

Perfluorinated Chemicals in Minnesota's Ambient Groundwater, 2013



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Executive summary

This report presents the results from a 2013 assessment of perfluorinated chemicals (PFCs) in the ambient groundwater throughout Minnesota. The term “ambient groundwater” refers to the general or background conditions of this resource. Any contamination in the ambient groundwater is contributed by the typical use of chemicals not by chemical spills, leaks, or disposal sites, although an ambient monitoring network can catch contamination from these sources if they affect a large area. In this assessment of the ambient groundwater, the Minnesota Pollution Control Agency (MPCA) sampled almost 200 wells across the state for 13 different PFCs. The study did not directly assess the known industrial PFC contamination in Washington County in the Twin Cities Metropolitan Area (TCMA); however, some of the sampled wells were located within the 100+ square mile area that is affected by this contamination plume.

PFCs, such as perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorobutanoic acid (PFBA) and others, are part of a class of approximately 3,000 manmade chemicals used worldwide to manufacture products that are heat and stain resistant and repel water. These chemicals are in a wide variety of products including fabric, carpet, paper coatings, floor polish, personal care products, non-stick surfaces, fire-fighting foam, and certain insecticides. PFCs are widespread and persistent in the environment and have been found in wildlife and people all over the globe. These chemicals also are of concern because of their toxicity and ability to bioaccumulate. Scientists only have studied the toxicity of a few of these chemicals. PFOA and PFOS are the two most studied chemicals, and the best available science indicates they cause several human health effects including developmental problems to fetuses during pregnancy, cancer, liver damage, and immune and thyroid effects. To protect against these adverse effects in drinking water, the U.S. Environmental Protection Agency (EPA) set lifetime health advisories for PFOA and PFOS at 70 ng/L in May 2016. One year later, in May 2017, the Minnesota Department of Health (MDH) updated their human health guidance for PFOA and PFOS. The PFOA health based value (HBV) was lowered to 35 ng/L, and the PFOS HBV was lowered to 27 ng/L. These values protect human health during short time periods such as pregnancy and breastfeeding as well as protect against a lifetime of exposure to these chemicals.

The most well-known PFC contamination in Minnesota comes from past manufacturing and waste disposal by the 3M Company. 3M manufactured PFOS and PFOA at its Cottage Grove facility in Washington County (located in the southeastern part of the TCMA) from the late 1940s until 2002. PFC wastes were disposed at four sites in Washington County ultimately resulting in a 100+ square mile contamination plume that has polluted the groundwater in a large part of the county and affected many city and private drinking water wells. PFCs also were discharged for decades to the Mississippi River via the 3M wastewater treatment plant in Cottage Grove.

In 2007, 3M entered into a Consent Order with the MPCA to investigate and conduct remediation, the implementation of which is ongoing. As part of this work, the MPCA detected PFC contamination in Minnesota waters besides the Mississippi River. Some of this pollution is attributable to the use of PFC-containing materials in chrome plating and fire-fighting foams in training and fire suppression.

This investigation of PFCs in the ambient groundwater mostly used samples collected from the MPCA's Ambient Groundwater Monitoring Network. The agency designed this network to characterize non-agricultural contaminants in the groundwater and further developed it to characterize current groundwater quality conditions and track any trends in concentrations over time. Some drinking water wells were sampled as part of this study, but the data do not necessarily characterize the water that is consumed because all samples were collected from the outside spigot, which typically is not passed through any in-home water treatment systems that may be present.

To conduct this study, the MPCA purposely sampled wells where scientists expected to find PFCs due to the vulnerability of the aquifers to pollution from above ground. Most of the sampled wells were located in urban areas and installed in the shallow water table, bedrock, or deep sand and gravel aquifers; the sampled aquifers typically were vulnerable to pollution. Twenty-six of the sampled wells were located in settings where there was known PFC pollution, mostly within the 100+ square mile plume of industrial pollution in Washington County related to the 3M PFC disposal sites, although none were immediately adjacent to the most contaminated areas.

This investigation found that PFCs in the ambient groundwater generally do not occur at concentrations that adversely affect human health. One or more types of PFCs were detected in almost 70% of the wells that were sampled. The measured PFC concentrations were thirty to several thousand times lower than those found in wells in the areas most contaminated by the 3M PFC manufacturing and waste disposal sites in Washington County. PFBA generally was measured at the highest concentrations of all the PFCs analyzed in this study, although none exceeded the health risk limit set in 2011 by the Minnesota Department of Health (MDH). Eight percent of the sampled wells had concentrations that exceeded the PFOA and PFOS HBVs of 35 and 27 ng/L that were set by the MDH in 2017 or the interim surrogate value for PFHxS (27 ng/L). Most of the concentrations exceeding these limits were measured in shallow monitoring wells in residential areas. Four of the 50 sampled water-supply wells had a concentration that exceeded the MDH HBVs for PFOA and PFOS. Two of these wells were located near the known industrial PFC contamination in Washington County.

The greatest number of individual PFCs and the highest concentrations of PFCs were generally detected in wells located within the 100+ square mile area influenced by the industrial PFC contamination plume in Washington County related to the 3M disposal sites or by two closed landfills in the northern TCMA. The median number of PFCs detected in the wells located in the vicinity of these known areas of contamination was five, and the corresponding median total PFC concentration was 71 ng/L. In contrast, the median total PFC concentration was 0 ng/L in the sampled wells that were not in these areas.

PFC detections and concentrations in the ambient groundwater also were associated with urban land use. One or two PFCs typically were detected in the shallow groundwater underlying the urban areas but were not typically detected in the groundwater underlying undeveloped areas.

More information on MPCA and MDH activities related to PFCs can be found on these websites:

<https://www.pca.state.mn.us/waste/perfluorochemicals-pfcs> and
<http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html>.

Introduction

An array of popular consumer products, including non-stick cookware; water repellent clothing; grease resistant food packaging; microwave popcorn bags; and stain resistant carpets, are made using fluorinated chemicals. Table 1 lists just a few of the compounds in this very large class of over 3,000 chemicals. Many products are manufactured using fluorinated chemicals because of their unique properties. Fluorinated chemicals are unlike most others in that they repel water, oil, and grease and can withstand high heat and most acids, bases, and solvents without breaking down. These chemicals also have surfactant properties that lower the surface tension of water. This allows liquids to easily fill in extremely tiny cracks and pores. Paints, polishes, and other products often contain surfactants to more easily allow them to coat the surfaces to which they are applied.

Table 1. Commonly measured fluorinated chemicals in the environment.

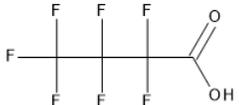
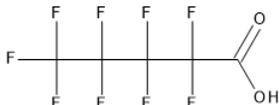
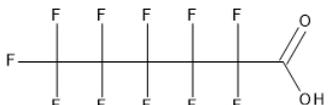
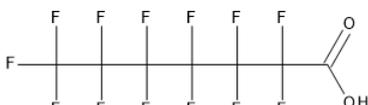
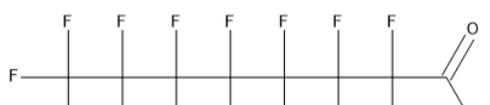
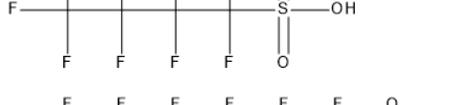
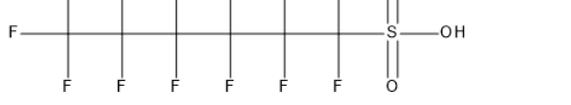
Chemical name	Structure
Perfluorobutanoic acid (PFBA)	
Perfluoropentanoic acid (PFPeA)	
Perfluorohexanoic acid (PFHxA)	
Perfluoroheptanoic acid (PFHpA)	
Perfluorooctanoic acid (PFOA)	
Perfluorononanoic acid (PFNA)	
Perfluorobutanesulfonate (PFBS)	
Perfluorohexanesulfonate (PFHxS)	
Perfluorooctanesulfonate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

Table 1. Commonly measured fluorinated chemicals in the environment. (continued)

Chemical name	Structure
8:2 Fluorotelomer acid (8:2 FTOH)	
N-methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)	
N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE)	

A fluorinated chemical's unique properties are due to its chemical structure. Fluorinated chemicals basically consist of a functional group attached to a "perfluorinated chain" of varying length. The functional group allows the chemical to dissolve in water (and some oils); it is often a carboxylate (COOH), sulfonate (SO₃H), or alcohol (OH). The perfluorinated chain is a linear backbone of carbon atoms that is fully saturated with fluorine. This chain gives a fluorinated chemical its unique ability to repel both oil and water and its extreme chemical and temperature stability. The multitude of carbon-fluorine bonds present in the perfluorinated chain makes these chemicals very stable and difficult to break down due to the extreme strength of this bond. Perfluorinated chemicals (PFCs) are just one of the many different types of fluorinated chemicals. What sets PFCs apart from the other fluorinated chemicals is that they contain as much fluorine as is chemically possible, which makes PFCs not just very stable but extremely stable.

Unfortunately, the PFC's extreme chemical stability also facilitates their widespread and persistent presence across the globe. PFCs have been measured in all sampled media throughout the world, including groundwater, surface water, air, soil and sludge, urban runoff, indoor and outdoor dust, and in animals and people. (U.S. Environmental Protection Agency, 2016a, 2016b).

