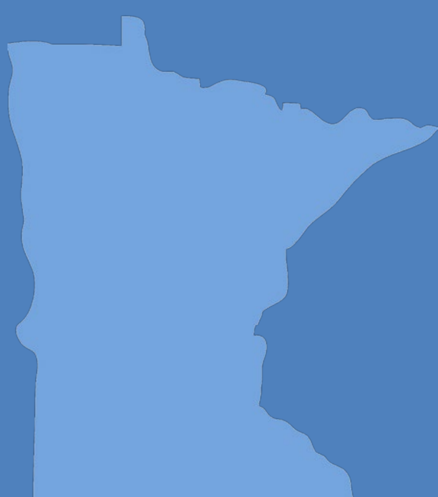
The Condition of Minnesota's Groundwater, 2007 - 2011



Minnesota Pollution Control Agency

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Acronyms

CEC – Contaminant of Emerging Concern

Cl/Br – Chloride/Bromide ratio

EAC – Endocrine Active Chemical

EDC – Endocrine Disrupting Chemical

HRL – Health Risk Limit

MCL – Maximum Contaminant Level

MDA – Minnesota Department of Agriculture

MDH – Minnesota Department of Health

MDNR – Minnesota Department of Natural Resources

mg/L – milligrams per liter

MPCA – Minnesota Pollution Control Agency

SMCL – Secondary Maximum Contaminant Level

TCMA – Twin Cities Metropolitan Area

ug/L – micrograms per liter

USEPA – United states Environmental Protection Agency

USGS – United states Geological Survey

VNMN – Volunteer Nitrate Monitoring Network

VOC – Volatile Organic Compound

Executive summary

Background

Sufficient amounts of clean groundwater are vital to the state of Minnesota. Groundwater supplies drinking water to about 75 percent of all Minnesotans and almost all of the water used to irrigate the state's crops. The inflow of groundwater also is important to maintain the water level, pollution assimilative capacity, and/or temperature in Minnesota's streams, lakes, and wetlands. Groundwater also must be clean to meet most Minnesotans' needs. Polluted groundwater often is unsuitable for drinking and usually is very expensive to clean up. It also costs more to construct water-supply wells in areas with polluted groundwater since wells may need to be drilled deeper to tap uncontaminated aquifers in these areas. In some instances, water treatment devices or additional water testing may be required before a new water-supply well can be used in areas with polluted groundwater.

The Minnesota Pollution Control Agency (MPCA) assesses the condition of Minnesota's groundwater as part of the agency's overall vision for clean water in its Strategic Plan, such that "Minnesota's clean water supports aquatic ecosystems, healthy communities and a strong economy" [*Minnesota Pollution Control Agency*, 2013]. This report describes the condition of Minnesota's groundwater, including temporal trends for selected constituents, and emphasizes the water quality in heavily-used aquifers for water-supply that are vulnerable to human-caused contamination. This report builds upon the last MPCA assessment of ambient groundwater quality that was published in 2007 [*O'Dell*, 2007]. The constituents assessed in this report are nitrate, phosphorus, sulfate, chloride, arsenic, iron, manganese, a suite of 68 volatile organic compounds (VOCs), and a suite of over 100 contaminants of emerging concern (CECs). The water-quality assessments in this report primarily were based on ambient monitoring data collected from 2007-2011 by the MPCA, Minnesota Department of Agriculture (MDA), and a volunteer nitrate monitoring network in Southeastern Minnesota. Data collected prior to 2007 by the MPCA, MDA, and US Geological Survey (USGS) also were analyzed to determine any trends in water quality.

Summarized finding for specific types of pollutants

The groundwater in the shallow sand and gravel aquifers in selected parts of Minnesota continues to be impacted by high *nitrate* concentrations. The shallow sand and gravel aquifers contained the highest median nitrate concentrations compared to all of the other aquifers assessed in this report. The highest nitrate concentrations occurred in the aquifers in Central and Southwestern Minnesota. In Central Minnesota, about 40 percent of the shallow sand and gravel aquifer wells contained water with nitrate concentrations that were greater than the Maximum Contaminant Level (MCL) of 10 milligrams per liter (mg/L) set by the U.S. Environmental Protection Agency (USEPA) for drinking water. The limited available data in Southwestern Minnesota showed that about 20 percent of the shallow sand and gravel aquifer wells contained water with nitrate concentrations that exceeded the MCL of 10 mg/L.

Some wells installed in the uppermost bedrock aquifers in Southeastern Minnesota had nitrate concentrations that exceeded the MCL of 10 mg/L. These high concentrations occurred in selected wells in the Upper Carbonate, St. Peter, Prairie du Chien, and Jordan aquifers, and all occurred in areas where the aquifers are naturally susceptible to contamination.

Nitrate concentrations in the sand and gravel aquifers varied with land use and depth. The groundwater underlying both agricultural and urban lands contained higher nitrate concentrations compared to the groundwater underlying undeveloped land. The highest nitrate concentrations observed in this investigation typically were in the shallow groundwater underlying agricultural lands. The median concentration in the shallow groundwater underlying agricultural areas was about 9 mg/L; whereas, the median concentration in the groundwater underlying a variety of urban land uses ranged from 2-3 mg/L. Data from the MDA suggested the high nitrate concentrations in the state's sand and gravel aquifers may be restricted to the uppermost parts. In deeper parts of the sand and gravel aquifers, the nitrate may be removed by a natural, microbially-mediated processed called denitrification, or the groundwater in these parts of the sand and gravel aquifers may be so old that nitrate contamination that originated from the land surface has not yet percolated down to these depths.

The amount of nitrate contamination in Minnesota's groundwater generally has not changed over the last 15 years. There was sufficient data to quantify trends from about 90 wells, which primarily were sampled from 1997-2011. Nitrate concentrations did not significantly change in the majority of the wells.

In contrast, *phosphorus* concentrations in the ambient groundwater were minimally affected by human factors compared to nitrate. There was no significant difference between phosphorus concentrations in the sand and gravel and Prairie du Chien-Jordan aquifers. The median concentration in both aquifers was about 30 micrograms per liter (ug/L). Concentrations tended to be higher in sand and gravel aquifers composed of calcareous sediments compared to those composed of siliceous sediments. This is consistent with the calcareous sediments in the state containing more phosphorus-bearing minerals, such as shale.

Groundwater in the shallow sand and gravel aquifers in the Twin Cities Metropolitan Area (TCMA) is impacted by high *chloride* concentrations. Chloride concentrations as high as 8,900 mg/L were measured in the shallow groundwater underlying the TCMA. The median chloride concentration in the sand and gravel aquifers in the TCMA was 86 mg/L, which was about five times greater compared to the sand and gravel aquifers throughout the rest of the state. Twenty-seven percent of the monitoring wells installed in the sand and gravel aquifers in the TCMA had chloride concentrations that were greater than the secondary maximum contaminant level of 250 mg/L, and thirty percent of the wells had chloride concentrations greater than the chronic water-quality standard of 230 mg/L. In contrast, very few wells outside the TCMA contained water with chloride concentrations that exceeded either drinking water or the chronic water-quality standard.

Chloride concentrations were significantly greater in groundwater underlying urban land compared to those underlying undeveloped areas. The source of the high chloride concentrations in the shallow sand and gravel aquifers in the TCMA likely was from the application of winter de-icing chemicals, since over 60 percent of the sand and gravel aquifer wells in the TCMA had a chemical signature consistent with halite, which typically is applied to de-ice roadways during the winter in Minnesota. The data compiled for this report suggested that the source of chloride was often halite in groundwater with concentrations greater than 30 mg/L.

Chloride concentrations were found to have increased in about one-third of the wells that had sufficient data for trend analysis. In some wells, chloride concentrations have increased by about 100 mg/L in the last 15-20 years. Most of the wells with increasing trends were shallow wells tapping the sand and gravel aquifers; however, increasing concentrations were found in two deep wells in the TCMA. If these trends continue, the water from more wells likely will have concentrations that exceed drinking water and water-quality standards in the future.

Iron and *manganese* concentrations were detected in about one-half of the sampled wells. About one-third of these wells contained concentrations that were high enough to cause human-health or aesthetic problems. High iron and manganese concentrations generally were related to geochemical conditions in the groundwater, specifically low oxygen concentrations.

The monitoring of *volatile organic compounds (VOCs)* in the state's ambient groundwater from 2007-2011 did not identify any areas that required cleanup or remediation. VOCs comprise a wide variety of chemicals that are refined from petroleum or otherwise synthesized and have many industrial, commercial, and household applications, including chemicals found in gasoline, solvents, refrigerants, and many commonly-used household products. VOCs were detected less frequently in the ambient groundwater compared to near sites with known spills or releases of these chemicals. Twelve VOCs were detected in the ambient groundwater, whereas 34 VOCs were detected in the groundwater in the immediate vicinity of known petroleum product or chemical spills. VOC concentrations in the ambient groundwater were low, and no concentrations exceeded any applicable human-health guidance.

Selected data on *contaminants of emerging concern (CECs)* that were collected from 2009-2010 were summarized in this report. These mostly included chemicals found in commonly-used household products, such as fire retardants, fragrances, an insect repellant, detergents and their associated degradates, prescription and non-prescription medications, and hormones. There was limited data on antibiotics; this analysis was restricted to two compounds. CECs were detected in about one-third of the sampled wells. No concentrations exceeded any applicable human-health guidance set by the state of Minnesota. The most-frequently detected chemicals were the fire retardant tris (dichloroisopropyl) phosphate, the antibiotic sulfamethoxazole, and the plasticizers bisphenol A and tributyl phosphate. Endocrine active chemicals were detected in three of the sampled wells. Two of these three wells tapped landfill-leachate plumes, and the third was a shallow well that provided drinking water to a residence.

Key results

The ambient monitoring conducted by the MPCA, MDA, and others continues to provide valuable, long-term information on water-quality conditions in aquifers vulnerable to human-caused contamination across Minnesota. As demands for Minnesota's groundwater increase, this record of ambient groundwater quality will become increasingly important for the proper use and management of the state's groundwater resources.

The analyses presented in this report give us a baseline to work from for future assessments of groundwater quality; chloride and nitrate concentrations in the state's aquifers especially should be watched. The high chloride concentrations in the state's shallow groundwater in the TCMA either will be discharged into streams and lakes, or this chloride-laden groundwater will move downward to the aquifers that supply the state's drinking water. The inflow of groundwater containing chloride concentrations that exceed the chronic water-quality standard (230 mg/L) to streams may cause any chloride impairments to occur during baseflow conditions as well as during the usual winter period [*Wenck Associates*, 2009]. In some streams in the TCMA, chloride concentrations already have begun to increase during baseflow conditions [*Asleson et al.*, 2011]. The chloride in the groundwater that does not reach streams or lakes will be transported downward into the aquifers that provide the state's drinking water. The analyses presented in this report have demonstrated that chloride concentrations in a bedrock aquifer in the TCMA have increased over the last decade. If these trends continue, more bedrock aquifer wells may be impacted by chloride, and the water may become unsuitable for drinking without treatment. The high nitrate concentrations found in some the state's groundwater in this report also need to be watched in the future, especially since some communities have had problems with high nitrate concentrations in their water supplies [*O'Dell*, 2007; *Robertson*, 2009]. The presence of CECs in the groundwater, even though these are low in concentration, bears watching because this monitoring identifies chemicals in Minnesota's groundwater that have no health-based drinking water standard.

Introduction

Sufficient amounts of clean groundwater are vital to the state of Minnesota. Groundwater supplies drinking water to about 75 percent of all Minnesotans and almost all of the water used to irrigate the state's crops. The inflow of groundwater also is important to maintain the water level, pollution assimilative capacity, and/or temperature in Minnesota's streams, lakes, and wetlands. Groundwater must be clean to meet most Minnesotans' needs. Polluted groundwater often is unsuitable for drinking and usually is very expensive to clean up. In addition, it costs more to construct water-supply wells in areas with contaminated groundwater. Wells may need to be drilled deeper to tap uncontaminated aquifers in areas with polluted groundwater, or in some instances, water treatment devices or additional water testing may be required before a new water-supply well can be used in these areas.

Purpose and scope

This report describes the current baseline condition of Minnesota's groundwater resources and determines, to the extent possible, whether groundwater conditions have changed over time. The quality of the state's groundwater is the focus of this report. Trends in groundwater levels are briefly described since groundwater quality and quantity concerns often are interrelated.

The most-heavily used aquifers for water supply primarily were assessed in this report. These aquifers often are the most vulnerable to human-caused pollution since they can contain young groundwater. Some of the deep aquifers in the state contain water that is hundreds to thousands of years old and generally are not as vulnerable to human-caused pollution. The groundwater level discussion primarily focuses on the bedrock aquifers in the Twin Cities Metropolitan Area (TCMA) because the most-detailed published reports are from this area.

The assessments in this report were based on ambient monitoring data or previously published reports. The groundwater quality assessments were based on ambient monitoring data collected by the Minnesota Pollution Control Agency (MPCA), the Minnesota Department of Agriculture (MDA), and a volunteer nitrate monitoring network (VNMN) in Southeastern Minnesota. The description of groundwater level trends was based on reports from the Minnesota Department of Natural Resources (MDNR) and US Geological Survey (USGS).

The water-quality assessment included traditional pollutants known to adversely affect the potability of the groundwater, such as nitrate, chloride, trace elements such as arsenic, and volatile organic compounds (VOCs). Other pollutants, such as phosphorus and sulfate, were assessed because groundwater inflow containing these constituents has the potential to adversely affect surface waters. This report also included some newly-recognized pollutants, such as medicines, insect repellents, and fire retardants. The effects of these new pollutants , which are often referred to as contaminants of emerging concern or CECs, to human and aquatic life are not fully understood at this point, but these chemicals are not naturally-occurring and their presence indicates human impact.

Current groundwater quality conditions generally were determined using data collected from wells that were sampled from 2007-2011. Most of these data were collected as part of the MPCA's ambient groundwater monitoring; however, a large amount of nitrate data was compiled from the MDA and Southeastern Minnesota VNMN. The assessments of nitrate, chloride, sulfate, and VOCs were made using data from 2007-2011. The phosphorus, CEC, and some of the trace element assessments used data collected over a shorter period of time because these constituents were not analyzed in earlier water samples. Phosphorus concentrations were described using data from 2008-2011. Arsenic concentrations were described using data from 2010-2011, and CEC concentrations generally were described using data from 2010. Temporal trends in groundwater quality conditions were determined using wells with data spanning a period of at least 10 years.

This report builds upon the MPCA assessment of the overall condition of Minnesota's groundwater that was published five years ago [*O'Dell*, 2007]. This report assesses additional constituents and includes a current analysis of the effect of land use on groundwater quality. These improvements in reporting resulted from enhancements to the MPCA's ambient monitoring network made possible through the Clean Water Fund. From 2007-2011, the number of chemicals analyzed in groundwater samples collected from the MPCA's Ambient Groundwater Monitoring Network increased from 70 to more than 200. Since 2010, about 70 new wells were installed in various urban and undeveloped settings for the MPCA's network. The sampling of these wells has resulted in an enhanced discussion of the effects of land use on water quality.

Minnesota's aquifers

Minnesota's groundwater occurs in aquifers that were formed throughout the state's geologic history. Some of these aquifers were formed long ago when Minnesota's landscape looked vastly different than it does today. The state's oldest aquifers were formed when Minnesota had active volcanoes and earthquakes commonly shook the land surface. The Earth's continents were just beginning to form during this time. Some of the state's most important bedrock aquifers were later formed when Minnesota enjoyed a hot, subtropical to tropical climate and was covered by a vast sea. Even later, the youngest aquifers were formed when the state had a very cold climate and was covered by glaciers.

The state's oldest aquifers are composed of crystalline bedrock and are important sources of groundwater, mainly in Northern and Southwestern Minnesota. These aquifers generally were formed from the sands and silts that were weathered and eroded from ancient volcanic rocks. These weathered materials were ultimately cemented together and transformed into crystalline rocks by the heat from long-extinct volcanoes. The rocks that form these aquifers are the oldest in the state and are at least 600 million to several billion years old. The crystalline bedrock aquifers include the North Shore Volcanic, Proterozoic metasedimentary, Biwabik Iron-formation, Sioux Quartzite, and Undifferentiated Precambrian aquifers. The first three aquifers (North Shore Volcanic, Proterozoic metasedimentary, and Biwabik Iron-formation aquifers) only occur in Northeastern and North-Central Minnesota, and the Sioux Quartzite aquifer only occurs in Southwestern Minnesota. The Undifferentiated Precambrian aquifers form the basement or lowermost rocks throughout the state and are used locally as aquifers everywhere except Southeastern Minnesota. In Southeastern Minnesota, the Undifferentiated Precambrian aquifers are too deeply buried by other very productive aquifers and are not tapped as a water supply.

The Paleozoic-age sandstone and carbonate rock aquifers are the state's most important bedrock aquifers and are major sources of groundwater in Southeastern Minnesota. The sandstone and carbonate rock bedrock aquifers were formed when seas covered Minnesota about 500 million years ago and include the Upper Carbonate, Red River-Winnipeg, St. Peter, Prairie du Chien-Jordan, Tunnel City/Wonewoc, and Mount Simon-Hinckley aquifers. The Red River-Winnipeg aquifer only is present in Northwestern Minnesota and contains salty water. The others form a sequence of aquifers in Southeastern Minnesota (Figure 1).

The Upper Carbonate aquifer is the uppermost and youngest in the series of Paleozoic-age aquifers in Southeastern Minnesota. This aquifer is located in extreme Southern Minnesota and extends only about 80 miles north into Minnesota from the Iowa border. The Upper Carbonate aquifer, as the 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 aquifer 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 the St. Peter aquifer is intergranular. This aquifer typically is not used for public water supplies because it is not continuous within the TCMA and the underlying bedrock aquifers are more productive.

The Prairie du Chien-Jordan aquifer is the third in the series of Paleozoic-age bedrock aquifers in Southeastern Minnesota and is a major source of water supplies. The Prairie du Chien-Jordan aquifer is present throughout Southeastern Minnesota and extends to the TCMA. This aquifer consists of two different units: the Prairie du Chien Group, which is a sandy dolomite, and the Jordan sandstone. These two units often have a hydraulic connection, so many studies consider both units as a single aquifer. However, the lower part of the Prairie du Chien Group can serve locally as a confining unit for the Jordan sandstone. The Prairie du Chien-Jordan aquifer is used heavily as a source of water supply for the TCMA, and wells tapping the aquifer can yield as much as 2,700 gallons per minute [*Adolphson et al.*, 1981].

The Tunnel City/Wonewoc aquifer (formerly referred to as the Franconia/Ironton/Galesville aquifer) is the fourth in the series of Paleozoic-age bedrock aquifers in Southeastern Minnesota. This aquifer is present throughout Southeastern Minnesota and extends just slightly beyond the TCMA. The Tunnel City/Wonewoc aquifer underlies the Prairie du Chien-Jordan and consists of very fine to coarse sandstone interbedded with shale, dolomitic sandstone, and dolomitic siltstone. Traditionally, the Tunnel City/Wonewoc has been treated as one aquifer. However, flow in the upper part of the aquifer primarily is through bedding plane features, and flow in the lower part of the aquifer primarily is intergranular. The upper and lower parts of the Tunnel City/Wonewoc aquifer are separated by a confining unit.

The Mount Simon-Hinckley is the fifth in the series of Paleozoic-age bedrock aquifers in Southeastern Minnesota. This aquifer is present throughout Southeastern Minnesota and extends almost as far north as Duluth, Minnesota. The Mount Simon-Hinckley is the deepest of Paleozoic-age bedrock aquifers and overlies the crystalline basement rocks. The aquifer consists of two sandstone formations, the Mount Simon and Hinckley sandstones, that have similar hydraulic characteristics [*Schoenberg*, 1984]. North of the TCMA, the Mount Simon-Hinckley is the uppermost bedrock aquifer. South of the TCMA, the Mount Simon-Hinckley aquifer is overlain by other Paleozoic-age bedrock aquifers.

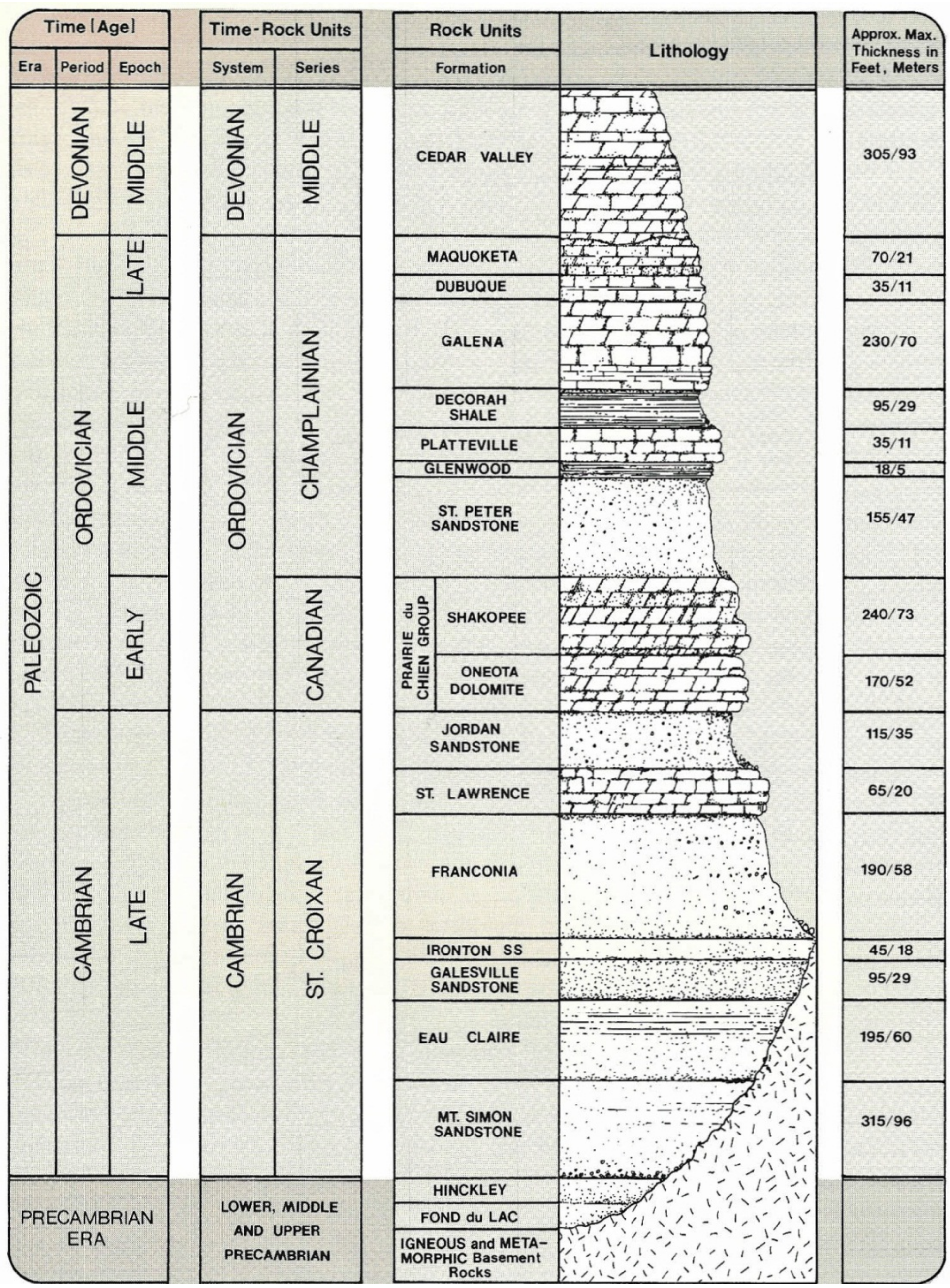


Figure 1. Stratigraphic column of the bedrock aquifers in Southeastern Minnesota [Ojakangas et al., 1982]

The Cretaceous aquifers are an important source of water in Southwestern Minnesota. These aquifers were formed about 65 to 145 million years ago (this is the same time period when dinosaurs roamed the state) and consist of discontinuous lenses of sandstones that usually are located within shale. The water in the aquifers usually is confined either by shale or by glacial till in places where the shales are absent due to erosion. The Cretaceous aquifers are located throughout Western and North-Central Minnesota where they overlie either the crystalline basement rocks or Paleozoic-age sandstone and limestone aquifers but are most extensive in Southwestern Minnesota. Most of the wells that tap this aquifer for water supplies are located in Southwestern Minnesota, primarily southwest of the Minnesota River.

