitoring and domestic water-supply wells in Washington County. The PFOA and PFOS concentrations increased by more than 50% in one monitoring well in Washington County (well #778336, Table 10).

Table 10. PFHxS, PFOA, and PFOS concentrations measured in selected wells in 2013 and 2017.

Well	County	PFHxS		PFOA		PFOS	
		2013	2017	2013	2017	2013	2017
404244	Washington	<5.68	<5.0	8.51-12.8	14.6	<4.72-7.05	8.66
406163	Washington	< 4.93	5.12	29.3	27.3	31.4	29
474571	Wabasha	< 4.51	< 5.1	2.49	< 2.55	23.2	10.6
560422	Hennepin	337	27.3	25	12.4	45.9	16.9
560426	Hennepin	26.6	39.1	11.4	5.6	98.8	114
778334	Washington	9.23	11.2	45.1	67.8	< 5.01	< 4.83
778336	Washington	< 5.22	6.76	26.7	69.2	10.3	63.1
778353	Washington	<6.11	<4.89	43.8	29.2	< 6.11	< 4.89
785653	Anoka	3580	1580	26.7	26.4	98	745
785656	Crow Wing	118	<5.03	60.5	<2.52	66.1	< 5.03
786964	Crow Wing	9.99	<4.83	7.58	2.64	59.4	14.6

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.

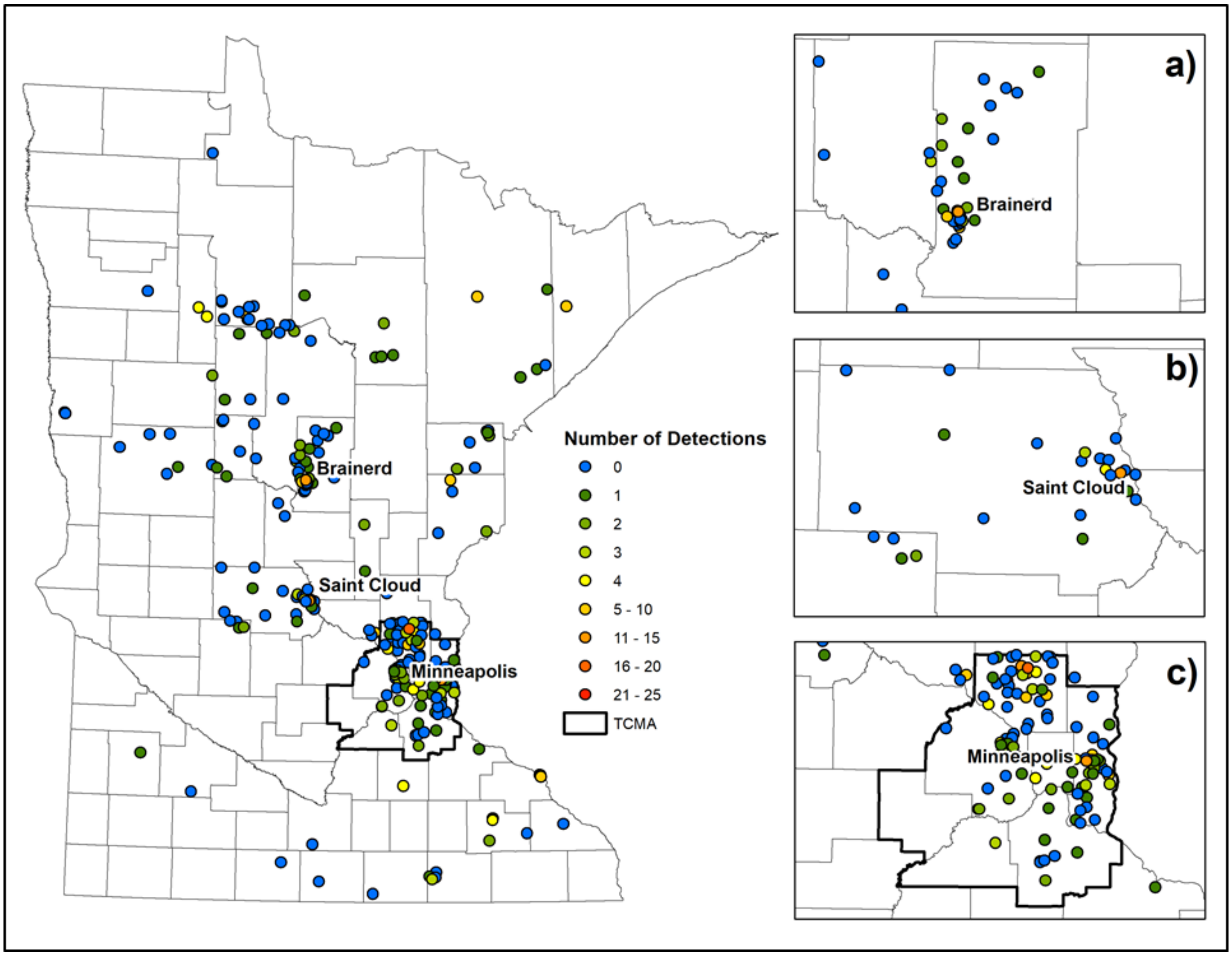
The release of CECs into the environment is of a particular concern because they may affect ecological or human health. The effect of chronic exposure to low levels of most of these chemicals to human or aquatic life often is not known. In addition, some of these chemicals function as endocrine active chemicals (EACs). EACs 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) were 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 132 CECs by SGS

AXYS Analytical Services in British Columbia. This change was made to maintain consistency between the CECs analyzed in the agency's groundwater and surface water monitoring programs. A complete list of contaminants analyzed and the analytical methods are included in Appendix D.

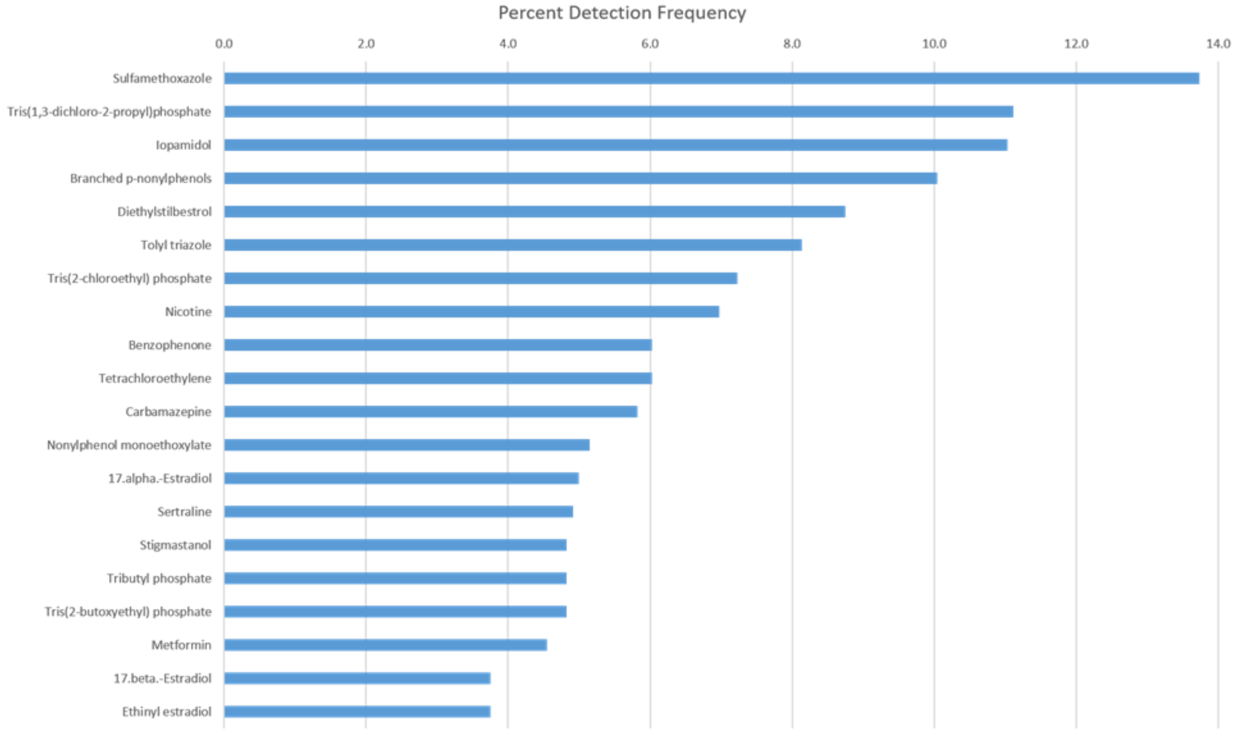
CECs were detected in a substantial number of the network wells, which again mainly were located in settings that are naturally vulnerable to human-caused pollution. From 2013-2017, CECs were detected in 124 of the 262 wells sampled for these chemicals (Figure 21). The number of CEC detections in these wells ranged from one to 23. The two wells with the greatest number of detections specifically were installed to monitor contamination near old, unlined landfills, which are a known CEC source (Cordy et al. 2004, Masoner et al. 2016). The number of CEC detections was smaller in most of the other sampled wells. Ninety-five percent of the sampled wells had seven or fewer CEC detections in them, and the average number detected in a well was 1.6.