The highest PFC concentrations in the environment usually are found near facilities where these chemicals were manufactured or places that were contaminated by the application or disposal of fluorochemical manufacturing wastes (Lindstrom, Strynar, & Libelo, 2011; Prevedouros, Cousins, Buck, & Korzeniowski, 2006; Rumsby, Young, Hall, & McLaughlin, 2010). In the United States, PFC contamination has been measured near many places where fluorochemicals are manufactured (i.e. Minnesota and Alabama) or used in secondary manufacturing processes (i.e. West Virginia and New York). Environmental contamination by PFCs also has been documented in Europe and Asia.

Landfill leachate and wastewater are two other important sources of PFCs to the environment. These contain PFCs due to the use and disposal of the many products that contain fluorochemicals. The MPCA detected PFCs in almost every landfill sampled in Minnesota (Minnesota Pollution Control Agency, 2010), and PFCs have also been found in landfill leachate in Germany (Busch, Ahrens, Sturm, & Ebinghaus, 2010). Several studies have documented that wastewater contains PFCs and causes increased PFC concentrations in the environment. Surface water studies in both the U.S. and Europe (Boulanger, Vargo, Schnoor, & Hornbuckle, 2005; Huset et al., 2008; Konwick et al., 2008) found substantial increases in PFC concentrations at sites downstream of wastewater treatment plant outfalls.

Aqueous film-forming foams (AFFFs) are another source of PFC contamination to the environment. These chemicals were developed in the 1960s to extinguish fires of flammable liquids, such as gasoline, and fluorinated chemicals are a key component of some AFFF formulations (Moody & Field, 2000). Several studies within Minnesota and in other parts of the U.S. (Antea Group, 2011; Moody, Hebert, Strauss, & Field, 2003; Weiss, Wiesmuller, & A, 2012) have reported high concentrations of PFCs in the biota and groundwater near fire fighter training areas where AFFFs were used.

Atmospheric deposition is yet another documented source of PFCs to the environment. In West Virginia, groundwater contamination by PFCs was traced to the air emissions from a fluoropolymer manufacturing facility (Davis, Aucoin, Larsen, Kaiser, & Hartten, 2007; Shinn et al., 2011). Atmospheric deposition also is thought to be a source of PFCs to extremely remote areas, such as the Arctic (Ellis et al., 2004; Rankin, Mabury, Jenkins, & Washington, 2016).

The presence of PFCs in the environment is problematic because these chemicals bioaccumulate and some are known to harm health. Giesy and Kannan first reported in 2001 that perfluorooctane sulfonate (PFOS) was globally distributed in wildlife, even in animals that inhabit very remote areas of the world such as the Arctic Circle. Subsequent studies confirmed the presence of PFCs in people and animals throughout the world (U.S. Environmental Protection Agency, 2016a, 2016b). Animal studies have found that exposure to some PFCs causes health effects, including changes in development, liver, thyroid, and immune function, and cancer in some organs following high dose exposures (Minnesota Department of Health, 2016b). Scientists continue to study human health problems associated with exposure to PFCs. To date, scientists have studied human health exposure to perfluorooctanoic acid (PFOA) and PFOS the most.

From 2005-2013, as part of a class action lawsuit settlement in West Virginia, a panel of scientists conducted research to determine whether there was any association between PFOA (and PFOS) and human disease in a high exposure community. This panel concluded that a probable link (association) exists between PFOA exposure and high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, and pregnancy-induced hypertension, while finding no probable link to numerous other examined health endpoints (U.S. Environmental Protection Agency, 2016a, 2016b).

To protect against known or anticipated human health effects from drinking water, the U.S. Environmental Protection Agency (EPA) set health advisories for PFOA and PFOS. A health advisory is the concentration of a contaminant in drinking water at which adverse health effects are not anticipated to occur. In May 2016, EPA updated its lifetime health advisories for PFOA and PFOS (provisional health advisories for these two chemicals were initially set in 2009), setting both at 70 ng/L. When both chemicals are found in drinking water, the combined concentration also should not exceed 70 ng/L. These health advisories were derived to provide protection against the spectrum of possible adverse health effects, including developmental effects to fetuses during pregnancy, cancer, liver damage, and immune and thyroid effects (U.S. Environmental Protection Agency, 2016a, 2016b). While health advisories are non-enforceable technical guidance, the EPA recommends that drinking water systems take steps to reduce exposure when concentrations exceed this guidance such as closing contaminated wells, blending water sources, or treating the water to remove PFOA and PFOS (U.S. Environmental Protection Agency, 2016c).

Similarly, the Minnesota Department of Health (MDH) establishes health risk limits (HRLs) and health based values (HBVs) for PFCs. These are similar to the EPA's health advisory; it is the concentration of a chemical in drinking water that poses little or no risk to humans. The MDH calculates HBVs and HRLs by the same method which is published in the state statutes. The HRLs are adopted using a formal rulemaking process. The MDH develops each HBV and HRL for a variety of exposure durations, ranging from a single incident of very short duration to long-term exposure to a chemical over many years.

The MDH set HBVs and HRLs for four PFCs. Updated HBVs for PFOA and PFOS were set in May 2017 (HRLs for these two chemicals were originally set in 2009). The updated value for PFOA is 35 ng/L, and the updated value for PFOS is 27 ng/L. These updated values reflect new state-level analysis of the potential for mothers to pass along these chemicals to fetuses and infants. The values are lower than the EPA lifetime health advisories because the MDH values apply to the short time period (e.g. weeks to months) during pregnancy and breastfeeding as well as a lifetime of exposure. The MDH set the HRLs for PFBA and PFBS in 2011, to protect from effects in the thyroid, blood, liver, and/or kidney systems. The chronic HRLs for both of these chemicals are 7,000 ng/L. MDH also evaluates the additive health risk when two or more PFCs are present in drinking water, using a calculation that divides each PFC by its HRL or HBV and then sums all the results. If the sum (referred to as the Hazard Index) is greater than one, the MDH considers it the same as a single PFC exceeding its individual HRL or HBV.

The MDH has also reviewed the toxicological information available for perfluorohexane sulfonate (PFHxS) but determined there currently is not enough available information to set a HRL for this chemical. However, because PFHxS has a longer half-life in the human body than PFOS and appears to have similar toxic effects, in 2013 MDH began using the PFOS HRL as a surrogate value for PFHxS when evaluating drinking water where multiple PFCs are present. With the issuance of the MDH HBV of 27 ng/L for PFOS, MDH now uses that level as the “surrogate” value for PFHxS when evaluating PFC mixtures.

In Minnesota, PFCs are of particular interest because this is one of the few places in the nation where these chemicals are manufactured. In addition, the disposal of fluorochemical manufacturing wastes several decades ago caused contamination of some of the state’s drinking water supplies, surface waters, and fish. The 3M Company manufactured PFOA and PFOS at its Cottage Grove facility in Washington County (Figure 1) from the late 1940s until 2002, when 3M voluntarily phased out the production of these chemicals. During this time, 3M disposed of PFC manufacturing wastes at four Washington County sites. In addition, 3M released large quantities of PFCs into the Mississippi River in effluent from the company’s wastewater treatment plant. The PFCs present in the wastes disposed of at the four sites in Washington County seeped into the underlying groundwater. An area of approximately 100+ square miles is known to be affected by this contamination (Minnesota Department of Health, 2012), including many private and city wells. A number of lakes and streams in Minnesota also are affected by PFC contamination from both 3M wastes and other sources (Minnesota Pollution Control Agency, 2008). Fish from Pool 2 of the Mississippi River and several lakes and streams, mainly in the Twin Cities Metropolitan Area (TCMA), contain high enough PFC concentrations for the MDH to issue fish consumption advice (Minnesota Department of Health, 2016b; Monson, 2013).

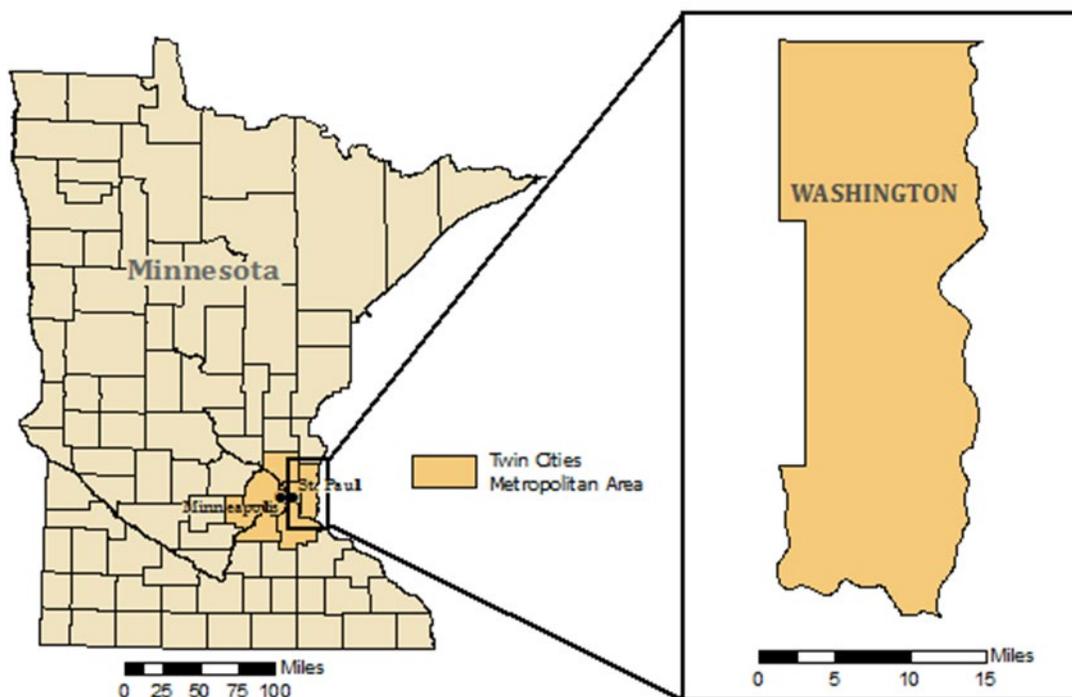


Figure 1. Location of Washington County and the Twin Cities Metropolitan Area, Minnesota.