The sand and gravel aquifers are the youngest in the state and important sources of groundwater throughout Minnesota. Unlike the bedrock aquifers described in the preceding paragraphs, the sand and gravel aquifers are composed of sediments that are not yet cemented together to form a rock. The sand

and gravel aquifers were formed when Minnesota had a very cold climate and was covered by glaciers from about two million to 12,000 years ago. The sand and gravel aquifers were formed in places where the melting water from the glaciers left sandy or gravelly sediments. These deposits can either be near the land surface or may be buried within clays. The buried sand and gravel aquifers occur when glaciers traversed the same area several times. The sand and gravel aquifers occur throughout Minnesota but are concentrated in the central part of the state.

Minnesota's groundwater resources are very unevenly distributed across the state due to the differences in how much water the various aquifers are able to transmit. Central and Southeastern Minnesota have the most abundant groundwater supplies (Figure 2) because the sandstone, limestone, and sand and gravel aquifers in these parts of the state yield good amounts of water. Northeastern Minnesota generally has only crystalline bedrock aquifers available, with limited groundwater resources because groundwater only is transmitted through fractures, faults, or weathered zones. Western Minnesota also has limited groundwater resources. The only aquifers present in this part of the state are a few surficial sand and gravel aquifers and the Sioux Quartzite aquifer.

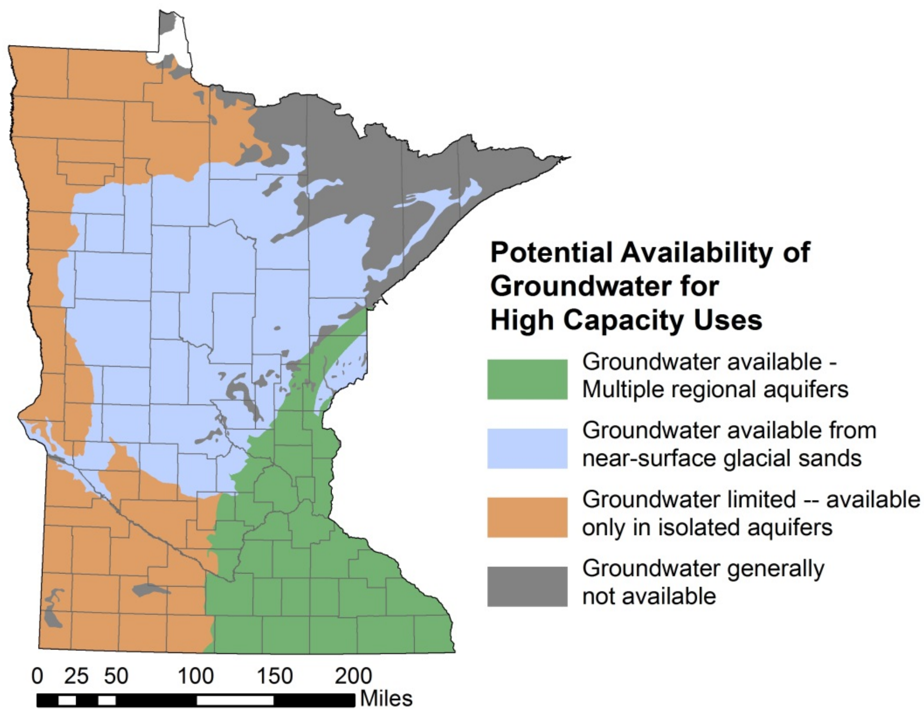


Figure 2. Potential groundwater availability in the state of Minnesota
[Data from the Minnesota Department of Natural Resources]

Minnesota's environmental setting

The state's environmental setting affects the presence and distribution of pollutants in the groundwater. Land use and cover probably are two of the most important features of the environmental setting that affect the presence and distribution of pollutants. Non-agricultural chemicals, such as VOCs and chloride, generally are used more-frequently in urban settings and are expected to be found at the greatest concentrations in these areas. Other constituents, such as nitrate, are used in both agricultural and non-agricultural areas and may be present in the groundwater underlying both settings.

Climate

Minnesota has a continental climate that is characterized by a wide range in temperature. The state's winters are very cold. The air temperature can be -30 degrees Fahrenheit or less when arctic air masses occasionally reach the state. The summers typically are warm and humid. The average temperature during this time typically is about 70-75 degrees Fahrenheit, and the dew point ranges from about 65-80 degrees Fahrenheit. The state usually receives about 29 inches of precipitation each year, though there is significant variation on a generally increasing west to east gradient. About two-thirds of the annual precipitation falls during the growing season for crops from May-September.

Land use and land cover

Most of Minnesota is covered by forests, wetlands, and agricultural lands. Forty-one percent of the state is covered by forests and wetlands, which are concentrated in the north [*Fry et al.*, 2011]. Agricultural land encompasses 45 percent of the state and is concentrated in the southern and western parts. Corn and soybeans are the primary crops grown. Cattle, hogs, and poultry are the primary livestock raised. Urban land use comprises about five percent of Minnesota and is concentrated in the TCMA, although small localized urban areas occur throughout the state. The remainder of the land in the state is comprised of open water, barren land, and grasslands.

Population and groundwater use

The state's population is concentrated in the TCMA. In 2011, there were 5.3 million people in Minnesota [*U.S. Census Bureau*, 2011], and about one-half of these people resided within the TCMA.

Groundwater primarily is used by Minnesotans as a drinking water supply and for crop irrigation. Water appropriations data collected by the MDNR shows that about 220 billion gallons of groundwater was withdrawn from the state's aquifers in 2010. Over 80 percent of this groundwater was used for drinking water supplies or crop irrigation. The majority of the groundwater withdrawn (57 percent) was used for public water supply, in which the water may be used for drinking or for other uses such as lawn watering or car washing. About one-quarter of the groundwater withdrawals in 2010 were used to irrigate crops. Industrial processing, power generation, air conditioning, or other uses accounted for less than 20 percent of the groundwater withdrawn.

The Prairie du Chien-Jordan and the sand and gravel aquifers are two of the most important sources of groundwater in Minnesota. These two aquifers generally account for over 80 percent of the groundwater withdrawn in the TCMA. The Prairie du Chien-Jordan aquifer generally supplies about 60 percent of the groundwater in the TCMA, and the sand and gravel aquifers account for about 20 percent of the groundwater withdrawn [*Minnesota Department of Natural Resources*, 2010]. Outside of the TCMA and Southeastern Minnesota, the sand and gravel aquifers typically are the most important sources of groundwater [*Lindgren*, 2002; *Lindgren and Landon*, 2000; *Stark et al.*, 1991].

Minnesota's ambient groundwater monitoring approach

Monitoring is essential to ensure the state of Minnesota has enough clean groundwater to meet its citizens' needs. Water managers need the monitoring data to understand where the groundwater flows and ensure that groundwater extracted for public water supplies or irrigation will be replenished so it can be used by future generations. It also is critical to monitor the amount of chemicals in the state's groundwater to ensure our land use practices do not degrade its quality and that practices put in place to minimize groundwater pollution are working. Once degraded, it usually is very expensive to restore groundwater quality to the appropriate levels.

There are several different types of groundwater monitoring. Problem investigation monitoring assesses localized areas of contamination, such as gasoline spills or Superfund sites. Ambient monitoring is used to understand the overall condition of the groundwater, identify any changes that have occurred over time, and identify any regional-scale problems. Ambient monitoring is done outside of known areas with chemical spills or releases and is the focus of this report.

Ambient groundwater monitoring in Minnesota is not the work of the MPCA alone but a coordinated effort among several state agencies. Each agency's role in ambient monitoring is defined by state statutes and federal requirements.

The MDNR monitors the ambient groundwater to understand how much is available for a variety of uses, including drinking water, crop irrigation, or maintaining streamflow or lake levels during dry periods. To meet this objective, the MDNR maintains the state's groundwater level monitoring network and tracks the amount of groundwater withdrawn.

Three agencies jointly monitor the chemicals present in Minnesota's groundwater based on their individual state and federal authorities and requirements. The MDA conducts ambient monitoring in agricultural areas of the state mainly to determine whether routine nitrogen fertilizer and pesticide use pollutes the state's groundwater. The MPCA maintains an ambient monitoring network to determine whether non-agricultural chemical pollution is present in the groundwater and to track any trends in pollution. The MDA and MPCA's monitoring networks focus on these specific chemical types because of their state and federal authorities and requirements. The MDA's monitoring compliments its charge to regulate the use of agricultural chemicals in the state, and the MPCA's monitoring compliments its charge to minimize groundwater contamination from all other chemicals. The Minnesota Department of Health (MDH) works with both the MPCA and MDA to ensure that any chemicals in the state's groundwater do not threaten human health. The MDH's activities include setting human health guidance for chemicals detected in the state's groundwater and monitoring the drinking water in the state's public water supplies in cooperation with the public water supply systems.

Minnesota Pollution Control Agency's Network

The MPCA maintains an Ambient Groundwater Monitoring Network that monitors the aquifers that are most likely to be polluted with non-agricultural chemicals. This network primarily targets the shallow aquifers that underlie the urban parts of the state. Typically, the shallow aquifers are sampled because these tend to be the most vulnerable to pollution. Some of the state's deep aquifers are naturally protected by materials that do not allow water and its associated pollution to percolate through it, such as clay or shale. As a result, some of these naturally-protected aquifers contain water that is thousands of years old, and any human-caused pollution introduced at the land surface has not been present in the groundwater long enough to reach these aquifers.

The MPCA's Ambient Groundwater Monitoring Network as of 2013, when this report was produced, consisted of about 200 wells that primarily are located in the sand and gravel and Prairie du Chien-

Jordan aquifers. About 80 percent of the network wells are located in the sand and gravel aquifers, and the remainder primarily are located in the Prairie du Chien-Jordan.

Some wells in the MPCA's network are used to discern the effect of urban land use on groundwater quality and comprise an early warning network. When this report was produced, the early warning network consisted of about 130 shallow wells placed near the water table in the sand and gravel aquifers. Most wells in this early warning network contain water that was recently recharged into the groundwater. The results of testing to determine the groundwater's age has determined that it is less than one year old in some wells in the early warning network. The wells in the early warning network are distributed among several different settings to determine the effect land use has on groundwater quality. These assessed land use settings are: 1) sewered residential, 2) residential areas that use subsurface sewage treatment systems (SSTS) for wastewater disposal, and 3) commercial or industrial, and 4) undeveloped. The data collected from the wells in the undeveloped areas provide a baseline to assess the extent of any pollution from all other land use settings.

Water samples from the MPCA's Ambient Groundwater Monitoring Network wells generally are collected annually by MPCA staff. This sampling frequency provides sufficient information to determine trends in groundwater quality. The water samples are analyzed to determine the concentrations of over 100 chemicals, including nitrate, chloride, and VOCs.

Minnesota Department of Agriculture's Network

The MDA monitors aquifers that are likely to be impacted by agricultural chemicals. Similar to the MPCA's network, the MDA's groundwater monitoring well network primarily targets the shallow aquifers, but those that underlie the agricultural parts of the state. The monitoring well network focuses on the upper portion of the sand and gravel aquifers and consists of over 100 wells that typically are located at the edge of farm fields. Although MDA's groundwater monitoring network was designed for pesticides, the MDA 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 in the state. About eighty of these wells are located in Central Minnesota, and the remainder are located in agricultural areas in other parts of the state. Approximately 10 springs and 10 domestic wells are sampled in lieu of monitoring wells in Southeastern Minnesota.

Water samples generally are collected at least annually from all network monitoring sites by MDA staff. The sampling frequency varies among the monitoring sites. Some sites are sampled as frequently as four times each year. The sampling frequency for all sites is listed in annual work plans published by the MDA, which can be found online at: http://www.mda.state.mn.us/monitoring. All water samples are analyzed at the MDA laboratory for nitrate and a suite of over 100 pesticides and their degradates.

Southeastern Minnesota Volunteer Nitrate Monitoring Network

In Southeastern Minnesota, a large amount of groundwater quality data has been collected by a VNMN. The Southeastern Minnesota VNMN was designed to assess the quality of the groundwater consumed by private well owners. In this part of the State, approximately two-thirds of the population consumes water from wells installed before the Minnesota state well code was adopted in 1974 [*Southeast Minnesota Water Resources Board*, 2009]. In addition, the nitrogen loading in this area is high, and the sensitivity of some of the aquifers to human-caused pollution is very high. Over 500 wells were sampled to determine nitrate concentrations by citizen volunteers as part of the VNMN. These included wells that were constructed before and after the Minnesota well code implementation. Many of these wells, especially those constructed before 1974, lacked well construction or geologic information.

The data collected by the VNMN provided a good indication of the extent of nitrate contamination in Southeastern Minnesota despite the limitations of this data set. The sample collection, handling, and analysis methods likely caused more uncertainty in the measured nitrate concentrations compared to those measured by the MPCA and MDA networks. All water samples collected by the VNMN came from citizens who received some general training in sample collection, whereas professional staff collected all of the water samples for the MPCA and MDA monitoring networks in accordance with standard operating procedures. The water samples collected for the VNMN were not shipped in coolers to the laboratory, and some of the samples arrived at the laboratory warm [*Southeast Minnesota Water Resources Board*, 2009]. The nitrate samples collected for the VNMN also were not analyzed at a facility that was certified by the State of Minnesota. Despite these limitations, any high nitrate concentrations reported by the VNMN still indicate areas of concern.

Data compilation and analysis methods

The water-quality data analyzed in this report were compiled from several national, statewide, and regional groundwater monitoring networks. The majority of the data analyzed in this report were from the MPCA's Ambient Groundwater Monitoring Network. A large amount of nitrogen data also were compiled from the MDA's ambient monitoring network and the Southeastern Minnesota VNMN. Only nitrogen data were compiled from the MDA's network and the Southeastern Minnesota VNMN because no other inorganic constituents, VOCs, or CECs were analyzed in water samples collected from these networks. In addition, nitrate data only were compiled from the VNMN if the well had construction information either from a well log or inferred through analyses conducted by the MDH. Selected data also were obtained from the USGS to augment the chloride and nitrogen trend records for some wells in the TCMA and the vicinity of Bemidji because the earliest data from these wells were collected for USGS studies.

Nitrogen data were available from a large number of wells and springs in the State. Over 850 wells and springs had nitrogen data collected from them during 2007-2011. These data were not evenly distributed across the state or among aquifers. Approximately one-half of the wells were located in Southeastern Minnesota, and the remainder primarily was located in Central Minnesota and the TCMA. Most of the compiled data was from the sand and gravel or Prairie du Chien-Jordan aquifers. Fifty-one percent of the monitored wells were installed in the sand and gravel aquifers, and twenty-six percent were installed in the Prairie du Chien-Jordan aquifer. The remainder of the wells primarily was installed in other Paleozoic-age bedrock aquifers in Southeastern Minnesota.

Nitrate was the only form of nitrogen measured in over 80 percent of the groundwater samples compiled for this report. Nitrate or nitrate plus nitrite nitrogen concentrations were measured in water samples collected by all of the monitoring networks. Throughout the remainder of this report, nitrate plus nitrite concentrations will be referred to simply as nitrate concentrations because nitrite concentrations in water typically are very small compared to nitrate concentrations. All samples collected by the MPCA from 2008-2011 also were analyzed to determine ammonia and total organic plus ammonia nitrogen concentrations.

The method reporting limits varied between the nitrate data sets compiled for this report. The method reporting limit associated with the MPCA nitrate data was 0.05 mg/L, and the method reporting limit associated with the MDA data was 0.4 mg/L. No method reporting limit was given for the data collected as part of the VNMN.

Chloride and VOC data were compiled from about 270 wells that were sampled from 2007-2011. These wells primarily tapped the sand and gravel aquifers in Central and Northern Minnesota and the Prairie du Chien-Jordan aquifer in Southeastern Minnesota. Most of the chloride and VOC data analyzed in this report were collected from the sand and gravel aquifers. About 76 percent of the wells were installed within the sand and gravel aquifers, and about 16 percent of the wells were installed in the Prairie du Chien-Jordan aquifer.

Phosphorus, sulfate, and trace element data were available from a smaller number of wells compared to nitrate, chloride, and VOCs because measurements of these constituents began later. Phosphorus, sulfate, and trace element data were compiled from about 150 wells for this report. These wells primarily tapped the sand and gravel aquifers. About 75 percent of the wells were installed within the sand and gravel aquifers, and about 15 percent of the wells were installed in the Prairie du Chien-Jordan aquifer. The remaining wells were installed in the St. Lawrence, Galena, Tunnel City/Wonewoc, or St. Peter aquifers.

The data were analyzed using several different techniques. In many instances, the reported concentrations were compared to applicable health-guidance values or surface water-quality standards to determine whether the groundwater was suitable for drinking or would present a risk to surface waters if discharged as groundwater inflow. The data also were analyzed to determine the source of contaminants, either by determining contaminant ratios or through an assessment of the distribution of concentrations in the groundwater. Finally, several statistical tests were performed to quantify differences in contaminant concentrations among aquifers or land-use settings or quantify any temporal trends in concentrations.

Most of the water-quality data compiled for this report were analyzed in a manner that evenly weighted the results among all of the monitoring sites and represented the most current water-quality conditions. The concentrations of many constituents were measured at least annually at many sites from 2007-2011. Many sites, however, were not sampled as long or even just once. To avoid biasing the data interpretations in this report to the most-frequently sampled sites, only the last water-quality measurement from each well was compiled for data analyses in this report, except for trend analysis. This method of compiling data also provided an analysis of the most recent water-quality conditions.

In this report, a well was considered to have sufficient data for trend analysis if five or more measurements were collected from it over at least a 10-year period. Data collected by the USGS were used to augment the records from many of the wells in Bemidji and the TCMA because the earliest data from these two sets of wells were collected for USGS studies [*Andrews et al.*, 1998; *Stark et al.*, 1991]. The inclusion of these additional records extended the amount of data back to the mid-1990s for the wells in the northwestern part of the TCMA and as far back as the late 1980s for the wells in the vicinity of Bemidji. The data from most of the analyzed wells was collected on an annual basis. Some wells located in the St. Cloud area were sampled more frequently. In the 1990s, data was collected from some of the wells in this area on a quarterly basis. To avoid biasing the trend results to the more frequently sampled periods and meet the criteria for the statistical test used to quantify trends, all data sets were reduced to an annual frequency; only the values collected closest to July were retained for analysis.

The source of the chloride in the Minnesota's groundwater was determined using the ratio of the chloride to bromide concentrations. In this report, chloride/bromide (Cl/Br) ratios were calculated for all wells that had both detectable chloride and bromide concentrations. The Cl/Br ratio is used to ascertain chloride sources because it differs among several common sources in the environment. Chloride derived from halite, commonly known as rock salt, has a Cl/Br ratio between 1,000 and 10,000 [*Davis et al.*, 1998]. This large ratio results from halite being depleted in bromide. Bromide is slightly more soluble than chloride and remains dissolved in the water after sodium and chloride precipitates out as rock salt or halite. Cl/Br ratios ranging from 300-1,000 may indicate that wastewater is the chloride source or the groundwater contains a mixture of halite and native groundwater. Groundwater unaffected by human-caused contamination has a Cl/Br ratio that is less than 200 [*Davis et al.*, 1998].

The water-quality data compiled for this report were analyzed using several statistical tests. The Kruskal-Wallis test and non-parametric multiple comparison test [*Helsel and Hirsch*, 1991] were used to determine whether there were significant differences among land-use settings or aquifers. Kendall-tau correlation coefficients were used to quantify whether there was any relation among the various water-quality constituents. Finally, long-term temporal trends were quantified using the Mann-Kendall test [*Helsel and Hirsch*, 1991].

Minnesota's groundwater elevations

The elevation of water measured in a well is related to the volume of water in the aquifer. Declines in water elevations indicate that there is less groundwater available for use. Groundwater elevation declines can be caused by both natural and man-made conditions, from decreasing rainfall or increased pumping.

The most detailed information on changes in groundwater elevations is from the Prairie du Chien-Jordan and Mt. Simon-Hinckley aquifers in the TCMA. Changes in groundwater elevations in these aquifers from 1980-1990 were quantified by *Andrews et al.* [1995]. During this period, groundwater elevations declined by an average of 2 and 43 feet, respectively, in the Prairie du Chien-Jordan and Mt. Simon-Hinckley aquifers, largely because the pumping of groundwater increased. The changes in groundwater elevations in these same two aquifers from 1988-2008 were quantified by *Sanocki et al.* [2009]. From 1988-2008, water levels in the Prairie du Chien-Jordan aquifer continued to decline in parts of the TCMA but rose in others. Groundwater elevations declined as much as 8 feet in Central Hennepin, 31 feet in Northwestern Dakota, and 13 feet West-Central Washington Counties, and rose as much as 17 feet in Central Ramsey, 48 feet in Southern Washington, and 35 feet Southern Dakota Counties. Groundwater elevations in the Mt. Simon-Hinckley aquifer continued to decline slightly from 1988-2008. The average decline in groundwater elevations in the Mt. Simon-Hinckley aquifer during this period was 0.45 feet. Changes in the groundwater elevations in individual wells ranged from an increase of 57 feet in Southern Anoka County to a decrease of 56 feet in Northeastern Scott County.