Figure 21. Number of contaminants of emerging concern detected in the ambient groundwater statewide and in three urban areas, 2013-2017. a) Brainerd, b) Saint Cloud, and c) Minneapolis-St. Paul Metropolitan Area



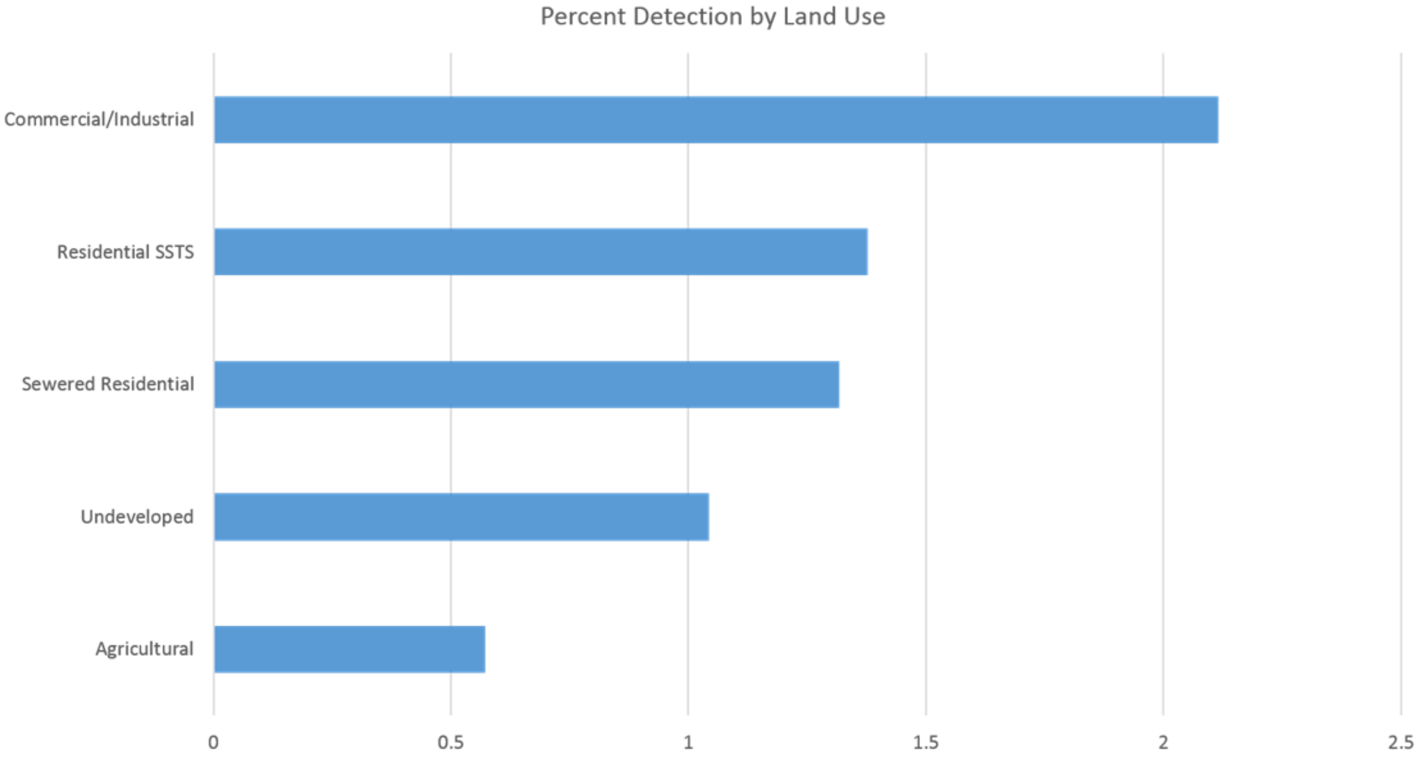
The most commonly detected CECs in the ambient groundwater were chemicals that are known to be persistent in the environment. Seventy-seven CECs were detected in the groundwater from 2013-2017 with frequency of 1.0% and greater. The most-frequently detected CECs were sulfamethoxazole, tris (1,3-dichloro-2-propyl)phosphate (TDCPP), iopamidol, and branched p-nonylphenols (Figure 22). These chemicals have very different uses. Sulfamethoxazole is an antibiotic used to treat bacterial infections. Iopamidol is a radio-opaque contrast agent, which is used for x-ray imaging, such as computed tomography (CTs), projectional radiography, and fluoroscopy. TDCPP is a chlorinated organophosphate and is commonly used as a flame retardant as well as a pesticide, plasticizer, and nerve gas. Branched p-nonylphenols are not a single chemical but a mixture of nonylphenols (U.S. Environmental Protection Agency 2010). These chemicals consist of a phenol ring that typically has a branched nonylphenol group attached to it in the *para*- position. The main use of nonylphenols is to manufacture nonanionic surfactants and nonylphenol ethoxylates (NPE), but they also are found in lubricants. NPE was used to make both household and industrial detergents; however, its use in household detergents has been eliminated (U.S. Environmental Protection Agency 2010). Nonylphenols also are considered an EAC. Common features among these four CECs is that they are widely used, resistant to degradation, and persist in the environment (Ternes and Hirsch 2000, Mao et al. 2012, Saint-Hilaire and Jans 2013, Wendel et al. 2014). All detections were within the applicable human health limits set by the EPA and MDH.

Figure 22. Detection frequencies for selected CECs in the ambient groundwater, 2013-2017.



Land use also was a factor in the number of CECs detected in the groundwater. To better understand the effect of land use on the occurrence of CECs in the groundwater, the data from the MPCA's early warning subnetwork and data collected from fifteen wells in the MDA's ambient monitoring network in 2015 was analyzed. The MDA network wells selected for sampling generally were located in the immediate vicinity of confined animal feeding operations, although none were specifically installed to monitor contamination emanating from a known plume. The results indicate that commercial/industrial land use had the greatest percent detection of CECs (2.12%), followed by residential SSTS (1.38%), sewered residential (1.32%), undeveloped land use (1.04%), and agricultural (0.57%) (Figure 23). This assessment of CECs did not assess other settings susceptible to contamination, such as feedlot plumes (Meyer et al. 2000) or agricultural lands amended with biosolids from wastewater treatment facilities (Kinny et al. 2006).

Figure 23. Percent detection of CECs by land use [the number next to each bar is the number of wells]



Pesticides

Pesticides are chemical substances, biological agents, or mixtures of substances that prevent, destroy, repel, or lessen the damage of any pest. Pesticides often are used to control weeds, insects, and plant diseases. Many agricultural producers use pesticides to protect crops and increase yields. Homeowners and municipalities use pesticides to manage pests around homes and in lawns, gardens, and parklands. Lake managers and lakeshore owners also use pesticides at times to control aquatic plants or other aquatic organisms that are causing nuisance conditions.

The MDA's ambient groundwater program monitoring data from 2017 showed that herbicide degradates were the most frequently detected pesticide-related compound (Minnesota Department of Agriculture 2018). Over sixty-five percent of the detections were degradates of acetochlor, alachlor, atrazine, metolachlor, and metribuzin. These pesticides have been placed in "common detection" status by the MDA. The common detection designation triggers heightened scrutiny and management activities, such as the development and promotion of pesticide-specific best management practices (BMPs). Three neonicotinoid insecticides (clothianidin, imidacloprid, and thiamethoxam), as well as the fungicide metalaxyl, were also among the top pesticide detections, based on the 2017 MDA groundwater data. These compounds were detected in eight to 16% of the groundwater samples that were analyzed.

The MDA's Private Well Pesticide Sampling (PWPS) Project has also showed that the majority of the wells sampled had a pesticide detection. Based on the data collected in 2017 for the PWPS project, pesticides were detected in 64% of the wells (Minnesota Department of Agriculture 2018). Thirty-eight percent of the well water samples had between two to six pesticide detections. Herbicide degradates were also the type of pesticide that was detected most frequently in the private well groundwater samples. Much like the wells in the agency's ambient groundwater monitoring network, the private wells sampled were located in agricultural areas considered to be vulnerable to contamination from the land surface.

Pesticide concentrations in the state's groundwater generally did not exceed any applicable human health-based guidance set by the MDH. No concentrations measured in the MDA's ambient groundwater monitoring network in 2017 exceeded an applicable MDH human health-based guidance. Only two of the 1,103 samples collected as part of the MDA's PWPS Project had a pesticide concentration that was greater than a human health-based guidance value. It should be noted, however, that confirmation sampling performed later at these two wells showed that the pesticides in question were not detected.

Appendix A

Regional Kendall Nitrate Temporal Trends Test Results

Trend Test Results for Nitrate Concentrations in the Ambient Groundwater by Selected Major Watersheds, 2005-2017

Region	Number of Sites	Rate of Change per year (in mg/L/year)	Kendall's tau	p-value
Minnesota River Basin	8	0.0000	-0.0633	0.3026
Lower Mississippi River Basin	9	0.0263	0.1536	0.0263
Red River Basin	13	0.0000	-0.0564	0.2551
Twin Cities Metropolitan Area	29	0.0000	-0.1013	0.0054
Upper Mississippi River Basin	55	-0.0005	-0.0274	0.2637

There were insufficient data in the Big Sioux and Rock, Des Moines, Little Sioux, Rainy, St. Croix, Upper Iowa, Wapsipnicon, and Western Lake Superior River Basins to determine temporal trends in nitrate concentrations in the ambient groundwater.

Trend Test Results for Nitrate Concentrations in the Ambient Groundwater by Selected Major Watersheds, 2005-2017

Land Use	Number of Sites	Rate of Change per year (in mg/L/year)	Kendall's tau	p-value
Agricultural	55	0.0000	-0.0217	0.3754
Sewered Residential	14	0.0000	-0.0924	0.0695

There were insufficient data in the commercial/industrial, residential areas using subsurface sewage treatment systems for wastewater treatment and disposal, and undeveloped areas for trend analysis.

Appendix B

Chloride Concentrations in the Galena and St. Peter aquifers, 2013-2017

Figure B 1. Chloride concentrations in the Galena Aquifer, 2013-2017.