The Minnesota Pollution Control Agency (MPCA), MDH, and 3M (under a 2007 Consent Order with the MPCA), and the affected municipalities have made efforts to identify all polluted wells and provide clean drinking water to the people affected by the contamination in Washington County. Public water supply systems and some residences served by private wells where contaminant levels exceeded the MDH HRLs were outfitted with additional treatment systems to remove the PFCs, and hundreds of residences served by private drinking water wells were connected to nearby public water supply systems. In response to the issuance of more stringent lifetime health advisory levels and HBVs by EPA and MDH, the MPCA and MDH expanded the scope of well testing and identified additional public and private wells that exceed levels of health concern. The affected people are being supplied with bottled water until treatment systems for their well water are installed. As of early 2012, all required major soil waste excavation work was completed to remove contaminated soil from the former 3M fluorochemical waste disposal sites. Three of the waste sites have groundwater “pump-and-treat” systems installed and operating to prevent PFCs from moving offsite. These systems have been, or are in the process of being, upgraded to increase their effectiveness while avoiding excessive groundwater pumping. At the fourth site (a former landfill where 3M fluorochemical waste was disposed), the PFC waste has been excavated and placed in lined cells that isolate it from the groundwater. Additional long-term work remains to monitor the effectiveness of these cleanup activities.

This report presents an updated assessment of PFCs in Minnesota’s ambient groundwater. The last assessment of PFCs in Minnesota’s ambient groundwater was conducted from 2006-2007 (Minnesota Pollution Control Agency, 2008) and included approximately 30 wells. This assessment was conducted in 2013, and expands the number of sampled wells to almost 200. Most of these wells are part of the MPCA’s Ambient Groundwater Monitoring Network; however, two of the sampled wells monitor closed (no longer operating) landfills located outside of Washington County.

Study area

The state's environmental setting affects the presence and distribution of pollutants in the groundwater. Land use and cover is one important feature of the environmental setting that is associated with pollutants such as PFCs because these chemicals generally are used more frequently in urban settings and are expected to be found at the greatest concentrations in these areas.

Land use and land cover

Most of Minnesota is covered by forests, wetlands, and agricultural lands. The National Land Cover database (Fry et al., 2011) shows that 41% of the state is covered by forests and wetlands, which are concentrated in the north. Agricultural land encompasses 45% of the state. These lands mainly are concentrated in southern and western Minnesota, and corn and soybeans are the primary crops. The primary livestock raised in the state are cattle, hogs, and poultry. Urban land use comprises only about 5% 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 composed of open water, barren land, and grasslands.

Aquifers

Minnesota's groundwater is obtained from aquifers formed from crystalline bedrock, sandstone, carbonate rock, and sand and gravel deposits. Crystalline bedrock aquifers are important sources of groundwater, mainly in northern and southwestern Minnesota. The rocks that form these aquifers are the oldest in the state and are at least 600 million years old, ranging to several billion years old. The sandstone and carbonate rock aquifers are the most productive in the state and are major sources of groundwater in southeastern Minnesota. These rocks form a sequence of aquifers separated by less permeable layers (often clay or shale) referred to as aquitards (Figure 2). The Prairie du Chien-Jordan is a notable aquifer in this sequence because it provides a substantial amount of drinking water to the TCMA. The sand and gravel aquifers are the youngest in the state and important sources of groundwater throughout Minnesota. These aquifers tend to be the primary source of drinking water in western and central Minnesota. Unlike the bedrock aquifers described above, the sand and gravel aquifers are composed of sediments that are not yet cemented together to form rock.

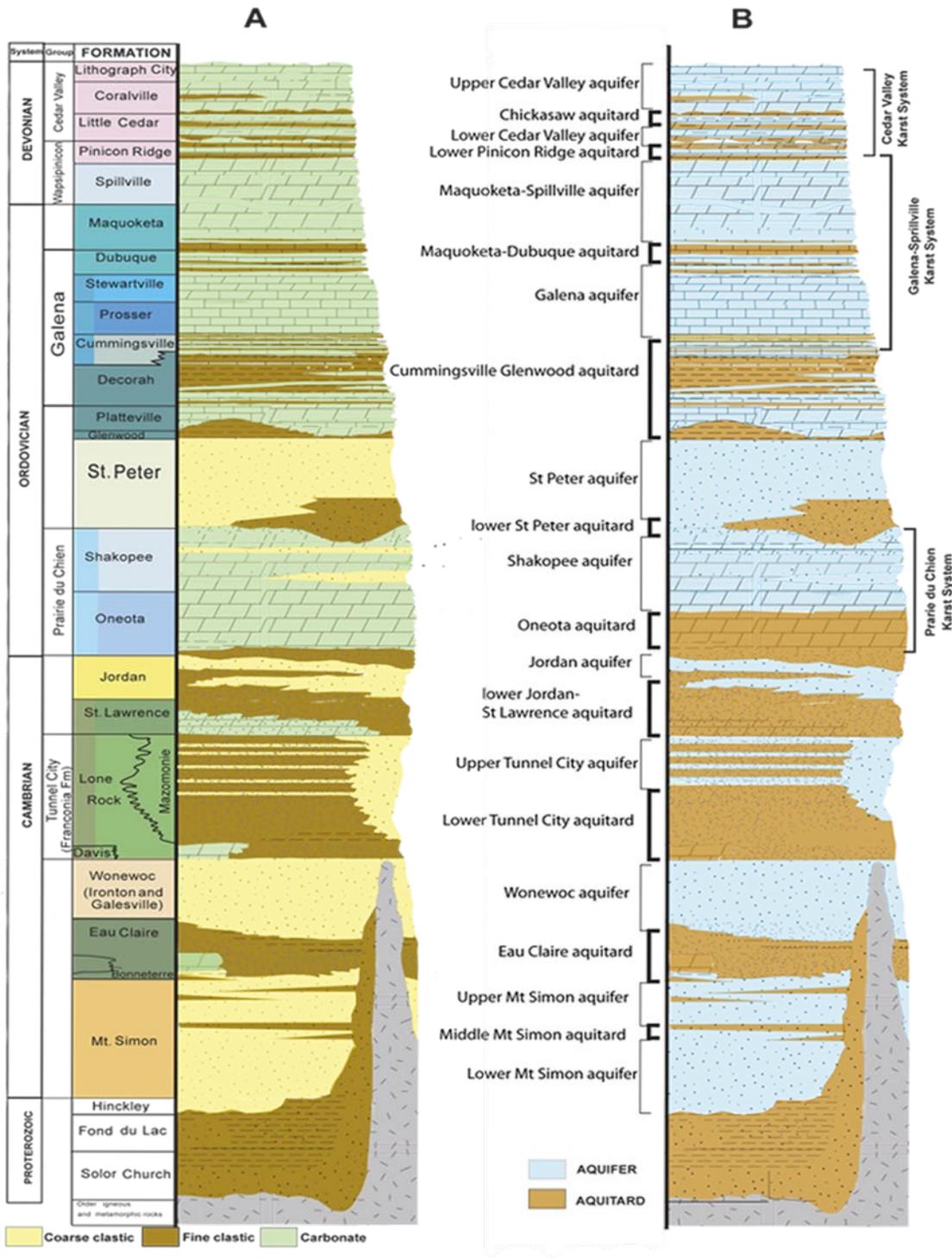


Figure 2. Stratigraphic column of the bedrock aquifers in Southeastern Minnesota [Modified from Runkel, Steenberg, Tipping, and Retzler (2014)].

Methods

Sampling design

This study was designed to measure the extent of PFC pollution present in Minnesota's aquifers. The investigation focused on the ambient groundwater which is not directly impacted by known point sources of PFC pollution such as landfills or wastewater disposal sites.

This report does not provide detailed assessments of the PFC pollution that emanates from the former 3M fluorochemical manufacturing waste disposal sites in Washington County. More detailed information about these contaminant plumes can be found in several reports published on the MPCA and MDH websites (<https://www.pca.state.mn.us/waste/perfluorochemicals-pfcs>, <http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html>).

In addition, this study did not monitor all of Minnesota's groundwater resources. Instead, two aquifers that rapidly recharge were sampled, primarily the sand and gravel aquifers and parts of the Prairie du Chien-Jordan that are vulnerable to human-caused contamination. These aquifers were chosen because of their susceptibility to contamination, making them likely to have a high number of PFC detections and concentrations.