There is more limited information on the changes in groundwater elevations in the rest of the state. A 2010 study of water availability [*Minnesota Department of Natural Resources*, 2010] assessed long-term changes in groundwater elevations using data from seven wells that were considered representative of different parts of the State. Groundwater elevations in most of these wells declined over time. The time period over which groundwater elevations were measured in the assessed wells varied and ranged from about the last 20 to 50 years. The well in Northeastern Minnesota was the only one that had no declines in the groundwater elevations.

There are groundwater quantity concerns in several parts of the state. The Interstate-94 (I-94) corridor from the TCMA to St. Cloud is one of these areas. This is one of the fastest growing areas of Minnesota. Some counties within the I-94 corridor have doubled or more in population over the last decade. This increased growth will lead to an increased demand for water supplies in this area, which already has high agricultural irrigation and industrial usage. The Bonanza Valley, which is located in the vicinity of the towns of Brooten and Belgrade in Southwestern Stearns County, is another area with groundwater quantity concerns. In this area, some residents' wells dried up due to increased pumping from irrigation wells. These problems have since been resolved but called attention to the importance of managing the groundwater resources in this part of the state. Southwestern Minnesota has limited groundwater resources. The only aquifers available to use for water supply in this part of the state are a few surficial sand and gravel aquifers and the Sioux Quartzite aquifer. Because of these limited groundwater supplies, a rural water system pumps groundwater from three wellfields to communities in about 10 counties in Southwestern Minnesota. These wellfields, however, are at or near their production capacity.

Minnesota's groundwater quality

Groundwater that is contaminated may be unsuitable as a drinking water source and contribute to the degradation of stream or lake water quality. Groundwater that contains chemicals with concentrations that exceed the state's human health guidance poses a health risk to people if it is consumed. In Minnesota, the MDH has published health-based guidance, found on the Internet at http://www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html. In some situations, the groundwater may transport substantial amounts of contaminants to streams and lakes. This usually occurs when the stream or lake water budget is dominated by groundwater inflow, and the contaminants are very soluble in water, such as nitrate or chloride. A groundwater source of contamination also may result in a longer time frame to clean up pollution in a stream or lake because it often takes much longer for a pollutant applied to the land surface to eventually reach streams or lakes if it is transported with the groundwater, compared to more "quick" pathways such as overland flow.

The distribution of a contaminant in the groundwater also may indicate whether it occurs naturally or results from human activities. Constituents in the groundwater that are affected by human-caused contamination share a couple of common characteristics. The concentrations typically vary with land use and usually are higher in the uppermost aquifers compared to the underlying aquifers because any human-caused contamination usually emanates from the land surface.

This section of the report describes the occurrence and distribution of several water-quality constituents in Minnesota's groundwater. This includes a discussion of some commonly-known contaminants, such as nitrate, chloride, and VOCs. These three chemicals were discussed in the previous MPCA statewide assessment of groundwater quality conditions [*O'Dell*, 2007]. The occurrence and distribution of some contaminants which have both natural and human-caused sources also is discussed. High concentrations of some of these constituents, such as arsenic and manganese, adversely affect human-health, whereas high concentration of other constituents, such as phosphorus, promote the growth of nuisance algal blooms and adversely affect surface water quality. Finally, there is a discussion of the occurrence of some previously unmonitored and unregulated contaminants. These contaminants include medicines, hormones, and other chemicals in commonly-used household products.

Nitrogen

Nitrogen is an essential nutrient for plant and animal growth. This nutrient is needed by plants and animals to form all of the proteins, enzymes, and metabolic processes involved in the synthesis and transfer of energy. In plants, nitrogen is an important part of chlorophyll, which is the green pigment that is responsible for photosynthesis. Nitrogen also helps promote rapid growth in plants and also increases seed and fruit production.

An overabundance of nitrogen in water, however, adversely affects human health and aquatic life. High concentrations of nitrate in drinking water cause a medical condition in humans called methemoglobinemia. This is a blood disorder that usually affects infants. In this disorder, the blood is unable to carry oxygen to the rest of the body which results in the skin turning a blue color and can even result in death. To protect human health, the EPA established a maximum contaminant level (MCL) of 10 mg/L for nitrate. A MCL is a legally enforceable standard that applies to public drinking water systems and is the highest contaminant concentration that is allowed in drinking water. High nitrate concentrations also are toxic to certain aquatic life. To protect these organisms, the MPCA has developed draft nitrate water quality standards [*Monson and Preimesberger*, 2010].

Sources and fate of nitrogen in groundwater

Several natural and human-caused sources contribute nitrogen to Minnesota's groundwater. Undisturbed landscapes contribute small amounts of nitrogen to water. Human activities can release large amounts of nitrogen into the groundwater. Fertilizers, animal waste, and contaminated rainfall are some important human-caused sources of nitrogen. Nitrogen fertilizers commonly are applied to the state's agricultural crops and urban landscapes to enhance crop yields and maintain optimal turfgrass and landscape plant growth. Animal and human wastes can reach the state's water resources if not properly managed. Rainfall also contains both naturally and human-caused nitrogen; however, most of the nitrogen in rainfall is due to the combustion of fossil fuels, such as coal and oil [*Puckett*, 2004].

Nitrogen exists as several different forms in these sources. In organic matter, nitrogen is present as a diverse mixture of natural organic compounds [*Aiken*, 2002]. In human and animal wastes, nitrogen mainly is present as part of organic compounds and as ammonium (NH_4+). Fertilizers contain nitrogen in a variety of forms. Prior to the 1920s, the nitrogen in most fertilizer was in the form of nitrate (NO_3^-) because, at this time, most of the world's fertilizer was mined from natural salt peter deposits in Chile [*Kramer*, 2004]. Fertilizers derived from ammonia, such as anhydrous ammonia, ammonium nitrate (NH_4NO_3), ammonium sulfate (NH_4SO_4), and urea (NH_2CONH_2), became the main sources of fertilizer nitrogen beginning in the 1950s after the Haber-Bosch process was developed which produced ammonia from atmospheric nitrogen.

The form nitrogen takes dictates how quickly it will be transported to the groundwater. The very soluble forms of nitrogen, such as nitrate and nitrogen contained in dissolved organic matter, may be directly transported through the soils to the groundwater. Other forms of nitrogen are not very soluble and do not readily move to the groundwater. For example, ammonium has a positive charge and readily sorbs onto most soils, organic matter, and aquifer materials.

The various forms of nitrogen present in the groundwater are easily changed by many natural processes. These processes include assimilation, mineralization, nitrification, denitrification, and volatilization. The combination of all the processes is called the Nitrogen Cycle. Assimilation is the incorporation of ammonium, nitrate, or nitrite (NO_2^-) into plants, animals, or microorganisms. Mineralization converts nitrogen contained in organic matter into ammonium. In this process, bacteria break down the organic matter in order to obtain energy and ultimately release ammonium. Nitrification is a microbially-mediated process that proceeds rapidly in warm, moist, well-aerated soils and converts ammonium to nitrate. Denitrification is another microbially-mediated process that converts nitrate to nitrogen gas. This is the main process that removes nitrogen from the groundwater. Volatilization is the loss of ammonia gas from the soils to the atmosphere.

Nitrogen forms in Minnesota's groundwater

Nitrate is the main form of nitrogen that is present in Minnesota's groundwater, and the form that is discussed in the remainder of this report. This was demonstrated with the available nitrate, ammonium, and organic nitrogen data from almost 150 wells that were sampled by the MPCA from 2007-2011. The sum of these three nitrogen compounds represents the total concentration of nitrogen in the water. One of the three nitrogen compounds was considered to be the main form present if it comprised 75 percent or more of the total nitrogen concentration in the well water sample. Nitrate was the main form of nitrogen present in the water from almost 70 percent of the wells. In contrast, organic nitrogen was the main form of nitrogen in about eight percent of the wells, while ammonium was the main form in only about four percent of the wells.

Natural distribution of nitrate in the state's aquifers

Data collected by the MPCA's early warning network indicated that nitrate concentrations naturally are very low in the groundwater which recharges Minnesota's sand and gravel aquifers. The nitrate concentration in the water from the wells in undeveloped parts of the state, mainly in the forested northern part, ranged from less than the method reporting limit (0.05 mg/L) to 1.1 mg/L, and the median concentration was 0.05 mg/L (the measured concentration was at the method reporting limit).

Geographic distribution of nitrate in the state's aquifers

Nitrate concentrations in Minnesota's groundwater were highest in the sand and gravel aquifers. The median concentration in the sand and gravel aquifers, based on data from 2007-2011, was over 2 mg/L. This was higher than those in the bedrock aquifers (Figure 3). In addition, the maximum concentration measured in the sand and gravel aquifers, 82 mg/L, was over twice as high compared to the maximum concentration measured in the state's bedrock aquifers, 34 mg/L.

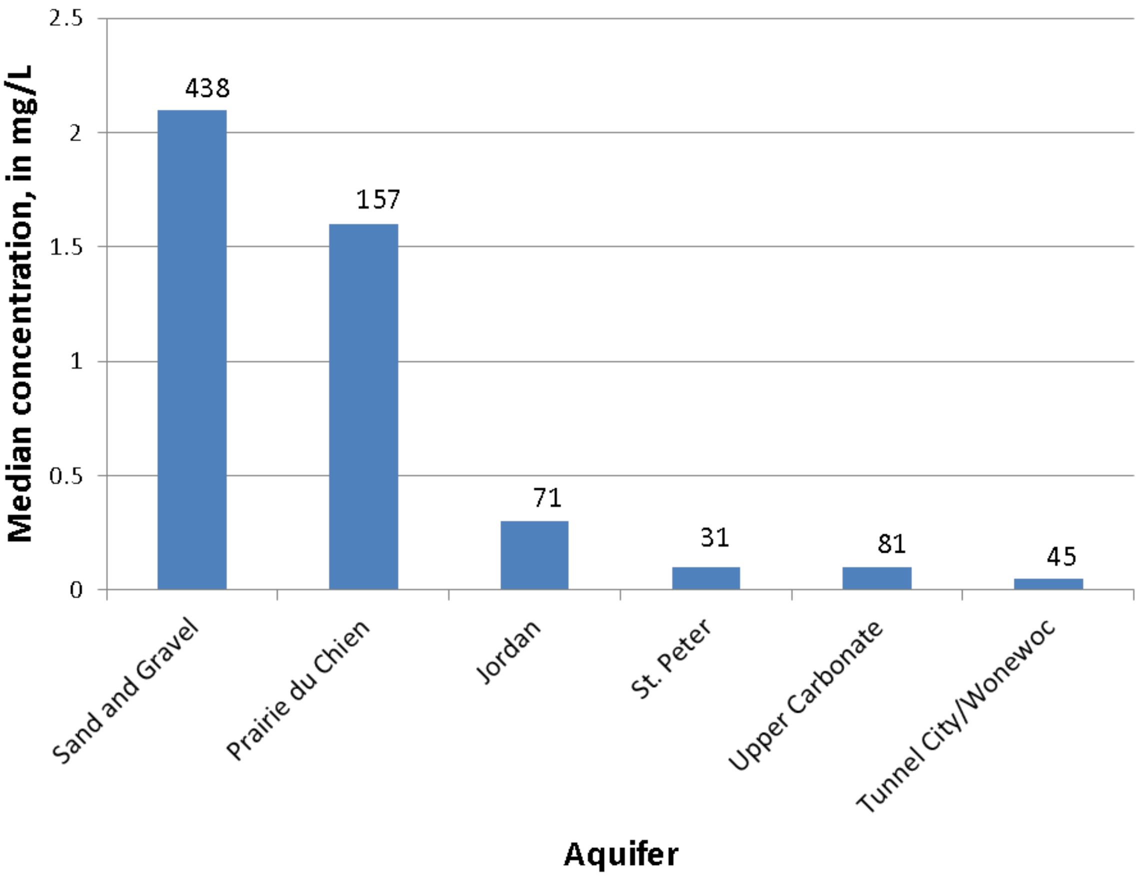


Figure 3. Median nitrate concentrations in Minnesota's ambient groundwater by aquifer, 2007-2011
[The number above each bar lists the number of samples. Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network, Minnesota Department of Agriculture's Ambient Groundwater Monitoring Network, and the Southeast Minnesota Volunteer Nitrate Monitoring Network].

Most of the sand and gravel aquifers with nitrate concentrations that exceeded human-health guidance were located in Central and Southern Minnesota. The sand and gravel aquifers in these parts of the state had the largest percentage of wells that contained water with nitrate concentrations greater than the MCL of 10 mg/L (Figure 4). High nitrate concentrations in these sand and gravel aquifers were not unexpected since previous studies that were conducted about 20 years ago showed that high nitrate concentrations occurred in the groundwater in these areas [*Anderson*, 1993; *Minnesota Pollution Control Agency and Minnesota Department of Agriculture*, 1991]. The data compiled from 2007-2011 for this report showed over 40 percent of the wells in Central Minnesota (81 of the 192 wells) had nitrate concentrations that were greater than or equal to the MCL of 10 mg/L. These concentrations mainly were measured in shallow wells installed in the uppermost part of the aquifers. There was more limited groundwater quality information available in Southwestern Minnesota. The available data indicated 4 out of the 22 sampled wells had nitrate concentrations of 10 mg/L or greater.

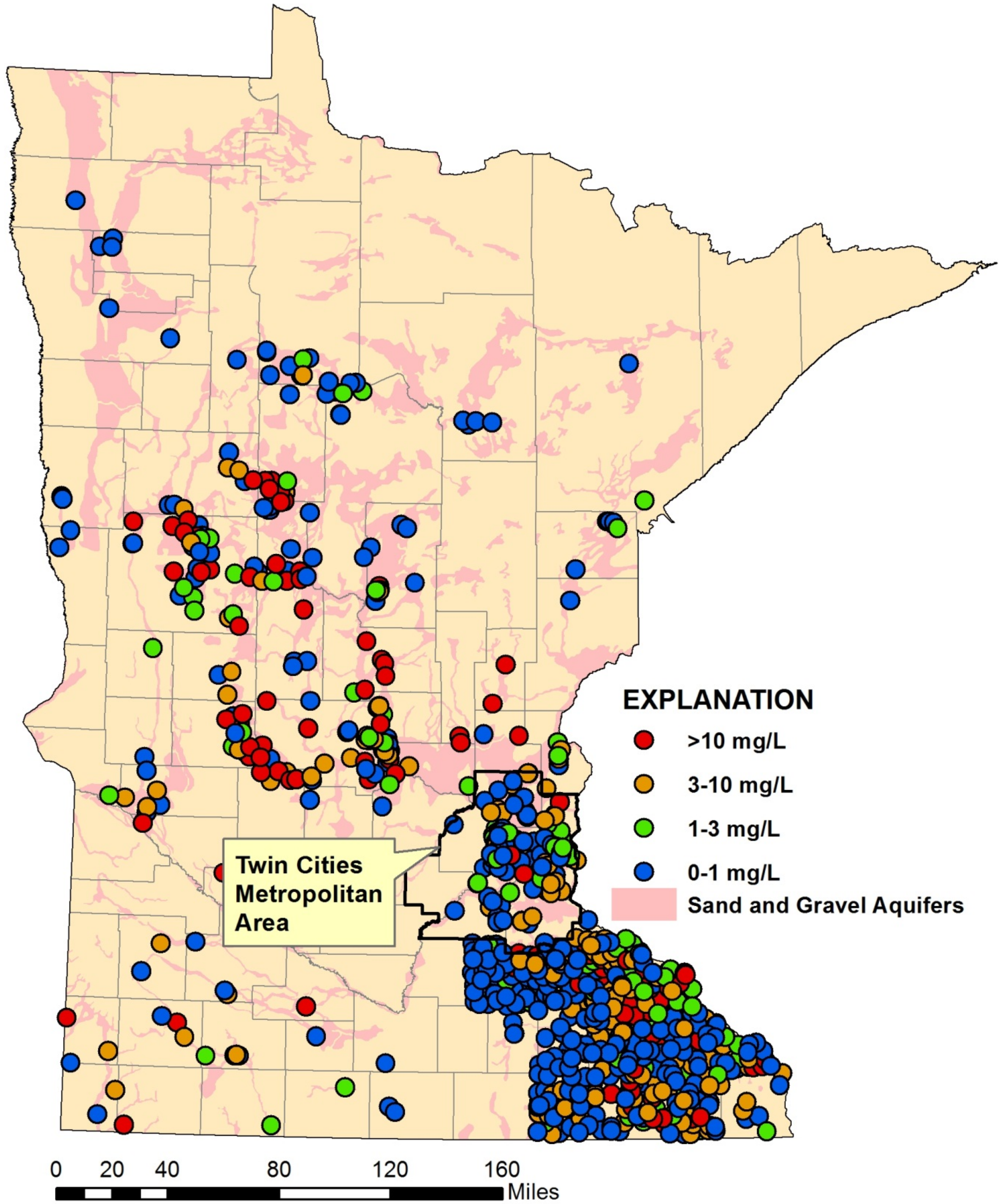


Figure 4. Nitrate concentrations in Minnesota's ambient groundwater, 2007-2011

Data from the MDA's monitoring network and Central Sands Private Well Monitoring Network suggests that high nitrate concentrations in the state's sand and gravel aquifers may be restricted to the uppermost parts. The MDA began the Central Sands Private Well Monitoring Network in 2011 [*Kaiser*, 2012]. This assessment was similar to the Southeastern Minnesota VNMN and used citizen volunteers to collect nitrate samples from private drinking water wells in Central Minnesota. This dataset has a similar uncertainty as the previously discussed VNMN due to the sample collection, handling, and analysis methods. The wells sampled as part of the Central Sands Private Well Monitoring Network typically were much deeper compared to those sampled by the MPCA's and MDA's ambient groundwater monitoring networks, which typically sample wells screened near the water table. Most of the wells sampled by the Central Sands Private Well Monitoring Network were screened at depths of 50 to 300 feet [*Kaiser*, 2012], and some were greater than 300 feet deep. The aquifer in which the wells drew water from was not tracked as part of this study; however, data from the County Well Index [*Wahl and Tipping*, 1991] showed that 94 percent of the wells in the 10 counties included in the Central Sands Private Well Monitoring Network were installed in a sand and gravel aquifer. So, it is very likely that most of the wells in this network measure water from deeper parts of the sand and gravel aquifers. Almost 90 percent of the wells sampled by the Central Sands Private Well Monitoring Network had nitrate concentrations that were less than 3 mg/L [*Kaiser*, 2012]. In contrast, only 14 percent of the wells sampled by the MDA's ambient groundwater monitoring network in this same area from 2000-2010 contained water with nitrate concentrations that were less than 3 mg/L. An analysis of eight paired shallow and deep wells that were installed as part of the MDA's monitoring network also found that median nitrate concentrations were about twice as high in the shallow wells compared to the deep ones [*Minnesota Department of Agriculture*, 2012].

There are a couple of reasons why nitrate concentrations may be lower in water from deep wells in the sand and gravel aquifers. The nitrate in these aquifers may be removed naturally at depth by denitrification, or the groundwater could be sufficiently old that any human-caused nitrate contamination has not yet percolated down into the deeper parts of these aquifers.

Nitrate concentrations exceeded the MCL of 10 mg/L in some wells installed in the bedrock aquifers in Southeastern Minnesota. In contrast to the monitoring in Central and Southwestern Minnesota, most of the sampled wells in this part of the state were domestic wells that provided water supplies to private residences. Approximately 10 percent of the sampled wells (53 out of 499 wells) in Southeastern Minnesota had nitrate concentrations that exceeded the MCL of 10 mg/L. Nitrate concentrations that exceeded the MCL were measured in the four uppermost aquifers in this part of the state: 1) Upper Carbonate, 2) St. Peter, 3) Prairie du Chien, and 4) Jordan. About five percent of the wells tapping the Upper Carbonate aquifer had reported concentrations of 10 mg/L or greater. All of these wells were located in Northwestern Fillmore County. Almost ten percent of the wells tapping the St. Peter aquifer exceeded the MCL of 10 mg/L. These wells were located in Northeastern Rice County and Central Goodhue County. Seventeen percent of the wells tapping the Prairie du Chien aquifer had nitrate concentrations of 10 mg/L or greater. All of these wells were located in Northeastern Goodhue County, Wabasha County, Northeastern Olmsted County, Winona County, and South-Central Fillmore County. About four percent of the wells tapping the Jordan aquifer had nitrate concentrations of 10 mg/L or greater. All of these wells were located in Northeastern Fillmore County and Southeastern Winona County.

The high nitrate concentrations in the bedrock aquifers in Southeastern Minnesota generally occurred in areas where these aquifers are susceptible to human-caused contamination. All bedrock wells with nitrate concentrations of 10 mg/L or greater were installed in the uppermost bedrock aquifer and were located in areas where the aquifers were overlain by a thin layer (50 feet or less) of glacial deposits.

Effect of land use on nitrate concentrations

The effect of land use on nitrate concentrations in the groundwater was determined using the data from almost 300 wells sampled by the MPCA and MDA. Two-thirds of these wells were located in agricultural areas and were sampled by the MDA. The remaining wells were located in urban and undeveloped parts of the state and were part of the MPCA's early warning network. Most of these wells were installed across or near the water table in the sand and gravel aquifers. About 260 of the nitrate measurements compiled for this analysis were from wells that had depth information; and seventy-five percent of these wells were less than 40 feet deep.

The highest nitrate concentrations occurred in the shallow groundwater underlying agricultural parts of the state (Table 1). The median nitrate concentration in the wells tapping the shallow groundwater underlying agricultural areas was significantly greater than those in all other monitored land use settings and was at least three times greater compared to those in wells tapping the groundwater underlying the other land uses (Table 1). Similarly, the maximum nitrate concentration measured in the shallow groundwater underlying agricultural parts of the state from 2007-2011, 59.7 mg/L, was almost six times greater than those measured in the groundwater underlying the other land use settings. These results are consistent with past investigations in Minnesota by the MPCA [*O'Dell*, 2007; *Trojan et al.*, 2003] and US Geological Survey (USGS) [*Fong*, 2000] that found nitrate concentrations in shallow groundwater underlying agricultural areas was significantly greater compared to urban and undeveloped areas.