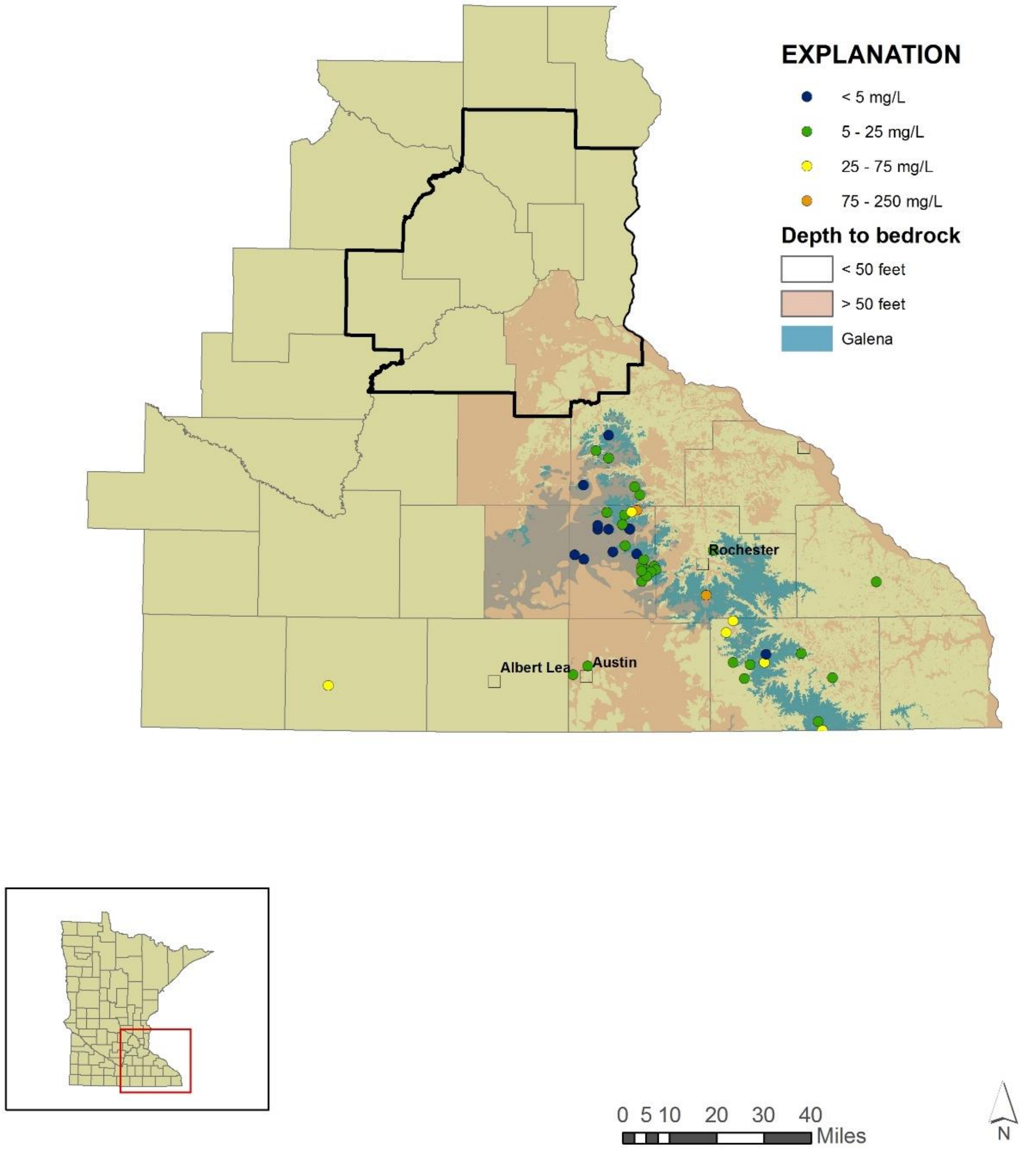
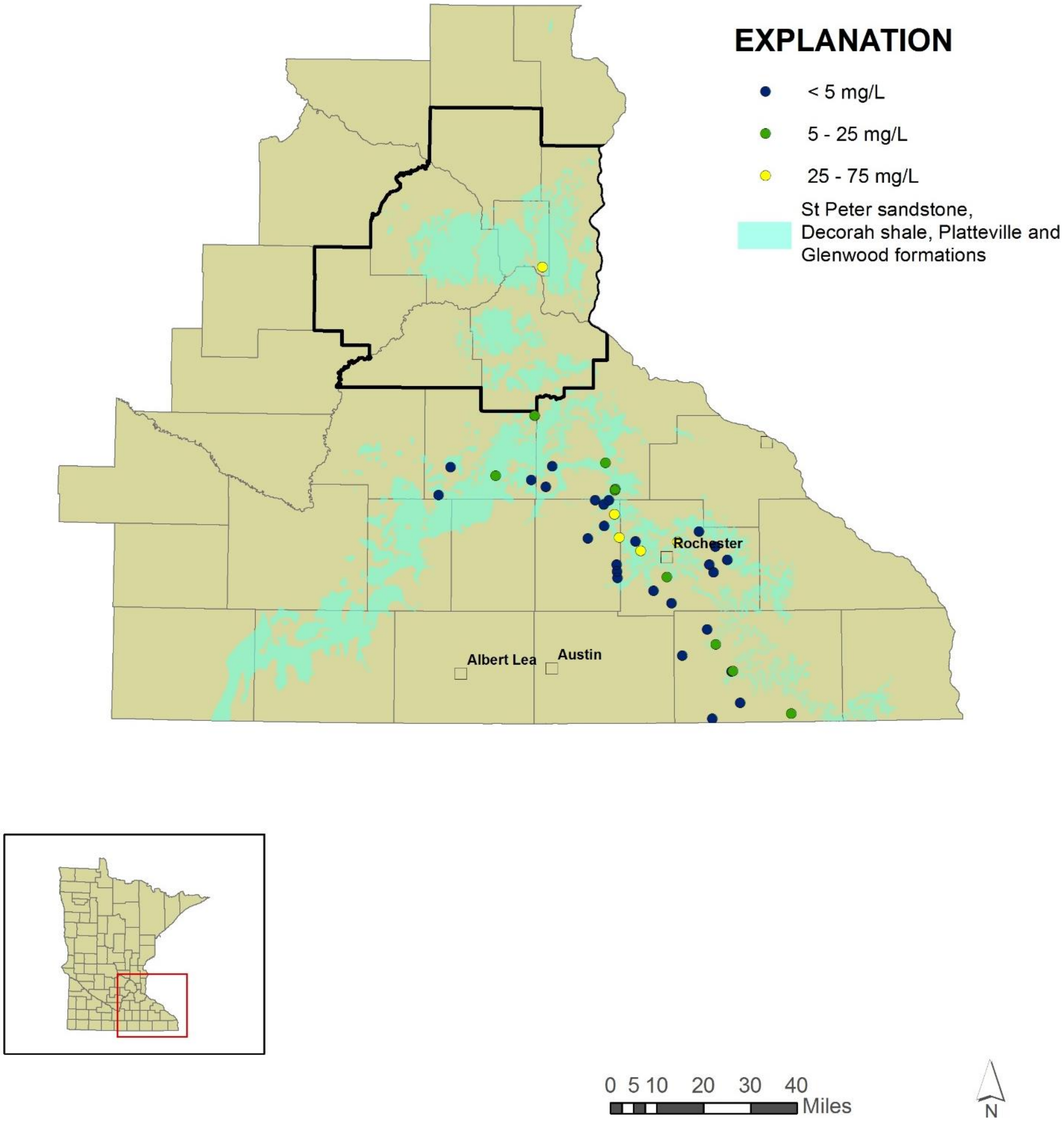


Figure B 2. Chloride concentrations in the St. Peter Aquifer, 2013-2017.



Appendix C

Volatile Organic Compounds Analyzed in Water Samples Collected for the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network, 2013-2017

Chemical	CAS number	Reporting Limit	Human health guidance value	Use/Source
1,1,1,2-Tetrachloroethane	630-20-6	0.2 – 0.4 ug/L	70 ug/L (HRL$_{93}$)	Solvent and in the production of wood stains and varnishes
1,1,1-Trichloroethane	71-55-6	0.2 – 0.4 ug/L	5,000 ug/L (HRL$_{18}$)	Solvent
1,1,2,2-Tetrachloroethane	79-34-5	0.2 - 0.4 ug/L	2 ug/L (HRL$_{94}$)	Solvent, Refrigerant
1,1,2-Trichloroethane	79-00-5	0.2 – 0.4 ug/L	3 ug/L (HRL$_{93}$)	Solvent, Chemical synthesis
1,1-Dichloroethane	75-34-3	0.2 – 0.4 ug/L	80 ug/L (RAA$_{16}$)	Chemical synthesis, Solvent, Degreaser
1,1-Dichloroethylene	75-35-4	0.5 – 1.0 ug/L	200 ug/L (HRL$_{11}$)	Chemical synthesis
1,1-Dichloropropene	563-58-6	0.2 – 0.4 ug/L		Not available
1,2,3-Trichlorobenzene	87-61-6	1-2 ug/L		Solvent
1,2,3-Trichloropropane	96-18-4	0.5 – 1 ug/L	0.003 ug/L (HRL$_{13}$)	Solvent
1,2,4-Trichlorobenzene	120-82-1	0.5 – 1 ug/L	4 ug/L (HRL$_{13}$)	Solvent
1,2,4-Trimethylbenzene	95-63-6	0.5 – 1 ug/L	30 ug/L (HBV$_{19}$)	Occurs naturally in coal tar and petroleum, Gasoline additive, Sterilizing agent, Manufacture of dyes, perfumes, and resins
1,2-Dibromo-3-chloropropane	96-12-8	2 – 4 ug/L		Soil fumigant
1,2-Dichloroethane	107-06-2	0.2 – 0.4 ug/L		Chemical synthesis, Solvent
1,2-Dichloropropane	78-87-5	0.2 – 0.4 ug/L	5 ug/L (HRL$_{94}$)	Chemical synthesis, Soil Fumigant, Solvent
1,3,5-Trimethylbenzene	108-67-8	0.5 – 1.0 ug/L	30 ug/L (HBV$_{19}$)	Solvent, Combustion product
1,3-Dichloropropane	142-28-9	0.2 – 0.4 ug/L		Soil Fumigant, Nematicide
2,2-Dichloropropane	594-20-7	0.5 – 1.0 ug/L		Not available
Acetone	67-64-1	20 – 40 ug/L	3,000 ug/L (HBV$_{17}$)	Solvent, Active ingredient in nail polish remover