This study primarily used wells from the MPCA's Ambient Groundwater Monitoring Network to monitor for PFCs. The MPCA established this network in 2004 to evaluate the current groundwater quality conditions and get the first look at any changes in water quality. It specifically was designed to monitor the distribution of non-agricultural chemicals, such as solvents and metals, since the MPCA is directed under state law to evaluate these types of chemicals in the groundwater (Minnesota Statutes 2015, chapter 103H, section 103H.251). To meet its objectives, the MPCA's monitoring network primarily assesses the shallow groundwater underlying urban parts of the state, where non-agricultural chemicals are most likely to be used and disposed. The MPCA typically does not assess the state's deep aquifers because many of them are generally naturally protected by aquitards, such as clay or shale that do not allow water to percolate through. As a result, these deep aquifers typically contain "old" water and have little or no human-caused pollution. Two of the wells sampled in this study were not part of the MPCA's monitoring network. These were installed to monitor groundwater that was affected by the leachate from two former landfills in Anoka County.

The MPCA's Ambient Groundwater Monitoring Network consists of two components. A large number of shallow wells in the network serve as an early warning system, and the remainder of the network is installed in deep bedrock and sand and gravel aquifers that are vulnerable to contamination.

The early warning system wells in the MPCA's groundwater network discern the effect of various urban land uses on groundwater quality and provide information on emerging groundwater chemistry trends. When the sampling for this study was conducted, the early warning system component of the network consisted of 126 shallow wells placed near the water table in the sand and gravel aquifers. These wells are distributed among several different settings to determine the effect land use has on groundwater quality. The land use areas include: 1) sewer residential, 2) residential areas that use subsurface sewage treatment systems (SSTS) for wastewater disposal, 3) commercial or industrial, and 4) undeveloped. The data collected in the undeveloped areas, mainly forested areas in northern Minnesota, provide a baseline to compare and assess the extent of pollution in all other land use settings. Most of the wells in the early warning system component of the network contain "young" water that recently fell as precipitation and recharged the groundwater. The results of testing to determine the age of the water extracted from selected wells in the early warning network has found

that it is less than one-year-old in over 80% of the tested wells. The maximum age of the tested water was 2.9 years.

The MPCA also uses deep wells in its network to assess water-quality conditions vertically within the aquifers. Sixty-one bedrock aquifer and deep sand and gravel aquifer wells were sampled for this study. These were fairly evenly split between the two-aquifer types. Most of the sampled bedrock aquifer wells were located in the eastern TCMA. These wells were on average about 180 feet deep and generally were in places where the aquifers are vulnerable to human-caused contamination, such as where the aquifer is near the land surface and only covered by a thin layer of sandy sediments. The deep sand and gravel aquifer wells sampled as part of the network were located throughout the state and were about 60 feet deep, on average. No information on the age of the water in these wells is available.

Due to this network's design, the results of this study should not be extrapolated to all of the state's groundwater. As previously mentioned, this study generally did not sample the aquifers that are naturally protected from human-caused contamination. In addition, not all land use settings in the state were represented as part of this assessment. For example, some aquifers that are located in the agricultural parts of the state also are vulnerable to contamination but were not monitored for this investigation.

Field and laboratory methods

Standard groundwater sampling procedures were used to collect water from each well. Prior to sample collection, each well was purged using a submersible pump outfitted with new polyethylene tubing. While the well was purged of any stagnant water in the casing, field measurements of water temperature, specific conductance, pH, and dissolved oxygen concentration were made. Water samples were drawn from each well for laboratory analysis only after these field measurements had stabilized. The samples for PFC analysis were collected, unfiltered, in 1-liter high-density polyethylene bottles provided by the analytical laboratory (AXYS Analytical Services Ltd., British Columbia, Canada).

AXYS Analytical analyzed all of the water samples for thirteen PFCs, which are listed in Table 2 below, using revision 10 of AXYS Analytical method MLA-060. The samples were prepared by first spiking them with deuterium or ¹³C-isotopically labeled analogs, and the samples were then extracted and cleaned up using solid phase extraction (SPE) and weak anion exchange cartridges. The resulting extracts were analyzed by high performance liquid chromatography/tandem-mass spectrometry. The final sample concentrations were determined by isotope dilution/internal standard quantification against extracted calibration standards in water. By the virtue of this method, all of the measured concentrations were recovery corrected for any possible losses during sample extraction and cleanup. The detection limits varied by the sample and the individual PFC analyzed because the method accounted for any matrix effects and the recovery achieved from sample preparation and analysis process. The range of sample specific detection limits for each analyzed PFC is listed in Table 2.

Table 2. Detection limits associated with the perfluorochemicals and analyzed in this study.

Chemical	Range of detection limits, in ng/L
Perfluorobutanoic acid (PFBA)	0.694 – 105
Perfluoropentanoic acid (PFPeA)	0.694 - 6.66
Perfluorohexanoic acid (PFHxA)	0.694 - 3.48
Perfluoroheptanoic acid (PFHpA)	0.694 - 3.48
Perfluorooctanoic acid (PFOA)	0.694 - 3.48
Perfluorononanoic acid (PFNA)	0.694 - 3.48
Perfluorodecanoic acid (PFDA)	0.694 - 3.48
Perfluoroundecanoic acid (PFUnA)	0.694 - 3.48
Perfluorododecanoic acid (PFDoA)	0.694 - 3.48
Perfluorobutanesulfonate (PFBS)	1.39 - 6.96
Perfluorohexanesulfonate (PFHxS)	1.39 - 6.96
Perfluorooctanesulfonate (PFOS)	1.39 - 6.96
Perfluorooctanesulfonamide (PFOSA)	0.694 - 3.48

The data collected in this study were analyzed using a geographic information system (GIS) and statistical tools. The GIS was used to plot each of the sampled wells and examine the distribution of PFC detections and concentrations across the state. Statistical methods were used to determine the relation between land use and PFC detections and concentrations as well as the proximity to the 3M PFC contamination plume in Washington County and the two sampled old landfills in Anoka County.

For the purposes of assessing the association between land use and PFC detections and concentrations in the ambient groundwater, the analysis only used data from the early warning component of the MPCA's Ambient Groundwater Monitoring Network. This assessment included the data from 115 wells. Wells located within the 100+ square-mile PFC plume in Washington County were not included to avoid biasing the results. The data were fairly evenly distributed among the various sampled urban and undeveloped land use settings. Twenty-five of the wells were located in commercial/industrial areas. Thirty-one of the wells were located in residential areas that use SSTS for wastewater disposal. Twenty-four wells were located in sewer residential areas, and 35 wells were located in undeveloped areas.

Total PFC concentrations were calculated in addition to examining the distribution of each individual measured chemical. The total PFC concentration measures the concentrations of all the PFCs present in the water, regardless of type. This value was calculated by summing all of the detected PFC concentrations in the sample; any concentrations below the laboratory method-reporting limit were assumed to be zero.

Statistical techniques applicable to environmental data and "censored" datasets were used in this study because the PFC data generally were heavily censored (i.e. contained many values reported as less than the detection limit) and had multiple laboratory method detection limits. Environmental water quality data, such as the PFC data interpreted in this report, usually are skewed due to a few high outlying values. These few outliers strongly influence the calculation of summary statistics such as the mean (i.e. average) and standard deviation. For this reason, this report uses median values instead of means to describe the central tendency of the PFC chemical detections and concentrations. Statistics that could account for "censored" values also were needed because of the nature of the PFC dataset. In some instances, the PFC method detection limits were higher than the measured concentrations. A statistical technique appropriate for this type of data set, robust regression on order statistics, was used to estimate median concentrations (Helsel & Cohn, 1988). This statistical method is applicable to any

dataset that contains zero to 80% censored values (Lee & Helsel, 2005). Any results obtained using a dataset with more than 80% censored values are labelled as “tenuous” in this report. The Wilcoxon rank sum test was used to determine whether differences between two groups of data were statistically significant. The Kruskal-Wallis test was used to quantify any differences among three or more groups of data, and the Dunn’s post hoc rank sum test using z statistics as directed by Siegal and Castellan (1988) was used to perform the subsequent multiple comparisons. The Wilcoxon rank sum and Kruskal-Wallis tests require data with just one detection limit. To use these two statistical tests, all PFC data were censored at the highest detection limit prior to analysis. R version 3.0.2 was used for all statistical analysis (R Core Development Team, 2008).

Results and discussion

This investigation found one or more PFCs detected in 69% of the wells sampled across the state (Figure 3). The wells with the greatest number of detections generally were located in urban areas, including the TCMA, Bemidji, Brainerd, Red Wing, Rochester, St. Cloud, and Wabasha. At least one PFC was measured in the water from 94% of the sampled wells in the TCMA and 10 of the 14 wells (over 70%) in the Brainerd area.