Table 1. Median nitrate concentrations in the sand and gravel aquifers in Minnesota by land use
[mg/L, milligrams per liter; MDA, Minnesota Department of Agriculture; MPCA, Minnesota Pollution Control Agency]

Land use	Median nitrate concentration, in mg/L	Number of wells	Data Source
Agriculture	8.75	212	MDA
Residential SSTS	2.82	13	MPCA
Sewered Residential	2.15	36	MPCA
Commercial/Industrial	1.96	9	MPCA
Undeveloped	0.05	18	MPCA

Nitrate concentrations also were increased in the shallow groundwater underlying urban areas. In the uppermost part of the sand and gravel aquifers, the median concentrations underlying commercial/industrial and residential areas (served by both municipal sewerage systems and SSTS) ranged from about 2-3 mg/L (Table 1), while the median concentration in the groundwater underlying undeveloped areas was 0.05 mg/L. These differences were determined to be statistically significant. There was no significant difference among the median nitrate concentrations measured in the groundwater underlying the different urban land use settings (residential SSTS, sewered residential, and commercial/industrial).

Temporal trends in nitrate concentrations

Eighty-eight wells in the MPCA's and MDA's ambient monitoring networks met the criterion for nitrate concentration trend analysis (Figure 5). Over one-half of the wells were located in agricultural areas in the Central Minnesota. The remaining wells primarily were located in residential areas in the vicinity of three areas: 1) Bemidji, 2) the TCMA, and 3) St. Cloud. Almost 90 percent of the nitrate concentration data analyzed for trends was collected from wells that tapped the sand and gravel aquifers and were less than 50 feet deep. Only three of the 88 assessed wells tapped bedrock aquifers. These three bedrock aquifer wells were located in the southeastern part of the TCMA.

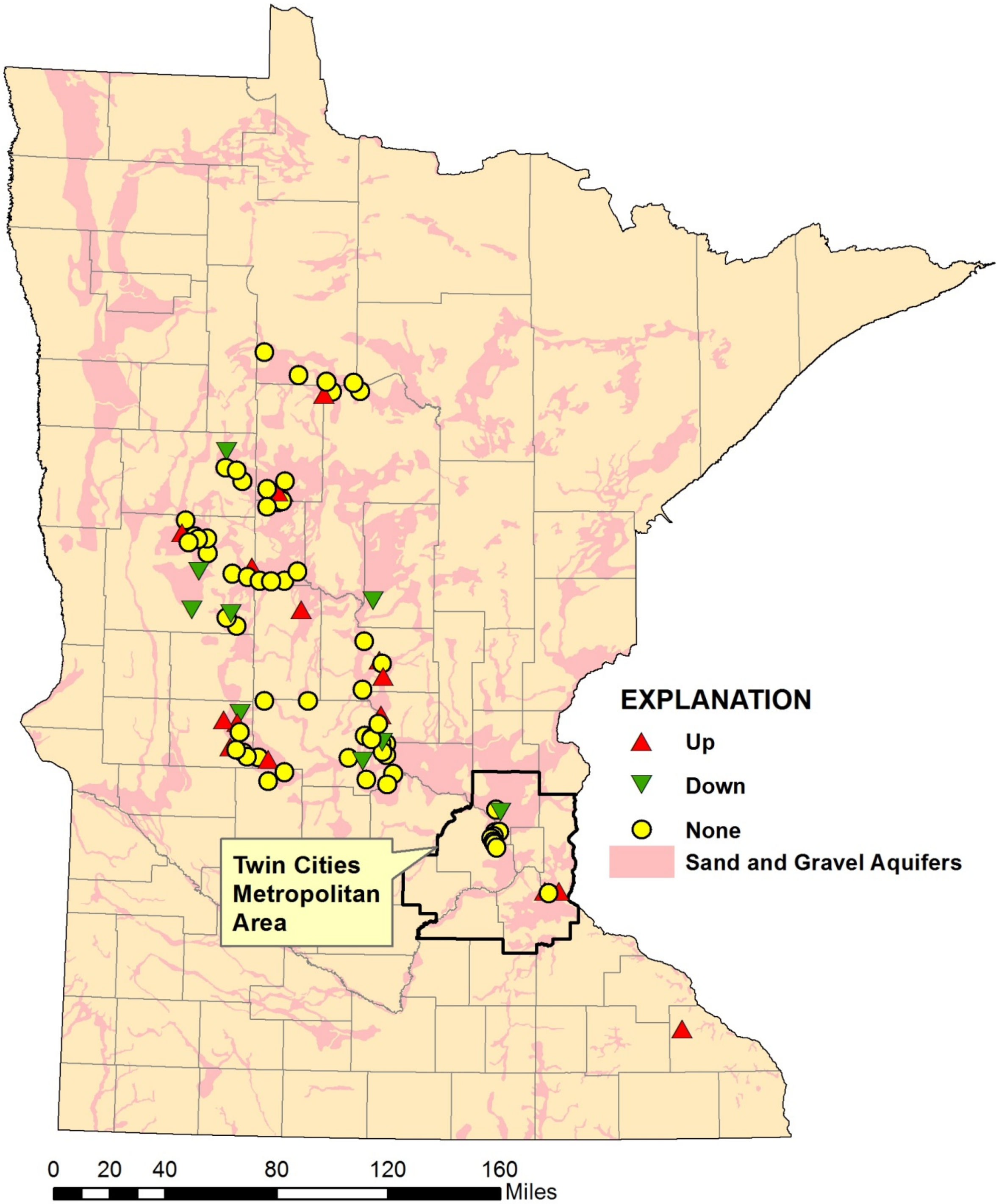


Figure 5. Temporal trends in nitrate concentrations, 2007-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network, Minnesota Department of Agriculture's Ambient Groundwater Monitoring Network, and the US Geological Survey].

Nitrate concentrations did not significantly change over time in most of the wells. The water from almost 75 percent of the analyzed wells (63 out of the 88 wells) had no significant change in nitrate concentrations.

Nitrate concentrations significantly increased in 15 wells. The majority of these wells were located in agricultural areas, and the nitrate concentrations in these wells increased, on average, about 1.5 mg/L each year. Two of the wells with an increasing trend in nitrate concentrations tapped bedrock aquifers in the TCMA. Both of the bedrock aquifer wells were located in the vicinity of the City of Cottage Grove. One of these wells tapped the Jordan aquifer, and the other well tapped the St. Lawrence aquifer. Nitrate concentrations increased much less in these two wells compared to the others with increasing trends. Concentrations in these two bedrock wells increased, on average, by about 0.3 mg/L each year.

Nitrate concentrations significantly decreased in 10 wells. These wells were located in both urban and agricultural areas. Four of the ten wells were in residential areas, and the remaining six wells were located in agricultural areas. Nitrate concentrations in the ten wells decreased, on average, about one mg/L each year.

Phosphorus

Phosphorus is another essential nutrient for the maintenance and growth of both plants and animals. This nutrient serves several important functions in plants. It stimulates plant and root growth and early plant maturity. Phosphorus also is necessary for seed production, and in animals, it is an important component of bones, teeth, and milk.

Too much phosphorus, however, is detrimental to stream and lakes because it accelerates the growth of algae and other aquatic plants. Nuisance algae reduce the water transparency and makes surface waters unsuitable for swimming or other recreational activities. In 2012, about 15 percent of the lakes and streams assessed in Minnesota were impaired for nutrients or eutrophication indicators [*Minnesota Pollution Control Agency*, 2012]. In addition, when these excessive amounts of algae die, their subsequent decay consumes the oxygen dissolved in the water. The biological communities may be stressed and fish kills may occur if too much oxygen is depleted by algal decay. Additionally, severe algal blooms that are triggered by excessive phosphorus in the water may release toxins that poison animals that ingest the water or cause allergic reactions in people who swim in it.

Sources and fate of phosphorus in groundwater

The weathering of minerals naturally contributes small amounts of phosphorus to Minnesota's water resources. Phosphorus-bearing minerals, such as apatite and phosphorite, occur within igneous, metamorphic, and sedimentary rocks. Extensive deposits of phosphorus minerals do not occur in Minnesota [*Hogan*, 2011]; however, small amounts are present in the state's soils, rocks, and glacial deposits.

Human activities can contribute large amounts of phosphorus to water resources. Major human-caused sources of phosphorus include fertilizer, livestock manure, and wastewater effluent [*Dubrovsky et a.,l* 2010]). These phosphorus sources are responsible for the cultural eutrophication of lakes and streams across the state [*Barr Engineering*, 2011; *Minnesota Pollution Control Agency*, 2008; *Wenck Associates*, 2012].

Phosphorus usually is not transported as quickly through the groundwater system as it is in streams and lakes. In the groundwater, phosphorus transport typically is limited because most phosphorus compounds are not very soluble and tend to precipitate, or the phosphorus sorbs to iron or aluminum oxides that often coat soil particles.

Certain circumstances, however, will allow phosphorus to be transported by the groundwater. Some soils contain little of the iron or aluminum oxides that retain phosphorus. High sulfate or silica concentrations in the groundwater also may limit the ability of the soils to sorb phosphorus because these constituents utilize the same sorption sites that phosphorus does. Low oxygen conditions in the groundwater also can dissolve iron oxides and permit any associated phosphorus to be released.

Occurrence and distribution of phosphorus in the state's aquifers

Phosphorus concentrations in the ambient groundwater were found to be low. Concentrations in the groundwater ranged from less than the reporting limit (3 ug/L) to 1,470 ug/L, and the median concentration was 30 ug/L. Only two of the sampled wells contained water with phosphorus concentrations exceeding 1,000 ug/L. An unfiltered water sample was submitted for analysis from one of these two wells, and the very high phosphorus concentration may have been caused by the presence of particles in the sample that contained phosphorus. These particles usually do not move with the groundwater. The water in the other well with the very high phosphorus concentration was known to be affected by landfill leachate. There was little difference in the phosphorus concentrations among the sampled aquifers. The median concentrations in the Prairie du Chien-Jordan and sand and gravel aquifers ranged from 0.029 to 0.033 ug/L and were not significantly different (p=0.463). These results are consistent with National-scale monitoring that found that almost 90 percent of the phosphorus concentrations in the groundwater were less than 100 ug/L, and there was no difference in concentrations between shallow and deep groundwater [*Dubrovsky et al.*, 2010].

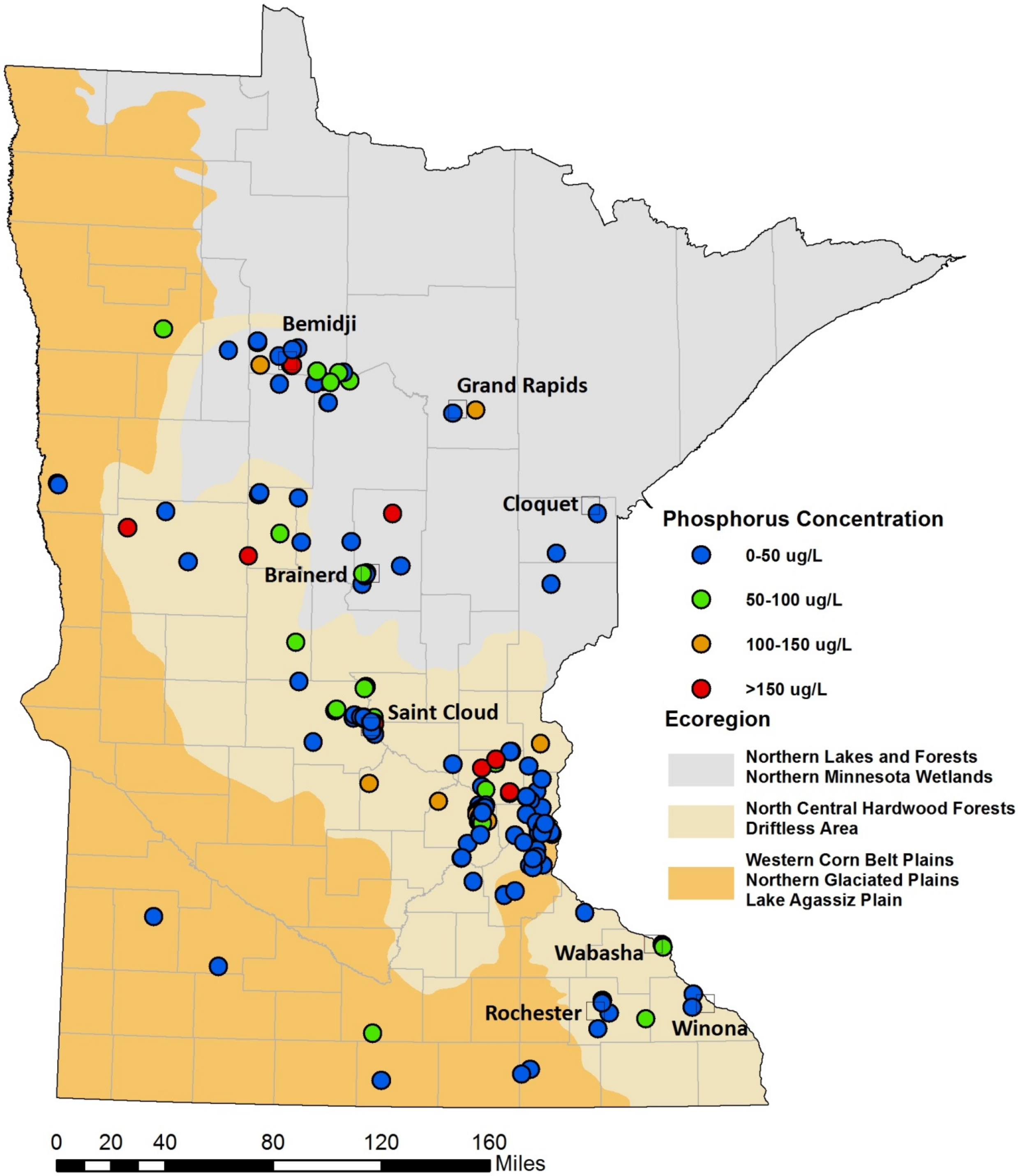


Figure 6. Phosphorus concentrations in Minnesota's ambient groundwater, 2008-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

The groundwater contains high enough phosphorus concentrations to cause the nuisance growth of algae in streams if it is transported to some streams in Northern and Central Minnesota. To minimize the growth of nuisance algae in streams and its subsequent problems, the MPCA developed draft stream nutrient criteria [*Heiskary et al.*, 2013]. Phosphorus concentrations that exceed these criteria in groundwater do not affect the suitability of the water for drinking. The draft phosphorus criteria for streams vary across the state by ecoregion and range from 50 to 150 ug/L (Table 2). Phosphorus concentrations in the ambient groundwater occasionally exceeded these draft criteria. About 20 percent of the wells sampled from 2008-2011 exceeded the draft criteria. The wells with exceedances of the draft phosphorus criterion were split between the North Central Hardwood Forests or Northern Minnesota Wetlands ecoregions, which have low draft criteria (Table 2). There were no exceedances of the draft criterion in wells located within the Driftless Area and Western Corn Belt Plains ecoregions. Phosphorus concentrations were not measured in any wells installed in the Northern Glaciated Plains or Lake Agassiz Plain ecoregions.

Table 2. Draft phosphorus criteria set for streams in Minnesota and the percentage of wells with concentrations that exceeded these criteria, 2008-2011

[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network]

Ecoregion	Draft total phosphorus criterion set for streams in Minnesota	Percentage of wells in the ecoregions exceeding the draft criteria
Northern Lakes and Forests Northern Minnesota Wetlands	50 ug/L	39%
North Central Hardwood Forests Driftless Area	100 ug/L	13%
Western Corn Belt Plains Northern Glaciated Plains Lake Agassiz Plain	150 ug/L	0%

Effect of land use on phosphorus concentrations in groundwater

The land use setting had little effect on the phosphorus concentration in the ambient groundwater. There was little difference in phosphorus concentrations in the groundwater underlying the various urban and undeveloped land use settings. The median concentrations in the groundwater underlying these settings ranged from 23 to 50 ug/L and were determined not to be significantly different ($p=0.270$).

Natural factors affecting phosphorus concentrations in groundwater

Phosphorus concentrations in Minnesota's ambient groundwater appear to be more affected by natural factors since there was no difference in concentrations among land use settings or aquifers. Constituents in the groundwater that are affected by human-caused contamination share a couple of common characteristics. The concentrations typically vary with land use and usually are higher in the uppermost aquifers compared to the underlying aquifers because any human-caused contamination usually emanates from the land surface.

Phosphorus concentrations tended to be higher in sand and gravel aquifers composed of calcareous sediments compared to those composed of siliceous sediments. The median concentration in the aquifers composed of calcareous sediments was 41 ug/L, whereas the median concentration in the aquifers composed of siliceous sediments was 28 ug/L. This likely results from differences in the mineral composition of the sand and gravel aquifers. The composition of the sand and gravel aquifers varies across Minnesota because the glaciers that formed them originated from areas with different rock types. Glaciers that originated from the northeast primarily traversed crystalline bedrock, and the sediments deposited by these glaciers are siliceous and contain little carbonate or shale. The glaciers that traversed the state from the west and northwest traversed an area with limestone, and the sediments deposited by these glaciers contain significant fractions of carbonate and shale. The high phosphorus concentrations in Minnesota's sand and gravel aquifers that have a calcareous composition are consistent with sources of phosphorus-bearing minerals such as shale.

Chloride

Excessive chloride concentrations in groundwater restrict its use for drinking and may degrade aquatic habitat if these are transported to surface waters. High chloride concentrations adversely affect drinking water because it imparts a salty taste to water that consumers find objectionable. To minimize taste problems with public drinking water supplies, the USEPA has set a Secondary Maximum Contaminant Level (SMCL) for chloride of 250 mg/L. SMCLs are not enforced by the EPA; this only is a guideline to assist public drinking water suppliers in managing their systems for aesthetic considerations. High chloride concentrations also are toxic to aquatic life, and streams and lakes with high 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 has set a chronic water quality standard of 230 mg/L and an acute water-quality standard of 860 mg/L.

Sources and fate of chloride in groundwater

Chloride naturally is present in Minnesota's groundwater due to the natural weathering of rocks. Most types of rocks contain some chloride. Igneous rocks that contain chloride include sodalite and apatite (Hem 1992). Sedimentary rocks, especially halite or rock salt, usually contain much more chloride compared to igneous rocks [*Hem*, 1992].

One of the most common pathways for chloride to enter the groundwater in the northern part of the United States is by the application of de-icing salts to roadways. This likely is the most important source of chloride contamination to the groundwater in Minnesota. Nationally, the largest use of salt, with the exception of the chloralkali chemical industry, is as a deicing chemical. About 70 percent of the salt distributed to Minnesota in 2010 was rock salt [*Kostick*, 2011], which primarily was used to de-ice roadways. Other sources of chloride contamination to the groundwater include fertilizer, water softening salt, and wastewater. Research by the University of Minnesota indicates a substantial amount of chloride may be seeping into the state's groundwater. A chloride budget for the TCMA [*Stefan et al.*, 2008] found that only a small amount of the applied chloride (22 percent) was exported by streamflow from the TCMA. This result indicated that almost 80 percent of the applied chloride is either transported to the groundwater or remains in the area soils, lakes, and wetlands.

Natural distribution of chloride in the state's aquifers

Naturally high chloride concentrations occur in some aquifers in Western Minnesota and a few other parts of the state. The sand and gravel aquifers and the underlying sedimentary bedrock aquifers in Northwestern Minnesota, from approximately Traverse County to the Canadian border, contain high concentrations of naturally-occurring chloride. Concentrations in these aquifers can be as high as 2,000 mg/L [*McClay et al.*, 1972]. These high chloride concentrations originate in the Red River-Winnipeg aquifer. The overlying sand and gravel aquifers in extreme Northwestern Minnesota also are impacted by the high concentrations because the groundwater in the Red River-Winnipeg aquifer naturally moves upward into the overlying sand and gravel aquifers [*Winter*, 1974]. High chloride concentrations also naturally occur in the some of the Cretaceous aquifers in Southwestern Minnesota, mainly southwest of the Minnesota River. In this part of the state, chloride concentrations in the Cretaceous aquifers can be as high as 1,500 mg/L [*Woodward and Anderson*, 1986]. Groundwater with naturally high chloride concentrations occurs sporadically in a few other parts of the state, including the Cretaceous aquifers in South-Central Minnesota and in some of the crystalline bedrock aquifers along Lake Superior in Northeastern Minnesota [*Winter*, 1974].

Geographic distribution of chloride contamination in the state's aquifers

The sand and gravel aquifers in the TCMA were found to be impacted by high chloride concentrations (Figure 7). In the TCMA, chloride concentrations were highly variable, ranging from less than the reporting limit (1 mg/L) to 8,900 mg/L; however, the median concentration in the TCMA (86 mg/L) was about five times greater than the median concentration in the sand and gravel aquifers in the rest of the state (17 mg/L). The largest number of wells with chloride concentrations exceeding the SMCL or water-quality standards were located in the TCMA. Twenty-seven percent of the wells installed in the sand and gravel aquifers in the TCMA had chloride concentrations that were greater than the SMCL of 250 mg/L, and thirty percent of the wells had chloride concentrations greater than the chronic water-quality standard of 230 mg/L. In contrast, only about one percent of the wells outside the TCMA contained water with chloride concentrations that exceeded either drinking water or the chronic water-quality standard.

In the TCMA, chloride concentrations of 250 mg/L or greater were measured in some sand and gravel aquifers that were about 50 feet below the land surface. Most groundwater with chloride concentrations that exceeded the SMCL of 250 mg/L was collected from wells that were 30 feet deep or less. However, chloride concentrations exceeding the SMCL in the TCMA were measured in two wells that collected groundwater from about 55 feet below the land surface.