Chemical	CAS number	Reporting Limit	Human health guidance value	Use/Source
Allyl Chloride	107-05-1	0.5 – 1.0 ug/L	30 ug/L (HRL$_{94}$)	Chemical synthesis
Benzene	71-43-2	0.2 – 0.4 ug/L	2 ug/L (HRL$_{09}$)	Natural constituent of crude oil, gasoline, and cigarette smoke; Chemical synthesis
Bromobenzene	108-86-1	0.2 – 0.4 ug/L		Chemical synthesis
Carbon Tetrachloride	56-23-5	0.2 – 0.4 ug/L	1 ug/L (HRL$_{13}$)	Chemical synthesis, Solvent, Refrigerant
CFC-11 (trichlorofluoromethane)	75-69-4	0.5 – 1.0 ug/L	2,000 ug/L (HRL$_{93}$)	Refrigerant
CFC-113	76-13-1	0.2 - 0.4 ug/L		Refrigerant
CFC-12 (dichlorodifluoromethane)	75-71-8	1 – 2 ug/L	500 ug/L (RAA$_{17}$)	Refrigerant
Chlorobenzene	108-90-7	0.2 – 0.4 ug/L	100 ug/L (HRL$_{93}$)	Chemical synthesis, Solvent
Chlorodibromomethane	124-48-1	0.5 – 1.0 ug/L	10 ug/L (HRL$_{93}$)	Disinfection byproduct, Flame retardant
Chloroethane	75-00-3	0.5 – 1.0 ug/L	Narrative RAA$_{16}$	Chemical synthesis
Chloroform	67-66-3	0.1 – 0.2 ug/L	20 ug/L (HRL$_{18}$)	Disinfection byproduct, Chemical synthesis, Solvent
Chloromethane	74-87-3	1 – 2 ug/L		Disinfection byproduct, Refrigerant, Chemical Synthesis
cis-1,2-Dichloroethylene	156-59-2	0.2 – 0.4 ug/L	6 ug/L (HRL$_{18}$)	Degradation product of tetrachloroethylene or trichloroethylene
cis-1,3-Dichloropropene	10061-01-5	0.2 – 0.4 ug/L		Soil Fumigant
Cumene (isopropyl benzene)	98-82-8	0.5 – 1.0 ug/L	300 ug/L (HRL$_{93}$)	Constituent of crude oil and gasoline
Dibromomethane	74-95-3	0.5 – 1.0 ug/L		Disinfection byproduct, Solvent, Chemical synthesis
Dichlorobromomethane	75-27-4	0.2 – 0.4 ug/L	3 ug/L (HBV$_{18}$)	Disinfection byproduct, Flame retardant
Ethyl ether	60-29-7	2 – 4 ug/L	200 ug/L (RAA$_{16}$)	Solvent
Ethylbenzene	100-41-4	0.5 – 1.0 ug/L	40 ug/L (HBV$_{19}$)	Constituent in crude oil and gasoline
Ethylene dibromide	106-93-4		0.004 ug/L (HRL$_{93}$)	Gasoline additive, Fumigant
Halon 1011 (bromochloromethane)	74-97-5	0.5 – 1.0 ug/L		Refrigerant

Chemical	CAS number	Reporting Limit	Human health guidance value	Use/Source
HCFC-21 (dichlorofluoromethane)	75-43-4	0.5 – 1.0 ug/L	20 ug/L (RAA_{17})	Refrigerant
Hexachlorobutadiene	87-68-3	1 – 2 ug/L	1 ug/L (HRL_{93})	Chemical synthesis, Solvent
m-Dichlorobenzene	541-73-1	0.2 – 0.4 ug/L		Chemical synthesis
Methyl bromide	74-83-9	1 – 2 ug/L	10 ug/L (HRL_{93})	Soil fumigant
Methyl ethyl ketone	78-93-3	10 – 20 ug/L	4,000 ug/L (HRL_{94})	Solvent
Methyl isobutyl ketone	108-10-1	5 – 10 ug/L	300 ug/L (HRL_{94})	Solvent
Methyl tert-butyl ether	1634-04-4	2 – 4 ug/L	60 ug/L (RAA_{13})	Gasoline additive
Methylene Chloride	75-09-2	0.5 – 1.0 ug/L	5 ug/L (HRL_{MCL})	Solvent, Chemical synthesis, Degreaser
Naphthalene	91-20-3	1 – 2 ug/L	70 ug/L (HRL_{13})	Natural constituent of coal and crude oil, Mothballs
n-Butylbenzene	104-51-8	0.5 – 1.0 ug/L		Not available
n-Propylbenzene	103-65-1	0.5 – 1.0 ug/L		Chemical synthesis, Solvent, Textile dyeing and printing, Fuel combustion
o-Chlorotoluene	95-49-8	0.5 – 1.0 ug/L		Solvent, Chemical synthesis
o-Dichlorobenzene	95-50-1	0.2 – 0.4 ug/L	600 ug/L (HRL_{93})	Solvent, Chemical Synthesis
o-Xylene	95-47-6	0.2 – 0.4 ug/L	300 ug/L (HRL_{11})	Constituent of crude oil and gasoline
p-Chlorotoluene	106-43-4	0.5 – 1.0 ug/L		Solvent, Chemical synthesis
p-Cymene (p-isopropyl toluene)	99-87-6	0.5 – 1.0 ug/L		Gasoline or oil combustion
p-Dichlorobenzene	106-46-7	0.2 – 0.4 ug/L	10 ug/L (HRL_{94})	Fumigant, Deodorant
sec-Butylbenzene	135-98-8	0.5 – 1.0 ug/L		Constituent of gasoline, Solvent, Chemical synthesis
tert-Butylbenzene	98-06-6	0.5 – 1.0 ug/L		Chemical synthesis, Solvent
Tetrachloroethylene	127-18-4	0.2 – 0.4 ug/L	4 ug/L (HBV_{14})	Solvent, Degreaser
Tetrahydrofuran	109-99-9	10 – 20 ug/L	600 ug/L (HRL_{18})	Solvent, Chemical synthesis
Toluene	108-88-3	0.2 – 0.4 ug/L	200 ug/L (HRL_{11})	Constituent of crude oil and gasoline, Solvent, Chemical synthesis

Chemical	CAS number	Reporting Limit	Human health guidance value	Use/Source
trans-1,2-Dichloroethylene	156-60-5	0.1 – 0.2 ug/L	40 ug/L (HRL_{13})	Degradation product of tetrachloroethylene or trichloroethylene
trans-1,3-Dichloropropene	10061-02-6	0.2 – 0.4 ug/L		Fumigant, Nematicide,
Tribromomethane (Bromoform)	75-25-2	0.5 – 1.0 ug/L	40 ug/L (HRL_{93})	Disinfection byproduct
Trichloroethylene	79-01-6	0.1 – 0.2 ug/L	0.4 ug/L (HRL_{15})	Solvent, Degreaser
Vinyl chloride	75-01-4	0.2 – 0.4 ug/L	0.2 ug/L (HRL_{18})	Chemical synthesis; Degradation product of tetrachloroethylene or trichloroethylene
meta and para Xylene mix	179601-23-1	0.3 – 0.6 ug/L	300 ug/L (HRL_{11})	Constituent of crude oil and gasoline
Styrene	100-42-5	0.5 – 1.0 ug/L		Chemical synthesis

Appendix D

Contaminants of Emerging Concern Analyzed in Water Samples Collected for the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network, 2013-2017