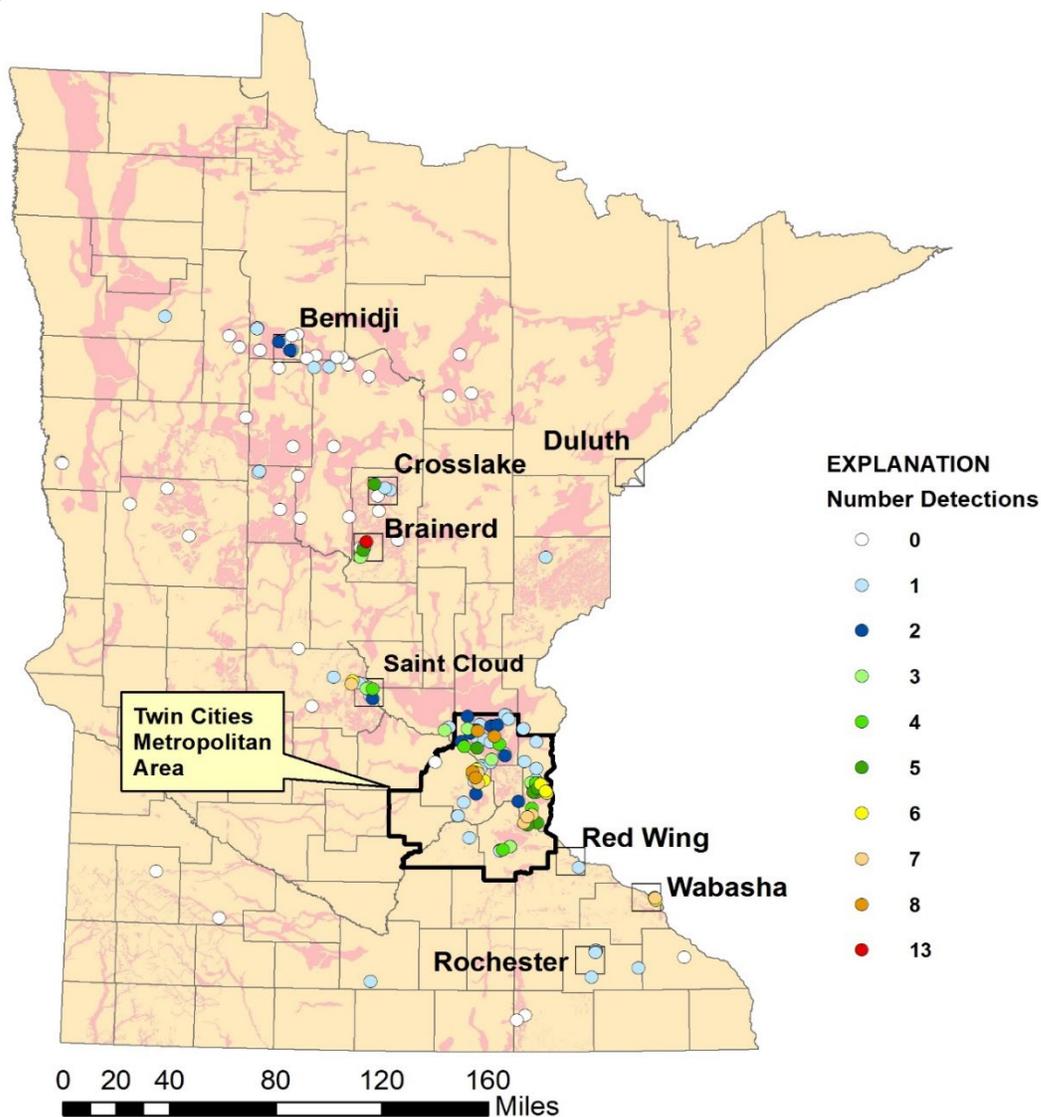


Figure 3. Number of perfluorochemicals detected in Minnesota’s ambient groundwater, 2013.

The wells with the most PFC detections generally were located within areas known to be contaminated with these chemicals. Twenty-six of the wells sampled in this study were located by areas known or very likely to be affected by PFC contamination. Twenty-four of these wells were located within the area affected by the 100+ square mile PFC contamination plume in Washington County, and two of the sampled wells specifically were installed to monitor the groundwater emanating from two old landfills in Anoka County. There were significantly more PFC detections in these wells compared to the others ($p=0.000$). The median number of PFCs detected in the water from the 26 wells located in the vicinity of known 3M PFC industrial waste disposal site contamination or old landfills was 4.5, whereas the median number of PFCs detected in the wells located in areas without any of these contamination sources was 1.

More PFCs also were detected in the ambient groundwater underlying urban areas compared to undeveloped land. The shallow groundwater underlying the commercial/industrial areas had the greatest number of PFC detections, with a median of 2.0. The median number of PFCs detected in the shallow groundwater underlying both types of residential areas (both sewered residential and residential areas using SSTS for wastewater treatment) was one. Very few PFCs were detected in the shallow groundwater underlying undeveloped areas. PFCs were detected in only nine of the 35 sampled wells located in the undeveloped, forested areas. The differences in the PFC detections in the shallow groundwater underlying all of the various land use settings were statistically significant ($p=0.000$). The number of PFC detections was significantly greater in the shallow groundwater underlying all of the urban land use settings compared to those underlying undeveloped land, but there was no significant difference in the PFC detections among the three urban land use settings.

The most-frequently detected PFCs were from a class of chemicals called perfluoroalkyl carboxylates. These PFCs all contain a carboxylate functional group. Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), PFOA, and perfluorohexanoic acid (PFHxA) were the most-frequently detected PFCs from this class; these chemicals were in about 68, 37, 30, and 26% of the sampled wells, respectively. These PFCs also all contained fluorinated chains composed of 4 to 8 carbons. Perfluoroalkyl sulfonates generally were detected less frequently compared to the perfluoroalkyl carbonates. The perfluoroalkyl sulfonates all contain a sulfonate functional group. PFOS, PFHxS, and perfluorobutanesulfonate (PFBS) were the most frequently detected perfluoroalkyl sulfonates. These three chemicals were detected in 12, 11, and 9% of the wells, respectively.

The more frequent detection of the perfluoroalkyl carboxylates may result from these chemicals having greater solubility and mobility in groundwater compared to the perfluoroalkyl sulfonates. Higgins and Luthy (2006) examined the sorption of several PFCs to sediments. Their research found that a PFC's structure, including the length of its perfluorinated chain and the functional group attached to the compounds, strongly influenced its sorption to sediments. PFCs with longer perfluorinated chains sorbed more strongly to sediments compared to those with shorter chains, and PFCs with sulfonate functional groups sorbed two times more strongly to sediments compared to an analogous compound containing a carboxylic acid group. Ahrens et al. (2009) found similar results. These researchers examined the partitioning of PFCs between the sediment and porewater in two sediment cores collected on Tokyo Bay, Japan. They also found that the length of the perfluorinated chain and the functional group attached to the PFC were the primary factors affecting the partitioning of the chemicals into the sediment. The perfluorinated carboxylates that had a perfluorinated chain of seven carbons or less, such as PFBA, PFPeA, or PFHxA, were found exclusively in the pore water. The perfluoroalkyl sulfonates, such as PFOS and PFHxS, comprised a much greater proportion of the total PFC concentration in the sediments compared to the pore water. Other research has shown the sorption of PFCs onto sediments is complex and also is affected by sediment organic matter, ferric oxide mineral content, pH, and calcium ion concentrations (Ferrey et al., 2012; Higgins & Luthy, 2006).

PFCs also were detected in the majority of the sampled water-supply wells, both within and outside of Washington County. Fifty water-supply wells located throughout the state were sampled as part of this study. All but one of these were domestic water supply wells that provided water to individual residences. The one non-domestic well was a public water supply well that provided drinking water to a park. One or more PFCs were detected in 68% of the sampled water-supply wells. PFCs were found in wells of a variety of depths; some were as deep as 285 feet. Thirteen of the tested water-supply wells were within the 100+ square mile PFC contamination plume in Washington County. The remaining 37 wells were in parts of the state that were unaffected by this industrial contamination; these wells primarily were located in urban areas, including the northern and southwestern parts of the TCMA, Rochester, St. Cloud, and Wabasha. Not surprisingly, PFCs were detected in all of the sampled water-supply wells that were located within the 100+ square mile PFC contamination plume; as many as seven different PFCs were detected in these wells. PFCs also were detected in many water-supply wells that were not affected by industrial contamination from the 3M waste disposal sites. One or more PFCs were detected in 21 of the 37 sampled water-supply wells that were in areas with no known industrial contamination sources. Most of these wells contained only one or two different PFCs. A few of these water-supply wells were located in rural areas in northwestern and southern Minnesota. A large number of PFCs were detected in a couple of the water-supply wells that were outside of Washington County. Seven individual PFCs were detected in one water supply well in the vicinity of St. Cloud. Three water-supply wells located near the City of Wabasha had detections of four or more individual PFCs, with one well containing seven different PFCs.

Concentrations

Wells located within the TCMA generally had the highest total PFC concentrations measured in this study. In these wells, the median total PFC concentration was 71 ng/L. The median total PFC concentration in all sampled wells outside of the TCMA was below the detection limits. A median concentration of zero ng/L indicates that PFCs were not detected in over one-half of the sampled wells. Twenty-one of the wells sampled in this study had a total PFC concentration that was greater than 300 ng/L (Figure 4). These were the highest total PFC concentrations sampled in this study. Most of the wells with PFC concentrations above 300 mg/L (18 of the 21) were located in the TCMA.