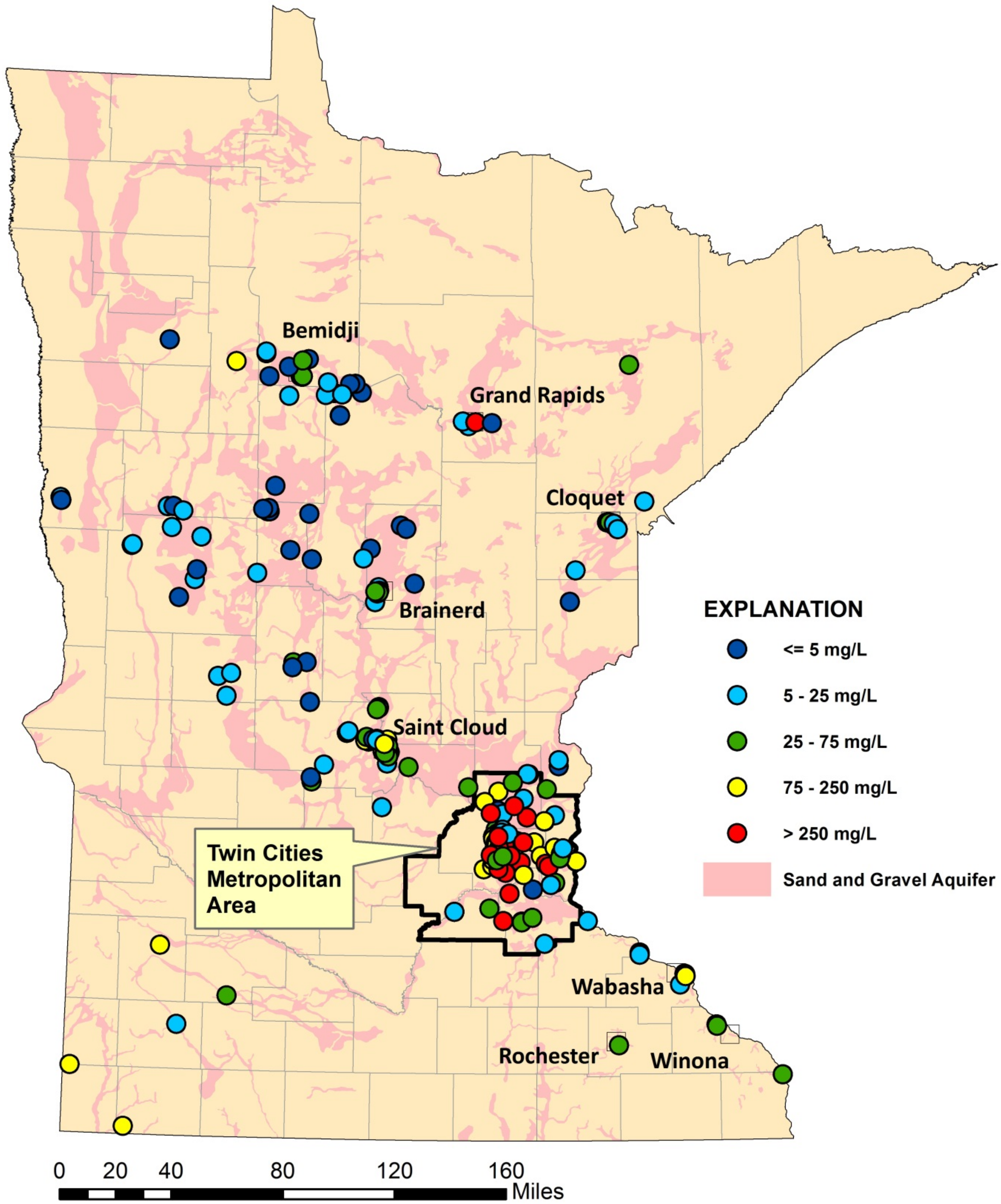


Figure 7. Chloride concentrations in the ambient groundwater from the sand and gravel aquifers, 2007-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

Chloride concentrations in the bedrock aquifers generally were low and usually did not exceed the SMCL or water-quality standards. The median concentration in the bedrock aquifers was 18 mg/L, and concentrations in each individual well ranged from less than the laboratory reporting limit (0.5 mg/L) to 680 mg/L (Figure 8). The only bedrock aquifer wells that contained chloride concentrations that exceeded the SMCL and the chronic water-quality standard were shallow, multi-aquifer wells that also drew water from the sand and gravel aquifers. The MPCA's Ambient Groundwater Monitoring Network sampled three multi-aquifer wells from 2007-2011. All three wells were located in the vicinity of Rochester and were very shallow, 25 feet deep or less. The chloride concentrations in these three wells ranged from 370 to 680 mg/L.

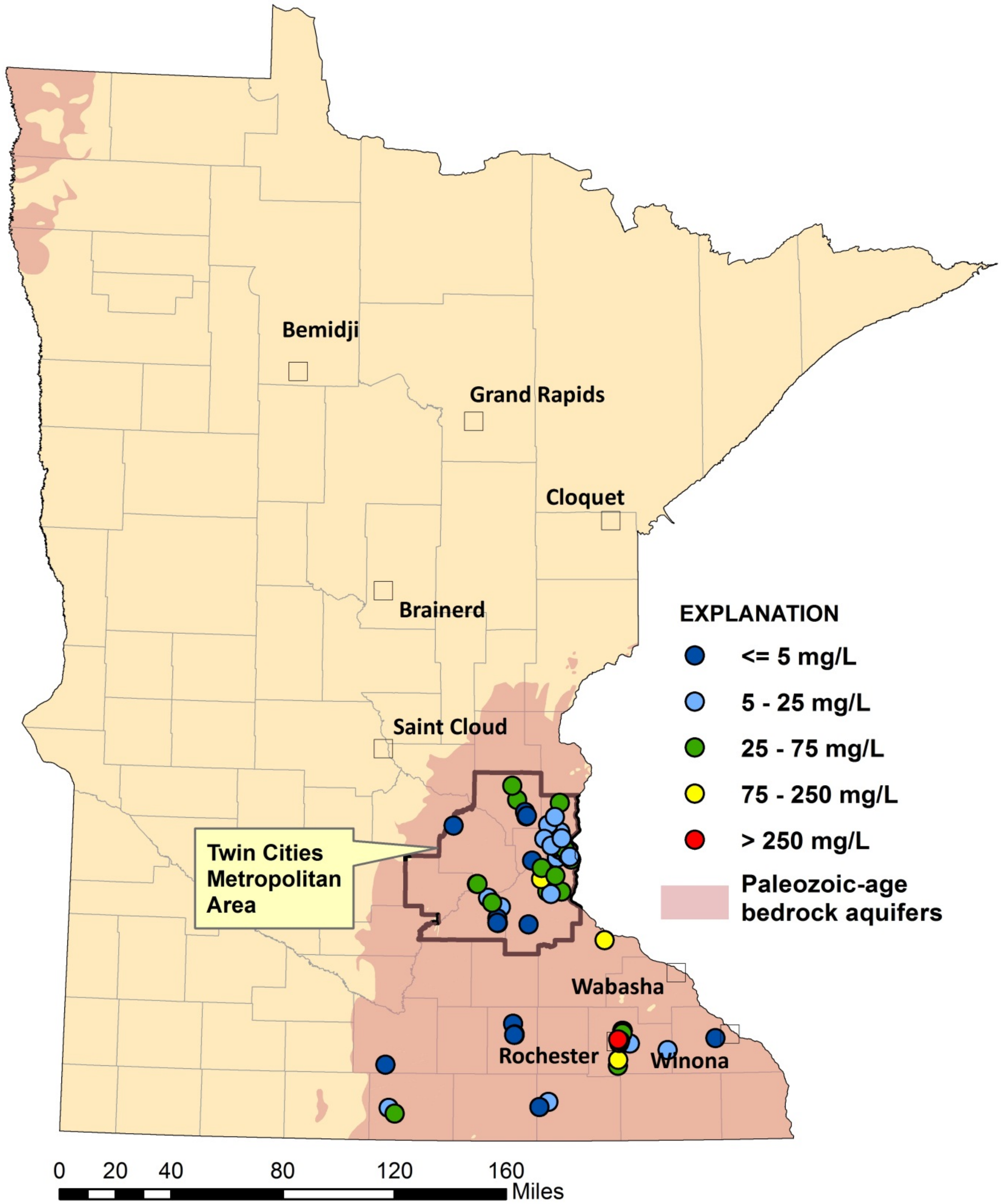


Figure 8. Chloride concentrations in the ambient groundwater from selected Paleozoic-age bedrock aquifers in Minnesota, 2007-2011
[Chloride concentration data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

The high chloride concentrations in the sand and gravel aquifers were associated with urban land use. In the early warning network, chloride concentrations generally were higher in all of the urban settings compared to those in undeveloped areas (Figure 9), and these differences were statistically significant. There was no significant difference in chloride concentrations in the groundwater underlying the various urban land use settings.

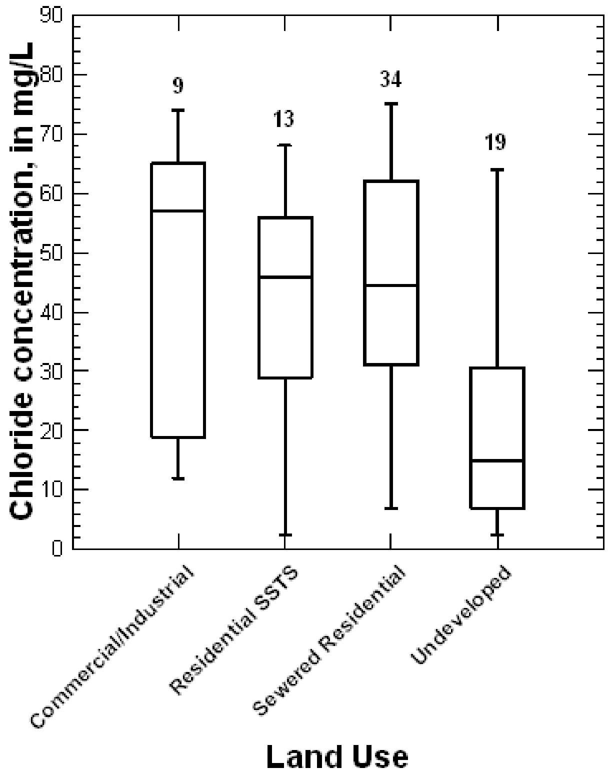


Figure 9. Boxplots showing chloride concentrations in the ambient groundwater from the sand and gravel aquifers in Minnesota by land use, 2007-2011

[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network; the number listed above each box plot indicates the number of measurements used to construct the plot].

Chloride sources

Halite, which likely was derived from road salt, was the most common source of chloride in the sand and gravel aquifers (Figure 10). Over one-half of the wells installed in the sand and gravel aquifers had a Cl/Br ratio greater than 1,000 which indicated a halite source. This halite likely was applied as a roadway de-icing chemical since the majority of the rock salt purchased in Minnesota is used for this purpose. Sand and gravel aquifer wells with a halite source of chloride were located throughout the state, including the TCMA and the cities of Bemidji, Brainerd, Grand Rapids, and St. Cloud. Almost one-third of the sand and gravel aquifer wells had a chemical signature that suggested the chloride source was wastewater or was a mixture of halite and native groundwater. Only 16 percent of the sand and gravel aquifer wells had a Cl/Br ratio that indicated there was no human-caused chloride source.

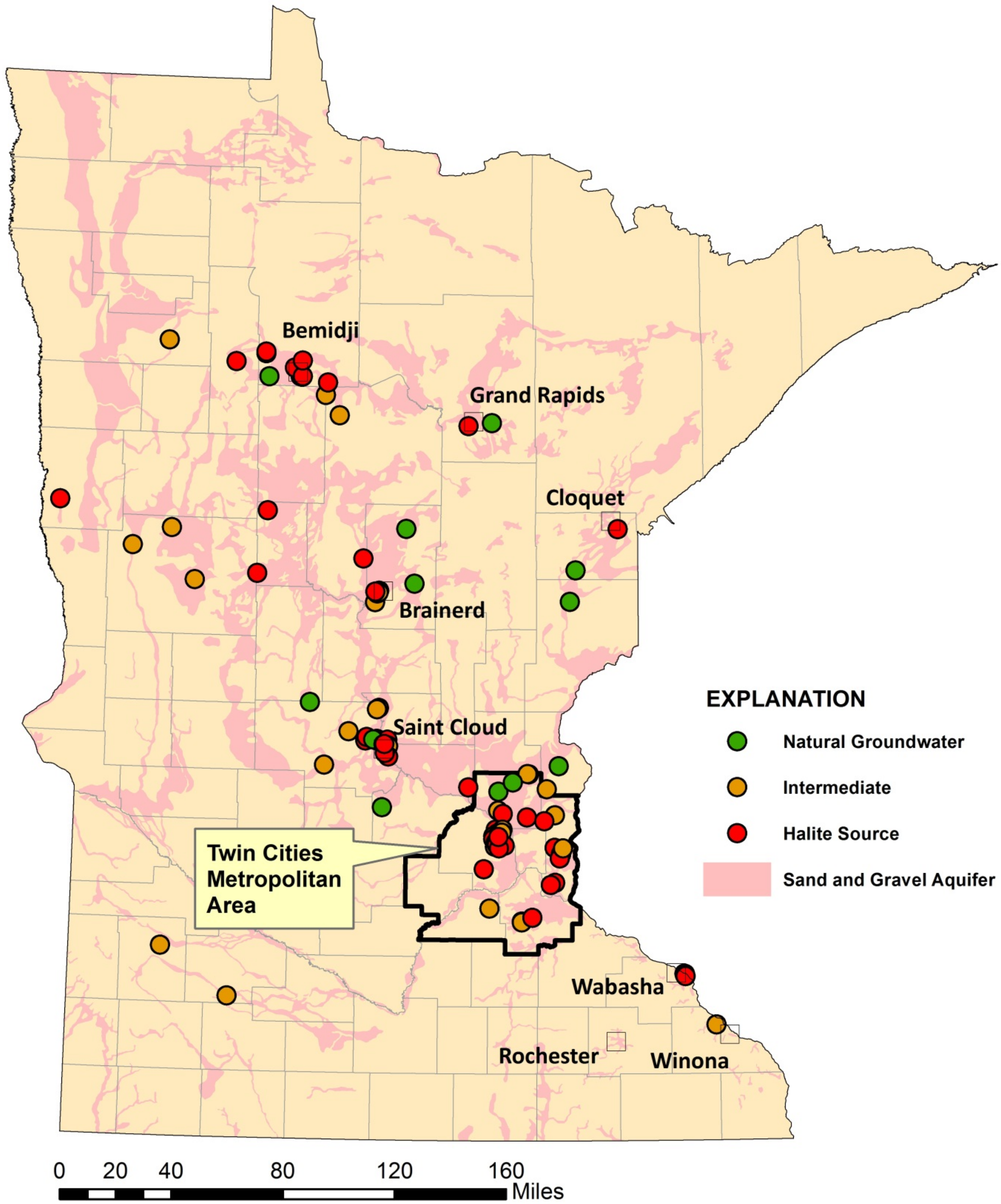


Figure 10. Chloride sources in the ambient groundwater from the sand and gravel aquifers in Minnesota, 2007-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

The water from most of the sampled bedrock aquifer wells also had a chemical signature that suggested the chloride originated either from a wastewater source or was a mixture of a halite and native groundwater. Thirty-four bedrock aquifer wells had sufficient data to calculate Cl/Br ratios. The chloride source was either wastewater or possibly a mixture of halite and native groundwater in almost 60 percent of the bedrock wells. Halite was the chloride source in almost one-third of the sampled wells. Most of the bedrock aquifer wells where the Cl/Br ratio suggested a halite source were located in the

TCMA. Only three of the bedrock aquifer wells had a chemical signature that indicated the water was unaffected by human-caused contamination.

The highest chloride concentrations measured by the MPCA's Ambient Groundwater Monitoring Network generally occurred in groundwater that was contaminated with halite. Groundwater that was unaffected by human-caused contamination generally had a chloride concentration that was less than 7 mg/L (Figure 11). This concentration is similar to values reported by [*Tipping*, 1994] and [*Mullaney et al.*, 2009]. In contrast, groundwater that was affected by halite contamination often had a chloride concentration that was 30 mg/L or greater.

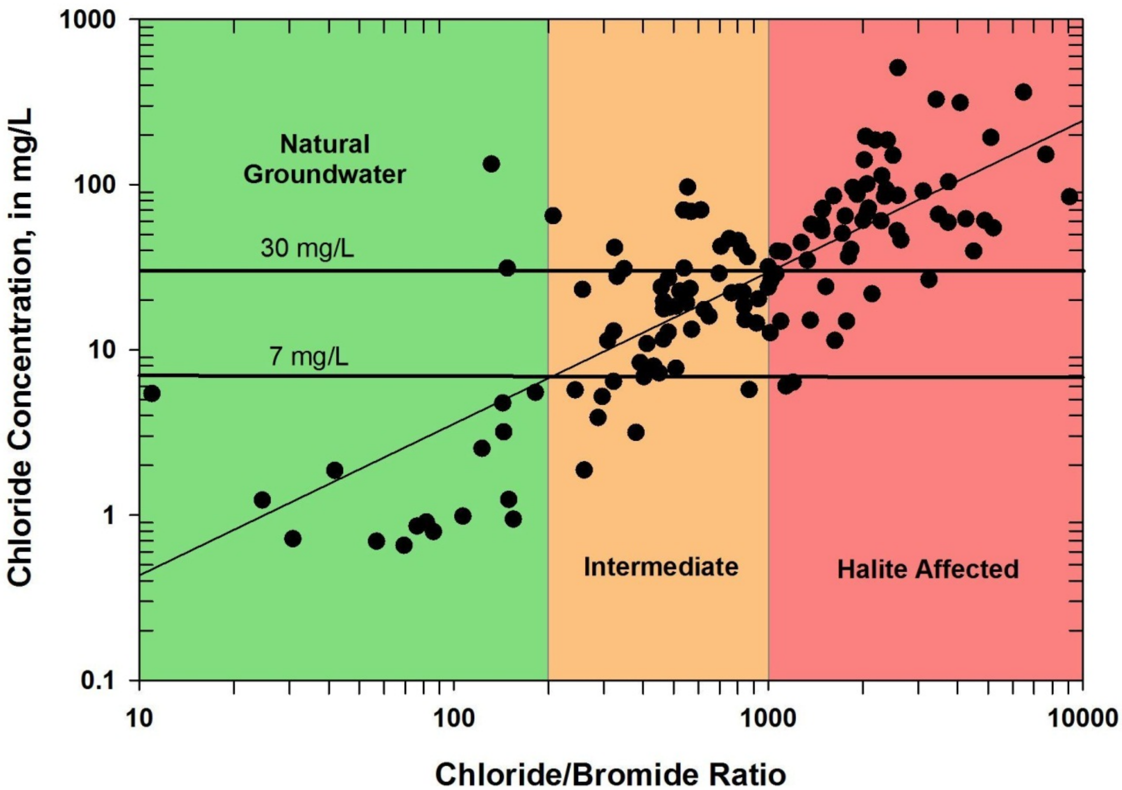


Figure 11. Chloride concentrations and the chloride/bromide concentration ratio in Minnesota's ambient groundwater, 2007-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

Temporal trends

There currently is limited data to determine whether chloride concentrations have changed in the state's ambient groundwater, even after compiling historical information collected by other agencies. Only a small number of wells (35) in the MPCA's Ambient Groundwater Monitoring Network met the criterion for trend analysis, despite the liberal criteria used to select the sites. The majority of these wells were located in sewered residential areas in the vicinity of three areas: 1) the City of Bemidji, 2) the City of St. Cloud, and 3) the TCMA.

Most of the wells that were analyzed for temporal trends in chloride concentrations were shallow and tapped the surficial sand and gravel aquifers. Almost 80 percent of the data assessed for trends was collected from monitoring wells that were less than 50 feet deep. All except three of the wells tapped the sand and gravel aquifers.

Over 30 percent of the analyzed wells had significant increases in chloride concentrations (Figure 12). Eleven of the 35 wells had a statistically significant upward trend in chloride concentrations. These wells were located in all land use settings-residential, commercial/industrial, and even in undeveloped areas. The majority of wells with upward trends in chloride concentrations were shallow (less than 30 feet deep) and located in sewered residential areas. The two wells in undeveloped areas that had upward trends in chloride concentrations both were located in the vicinity of the City of Bemidji.