Chemical name	CAS number	Analytical method	Reporting limit
Menthol	89-78-1	USGS METHOD O-1433-01	320 ng/L
beta-Sitosterol	83-46-5	USGS METHOD O-1433-01	4000 ng/L
Galaxolide	1222-05-5	USGS METHOD O-1433-01	52 ng/L
1,7-Dimethylxanthine	611-59-6	SGS AXYS METHOD MLA-075	58.1 - 120.0 ng/L
		USGS RESEARCH METHOD 9017	87.7 ng/L
		USGS METHOD O-2080-08	100 ng/L
		USGS METHOD O-2440-14	87.7 ng/L
11-Ketotestosterone	564-35-2	USGS METHOD 2434	2.0 ng/L
17 α-Estradiol	57-91-0	USGS METHOD 2434	0.8 ng/L
17 β-Estradiol	50-28-2	USGS METHOD 2434	0.8 ng/L
1-Methylnaphthalene	90-12-0	USGS METHOD O-1433-01	22 ng/L
2,6-Dimethylnaphthalene	581-42-0	USGS METHOD O-1433-01	60 ng/L
2-Methylnaphthalene	91-57-6	USGS METHOD O-1433-01	36 ng/L
3-Methylindole	83-34-1	USGS METHOD O-1433-01	36 ng/L
4-Androstenedione	63-05-8	USGS METHOD 2434	0.8 ng/L
4-tert-Octylphenol	140-66-9	USGS METHOD O-1433-01	0.14 µg/L
4-tert-Octylphenol diethoxylate	2315-61-9	USGS METHOD O-1433-01	1,000 ng/L
4-tert-Octylphenol monoethoxylate	2315-67-5	USGS METHOD O-1433-01	1,000 ng/L
5-Methyl-1H-Benzotriazole	136-85-6	USGS METHOD O-1433-01	1,200 ng/L
Abacavir	136470-78-5	USGS RESEARCH METHOD 9017	8.21 ng/L
		USGS METHOD O-2440-14	8.21 ng/L
Acetaminophen	103-90-2	SGS AXYS METHOD MLA-075	14.5-30.0 ng/L
		USGS RESEARCH METHOD 9017	7.13 ng/L
		USGS METHOD O-2080-08	120 ng/L
		USGS METHOD O-2440-14	7.13-80.0 ng/L
Acetophenone	98-86-2	USGS METHOD O-1433-01	400 ng/L
Acyclovir	59277-89-3	USGS RESEARCH METHOD 9017	22.2 ng/L
		USGS METHOD O-2440-14	22.2 ng/L
AHTN	21145-77-7	USGS METHOD O-1433-01	28 ng/L
Albuterol	18559-94-9	SGS AXYS METHOD MLA-075	0.293-3.28 ng/L
		USGS RESEARCH METHOD 9017	6.06 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
		USGS METHOD O-2080-08	80 ng/L
		USGS METHOD O-2440-14	6.7 ng/L
Alprazolam	28981-97-7	SGS AXYS METHOD MLA-075	0.281-0.589 ng/L
		USGS RESEARCH METHOD 9017	21.3 ng/L
		USGS METHOD O-2440-14	21.3 ng/L
Amitriptyline	50-48-6	SGS AXYS METHOD MLA-075	0.281-6.98 ng/L
		USGS RESEARCH METHOD 9017	37.2 ng/L
		USGS METHOD O-2440-14	37.2-80.0 ng/L
Amlodipine	88150-42-9	SGS AXYS METHOD MLA-075	1.41-2.95 ng/L
Amphetamine	300-62-9	SGS AXYS METHOD MLA-075	1.47-2.41 ng/L
		USGS RESEARCH METHOD 9017	8.14 ng/L
		USGS METHOD O-2440-14	8.14-80.0 ng/L
Amsacrine	51264-14-3	SGS AXYS METHOD MLA-075	0.0750-4.33 ng/L
Androsterone	53-41-8	USGS METHOD 2434	0.8-3.13 ng/L
Anthracene	120-12-7	USGS METHOD O-1433-01	10 ng/L
Anthraquinone	84-65-1	USGS METHOD O-1433-01	160 ng/L
Antipyrine	60-80-0	USGS RESEARCH METHOD 9017	116 ng/L
		USGS METHOD O-2440-14	116 ng/L
Atenolol	29122-68-7	SGS AXYS METHOD MLA-075	0.586-2.07 ng/L
		USGS RESEARCH METHOD 9017	13.3 ng/L
		USGS METHOD O-2440-14	13.3-80.0 ng/L
Atorvastatin	134523-00-5	SGS AXYS METHOD MLA-075	1.47-5.39 ng/L
Atrazine	1912-24-9	USGS RESEARCH METHOD 9017	19.4 ng/L
		USGS METHOD O-2440-14	19.4 ng/L
Azathioprine	446-86-6	SGS AXYS METHOD MLA-075	1.87-4.15 ng/L
Azithromycin	83905-01-5	SGS AXYS METHOD MLA-075	1.45-5.14 ng/L
		USGS OGRL LCAB	5 ng/L
Benzo[a]pyrene	50-32-8	USGS METHOD O-1433-01	60 ng/L
Benzophenone	119-61-9	USGS METHOD O-1433-01	80 ng/L
Benzoylecgonine hydrate	519-09-5	SGS AXYS METHOD MLA-075	0.281-0.589 ng/L
Benztropine	86-13-5	SGS AXYS METHOD MLA-075	0.469-3.33 ng/L
		USGS RESEARCH METHOD 9017	15.8 ng/L
		USGS METHOD O-2440-14	24.0 ng/L
Betamethasone	378-44-9	SGS AXYS METHOD MLA-075	1.41-9.82 ng/L
		USGS RESEARCH METHOD 9017	114.0 ng/L
		USGS METHOD O-2440-14	114.0 ng/L
Bisphenol A	80-05-7	SGS AXYS METHOD MLA-075	469.0-538.0 ng/L
		AXYS METHOD MLA-082	1.08-5.76 ng/L
		USGS METHOD 2434	100.0 ng/L
Branched p-nonylphenols	84852-15-3	AXYS METHOD MLA-004	0.918-9.78 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
		USGS METHOD O-1433-01	2,000 ng/L
Bromacil	314-40-9	USGS METHOD O-1433-01	360 ng/L
Bupropion	34911-55-2	USGS RESEARCH METHOD 9017	17.8-20.0 ng/L
		USGS METHOD O-2440-14	17.8 ng/L
Busulfan	55-98-1	SGS AXYS METHOD MLA-075	2.09-19.3 ng/L
Butylated hydroxyanisole	25013-16-5	USGS METHOD O-1433-01	600 ng/L
Caffeine	58-08-2	SGS AXYS METHOD MLA-075	14.5-30.0 ng/L
		USGS RESEARCH METHOD 9017	90.7 ng/L
		USGS METHOD O-1433-01	60 ng/L
		USGS METHOD O-2080-08	60 ng/L
		USGS METHOD O-2440-14	90.7-128.0 ng/L
Camphor	76-22-2	USGS METHOD O-1433-01	44 ng/L
Carbadox	6804-07-5	SGS AXYS METHOD MLA-075	1.45-9.1 ng/L
Carbamazepine	298-46-4	SGS AXYS METHOD MLA-075	1.47-3.0 ng/L
		USGS RESEARCH METHOD 9017	4.18 ng/L
		USGS OGRL LCAB	5 ng/L
		USGS METHOD O-2080-08	60 ng/L
		USGS METHOD O-2440-14	11.0 ng/L
Carbaryl	63-25-2	USGS METHOD O-1433-01	160 ng/L
Carbazole	86-74-8	USGS METHOD O-1433-01	30 ng/L
Carisoprodol	78-44-4	USGS RESEARCH METHOD 9017	12.5 ng/L
		USGS METHOD O-2440-14	12.5-80.0 ng/L
Cefotaxime	63527-52-6	SGS AXYS METHOD MLA-075	1.89-43.3 ng/L
Chloramphenicol	56-75-7	USGS OGRL LCAB	100 ng/L
Chlorpheniramine	132-22-9	USGS RESEARCH METHOD 9017	4.68 ng/L
		USGS METHOD O-2440-14	4.68 ng/L
Chlorpyrifos	2921-88-2	USGS METHOD O-1433-01	160 ng/L
Chlortetracycline	57-62-5	USGS OGRL LCAB	10 ng/L
Cholesterol	57-88-5	USGS METHOD 2434	200.0 ng/L
		USGS METHOD O-1433-01	2,000 ng/L
Cimetidine	51481-61-9	SGS AXYS METHOD MLA-075	0.593-1.25 ng/L
		USGS RESEARCH METHOD 9017	27.8 ng/L
		USGS METHOD O-2440-14	27.8-80.0 ng/L
Ciprofloxacin	85721-33-1	SGS AXYS METHOD MLA-075	5.81-57.3 ng/L
		USGS OGRL LCAB	5 ng/L
Citalopram	59729-33-8	SGS AXYS METHOD MLA-075	0.375-3.31 ng/L
		USGS RESEARCH METHOD 9017	6.58 ng/L
		USGS METHOD O-2440-14	6.58-80.0 ng/L
Clarithromycin	81103-11-9	SGS AXYS METHOD MLA-075	1.45-3.0 ng/L
Clinafloxacin	105956-97-6	SGS AXYS METHOD MLA-075	6.03-91.0 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
Clonidine	4205-90-7	SGS AXYS METHOD MLA-075	1.47-2.41 ng/L
		USGS RESEARCH METHOD 9017	60.8 ng/L
		USGS METHOD O-2440-14	60.8-80.0 ng/L
Clotrimazole	23593-75-1	SGS AXYS METHOD MLA-075	0.375-0.796 ng/L
Cloxacillin	61-72-3	SGS AXYS METHOD MLA-075	2.9-6.0 ng/L