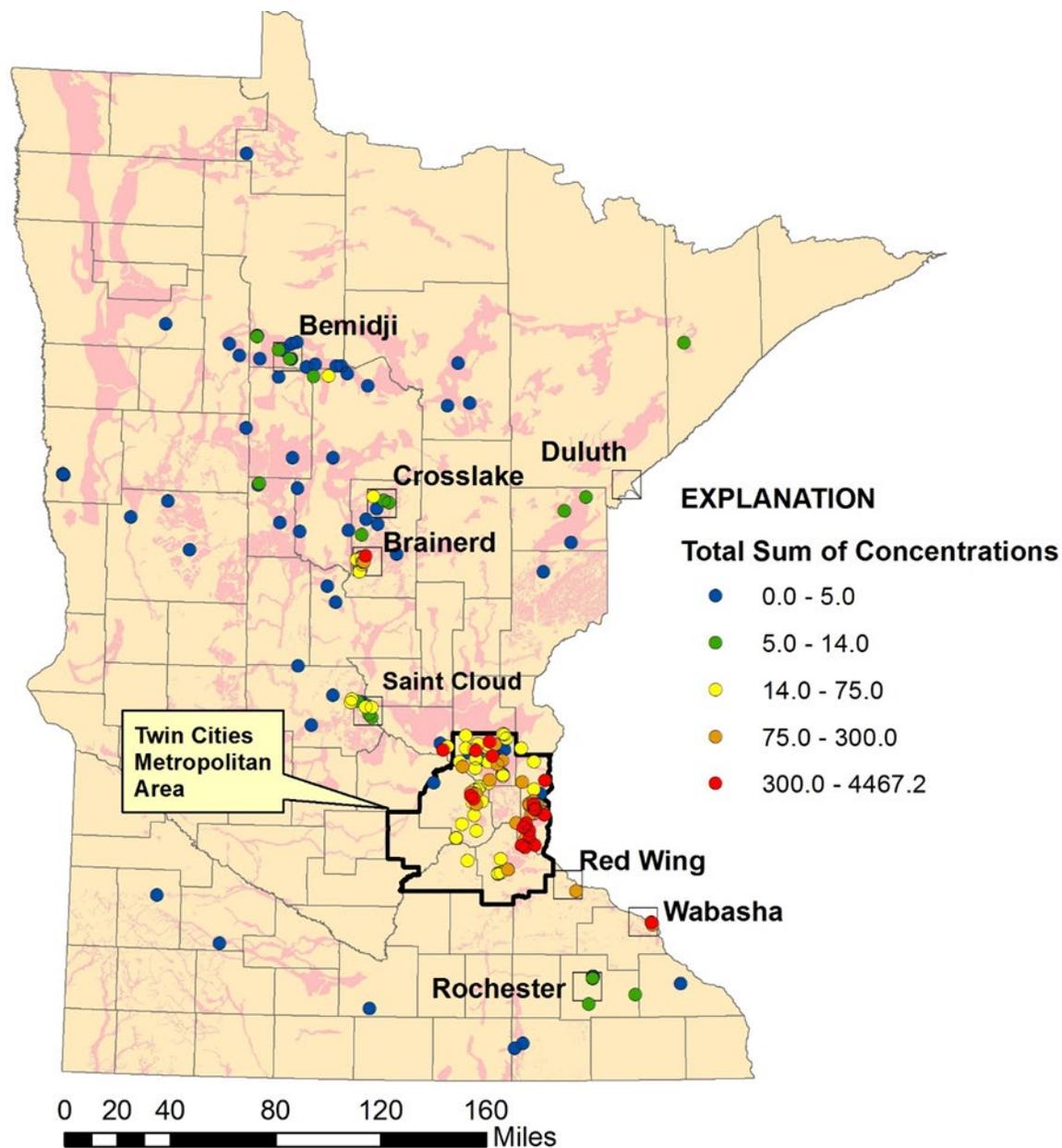


Figure 4. Total sum of perfluorochemical concentrations in the groundwater, 2013.

Similar to the results for the PFC detections, the wells with the highest total PFC concentrations generally were located in Washington County, where there is a 100+ square mile PFC contamination plume due to the past disposal by 3M of fluorochemical-manufacturing wastes. The median total PFC concentration in wells where the groundwater was affected by 3M PFC contamination or two old landfills in Anoka County was 313 ng/L. This was almost 40 times higher than the median concentration measured in the wells that are not known to be affected by these PFC contamination sources (8 ng/L), and these differences were statistically significant ($p=0.000$).

The groundwater underlying urban land had higher PFC concentrations compared to those measured in undeveloped areas. The median total PFC concentrations in the shallow groundwater underlying the various urban land use settings ranged from 21 ng/L in residential areas that use SSTS for wastewater disposal to 31 ng/L in sewered residential areas. In contrast, the median concentration in the

groundwater underlying the undeveloped areas was below the method detection limits. These differences were statistically significant. The concentrations in the shallow groundwater underlying all of the urban settings was significantly greater compared to those measured in undeveloped areas ($p=0.000$), but there was no statistically significant difference among the concentrations measured in the various urban land use settings.

A few wells located outside of the TCMA had high total PFC concentrations. Three wells in Crow Wing, Sherburne, and Wabasha Counties had a total PFC concentration that was greater than 300 ng/L (Figure 4). These all were shallow wells located in urban areas, ranging from 15 to 58 feet deep. Two of the wells were located in residential areas that use SSTS for wastewater disposal, and the remaining well was located in an industrial area where wastewater is sent to a centralized wastewater plant for treatment. Two of the wells were constructed specifically for monitoring; the water from these wells is not consumed. The 58-foot-deep well in Wabasha County, however, supplied drinking water to a residence. While this study did not investigate the exact cause for these high concentrations, it is likely that they come from typical urban sources, such as wastewater or the past use of fire-fighting foams that contained fluorinated surfactants.

The concentrations of each individual PFC were distributed differently in the state's groundwater. The concentrations of some PFCs generally were highest near known industrial sources of these contaminants, such as near the former 3M fluorochemical industrial waste disposal sites or two old landfills in the northern TCMA. In other instances, the highest concentrations of an individual PFC were found in residential areas.

PFBA generally was measured at the highest concentrations of all the PFCs analyzed in this study. The median PFBA concentration in the groundwater was 10.2 ng/L (Table 3). In contrast, the median concentrations of the other most-frequently detected PFCs in the groundwater were over 10 times lower compared to PFBA and ranged from 0.01 to 0.8 ng/L.

Table 3. Summary statistics of the perfluorochemical concentrations measured in groundwater in this study [--=not calculated due to insufficient data; NA = not applicable].

Chemical	Median	Minimum	Maximum	MDH Health Limit	EPA Health Advisory
Perfluorobutanoic acid (PFBA)	10.2 ng/L	<0.9 ng/L	1,680 ng/L	7,000 ng/L ¹	NA
Perfluorobutanesulfonate (PFBS)	0.02 ng/L ²	<1.4 ng/L	555 ng/L	7,000 ng/L ¹	NA
Perfluoropentanoic acid (PFPeA)	0.8 ng/L	<0.8 ng/L	87.4 ng/L	NA	NA
Perfluorohexanoic acid (PFHxA)	0.4 ng/L	<0.7 ng/L	124 ng/L	NA	NA
Perfluorohexanesulfonate (PFHxS)	0.01 ng/L ²	<1.4 ng/L	3,580 ng/L	27 ng/L ⁵	NA
Perfluoroheptanoic acid (PFHpA)	0.2 ng/L ²	<0.7 ng/L	123 ng/L	NA	NA
Perfluorooctanoic acid (PFOA)	0.7 ng/L	<0.7 ng/L	149 ng/L	35 ng/L ⁶	70 ng/L ⁴
Perfluorooctanesulfonate (PFOS)	0.2 ng/L ²	<1.4 ng/L	98.8 ng/L	27 ng/L ⁶	70 ng/L ⁴
Combined PFOA and PFOS	0 ng/L	<1.4 ng/L	162.6 ng/L	NA	70 ng/L ⁴
Perfluorooctanesulfonamide (PFOSA)	--	<0.7 ng/L	40.9 ng/L	NA	NA
Perfluorononanoic acid (PFNA)	--	<0.7 ng/L	41.8 ng/L	NA	NA
Perfluorodecanoic acid (PFDA)	--	<0.7 ng/L	24.2 ng/L	NA	NA
Perfluoroundecanoic acid (PFUnA)	--	<0.7 ng/L	17.1 ng/L	NA	NA
Perfluorododecanoic acid (PFDoA)	--	<0.7 ng/L	17.4 ng/L	NA	NA

1. Set by the MDH in 2011.
2. Median concentration estimate is tenuous due to a large amount of censored data.
3. Set by the MDH in 2009.
4. Set by the EPA in May 2016
5. Interim "surrogate" value used by MDH to evaluate drinking water with PFHxS since May 2017.
6. Set by the MDH in May 2017.

Since PFBA was measured most frequently and generally at the highest concentration, the distribution of PFBA concentrations in the ambient groundwater generally mirrored those shown for the total PFC concentrations. The groundwater underlying both rural and urban parts of the state contained measurable PFBA concentrations, which were as high as 1,680 ng/L (Table 3, Figure 5). The highest PFBA concentrations were generally seen in wells in urban areas, especially those within the 100+ square mile PFC contamination plume in Washington County. The maximum PFBA concentration measured in this study was in an approximately 200 foot deep domestic well in southern Washington County, which tapped the Prairie du Chien-Jordan aquifer. PFBA generally was measured at low concentrations (less than 30 ng/L) in the wells located in rural parts of Minnesota.