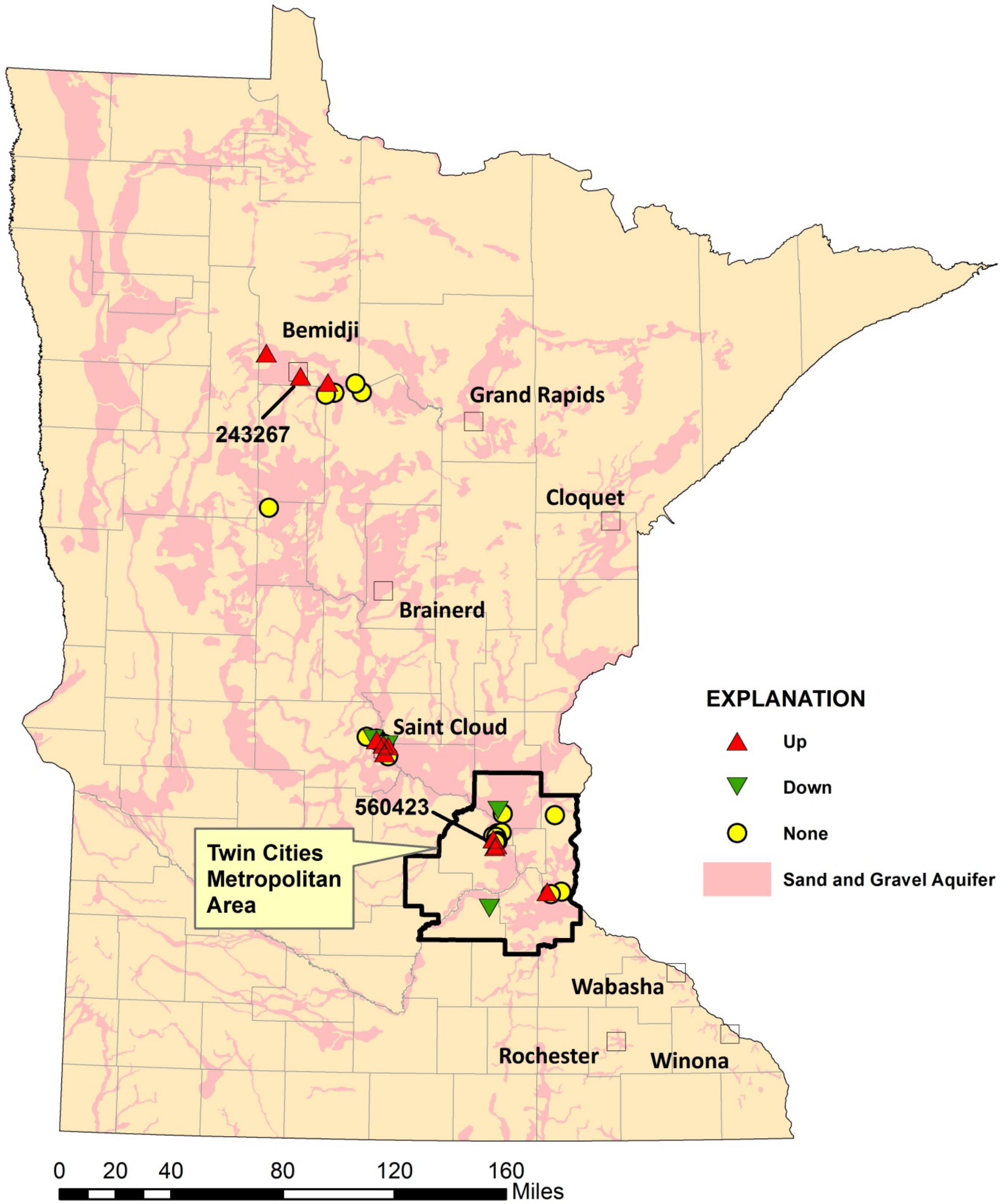
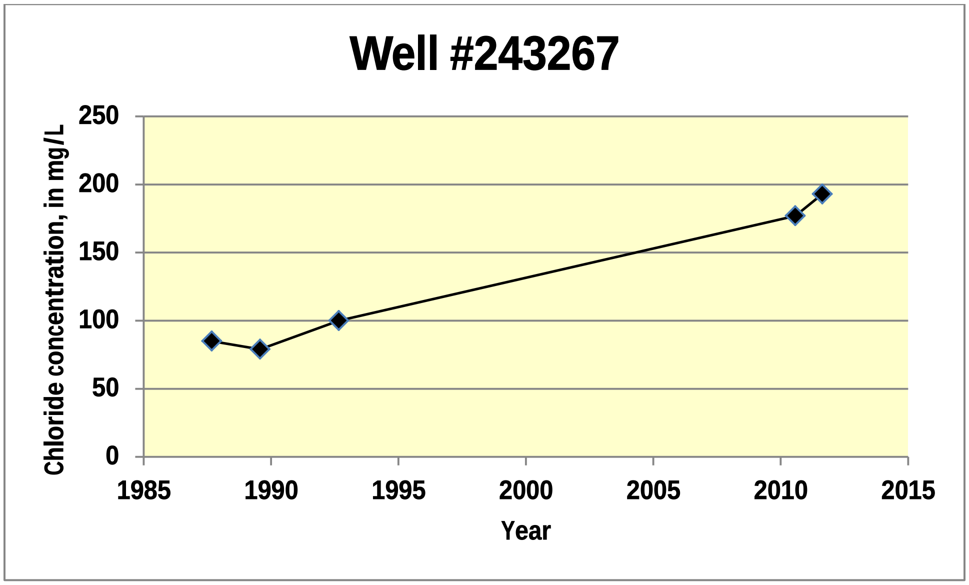


Figure 12. Chloride concentration trends in Minnesota's ambient groundwater, 1987-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network and the US Geological Survey].

Chloride concentrations increased by more than 100 mg/L in some of the wells in the state. These wells were located in sewered residential and commercial/industrial areas. The chloride concentrations in well 243267, which is located in a sewered residential area of Bemidji, increased from 85 mg/L in 1987 to 193 mg/L in 2011 (Figures 12, 13). Similarly, the chloride concentration in the water from well 560423, which is located in a sewered residential area of the TCMA, increased from 91 mg/L in 1996 to 196 mg/L in 2011 (Figures 12,13). On average, chloride concentrations in the sewered residential and commercial/industrial areas increased by 3.4 mg/L each year.



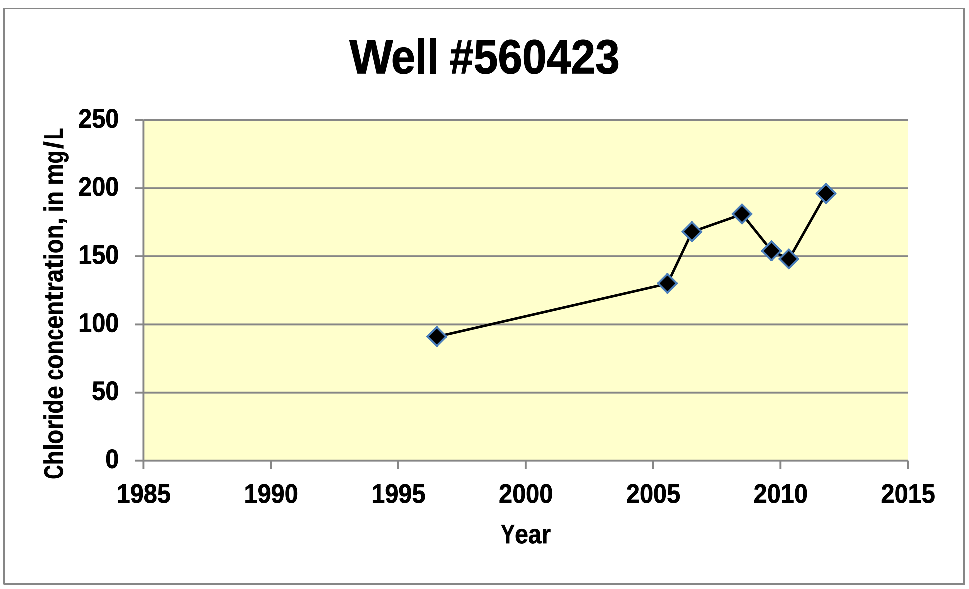


Figure 13. Chloride concentrations in selected wells from the MPCA's Ambient Groundwater Monitoring Network, 2007-2011 [Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network and the US Geological Survey].

The application of deicing chemicals likely resulted in the upward trend in chloride concentrations in two wells that were located in primarily undeveloped areas. Both of these wells had small increases in chloride concentrations. In these two wells, concentrations increased less than 1 mg/L each year, and the concentrations reported in both wells increased from about 3 mg/L in 1987 to 25 mg/L in 2011. Both of these wells were located near major roadways to which road salt may have been applied in the winter, and the Cl/Br ratios in both of the wells also suggested the presence of road salt in the water.

One of the wells had a Cl/Br ratio that was greater than 1,000 which strongly suggested the well water was affected by halite. The other well also had an elevated Cl/Br ratio (764) that is considerably greater compared to those found in groundwater that is not affected by human-caused contamination.

Upward trends in chloride concentrations were not just restricted to shallow wells that tapped the sand and gravel aquifers. Concentrations also significantly increased in two deep wells in the TCMA. One of these wells was 190 feet deep and tapped the Jordan aquifer in the vicinity of Cottage Grove. The other well was 72 feet deep and tapped a buried sand and gravel aquifer in Hennepin County. The Cl/Br ratios in both of these wells; 803 and 822, respectively; also was considerably greater than those expected in groundwater unaffected by human-caused contamination. In these two wells, chloride concentrations increased on average 1.8 mg/L each year. This translated into an increase of about 15-30 mg/L over approximately the past 15 years. Concentrations in the Jordan aquifer well increased from about 12 mg/L in 1999 to 41 mg/L in 2011, and concentrations in the buried sand and gravel aquifer wells increased from about 30 mg/L in 1996 to 46 mg/L in 2011.

Sulfate

Sulfate (SO_4) is a mineral that is essential for the growth of all living things. Plants and animals use it to form the proteins that are necessary for their growth.

Even though it is essential for life, too much sulfate in the water renders it unfit for human consumption. High sulfate concentrations cause drinking water to have a bitter or astringent taste. High concentrations also may cause laxative effects in people, especially when they are not acclimated to drinking it. To address these drinking water problems, the USEPA set a SMCL for sulfate of 250 mg/L.

Too much sulfate in the water also may harm wild rice plants. Wild rice is an important natural resource. This plant provides food for waterfowl and shelter for animals and fish. Wild rice also is a very important cultural resource to many Minnesotans and is economically important to those who harvest and market wild rice. An assessment of the effect of water chemistry on aquatic plant growth in Minnesota found that no large wild rice stands occur in waters that had a sulfate concentration greater than 10 mg/L, and wild rice generally was absent from waters that had a concentration greater than 50 mg/L [*Moyle*, 1956]. To protect waters where wild rice is grown, the state of Minnesota adopted a sulfate water-quality standard of 10 mg/L in 1973 (Minnesota Rules 7050.0224).

The effect of sulfate concentrations on wild rice growth has received a considerable amount of attention in Minnesota over the past few years. These concerns largely stem from proposals to mine nickel, copper, and other metals in the Iron Range in Northeastern Minnesota. There has been a tremendous demand for copper and nickel worldwide, and the Iron Range has one of the largest reserves of these metals on the Earth. A great concern with the proposed copper/nickel mines is that these metals are associated with sulfide minerals. The exposure of the sulfide minerals to water and air as a result of the mining potentially may result in runoff polluted with sulfate, acid, and other contaminants. The oxidation of sulfide minerals in the Eastern United states has been reported to produce runoff that contains sulfate concentrations as high as 3,000 mg/L [*Emrich and Merritt*, 1968], although the amount of contamination in the runoff varies widely and depends on the mineralogy of rock material [*U.S. Environmental Protection Agency*, 1994; *Wireman and Stover*, 2011]. In Minnesota, many of the lakes and streams where wild rice grows also are located near the proposed copper/nickel mines, and there are strong concerns that any additional sulfate transported from the mines to the surface waters will harm the growth of wild rice plants.

Sources and fate of sulfate in the groundwater

The weathering of minerals naturally releases sulfate to Minnesota's groundwater. Common sulfur-containing minerals include gypsum ($CaSO_4$) and pyrite (FeS_2). Gypsum is an evaporite mineral, which, as its name suggests, is formed by the extensive or total evaporation of water, and the dissolution of gypsum present in aquifer materials naturally releases sulfate into the groundwater. Pyrite is a sulfide mineral and usually is formed under anoxic conditions [*Hem*, 1992]. This mineral is present over a large part of the state. It occurs in some of the calcareous glacial deposits [*Wright et al.*, 1973] and in the Iron Range in Northeastern Minnesota. In the presence of water and oxygen, pyrite and other sulfide minerals readily oxidize and release sulfate.

Human activities also may contribute sulfate to Minnesota's groundwater. The combustion of fossil fuels contributes sulfur to the atmosphere that ultimately is transported to the land surface in the form of sulfate by precipitation. The state's groundwater ultimately is recharged by this sulfate-containing precipitation. Many commonly-used products also contain sulfate, including wallboard, chalk, cement, and plaster of Paris, commercial fertilizers, and soil amendments used to break up clayey soils. The sulfate in these products may reach the groundwater when these products are applied to or disposed of on the land surface and leached into the groundwater by precipitation. Some mining activities also may transport sulfate to the groundwater when sulfide minerals are extracted from the ground and exposed to oxygen, and water is allowed to leach the resulting sulfate into the ground.

Geographic distribution of sulfate in the state's aquifers

The groundwater naturally contains high sulfate concentrations in western Minnesota. *Winter* [1974] and *Ruhl* [1987] found sulfate concentrations in the sand and gravel aquifers were substantially higher in Southwestern and Northwestern Minnesota compared to the rest of the state. Concentrations as high as 4,000 mg/L were measured in Northwestern Minnesota by *Winter* [1974]. Similarly, *Woodward and Anderson* [1986] found high sulfate concentrations in the Cretaceous aquifers in Southwestern Minnesota. In some places, concentrations were as high as 1,700 mg/L. These high sulfate concentrations were attributed to the natural leaching of sulfur-rich minerals that are present in the aquifer materials in Western Minnesota and the inflow of highly mineralized groundwater from North and South Dakota.

The MPCA's Ambient Groundwater Monitoring network also showed high sulfate concentrations occurred in wells in Western Minnesota. Most of the wells with sulfate concentrations that were greater than 250 mg/L were in Northwestern or Southwestern Minnesota (Figure 14). These wells primarily were completed in the sand and gravel aquifers. One well was completed in the Prairie du Chien-Jordan aquifer. The sulfate concentration in all five of these wells exceeded the SMCL of 250 mg/L and ranged from 313 to 1,320 mg/L.

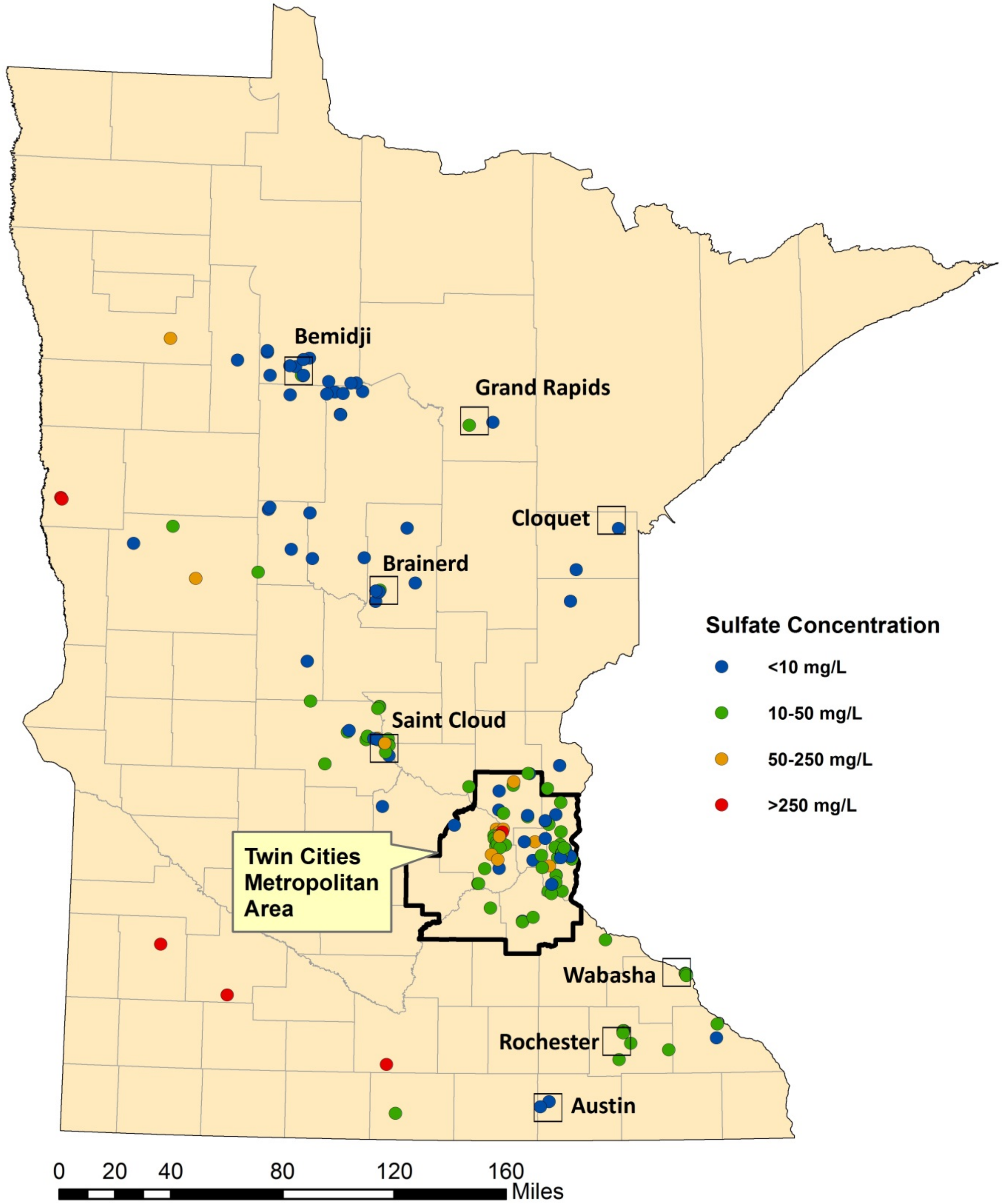


Figure 14. Sulfate concentrations in Minnesota's ambient groundwater, 2007-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

The sulfate concentrations in the groundwater in the rest of Minnesota generally were low. In Central and Southeastern Minnesota, sulfate concentrations in the groundwater ranged from less than one to 429 mg/L, and the median concentration was 13.2 mg/L. Water from only one well in this part of the state had a sulfate concentration that exceeded the SMCL of 250 mg/L. Sulfate concentrations generally were similar among the various sampled aquifers. The median concentrations ranged from 11.5 mg/L in the sand and gravel aquifers to 20.4 mg/L in the St. Peter.

Groundwater monitoring to determine sulfate concentrations was limited in Northeastern Minnesota from 2007-2011. Future groundwater monitoring network enhancements, however, will fill this information gap. The MPCA plans to add approximately 10 new monitoring wells to the network in this part of the state. Potential locations for these sites have been identified, and well installation likely will commence in 2013.

Effect of land use on sulfate concentrations in groundwater

The available data suggested that sulfate concentrations in the uppermost part of the sand and gravel aquifers naturally are very low in most of Minnesota. Nineteen wells located in undeveloped areas were sampled by the MPCA's early warning network to determine sulfate concentrations from 2007-2011. All of these wells were located in North-Central and Northeastern Minnesota and were screened near the water table in the sand and gravel aquifers. The sulfate concentration in these wells ranged from less than one to 8.2 mg/L, and the median concentration was 3.1 mg/L.

Urban land use affected sulfate concentrations in the groundwater. Sulfate concentrations in the shallow groundwater underlying urban areas were higher compared to those in the groundwater underlying undeveloped parts of the state (Figure 15). Sulfate concentrations were significantly different between the groundwater underlying urban and undeveloped land use settings. There were no significant differences in sulfate concentrations in the shallow groundwater underlying the three urban land use settings. Possible sources of sulfate to the shallow groundwater underlying urban areas include combustion of fossil fuels and the application and/or disposal of sulfur-containing products to the land surface.

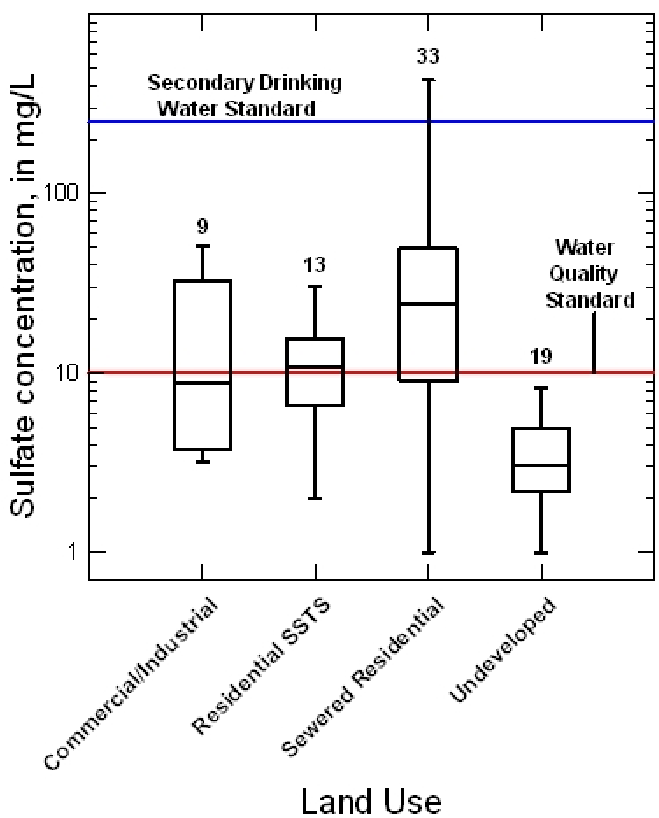


Figure 15. Sulfate concentrations in Minnesota's ambient groundwater by land use, 2007-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

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 naturally are present in rocks and are released to the environment through rock weathering. Human activities also release substantial amounts of trace elements to the environment. Trace elements have a variety of human uses and are present in steel and other metal alloys, pigments, batteries, electronic equipment, and many other products. In water, trace elements typically are measured at low concentrations, usually less than 1 ug/L, because the compounds these elements form typically are not very soluble. However, under certain geochemical conditions, such as low pH or low oxygen concentrations, most trace elements will 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 they may adversely affect human health or cause aesthetic problems with drinking water. Some trace elements, such as arsenic, are known to be toxic. Other trace elements, such as 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

In Minnesota, arsenic sorbed or stuck to the aquifer sediments, especially 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 yield water that is 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 under reducing conditions.

Human activities also may contribute arsenic to the groundwater, although most arsenic contamination in the groundwater is attributed to natural conditions [*Smedley and Kinniburgh*, 2002]. Arsenic is used 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 USEPA banned the use of lead arsenate as a pesticide in 1988 [*U.S. Environmental Protection Agency*, 1988], and most organic arsenic pesticide uses were cancelled by the USEPA in 2009 [*U.S. Environmental Protection Agency*, 2012].

High concentrations of arsenic in groundwater used for drinking are a concern because this element is known to be toxic. Inorganic arsenic is classified as a known human carcinogen by the EPA 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. To better protect the people from the long-term effects associated with consuming water containing arsenic, the EPA tightened the arsenic MCL from 50 to 10 ug/L in 2001 for public water suppliers.

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 percent of the sampled wells in the State have arsenic concentrations that exceed the USEPA's MCL of 10 ug/L. This analysis primarily was based on databases on 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 percent of the over 20,000 new wells drilled since about 2008 have concentrations that exceed the MCL [*Lundy*, 2013]. 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 MCL are scattered across Minnesota; however, some parts of the state have a high percentage of wells with water that contains 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 percent 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*, 2001].

The data from the MPCA's Ambient Groundwater Monitoring Network shows a low percentage of wells with arsenic concentrations that exceed the MCL due to the network's design. Only about six percent of these wells had concentrations that exceeded the arsenic MCL of 10 ug/L. This is substantially lower than the statewide percentage reported by others because the MPCA's network typically samples aquifers that are not expected to release any arsenic sorbed to the aquifer materials into the groundwater. Arsenic present in Minnesota's aquifer materials is thought to be released into the groundwater by a process called reductive dissolution, and one of the major conditions for this process to occur is that the water must contain little to no oxygen. The MPCA's network primarily samples shallow wells that contain recently-recharged groundwater to identify any human-caused contamination and groundwater quality trends. Recently-recharged groundwater typically contains oxygen, and the median dissolved oxygen and in the well water sampled by the MPCA was about 3 mg/L. The reductive dissolution process also results in iron being released into the groundwater along with the arsenic. Most of the wells sampled by the MPCA's network also do not contain iron. The median iron concentration in the wells sampled by the MPCA was less than the reporting limit of 20 ug/L.