Cocaine	50-36-2	SGS AXYS METHOD MLA-075	0.141-0.402 ng/L
Codeine	76-57-3	SGS AXYS METHOD MLA-075	2.93-4.82 ng/L
		USGS RESEARCH METHOD 9017	88.3 ng/L
		USGS METHOD O-2080-08	46 ng/L
		USGS METHOD O-2440-14	88.3 ng/L
Colchicine	64-86-8	SGS AXYS METHOD MLA-075	0.787-17.5 ng/L
Coprostanol	360-68-9	USGS METHOD 2434	200.0 ng/L
		USGS METHOD O-1433-01	1,800 ng/L
Cotinine	486-56-6	SGS AXYS METHOD MLA-075	1.47 - 2.41 ng/L
		USGS RESEARCH METHOD 9017	6.37 ng/L
		USGS METHOD O-1433-01	800 ng/L
		USGS METHOD O-2080-08	38 ng/L
		USGS METHOD O-2440-14	6.37-80.0 ng/L
Cumene	98-82-8	USGS METHOD O-1433-01	300 ng/L
Cyclophosphamide	50-18-0	SGS AXYS METHOD MLA-075	0.75-1.66 ng/L
Daunomycin	20830-81-3	SGS AXYS METHOD MLA-075	7.5-26.5 ng/L
DEET	134-62-3	SGS AXYS METHOD MLA-075	0.805-6.48 ng/L
		USGS METHOD O-1433-01	60 ng/L
Dehydronifedipine	67035-22-7	SGS AXYS METHOD MLA-075	0.581-2.08 ng/L
		USGS RESEARCH METHOD 9017	24.5 ng/L
		USGS METHOD O-2080-08	80 ng/L
		USGS METHOD O-2440-14	24.5 ng/L
Desmethyldiltiazem	84903-78-6	SGS AXYS METHOD MLA-075	0.141 - 2.5 ng/L
		USGS RESEARCH METHOD 9017	12.4 ng/L
		USGS METHOD O-2440-14	12.4 ng/L
Desvenlafaxine	93413-62-8	USGS RESEARCH METHOD 9017	7.49 ng/L
		USGS METHOD O-2440-14	7.49 ng/L
Dextromethorphan	125-71-3	USGS RESEARCH METHOD 9017	8.2 ng/L
		USGS METHOD O-2440-14	8.2 ng/L
Diatrizoic acid	117-96-4	SGS AXYS METHOD MLA-075	22.5-218.0 ng/L
Diazepam	439-14-5	SGS AXYS METHOD MLA-075	0.281-1.02 ng/L
		USGS RESEARCH METHOD 9017	2.24 ng/L
		USGS METHOD O-2440-14	2.24-4.0 ng/L
Diazinon	333-41-5	USGS METHOD O-1433-01	160 ng/L
Diethylstilbestrol	56-53-1	USGS METHOD 2434	0.8 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
Digoxigenin	1672-46-4	SGS AXYS METHOD MLA-075	5.93-267.0 ng/L
Digoxin	20830-75-5	SGS AXYS METHOD MLA-075	5.81-20.8 ng/L
Dihydrotestosterone	521-18-6	USGS METHOD 2434	4.0 ng/L
Diltiazem	42399-41-7	SGS AXYS METHOD MLA-075	0.29-1.02 ng/L
		USGS RESEARCH METHOD 9017	10.2 ng/L
		USGS METHOD O-2080-08	60 ng/L
		USGS METHOD O-2440-14	10.2-80.0 ng/L
Diphenhydramine	58-73-1	SGS AXYS METHOD MLA-075	0.581-2.05 ng/L
		USGS RESEARCH METHOD 9017	5.79 ng/L
		USGS METHOD O-2080-08	58 ng/L
		USGS METHOD O-2440-14	5.79 ng/L
D-Limonene	5989-27-5	USGS METHOD O-1433-01	80 ng/L
Doxorubicin	23214-92-8	SGS AXYS METHOD MLA-075	22.5-47.8 ng/L
Doxycycline	564-25-0	USGS OGRL LCAB	10 ng/L
Drospirenone	67392-87-4	SGS AXYS METHOD MLA-075	7.5 - 16.4 ng/L
Duloxetine	136434-34-9	USGS RESEARCH METHOD 9017	36.6 ng/L
		USGS METHOD O-2440-14	36.6-80 ng/L
Enalapril	75847-73-3	SGS AXYS METHOD MLA-075	0.293-3.03 ng/L
Enrofloxacin	93106-60-6	SGS AXYS METHOD MLA-075	2.9-30.8 ng/L
		USGS OGRL LCAB	5 ng/L
Epi-chlorotetracycline	14297-93-9	USGS OGRL LCAB	10 ng/L
Epi-iso-chlorotetracycline	EICTC	USGS OGRL LCAB	10 ng/L
Epi-oxytetracycline	14206-58-7	USGS OGRL LCAB	10 ng/L
Epitestosterone	481-30-1	USGS METHOD 2434	2.0 ng/L
Epi-tetracycline	23313-80-6	USGS OGRL LCAB	10 ng/L
Equilenin	517-09-9	USGS METHOD 2434	2.0 ng/L
Equilin	474-86-2	USGS METHOD 2434	8.0 ng/L
Erythromycin	114-07-8	USGS RESEARCH METHOD 9017	53.1 ng/L
		USGS OGRL LCAB	8 ng/L
		USGS METHOD O-2440-14	53.1-200.0 ng/L
Erythromycin-H20	114078-H2O	SGS AXYS METHOD MLA-075	2.23-4.6 ng/L
		USGS OGRL LCAB	5 ng/L
Estriol	50-27-1	USGS METHOD 2434	2.0 ng/L
Estrone	53-16-7	USGS METHOD 2434	0.8-4.87 ng/L
Ethinyl estradiol	57-63-6	USGS METHOD 2434	0.8-1.05 ng/L
Etoposide	33419-42-0	SGS AXYS METHOD MLA-075	1.87 - 4.01 ng/L
Ezetimibe	163222-33-1	USGS RESEARCH METHOD 9017	63.5 ng/L
		USGS METHOD O-2440-14	63.5-200.0 ng/L
Fadrozole	102676-47-1	USGS RESEARCH METHOD 9017	7.32 ng/L
		USGS METHOD O-2440-14	7.32 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
Famotidine	76824-35-6	USGS RESEARCH METHOD 9017	10.7 ng/L
		USGS METHOD O-2440-14	10.7-80.0 ng/L
Fenofibrate	49562-28-9	USGS RESEARCH METHOD 9017	6.28 ng/L
		USGS METHOD O-2440-14	6.28-80.0 ng/L
Fexofenadine	83799-24-0	USGS RESEARCH METHOD 9017	19.9 ng/L
		USGS METHOD O-2440-14	19.9 ng/L
Fluconazole	86386-73-4	USGS RESEARCH METHOD 9017	71.0 ng/L
		USGS METHOD O-2440-14	71.0-80.0 ng/L
Flumequine	42835-25-6	SGS AXYS METHOD MLA-075	1.45-5.24 ng/L
Fluocinonide	356-12-7	SGS AXYS METHOD MLA-075	5.62-52.8 ng/L
Fluoranthene	206-44-0	USGS METHOD O-1433-01	24 ng/L
Fluoxetine	54910-89-3	SGS AXYS METHOD MLA-075	1.45-5.22 ng/L
		USGS RESEARCH METHOD 9017	26.9 ng/L
		USGS METHOD O-2440-14	26.9-80.0 ng/L
Fluticasone propionate	80474-14-2	SGS AXYS METHOD MLA-075	1.87-3.93 ng/L
		USGS RESEARCH METHOD 9017	4.62 ng/L
		USGS METHOD O-2440-14	4.62-80.0 ng/L
Fluvoxamine	54739-18-3	USGS RESEARCH METHOD 9017	53.8 ng/L
		USGS METHOD O-2440-14	53.8-200.0 ng/L
Furosemide	54-31-9	SGS AXYS METHOD MLA-075	37.5-134.0 ng/L
Gemfibrozil	25812-30-0	SGS AXYS METHOD MLA-075	1.41-1.62 ng/L
Glipizide	29094-61-9	SGS AXYS METHOD MLA-075	5.62-6.46 ng/L
		USGS RESEARCH METHOD 9017	34.6 ng/L
		USGS METHOD O-2440-14	148.0 ng/L
Glyburide	10238-21-8	SGS AXYS METHOD MLA-075	2.81-3.23 ng/L
		USGS RESEARCH METHOD 9017	3.95 ng/L
		USGS METHOD O-2440-14	3.95-4.0 ng/L
Hydrochlorothiazide	58-93-5	SGS AXYS METHOD MLA-075	11.7-66.8 ng/L
Hydrocodone	125-29-1	SGS AXYS METHOD MLA-075	1.48-3.03 ng/L
		USGS RESEARCH METHOD 9017	10.5 ng/L
		USGS METHOD O-2440-14	10.5-80.0 ng/L
Hydrocortisone	50-23-7	SGS AXYS METHOD MLA-075	56.2-118.0 ng/L
		USGS RESEARCH METHOD 9017	147.0 ng/L
		USGS METHOD O-2440-14	147.0 ng/L
10-hydroxy-amitriptyline	1159-82-6	SGS AXYS METHOD MLA-075	0.141-0.343 ng/L
		USGS RESEARCH METHOD 9017	8.3 ng/L
		USGS METHOD O-2440-14	8.3 ng/L
2-hydroxy-ibuprofen	51146-55-5	SGS AXYS METHOD MLA-075	75.0-193.0 ng/L
Hydroxyzine	68-88-2	USGS RESEARCH METHOD 9017	7.43 ng/L
		USGS METHOD O-2440-14	7.43 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
Ibuprofen	15687-27-1	SGS AXYS METHOD MLA-075	14.1-41.1 ng/L
		USGS OGRL LCAB	0.05 µg/L
Iminostilbene	256-96-2	USGS RESEARCH METHOD 9017	145.0 ng/L