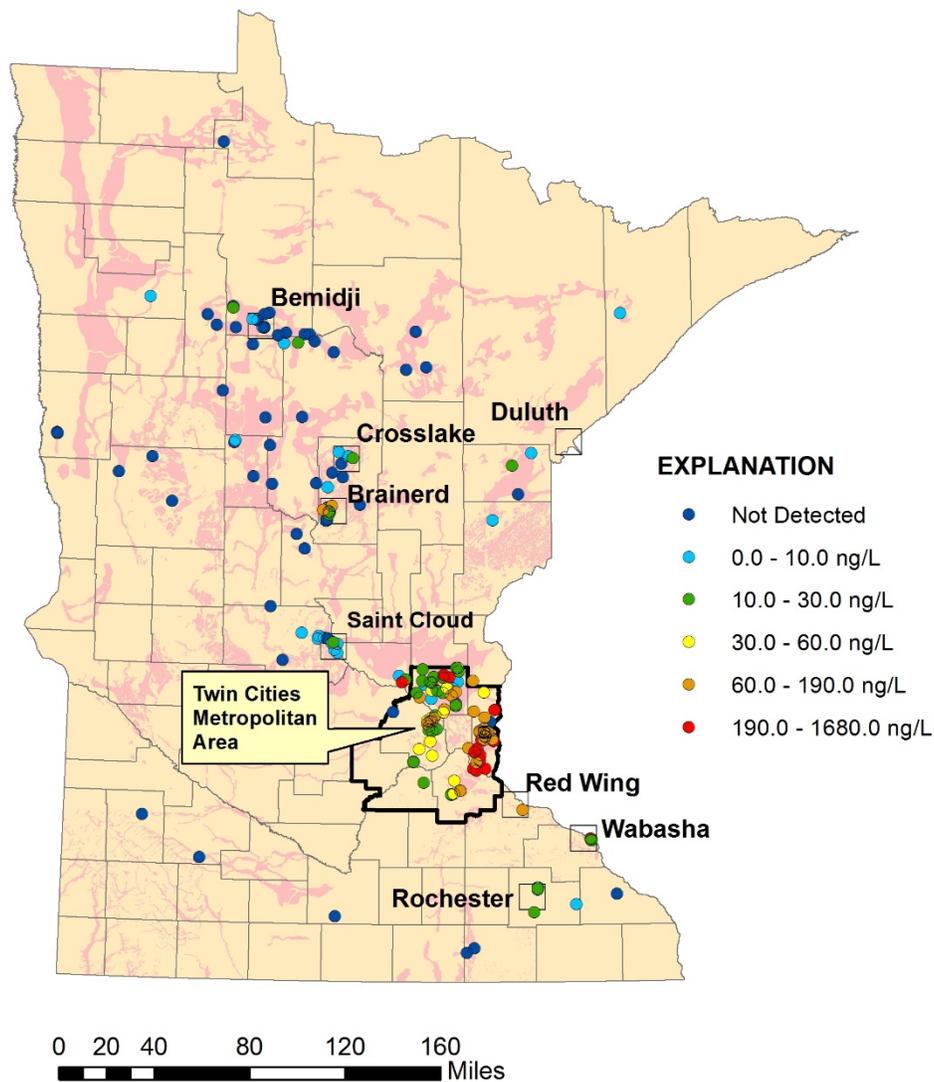


Figure 5. Perfluorobutanoic acid (PFBA) concentrations in the groundwater, 2013.

Similar to the results for PFBA, PFPeA concentrations generally were highest in the sampled wells that were located within the 100+ square mile PFC contamination plume in Washington County. The concentrations measured in this study ranged from below the laboratory method-reporting limit to 87.4 ng/L (Table 3, Figure 6). The highest concentrations generally were in wells in Washington County. In this part of the state, the PFPeA concentrations ranged from below the laboratory-reporting limit to 81.3 ng/L. However, the maximum concentration in the groundwater (87.4 ng/L) was measured in a well near Brainerd. This was a shallow (44 foot deep) monitoring well installed in a sand and gravel aquifers underlying a residential area.

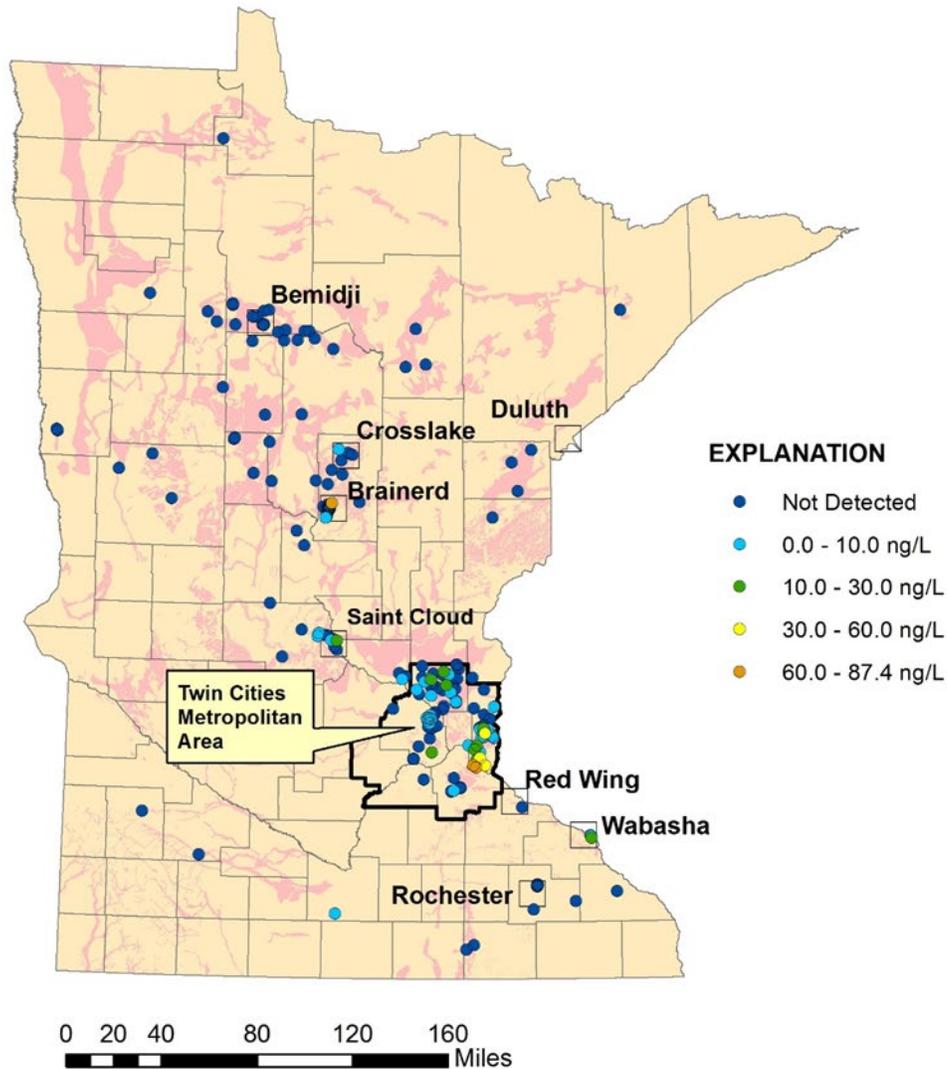


Figure 6. Perfluoropentanoic acid (PFPeA) concentrations in the groundwater, 2013.

The highest PFOA concentrations in the ambient groundwater occurred in wells located in the northern TCMA and the City of Wabasha (Figure 7). All of these wells were installed in the sand and gravel aquifers. The two wells in the northern TCMA had the highest PFOA concentrations measured in this study, ranging from 113 to 149 ng/L. Both of these wells specifically were installed to monitor contamination emanating from old closed landfills. The well with the high PFOA concentrations in Wabasha had a concentration of 74 ng/L. There also was one well in the vicinity of Brainerd and a cluster of wells in the southeastern TCMA that had elevated PFOA concentrations; the PFOA concentrations in these wells ranged from about 38 to 64 ng/L.

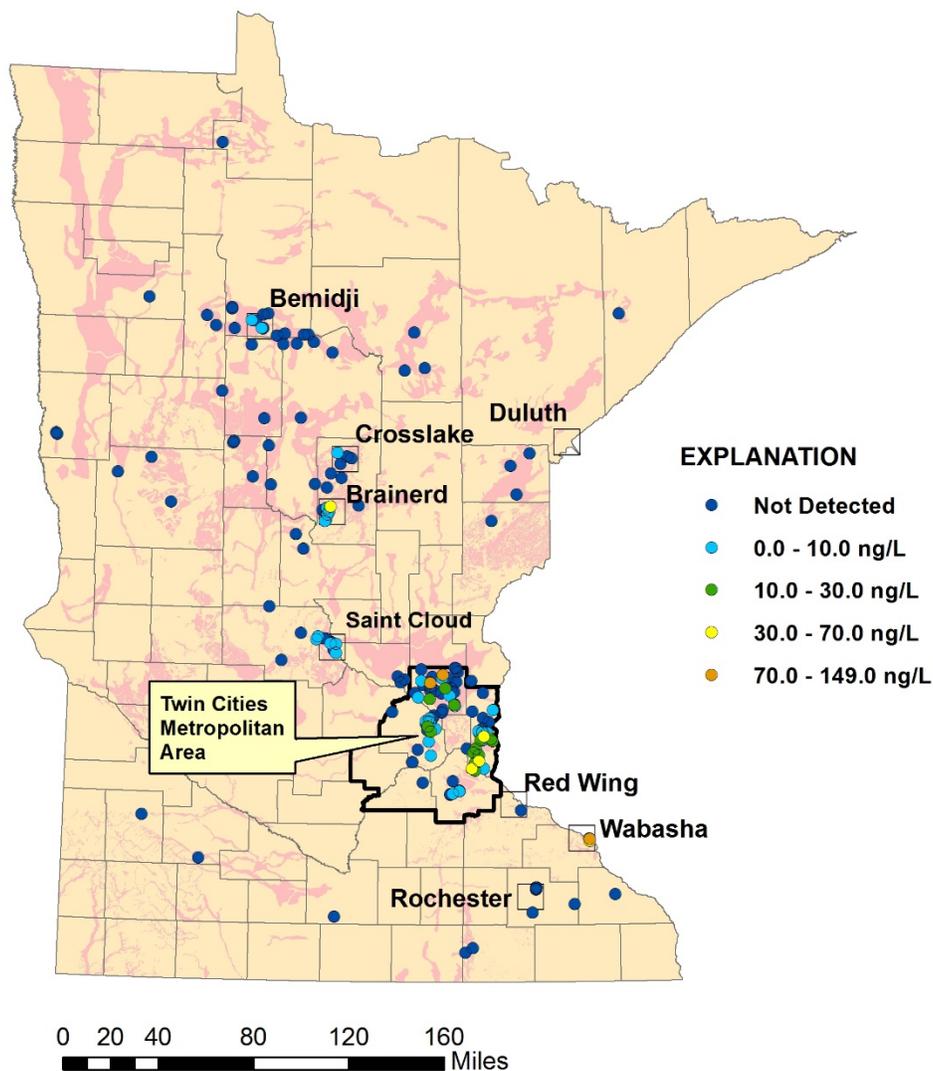


Figure 7. Perfluorooctanoic acid (PFOA) concentrations in the groundwater, 2013.