Research conducted in Minnesota [*Erickson and Barnes*, 2005b] also has identified the proximity of a well screen to a confining unit as a factor which affects the arsenic concentration in the water from the sand and gravel aquifers. This research showed arsenic concentrations are highest in wells with screens set within a short (less than 8 feet) distance from the upper confining unit, such as glacial till. Most of the aquifers sampled by the MPCA's network were shallow (the median well depth was about 30 feet) and lacked any confining layer like till that retards the downward flow of water and its associated contaminants.

Arsenic concentrations high enough to exceed the MCL of 10 ug/L only were measured in water from wells sampled by the MPCA's network that were installed in the sand and gravel aquifers. Arsenic concentrations exceeding the MCL, ranging from 11.4 to 74.7 ug/L, were measured in 10 wells. Four of the ten wells were drinking water supply wells. These wells mainly were located in Western Minnesota and ranged from 60 to 98 feet deep, and the arsenic concentrations measured in the water from these wells ranged from 11.4 to 50.4 ug/L. The remainder were shallow monitoring wells that ranged from 9 to 32 feet deep. The chemistry of the water from all of these wells was conducive to release any arsenic that was sorbed onto the aquifer sediments. The water from these wells typically contained little oxygen and increased iron concentrations. The measured dissolved oxygen concentrations were 0.6 mg/L or less, and the iron concentrations ranged from about 270 to 22,000 ug/L.

Two of the shallow monitoring wells with arsenic concentrations that exceeded the MCL were located downgradient of closed landfills. The high arsenic concentrations measured in these wells were consistent with a study of groundwater affected by landfill leachate in Oklahoma [*Cozzarelli et al.*, 2011]. *Stollenwerk and Colman* [2003] found the aquifer materials were the source of the arsenic and not the landfill itself. Human-induced changes in the groundwater chemistry as a result of the landfill leachate caused the oxygen dissolved in the groundwater to be depleted. This in turn resulted in the arsenic sorbed to the aquifer materials to be released into the groundwater.

Arsenic concentrations in Minnesota's groundwater likely are related to the source of the glacial materials that comprise the state's sand and gravel aquifers. Sixty-nine wells from the early warning network were sampled to determine arsenic concentrations. This data showed that arsenic was detected more frequently in wells installed in calcareous glacial deposits compared to those installed in siliceous glacial deposits. Arsenic was detected in 20 out of the 50 wells (40 percent) installed in calcareous glacial deposits. In contrast, arsenic only was detected in one of the 19 wells (five percent) installed in siliceous glacial deposits. These results are consistent with the findings of *Erickson and Barnes* [2005a] who determined that arsenic concentrations from public water supply wells located in glacial sediments which originated from a source area northwest of Minnesota had more exceedances of the arsenic MCL compared to public water supply wells located in glacial deposits which originated from other areas.

Human-caused contamination was not found to be the cause for high arsenic concentrations in Minnesota's groundwater. Land use did not affect arsenic concentrations in the early warning network wells. Only early warning network wells installed in calcareous glacial deposits were used in this analysis since there were few arsenic detections from the aquifers composed of siliceous glacial deposits. The median arsenic concentrations in the shallow groundwater underlying undeveloped, sewered residential and commercial/industrial areas were not significantly different. This is consistent with *Welch et al.* [2000] who reported that groundwater in Minnesota largely was unaffected by past applications of arsenical pesticides.

Iron and manganese

Plants and animals both require iron and manganese for life. Iron is part of the hemoglobin in human and animal blood, which carries oxygen throughout the body. Manganese is needed by several enzyme systems in the human body to function properly. Manganese also helps form healthy cartilage and bones and plays a role in wound healing [*U.S. Department of Health and Human Services*, 2008]. Plants also require both iron and manganese for growth. Both of these metals are needed by plants to photosynthesize or obtain energy from the sun. Iron is required by plants to produce chlorophyll [*Hochmuth*, 2011], and manganese also plays a key role in photosynthesis [*Amesz*, 1983].

Excessive amounts of manganese in the groundwater make it harmful for people to consume. Too much manganese in the drinking water may cause neurological problems, such as lethargy, tremors, and slow speech [*U.S. Environmental Protection Agency*, 2004]. To prevent these problems, the MDH developed risk assessment advice for manganese in 2012. The MDH recommends manganese concentrations in drinking water be 100 ug/L or lower for formula-fed infants or infants that drink tap water, and the manganese concentration in drinking water is recommended to be 300 ug/L or lower for children and adults.

Iron in the groundwater generally is not considered to be harmful if ingested [*Minnesota Department of Health*, 2010], but excessive amounts of both iron and manganese in the water may result in colored precipitates that make the water unappealing for many uses. Iron usually forms a red precipitate, and manganese typically forms a black precipitate. These precipitates make the water unappealing to drink and may stain laundry and plumbing fixtures. To minimize excessive color in the water and staining, the USEPA set SMCLs for iron and manganese in public water supply systems of 300 and 50 ug/L, respectively [*U.S. Environmental Protection Agency*, 2012].

The weathering of rocks naturally contributes iron and manganese to Minnesota's environment. Iron and manganese are two of the most abundant metals on the earth and are contained in a variety of rocks and minerals. In the earth's crust, iron and manganese are the second- and fifth-most abundant metals [*Hem*, 1992; *U.S. Department of Health and Human Services*, 2008]. Iron ores (i.e. hematite and magnetite) and sufide minerals, such as pyrite, are common iron-containing minerals. Substantial amounts of manganese are found in the minerals that comprise some igneous and metamorphic rocks, such as basalt, olivine, pyroxene, and amphibole.

The chemistry of the aquifer determines whether iron and manganese will be released or removed from the groundwater. Both iron and manganese can be released from the aquifer materials when the water contains little oxygen. Low dissolved oxygen concentrations naturally can occur in the groundwater when the aquifer matrix contains materials such as pyrite or organic matter that react with oxygen over time. In many cases, this groundwater occurs in deep wells that contain old water or aquifers with an overlying confining unit, such as clay or shale, which retards the downward transport of oxygen-containing water. Oxygen also may be depleted when the aquifer is contaminated with organic compounds from petroleum spills [*Chapelle et al.*, 2002; *Essaid et al.*, 2011] or the discharge of wastewater [*LeBlanc*, 1984]. Iron also forms many complexes with organic matter and may be transported through the groundwater by this mechanism. Under certain conditions, iron and manganese can be removed from the groundwater. For example, when the dissolved oxygen concentration is low and sulfur is present in the groundwater, iron and manganese may form relatively insoluble sulfide compounds that precipitate out of the water.

Iron or manganese was detected in almost one-half of the wells sampled by the MPCA's Ambient Groundwater Monitoring Network. Iron was detected in about 42 percent of the wells sampled, and manganese was detected in 48 percent of the sampled wells.

About one-third of the wells sampled by the MPCA contained high enough iron or manganese concentrations to cause aesthetic or human-health problems. Twenty-six percent of the sampled wells had iron concentrations greater than the SMCL of 300 ug/L (Figure 16). Thirty-four percent of the sampled wells had manganese concentrations greater than the SMCL of 50 ug/L (Figure 17). Most of the wells that contained water that exceeded the iron or manganese SMCLs tapped the sand and gravel aquifers. About 81 percent of the wells with water that exceeded the SMCL for iron tapped the sand and gravel aquifers, and about 85 percent of the wells that contained water that exceeded the SMCL for manganese tapped the sand and gravel aquifers.

The water from some of the wells contained manganese concentrations high enough to affect human health. Twenty-nine percent of the wells contained water with manganese concentrations that exceeded the state of Minnesota's risk assessment advice for infants. Eighteen percent of the wells contained water with manganese concentrations that exceeded the state of Minnesota's risk assessment advice for children and adults. The wells with manganese concentrations exceeding the state's risk assessment advice were located throughout Minnesota.

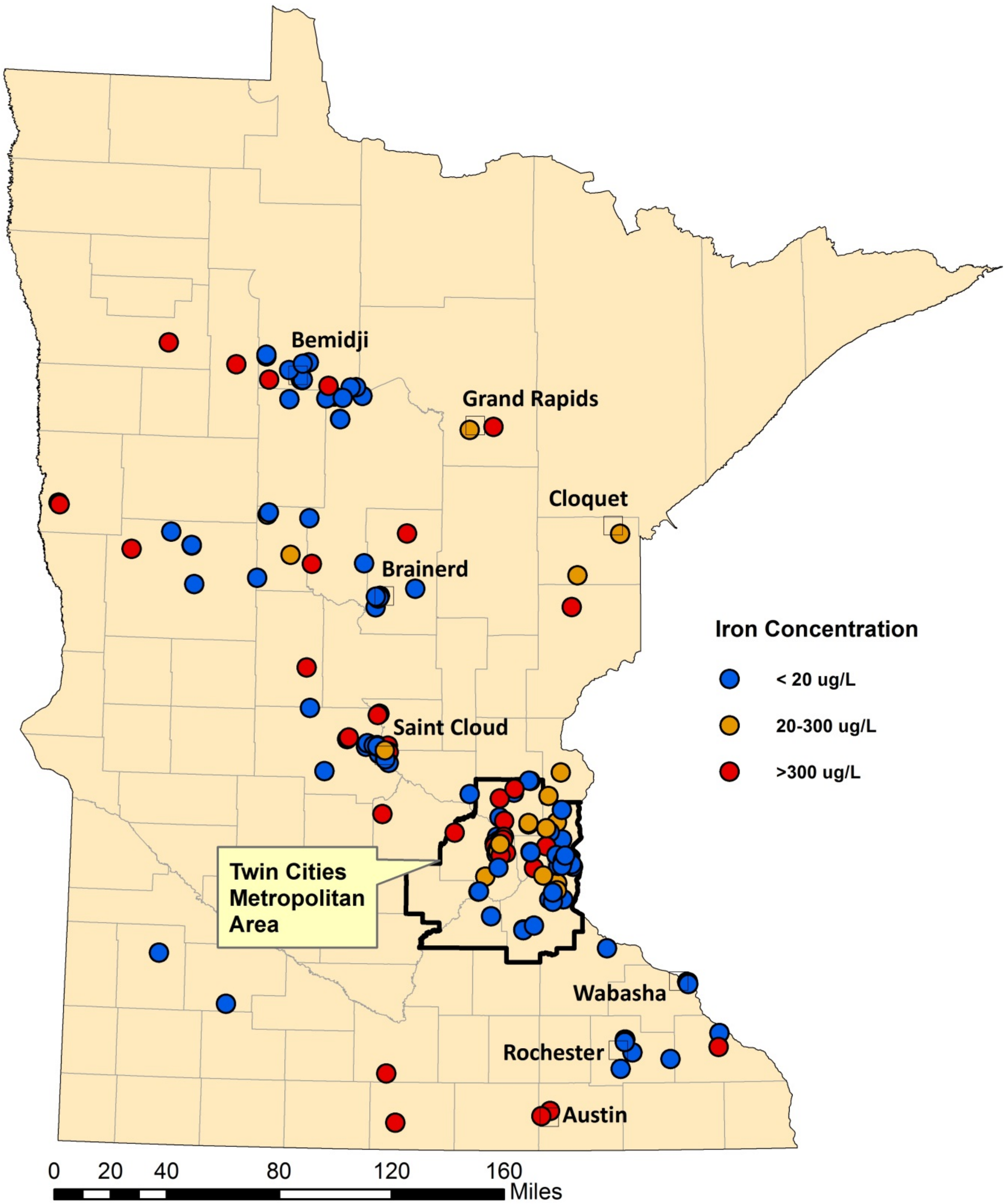


Figure 16. Iron concentrations in Minnesota's ambient groundwater, 2007-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

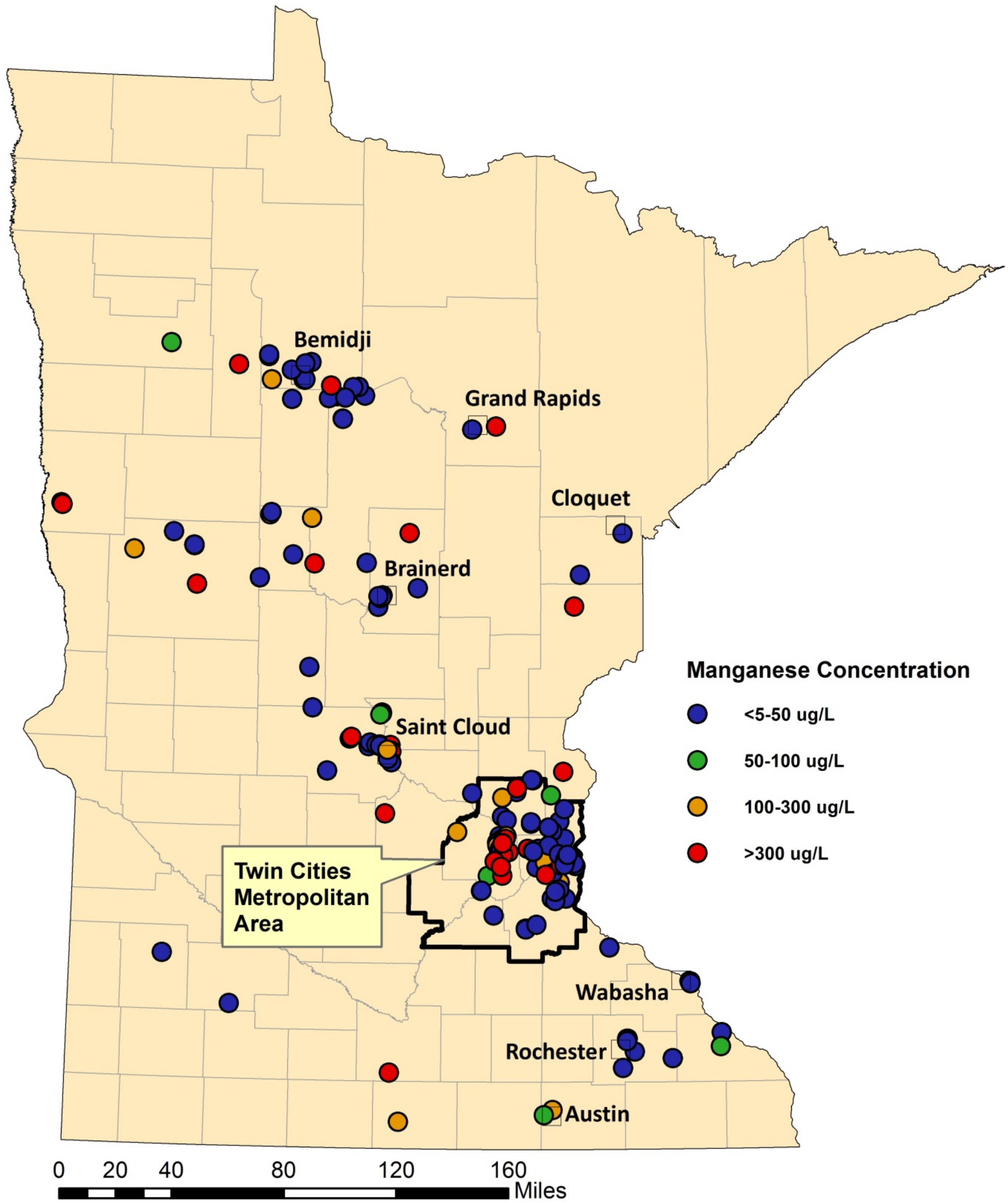


Figure 17. Manganese concentrations in Minnesota's ambient groundwater, 2007-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

High iron and manganese concentrations were related to low oxygen concentrations in the groundwater. There was a significant negative correlation between iron and dissolved oxygen concentrations (Kendall's tau=-0.4251, p=0.000). There also was a significant correlation between manganese and dissolved oxygen concentrations (Kendall's tau=-0.3948, p=0.000). There was no correlation between well depth and iron (Kendall's tau=-0.0168, p=0.7261) and manganese concentrations (Kendall's tau=-0.0885, p=0.0786). The land use setting did not significantly affect the iron or manganese concentrations in the groundwater. There also was no significant difference between manganese concentrations in the groundwater and the source of the glacial materials that comprise the surficial sand and gravel aquifers (p=0.107).

There was a significant difference between iron concentrations in sand and gravel aquifers comprised of calcareous sediments compared to those comprised of siliceous sediments (p=0.0184). The median iron concentration in the calcareous sand and gravel aquifers was estimated to be 35.9 ug/L. In contrast, the median iron concentration in the siliceous sand and gravel aquifers was estimated to be 0.001 ug/L. This difference in iron concentrations may be due to the amount of oxygen in the sand and gravel aquifers. Almost one-third of the wells tapping the calcareous sand and gravel aquifers had dissolved oxygen concentrations less than one mg/L. In contrast, only about five percent of the wells tapping the siliceous sand and gravel aquifers had dissolved oxygen concentrations less than one milligram per liter.

Volatile organic compounds

VOCs comprise a wide variety of chemicals that are refined from petroleum or otherwise synthesized and have many industrial, commercial, and household applications. These include the chemicals found in gasoline, solvents, refrigerants, and many commonly-used household products such as paints, spot cleaners, and glue. Some VOCs, called disinfection byproducts, are produced when drinking water is treated with chlorine to kill any organisms in the water that may make people sick. The presence of VOCs in groundwater 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. The VOCs generally are not naturally occurring, so the detection of any of these chemicals in groundwater indicates human impact.

Sources and fate of VOCs in groundwater

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 Resource Conservation and Recovery Act, commonly referred to as 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.

Sites where large quantities of VOCs were disposed of in the past became the focus of major efforts of groundwater remediation. Over the past 20 years, state or federal programs have addressed groundwater 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 groundwater contamination area that is smaller than one acre.

Once released into the soil, VOCs readily leach into the underlying groundwater. Most VOCs in the groundwater will degrade over time, depending on aquifer conditions. The VOCs that contain more than two chlorine atoms, such as tetrachloroethylene or trichloroethylene, usually slowly degrade when the groundwater contains no oxygen. If the groundwater is oxygenated, these chemicals typically persist for many years. The VOCs that are associated with petroleum spills will often break down over time in soil and groundwater.

Occurrence and distribution of VOCs in groundwater

Common uses of the VOCs that were analyzed in the groundwater samples compiled for this report are listed in Table 3. Some of the uses of these chemicals have declined over time or been phased out. The MDH has developed Health Risk Limits (HRLs) for many of these chemicals based on their toxicity to humans. A HRL represents the concentration of a chemical in groundwater above which it is unsafe to consume.

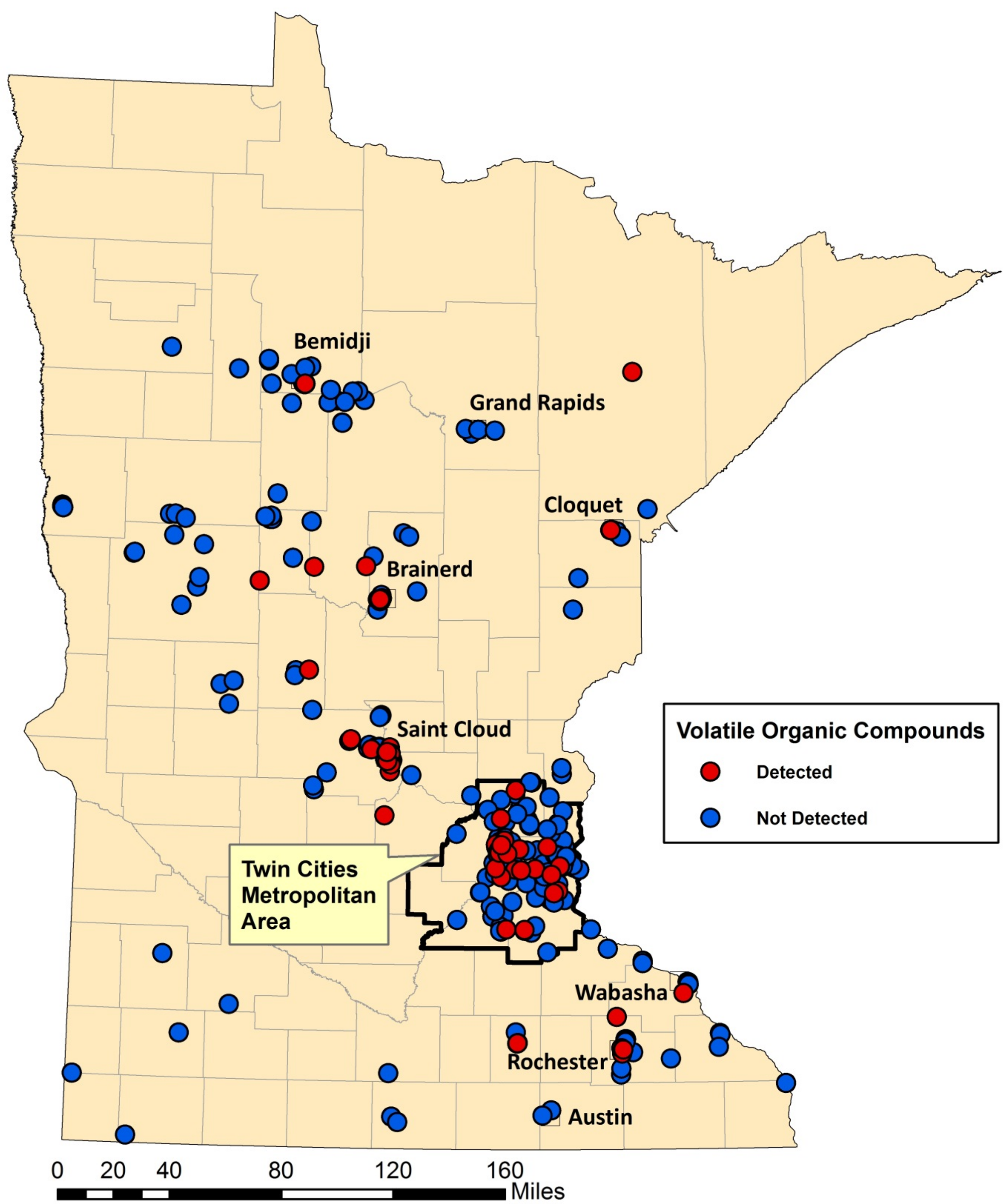


Figure 18. Volatile organic compounds in Minnesota's groundwater, 2007-2011
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

Table 3. Volatile organic compounds analyzed in water samples collected for the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network, 2007-2011 [N/A, not available]