		USGS METHOD O-2440-14	145.0-200.0 ng/L
Indole	120-72-9	USGS METHOD O-1433-01	80 ng/L
Iopamidol	60166-93-0	SGS AXYS METHOD MLA-075	75.0-529.0 ng/L
Isoborneol	124-76-5	USGS METHOD O-1433-01	80 ng/L
Iso-chlorotetracycline	514-53-4	USGS OGRL LCAB	32 ng/L
Isophorone	78-59-1	USGS METHOD O-1433-01	32 ng/L
Isoquinoline	119-65-3	USGS METHOD O-1433-01	46-800 ng/L
Ketoconazole	65277-42-1	USGS RESEARCH METHOD 9017	113.0 ng/L
		USGS METHOD O-2440-14	113.0 ng/L
Lamivudine	134678-17-4	USGS RESEARCH METHOD 9017	16.1 ng/L
		USGS METHOD O-2440-14	16.1-80.0 ng/L
Lidocaine	137-58-6	USGS RESEARCH METHOD 9017	15.2 ng/L
		USGS METHOD O-2440-14	15.2 ng/L
Lincomycin	154-21-2	SGS AXYS METHOD MLA-075	2.9-6.0 ng/L
		USGS OGRL LCAB	5 ng/L
Lomefloxacin	98079-51-7	SGS AXYS METHOD MLA-075	2.9-30.5 ng/L
		USGS OGRL LCAB	5 ng/L
Loperamide	53179-11-6	USGS RESEARCH METHOD 9017	11.5 ng/L
		USGS METHOD O-2440-14	11.5 ng/L
Loratadine	79794-75-5	USGS RESEARCH METHOD 9017	6.95 ng/L
		USGS METHOD O-2440-14	6.95 ng/L
Lorazepam	846-49-1	USGS RESEARCH METHOD 9017	116 ng/L
		USGS METHOD O-2440-14	116.0-200.0 ng/L
Medroxyprogesterone acetate	71-58-9	SGS AXYS METHOD MLA-075	3.75-10.1 ng/L
Melphalan	148-82-3	SGS AXYS METHOD MLA-075	23.2-289.0 ng/L
Meprobamate	57-53-4	SGS AXYS METHOD MLA-075	3.75-7.85 ng/L
		USGS RESEARCH METHOD 9017	86.0 ng/L
		USGS METHOD O-2440-14	86.0 ng/L
Mestranol	72-33-3	USGS METHOD 2434	0.8-1.11 ng/L
Metalaxyl	57837-19-1	USGS METHOD O-1433-01	120 ng/L
Metaxalone	1665-48-1	USGS RESEARCH METHOD 9017	15.6 ng/L
		USGS METHOD O-2440-14	15.6-80.0 ng/L
Metformin	657-24-9	SGS AXYS METHOD MLA-075	2.98-29.5 ng/L
		USGS RESEARCH METHOD 9017	13.1-20.0 ng/L
		USGS METHOD O-2440-14	13.1 ng/L
Methadone	76-99-3	USGS RESEARCH METHOD 9017	7.61 ng/L
		USGS METHOD O-2440-14	7.61-80.0 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
Methocarbamol	532-03-6	USGS RESEARCH METHOD 9017	8.72 ng/L
		USGS METHOD O-2440-14	8.72-10.0 ng/L
Methotrexate	59-05-2	USGS RESEARCH METHOD 9017	52.4 ng/L
		USGS METHOD O-2440-14	52.4-80.0 ng/L
Methyl salicylate	119-36-8	USGS METHOD O-1433-01	44 ng/L
Methylprednisolone	83-43-2	SGS AXYS METHOD MLA-075	3.75-24.2 ng/L
Metolachlor	51218-45-2	USGS METHOD O-1433-01	28 ng/L
Metoprolol	51384-51-1	SGS AXYS METHOD MLA-075	1.45-17.7 ng/L
		USGS RESEARCH METHOD 9017	27.5 ng/L
		USGS METHOD O-2440-14	27.5 ng/L
Metronidazole	443-48-1	SGS AXYS METHOD MLA-075	3.75-15.7 ng/L
Miconazole	22916-47-8	SGS AXYS METHOD MLA-075	1.45-3.0 ng/L
Morphine	57-27-2	USGS RESEARCH METHOD 9017	14.0 ng/L
		USGS METHOD O-2440-14	14.0-80.0 ng/L
Moxifloxacin	151096-09-2	SGS AXYS METHOD MLA-075	3.87-111.0 ng/L
Nadolol	42200-33-9	USGS RESEARCH METHOD 9017	80.8 ng/L
		USGS METHOD O-2440-14	80.8 ng/L
Naphthalene	91-20-3	USGS METHOD O-1433-01	40 ng/L
Naproxen	22204-53-1	SGS AXYS METHOD MLA-075	2.81-10.7 ng/L
Nevirapine	129618-40-2	USGS RESEARCH METHOD 9017	15.1 ng/L
		USGS METHOD O-2440-14	15.1-80.0 ng/L
Nicotine	54-11-5	USGS RESEARCH METHOD 9017	57.8 ng/L
		USGS METHOD O-2440-14	57.8-80.0 ng/L
Nizatidine	76963-41-2	USGS RESEARCH METHOD 9017	19.0 ng/L
		USGS METHOD O-2440-14	19.0-80.0 ng/L
Nonylphenol diethoxylate	NP2EO	AXYS METHOD MLA-004	0.697-101.0 ng/L
		USGS METHOD O-1433-01	5,000 ng/L
Nonylphenol monoethoxylate	NP1EO	AXYS METHOD MLA-004	0.796-30.3 ng/L
Nordiazepam	1088-11-5	USGS RESEARCH METHOD 9017	41.4 ng/L
		USGS METHOD O-2440-14	41.4-80.0 ng/L
Norethisterone	68-22-4	USGS RESEARCH METHOD 9017	10.8-44.3 ng/L
		USGS METHOD 2434	0.8-0.9 ng/L
		USGS METHOD O-2440-14	10.9-80.0 ng/L
Norfloxacin	70458-96-7	SGS AXYS METHOD MLA-075	14.5-277.0 ng/L
		USGS OGRL LCAB	5 ng/L
Norfluoxetine	83891-03-6	SGS AXYS METHOD MLA-075	1.41-2.95 ng/L
		USGS RESEARCH METHOD 9017	199.0 ng/L
		USGS METHOD O-2440-14	199.0 ng/L
Norgestimate	35189-28-7	SGS AXYS METHOD MLA-075	2.9-15.8 ng/L
Norsertraline	87857-41-8	USGS RESEARCH METHOD 9017	192.0 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
		USGS METHOD O-2440-14	192.0-200.0 ng/L
Norverapamil	67018-85-3	SGS AXYS METHOD MLA-075	0.141-0.295 ng/L
		USGS RESEARCH METHOD 9017	8.58 ng/L
		USGS METHOD O-2440-14	8.58-80.0 ng/L
Ofloxacin	82419-36-1	SGS AXYS METHOD MLA-075	1.45-5.3 ng/L
		USGS OGRL LCAB	5 ng/L
Omeprazole/Esomeprazole mix	OMEPRAZOLE-MIX	USGS RESEARCH METHOD 9017	5.62 ng/L
		USGS METHOD O-2440-14	5.62-80.0 ng/L
Orlistat	96829-58-2	USGS RESEARCH METHOD 9017	52.0 ng/L
Ormetoprim	6981-18-6	SGS AXYS METHOD MLA-075	0.581-1.2 ng/L
		USGS OGRL LCAB	5 ng/L
Oseltamivir	196618-13-0	USGS RESEARCH METHOD 9017	14.6 ng/L
		USGS METHOD O-2440-14	14.6-20.0 ng/L
Oxacillin	66-79-5	SGS AXYS METHOD MLA-075	2.9-6.0 ng/L
Oxazepam	604-75-1	SGS AXYS METHOD MLA-075	3.75-7.96 ng/L
		USGS RESEARCH METHOD 9017	140.0 ng/L
		USGS METHOD O-2440-14	140.0-200.0 ng/L
Oxolinic acid	14698-29-4	SGS AXYS METHOD MLA-075	0.581-6.18 ng/L
Oxycodone	76-42-6	SGS AXYS METHOD MLA-075	0.593-3.78 ng/L
		USGS RESEARCH METHOD 9017	24.9 ng/L
		USGS METHOD O-2440-14	24.9-80.0 ng/L
Oxytetracycline	79-57-2	USGS OGRL LCAB	0.01 µg/L
Paroxetine	61869-08-7	SGS AXYS METHOD MLA-075	3.75-7.85 ng/L
		USGS RESEARCH METHOD 9017	20.6 ng/L
		USGS METHOD O-2440-14	20.6 ng/L
p-Cresol	106-44-5	USGS METHOD O-1433-01	0.08 µg/L
p-Cumylphenol	599-64-4	USGS METHOD O-1433-01	0.06 µg/L
p-Dichlorobenzene	106-46-7	USGS METHOD O-1433-01	0.04 µg/L
Penciclovir	39809-25-1	USGS RESEARCH METHOD 9017	40.2 ng/L
		USGS METHOD O-2440-14	40.2-80.0 ng/L
Penicillin G	61-33-6	SGS AXYS METHOD MLA-075	2.9-6.0 ng/L
Penicillin V	87-08-1	SGS AXYS METHOD MLA-075	2.9-6.0 ng/L
Pentoxifylline	6493-05-6	USGS RESEARCH METHOD 9017	9.35 ng/L
		USGS METHOD O-2440-14	9.35-10.0 ng/L
Phenanthrene	85-01-8	USGS METHOD O-1433-01	0.016 µg/L
Phenazopyridine	94-78-0	USGS RESEARCH METHOD 9017	13.3 ng/L
		USGS METHOD O-2440-14	13.3-40.0 ng/L
Phendimetrazine	634-03-7	USGS RESEARCH METHOD 9017	31.1 ng/L
		USGS METHOD O-2440-14	31.1-80.0 ng/L
Phenol	108-95-2	USGS METHOD O-1433-01	0.16 µg/L

Chemical name	CAS number	Analytical method	Reporting limit
Phenytoin	57-41-0	USGS RESEARCH METHOD 9017	188.0 ng/L
		USGS METHOD O-2440-14	188.0 ng/L
Piperonyl butoxide	51-03-6	USGS RESEARCH METHOD 9017	3.07 ng/L
		USGS METHOD O-2440-14	3.07-80.0 ng/L
p-Octylphenol	1806-26-4	AXYS METHOD MLA-004	0.117-5.54 ng/L
		USGS METHOD O-1433-01	0.06-0.08 µg/L
Prednisolone	50-24-8	SGS AXYS METHOD MLA-075	5.62-99.3 ng/L
		USGS RESEARCH METHOD 9017	150.0 ng/L
		USGS METHOD O-2440-14	150.0 ng/L
Prednisone	53-03-2	SGS AXYS METHOD MLA-075	18.7-325.0 ng/L
		USGS RESEARCH METHOD 9017	168.0 ng/L
		USGS METHOD O-2440-14	168.0-200.0 ng/L
Progesterone	57-83-0	USGS METHOD 2434	8.0 ng/L
Promethazine	60-87-7	SGS AXYS METHOD MLA-075	0.375-12.1 ng/L
		USGS RESEARCH METHOD 9017	50.0 ng/L
		USGS METHOD O-2440-14	50.0-80.0 ng/L
Prometon	1610-18-0	USGS METHOD O-1433-01	0.12 µg/L
Propoxyphene	469-62-5	SGS AXYS METHOD MLA-075	0.281-1.08 ng/L
		USGS RESEARCH METHOD 9017	17.2 ng/L
		USGS METHOD O-2440-14	17.2-80.0 ng/L
Propranolol	525-66-6	SGS AXYS METHOD MLA-075	1.87-3.93 ng/L
		USGS RESEARCH METHOD 9017	26.3 ng/L
		USGS METHOD O-2440-14	26.3 ng/L
Pseudoephedrine/Ephedrine mix	EPHED_PSEUDOEPH	USGS RESEARCH METHOD 9017	11.1 ng/L
		USGS METHOD O-2440-14	11.1 ng/L
Pyrene	129-00-0	USGS METHOD O-1433-01	0.042 µg/L
Quinine	130-95-0	USGS RESEARCH METHOD 9017	79.9 ng/L
		USGS METHOD O-2440-14	79.9-80.0 ng/L
Raloxifene	84449-90-1	USGS RESEARCH METHOD 9017	9.72 ng/L
		USGS METHOD O-2440-14	9.72-80.0 ng/L
Ranitidine	66357-35-5	SGS AXYS METHOD MLA-075	0.586-6.57 ng/L
		USGS RESEARCH METHOD 9017	192.0 ng/L
		USGS METHOD O-2440-14	192.0 ng/L
Rosuvastatin	287714-41-4	SGS AXYS METHOD MLA-075	3.75-8.32 ng/L
Roxithromycin	80214-83-1	SGS AXYS METHOD MLA-075	0.29-1.19 ng/L
		USGS OGRL LCAB	0.005 µg/L
Sarafloxacin	98105-99-8	SGS AXYS METHOD MLA-075	14.5-33.9 ng/L
		USGS OGRL LCAB	0.005 µg/L
Sertraline	79617-96-2	SGS AXYS METHOD MLA-075	0.375-0.907 ng/L
		USGS RESEARCH METHOD 9017	16.2 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
		USGS METHOD O-2440-14	16.2-80.0 ng/L
Simvastatin	79902-63-9	SGS AXYS METHOD MLA-075	18.7-208.0 ng/L
Sitagliptin	486460-32-6	USGS RESEARCH METHOD 9017	97.3 ng/L
		USGS METHOD O-2440-14	97.3 ng/L
Stigmastanol	19466-47-8	USGS METHOD O-1433-01	2.6 µg/L
Sulfachloropyridazine	80-32-0	SGS AXYS METHOD MLA-075	1.45-9.46 ng/L
		USGS OGRL LCAB	0.005 µg/L
Sulfadiazine	68-35-9	SGS AXYS METHOD MLA-075	1.45-3.0 ng/L
		USGS OGRL LCAB	0.005 µg/L
Sulfadimethoxine	122-11-2	SGS AXYS METHOD MLA-075	0.29-5.98 ng/L
		USGS RESEARCH METHOD 9017	65.5 ng/L
		USGS OGRL LCAB	0.005 µg/L
		USGS METHOD O-2440-14	65.5 ng/L
Sulfamerazine	127-79-7	SGS AXYS METHOD MLA-075	0.581-3.24 ng/L
Sulfamethazine	57-68-1	SGS AXYS METHOD MLA-075	0.586-9.05 ng/L
		USGS OGRL LCAB	0.005 µg/L
Sulfamethizole	144-82-1	SGS AXYS METHOD MLA-075	0.581-5.46 ng/L
		USGS RESEARCH METHOD 9017	104.0 ng/L
		USGS METHOD O-2440-14	104.0 ng/L
Sulfamethoxazole	723-46-6	SGS AXYS METHOD MLA-075	0.591-1.96 ng/L
		USGS RESEARCH METHOD 9017	26.1 ng/L
		USGS OGRL LCAB	0.005 µg/L
		USGS METHOD O-2080-08	0.091 µg/L
		USGS METHOD O-2440-14	26.1-80.0 ng/L
Sulfanilamide	63-74-1	SGS AXYS METHOD MLA-075	14.5-52.8 ng/L
Sulfathiazole	72-14-0	SGS AXYS METHOD MLA-075	1.45-5.07 ng/L
		USGS OGRL LCAB	0.005 µg/L
Tamoxifen	10540-29-1	SGS AXYS METHOD MLA-075	0.375-0.796 ng/L
		USGS RESEARCH METHOD 9017	52.4 ng/L
		USGS METHOD O-2440-14	80.0-181.0 ng/L
Temazepam	846-50-4	USGS RESEARCH METHOD 9017	18.4 ng/L
		USGS METHOD O-2440-14	18.4-80.0 ng/L
Teniposide	29767-20-2	SGS AXYS METHOD MLA-075	3.75-7.96 ng/L
Testosterone	58-22-0	USGS METHOD 2434	1.6 ng/L
Tetrachloroethylene	127-18-4	USGS METHOD O-1433-01	0.12 µg/L
Tetracycline	60-54-8	USGS OGRL LCAB	0.01 µg/L
Theophylline	58-55-9	SGS AXYS METHOD MLA-075	56.2-118.0 ng/L
		USGS RESEARCH METHOD 9017	41.5 ng/L
		USGS METHOD O-2440-14	41.5-200.0 ng/L
Thiabendazole	148-79-8	SGS AXYS METHOD MLA-075	1.45-15.9 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
		USGS RESEARCH METHOD 9017	4.1 ng/L
		USGS METHOD O-2080-08	0.06 µg/L
		USGS METHOD O-2440-14	4.1 ng/L
Tiotropium	186691-13-4	USGS RESEARCH METHOD 9017	43.1 ng/L
		USGS METHOD O-2440-14	43.1-200.0 ng/L
Tolyl triazole	29385-43-1	USGS RESEARCH METHOD 9017	141.0 ng/L
		USGS METHOD O-2440-14	141.0 ng/L
Tramadol	27203-92-5	USGS RESEARCH METHOD 9017	15.1 ng/L
		USGS METHOD O-2440-14	15.1 ng/L
Trenbolone	10161-33-8	SGS AXYS METHOD MLA-075	3.75-7.85 ng/L
Trenbolone acetate	10161-34-9	SGS AXYS METHOD MLA-075	0.281-2.48 ng/L
Triamterene	396-01-0	SGS AXYS METHOD MLA-075	0.293-1.04 ng/L
		USGS RESEARCH METHOD 9017	5.25 ng/L
		USGS METHOD O-2440-14	5.25-80.0 ng/L
Tribromomethane	75-25-2	USGS METHOD O-1433-01	0.1 µg/L
Tributyl phosphate	126-73-8	USGS METHOD O-1433-01	0.16 µg/L
Triclocarban	101-20-2	SGS AXYS METHOD MLA-075	2.81-3.23 ng/L
Triclosan	3380-34-5	SGS AXYS METHOD MLA-075	56.2-64.6 ng/L
		AXYS_MLA-083	4.69-11.0 ng/L
		USGS METHOD O-1433-01	0.2-1.28 µg/L
Triethyl citrate	77-93-0	USGS METHOD O-1433-01	0.16 µg/L
Trimethoprim	738-70-5	SGS AXYS METHOD MLA-075	1.45-3.0 ng/L
		USGS RESEARCH METHOD 9017	19.0 ng/L
		USGS OGRL LCAB	0.005 µg/L
		USGS METHOD O-2080-08	0.034 µg/L
		USGS METHOD O-2440-14	19.0-80.0 ng/L
Triphenyl phosphate	115-86-6	USGS METHOD O-1433-01	0.12 µg/L
Tris(1,3-dichloro-2-propyl)phosphate	13674-87-8	USGS METHOD O-1433-01	0.16 µg/L
Tris(2-butoxyethyl) phosphate	78-51-3	USGS METHOD O-1433-01	0.8-2.6 µg/L
Tris(2-chloroethyl) phosphate	115-96-8	USGS METHOD O-1433-01	0.1 µg/L
Tylosin	1401-69-0	SGS AXYS METHOD MLA-075	5.81-12.0 ng/L
		USGS OGRL LCAB	0.01 µg/L
Valacyclovir	124832-26-4	USGS RESEARCH METHOD 9017	163 ng/L
		USGS METHOD O-2440-14	163 ng/L
Valsartan	137862-53-4	SGS AXYS METHOD MLA-075	3.75-14.1 ng/L
Venlafaxine	93413-69-5	SGS AXYS METHOD MLA-075	0.387-6.37 ng/L
		USGS RESEARCH METHOD 9017	4.48 ng/L
		USGS METHOD O-2440-14	4.48 ng/L
Verapamil	52-53-9	SGS AXYS METHOD MLA-075	0.141-0.295 ng/L

Chemical name	CAS number	Analytical method	Reporting limit
		USGS RESEARCH METHOD 9017	15.5 ng/L
		USGS METHOD O-2440-14	15.5-80.0 ng/L
Virginiamycin M1	21411-53-0	SGS AXYS METHOD MLA-075	2.9-11.0 ng/L
		USGS OGRL LCAB	0.005 µg/L
Warfarin	81-81-2	SGS AXYS METHOD MLA-075	1.41-1.62 ng/L
		USGS RESEARCH METHOD 9017	6.03 ng/L
		USGS METHOD O-2080-08	0.08 µg/L
		USGS METHOD O-2440-14	6.03
Zidovudine	30516-87-1	SGS AXYS METHOD MLA-075	22.5 - 173.0

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