Chemical	Use/Source
1,1,1,2-Tetrachloroethane	Solvent and in the production of wood stains and varnishes
1,1,1-Trichloroethane	Solvent
1,1,2,2-Tetrachloroethane	Solvent, Refrigerant
1,1,2-Trichloroethane	Solvent, Chemical synthesis
1,1-Dichloroethane	Chemical synthesis, Solvent, Degreaser
1,1-Dichloroethylene	Chemical synthesis
1,1-Dichloropropene	N/A
1,2,3-Trichlorobenzene	Solvent
1,2,3-Trichloropropane	Solvent
1,2,4-Trichlorobenzene	Solvent
1,2,4-Trimethylbenzene	Occurs naturally in coal tar and petroleum, Gasoline additive, Sterilizing agent, Manufacture of dyes, perfumes, and resins
1,2-Dibromo-3-chloropropane	Soil fumigant
1,2-Dichloroethane	Chemical synthesis, Solvent
1,2-Dichloropropane	Chemical synthesis, Soil Fumigant, Solvent
1,3,5-Trimethylbenzene	Solvent, Combustion product
1,3-Dichloropropane	Soil Fumigant, Nematicide
2,2-Dichloropropane	N/A
Acetone	Solvent, Active ingredient in nail polish remover
Allyl Chloride	Chemical synthesis
Benzene	Natural constituent of crude oil, gasoline, and cigarette smoke; Chemical synthesis
Bromobenzene	Chemical synthesis
Carbon Tetrachloride	Chemical synthesis, Solvent, Refrigerant
CFC-11	Refrigerant
CFC-113	Refrigerant
CFC-12	Refrigerant
Chlorobenzene	Chemical synthesis, Solvent
Chlorodibromomethane	Disinfection byproduct, Flame retardant
Chloroethane	Chemical synthesis
Chloroform	Disinfection byproduct, Chemical synthesis, Solvent
Chloromethane	Disinfection byproduct, Refrigerant, Chemical Synthesis
cis-1,2-Dichloroethylene	Degradation product of tetrachloroethylene or trichloroethylene
cis-1,3-Dichloropropene	Soil Fumigant
Cumene	Constituent of crude oil and gasoline
Dibromomethane	Disinfection byproduct, Solvent, Chemical synthesis
Dichlorobromomethane	Disinfection byproduct, Flame retardant
Ethyl ether	Solvent
Ethylbenzene	Constituent in crude oil and gasoline
Ethylene dibromide	Gasoline additive, Fumigant
Halon 1011	Refrigerant
HCFC-21	Refrigerant
Hexachlorobutadiene	Chemical synthesis, Solvent
m-Dichlorobenzene	Chemical synthesis
Methyl bromide	Soil fumigant
Methyl ethyl ketone	Solvent
Methyl isobutyl ketone	Solvent
Methyl tert-butyl ether	Gasoline additive
Methylene Chloride	Solvent, Chemical synthesis, Degreaser

Naphthalene	Natural constituent of coal and crude oil, Mothballs
n-Butylbenzene	N/A
n-Propylbenzene	Chemical synthesis, Solvent, Textile dyeing and printing, Fuel combustion
o-Chlorotoluene	Solvent, Chemical synthesis
o-Dichlorobenzene	Solvent, Chemical Synthesis
o-Xylene	Constituent of crude oil and gasoline
p-Chlorotoluene	Solvent, Chemical synthesis
p-Cymene	Gasoline or oil combustion
p-Dichlorobenzene	Fumigant, Deodorant
sec-Butylbenzene	Constituent of gasoline, Solvent, Chemical synthesis
tert-Butylbenzene	Chemical synthesis, Solvent
Tetrachloroethylene	Solvent, Degreaser
Tetrahydrofuran	Solvent, Chemical synthesis
Toluene	Constituent of crude oil and gasoline, Solvent, Chemical synthesis
trans-1,2-Dichloroethylene	Degradation product of tetrachloroethylene or trichloroethylene
trans-1,3-Dichloropropene	Fumigant, Nematicide,
Tribromomethane	Disinfection byproduct
Trichloroethylene	Solvent, Degreaser
Vinyl chloride	Chemical synthesis; Degradation product of tetrachloroethylene or trichloroethylene
meta and para Xylene mix	Constituent of crude oil and gasoline
Styrene	Chemical synthesis

A small percentage of the wells sampled for VOCs (13 percent) were installed to monitor known areas of groundwater contamination. These wells were incorporated into the MPCA's Ambient Groundwater Monitoring Network in an attempt to utilize the wells that have been installed to monitor upgradient conditions at a multitude of remediation sites to describe ambient groundwater conditions. The wells sampled near remediation sites primarily were installed to monitor petroleum spills and were located in the sand and gravel aquifers. At remediation sites, wells are installed to monitor the most-contaminated areas, other wells are installed to determine the extent of any contamination, and some wells are installed to determine the amount of contamination that originated from areas upgradient of the contamination source. As a result of this monitoring scheme, the amount of VOC contamination measured in the vicinity of a remediation site can vary substantially. For this assessment, the least-contaminated wells associated with remediation sites generally were preferentially selected for sampling because these best represented ambient groundwater quality conditions.

Detection frequency of VOCs

The data collected by the MPCA shows that VOCs were detected in a small percentage of samples collected from the ambient groundwater. At least one VOC was detected in the water from 15 percent of the wells installed to monitor the quality of the ambient groundwater. In contrast, VOCs were detected in almost 40 percent of the wells installed to monitor known areas of contamination.

Only a small number the VOCs were detected in the ambient groundwater. Twelve of the 68 VOCs analyzed (18 percent) were detected in water from the wells installed to monitor the ambient groundwater, whereas thirty-four of the 68 VOCs (50 percent) were detected in water from the wells installed to monitor known areas of contamination.

There were distinct differences in the types of VOCs found in the groundwater affected by known contamination versus the ambient conditions. VOCs typically associated with petroleum spills, such as benzene, xylenes, and toluene, were the most-frequently chemicals detected in water from the wells installed to monitor remediation sites (Table 4). Disinfection byproducts (chloroform, bromodichloromethane, and chlorodibromomethane) were among the most-frequently detected VOCs in the ambient groundwater (Table 5). The infiltration of municipal drinking water used for a variety of purposes, such as lawn and garden irrigation or car washing, is one likely source of disinfection byproducts to the groundwater [*Squillace et al.*, 1999].

Table 4. Most-frequently detected volatile organic compounds in water from wells installed to monitor known contaminant spills, 2007-2011
[NA, not available; the health-based guidance for the chronic exposure duration was reported for the chemicals with multiple exposure durations].

Chemical	Detection frequency	Maximum Concentration	Health-based guidance[1]
Benzene	26%	12,000 ug/L	3 ug/L
n-Propylbenzene	26%	300 ug/L	NA
Sec-Butylbenzene	23%	18 ug/L	NA
1,2,4-Trimethylbenzene	20%	3,000 ug/L	100 ug/L
1,3,5-Trimethylbenzene	20%	790 ug/L	100 ug/L
Cumene	20%	30 ug/L	300 ug/L[2]
Naphthalene	20%	400 ug/L	70 ug/L
o-Xylene	20%	3,700 ug/L	300 ug/L
Para- and methyl-Xylenes mix	20%	9,400 ug/L	300 ug/L
Toluene	17%	22,000 ug/L	200 ug/L

1. Health-based guidance published by the Minnesota Department of Health as of January, 2013.
2. Health-based guidance currently is under review by the Minnesota Department of Health and may be revised.

Table 5. Most-frequently detected volatile organic compounds in water from wells installed to monitor the quality of the ambient groundwater, 2007-2011
[NA, not available; the health-based guidance for the chronic exposure duration was reported for the chemicals with multiple exposure durations]

Chemical	Detection frequency	Maximum Concentration	Health-based guidance[1]
Para- and methyl-Xylenes mix	9%	5.6 ug/L	300 ug/L
o-Xylene	6%	2.8 ug/L	300 ug/L
Chloroform	3.9%	11 ug/L	30 ug/L MCL
Bromodichloromethane	2.2%	6.4 ug/L	NA
Ethylbenzene	2.2%	0.92 ug/L	50 ug/L
Chlorodibromomethane	1.3%	2.6 ug/L	NA
Tetrachloroethene	1.3%	0.62 ug/L	5 ug/L
Toluene	1.3%	0.35 ug/L	200 ug/L
Tetrahydrofuran	0.8%	150 ug/L	NA

1. Health-based guidance published by the Minnesota Department of Health as of January, 2013.

The ambient groundwater contained mixtures of a smaller number of VOCs compared to the water from the wells installed to monitor areas of known groundwater contamination. The water from the wells installed to monitor ambient groundwater quality conditions contained a mixture of up to four different VOCs, whereas the water from the wells installed to monitor the remediation sites contained a mixture of up to 17 different VOCs.

Concentrations of VOCs in groundwater

In Minnesota's ambient groundwater, the measured VOC concentrations were low compared to those in wells that were located in the immediate vicinity of known chemical spills. The total sum of VOC concentrations in the ambient groundwater ranged from zero to 150 ug/L, and the highest concentrations were measured in one well that was located in the immediate vicinity of an old landfill. In contrast, the total sum of VOC concentrations in water from wells installed to monitor known chemical spills often were substantially higher compared to the ambient groundwater. The total sum of VOC concentrations in these wells sometimes were more than two orders of magnitude higher compared to the ambient groundwater, ranging from zero to over 55,000 ug/L. The VOC data presented in this report that was collected near remediation sites should not be construed as the typical ranges in VOC concentrations at remediation sites because the sampling primarily was biased toward the least-contaminated wells.

VOC concentrations in the ambient groundwater did not exceed any human-health guidance set by the MDH. The human-health guidance set by the MDH was exceeded for 10 chemicals measured in the water from wells installed to monitor known contamination: 1) chloroform, 2) o-Xylene, 3) toluene, 4) tetrachloroethylene, 5) ethylbenzene, 6) benzene, 7) trichloroethylene, 8) naphthalene, 9) 1,2,4-trimethylbenzene, and 10) vinyl chloride.

VOCs in drinking water wells

VOCs were detected in eight drinking water wells that were sampled by the MPCA's Ambient Groundwater Monitoring Network. All of these wells provided drinking water to a single residence, and disinfection byproducts primarily were the type of VOC that were measured. Five of the eight wells contained one or more of the disinfection byproducts: chloroform, chlorodibromomethane, dichlorobromomethane, or tribromomethane. There are a couple of different sources for disinfection byproducts in the groundwater. These chemicals either originated from the infiltration of treated water that was disposed on the land surface, or the chemicals could have been formed when the water-supply well was disinfected to minimize the presence of disease-causing organisms, such as bacteria, in the drinking water.

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 these chemicals to human or aquatic life generally 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.

In Minnesota, scientists have measured CECs in the state's water resources and unnatural endocrine activity in the state's aquatic life. Several studies conducted over the past decade have detected CECs in the state's feedlot lagoons, groundwater, lakes, landfill leachate, municipal wastewater, and streams [*Lee et al.*, 2004; *Writer et al.*, 2010]. Indicators of endocrine activity, such as the presence of vitellogenin in male fish, have been measured at more than 40 percent of the surface-water sites sampled in Minnesota [*Lee et al.*, 2010]. In Minnesota, unnatural endocrine activity was observed in fish exposed to wastewater treatment plant effluent as well as fish in diverse environmental settings, which suggests there are other sources of EACs to streams besides wastewater effluent, such as runoff from agricultural or urban lands, atmospheric deposition, or groundwater inflow.

The MPCA received appropriations from the Clean Water Fund from state fiscal years 2010-2013 to expand the monitoring of EACs and other CECs in the state's groundwater. The MPCA used funds from this appropriation to test approximately 40 wells each year for EACs and other contaminants of emerging concern as part of the agency's ambient groundwater monitoring. A full report on some of the initial findings from the first year of CEC sampling is found at: http://www.pca.state.mn.us/index.php/view-document.html?gid=17244 . A brief summary of the findings follows.

The results from the first round of sampling, which was from November 2009 to June 2010, were summarized by *Kroening* [2012]. During this period, the MPCA tested 40 wells primarily in urban settings to determine the extent of any contamination from EACs and other CECs in Minnesota's groundwater. The USGS laboratories tested the samples for almost 100 different chemicals. These included prescription and non-prescription medicines, hormones, fragrances, detergent breakdown products, and fire retardants. Two antibiotics were included in the set of chemicals analyzed by *Kroening* [2012]. Most of the sampled wells represented ambient groundwater quality conditions and tapped the shallow sand and gravel aquifers. Five wells of the sampled wells tapped the Prairie du Chien-Jordan aquifer.

The sampled wells purposely were selected because the well water contained increased boron concentrations or were located downgradient of landfills, which suggested the water may contain EACs and other contaminants of emerging concern. Boron has many sources in the environment but may be associated with wastewater contamination, in which EACs and other contaminants of emerging concern often are present. Three of the 40 sampled wells were sampled to characterize the extent of any contamination emanating from old landfills, which is another source of CECs in the environment. These wells were located within the landfills' contaminant plumes and were selected in consultation with hydrogeologists from the MPCA's Closed Landfill Program. None of the landfills were in operation at the time of sampling, and all of them ceased accepting waste 15 to 27 years prior to sample collection.

The results from the first round of sampling showed that twenty EACs and other CECs were detected in about one-third of the sampled wells (Figure 19). The number of chemicals detected in a single well ranged from one to ten. The most frequently detected chemicals were the fire retardant tris (dichloroisopropyl) phosphate, the antibiotic sulfamethoxazole, and the plasticizers bisphenol A and tributyl phosphate, which were detected in 20 percent or less of the sampled sites (Figure 20).

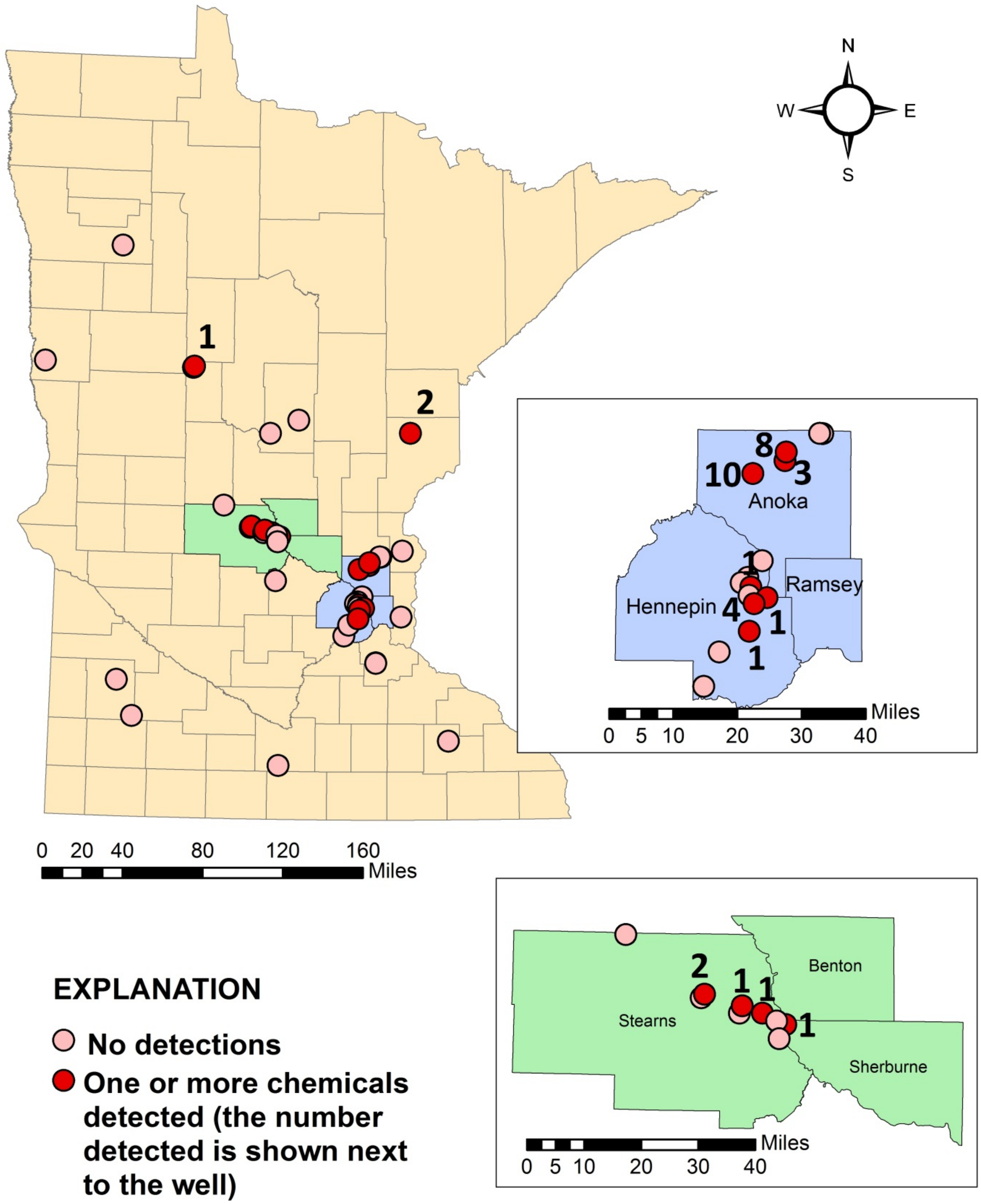


Figure 19. Wells with detections of contaminants of emerging concern in Minnesota's groundwater, 2009-2010
[Wells located in the vicinity of Anoka, Benton, Hennepin, Ramsey, Sherburne, and Stearns Counties are shown on the inset maps; Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

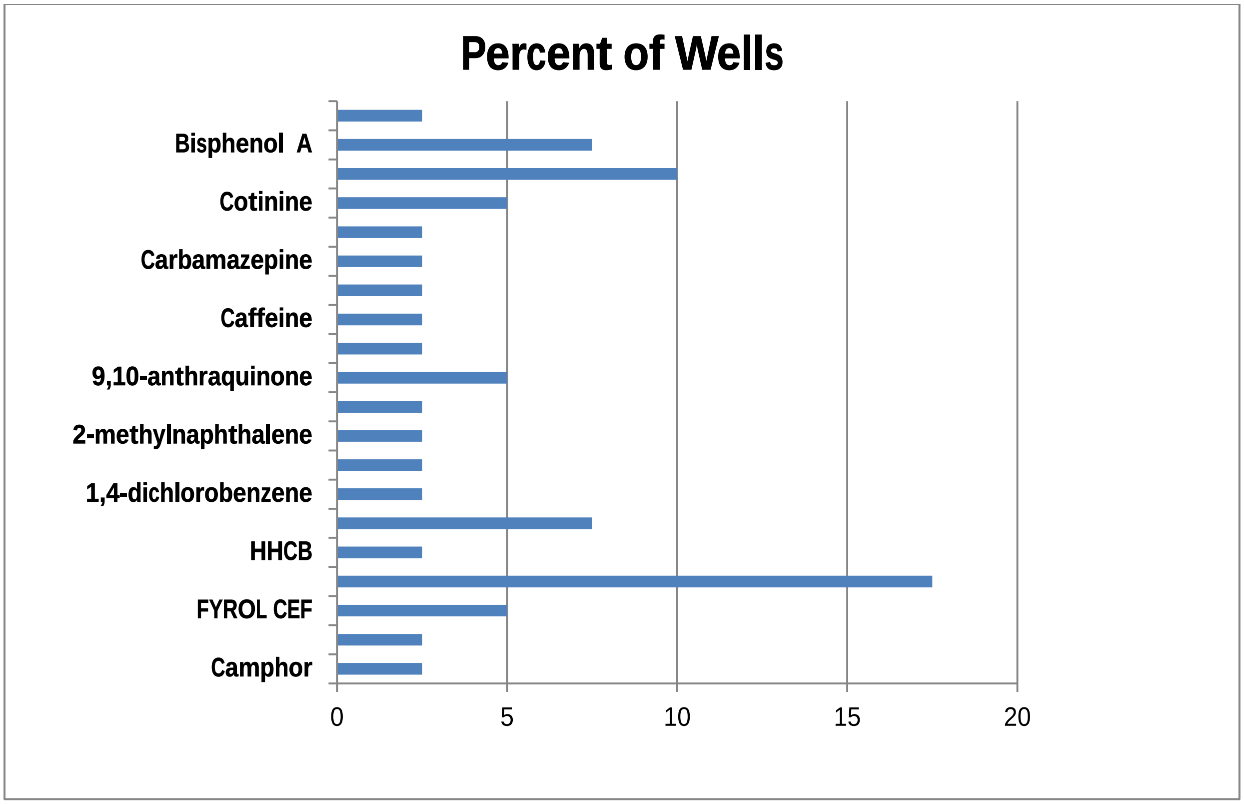


Figure 20. Detection frequency of contaminants of emerging concern in Minnesota's groundwater, 2009-2010
[Data from the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network].

EACs were detected in three of the sampled wells. The detected EACs were bisphenol A, trans-diethylstilbestrol, and 4-cumylphenol. Bisphenol A is used to manufacture polycarbonate plastics and epoxy resins. Epoxy resins are used in food and drink packaging, compact discs, and medical devices, and to coat products such as food cans, bottle tops, and water-supply pipes. Trans-diethylstilbestrol is a synthetic non-steroidal estrogen used to treat cold sores. 4-cumylphenol is a breakdown product of alkylphenol detergents. Two of the wells with detections of these chemicals tapped a landfill-leachate plume, and the remaining well was shallow and supplied water to a residence.

EACs and other CECs were present at low concentrations in the ambient groundwater underlying urban areas in Minnesota. Over 80 percent of the detected chemicals were measured at concentrations of less than one microgram per liter (µg/L). No concentrations exceeded any applicable human-health guidance established by the MDH.

The water from two wells affected by landfill leachate had the greatest number of detections of contaminants of emerging concern and the highest total sum of concentrations. These results suggested the state's continued efforts to properly close, monitor, and maintain landfills likely will help minimize the migration of the EACs and other contaminants of emerging concern to the groundwater.

Further data collection will refine this assessment of EACs and other CECs in Minnesota's groundwater. A limited number of wells in residential areas on SSTS were available for sampling from November 2009 to June 2010. The MPCA's Ambient Groundwater Monitoring Network currently (2013) is being enhanced to provide a better assessment of the effects of land use on groundwater quality. Additional wells in unsewered residential areas were installed for this monitoring network enhancement during the course of this study. These wells will be targeted for sampling as part of future monitoring. This assessment of CECs did not assess other settings susceptible to contamination, such as feedlots [***Meyer*** *et al.*, 2000] or agricultural lands amended with biosolids from wastewater treatment facilities [*Kinny et al.*, 2006].

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