PFHxA concentrations in the ambient groundwater had a distribution similar to that for PFOA. PFHxA concentrations ranged from below the method reporting limit to 124 ng/L (Table 3, Figure 8), and the highest concentrations were measured in water from three wells located in the northern TCMA and one well in the vicinity of the City of Brainerd. All of these were shallow wells installed in the sand and gravel aquifers and ranged from 15 to 44 feet deep. The wells with the highest PFHxA concentrations were located in residential areas that use SSTS for wastewater disposal, and the concentrations measured in these wells were 110 and 124 ng/L. In the northern TCMA, two of the wells with high PFHxA concentrations were installed to monitor contamination emanating from old closed landfills; the PFHxA concentrations in these two wells were 60 and 68 ng/L. There also was a cluster of wells with elevated PFHxA concentrations in the southeastern TCMA; concentrations as high as 46 ng/L were measured in this area.

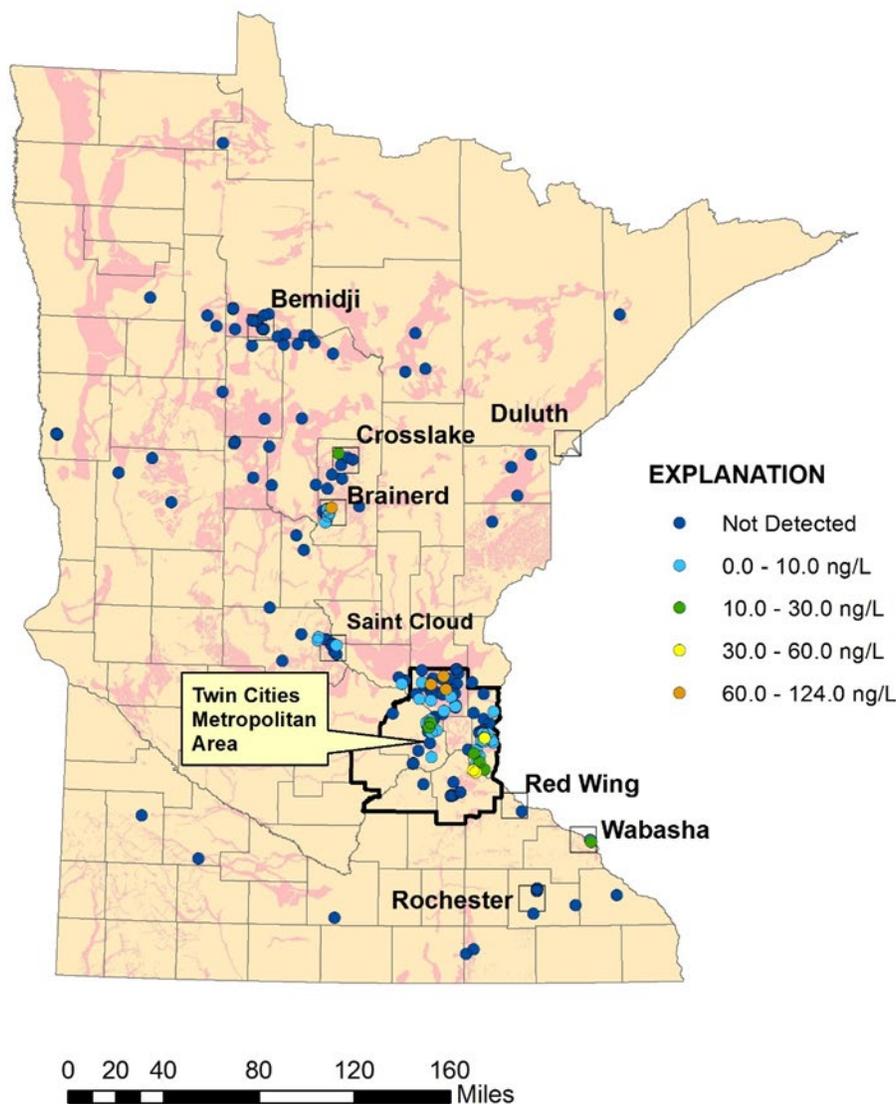


Figure 8. Perfluorohexanoic acid (PFHxA) concentrations in Minnesota’s ambient groundwater, 2013.

The PFOS concentrations measured in this study ranged from below the method-reporting limit to 98.8 ng/L (Table 3, Figure 9). The highest PFOS concentrations measured in this study (98.0-98.8 ng/L) were in two wells in the central and northern TCMA. Elevated concentrations also were found in wells in Brainerd and Washington County. Most of these were shallow monitoring wells, ranging from 15 to 44 feet deep, and located in residential areas. The Washington County wells were installed in the Prairie du Chien-Jordan aquifer.

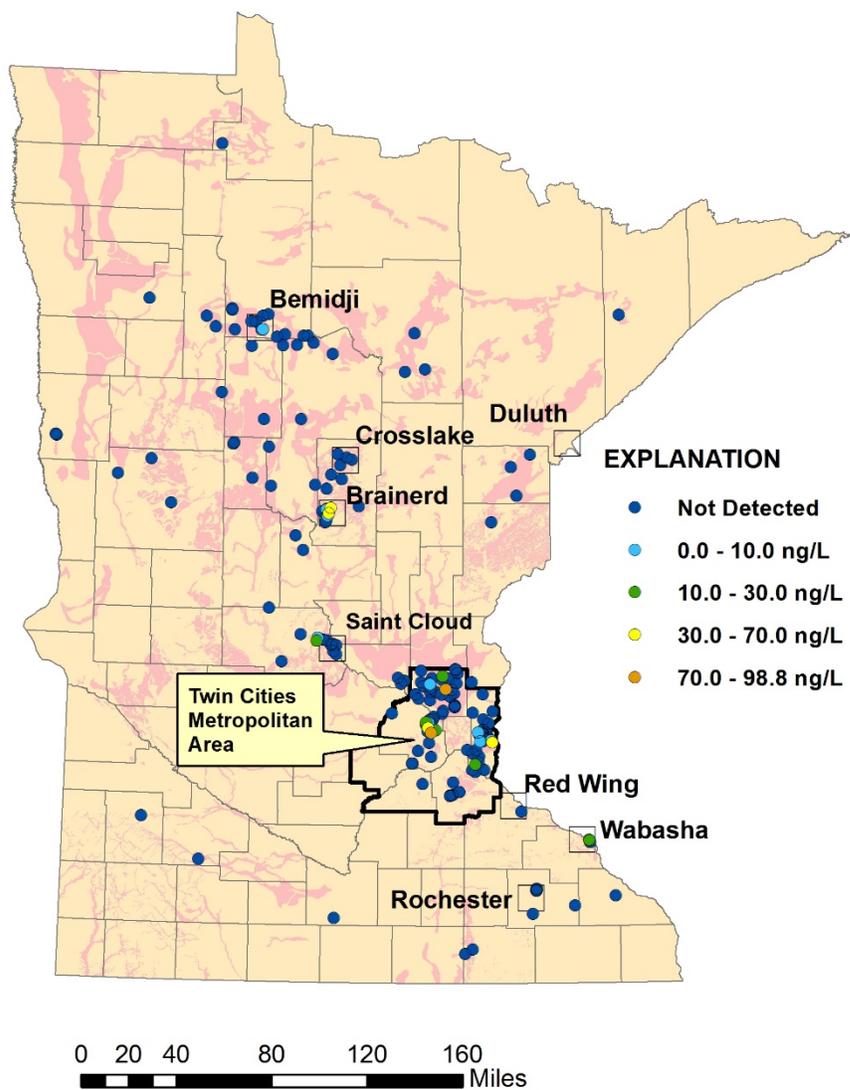


Figure 9. Perfluorooctane sulfonate (PFOS) concentrations in Minnesota’s ambient groundwater, 2013.

Similar to the results for PFOS, the highest PFHxS concentrations in the ambient groundwater also were in the central and northern TCMA (Table 3, Figure 10). These both were shallow wells installed in the sand and gravel aquifers in residential areas, ranging from 15 to 18 feet deep. The well with the maximum PFHxS concentration (3,580 ng/L) was located in the northern TCMA.

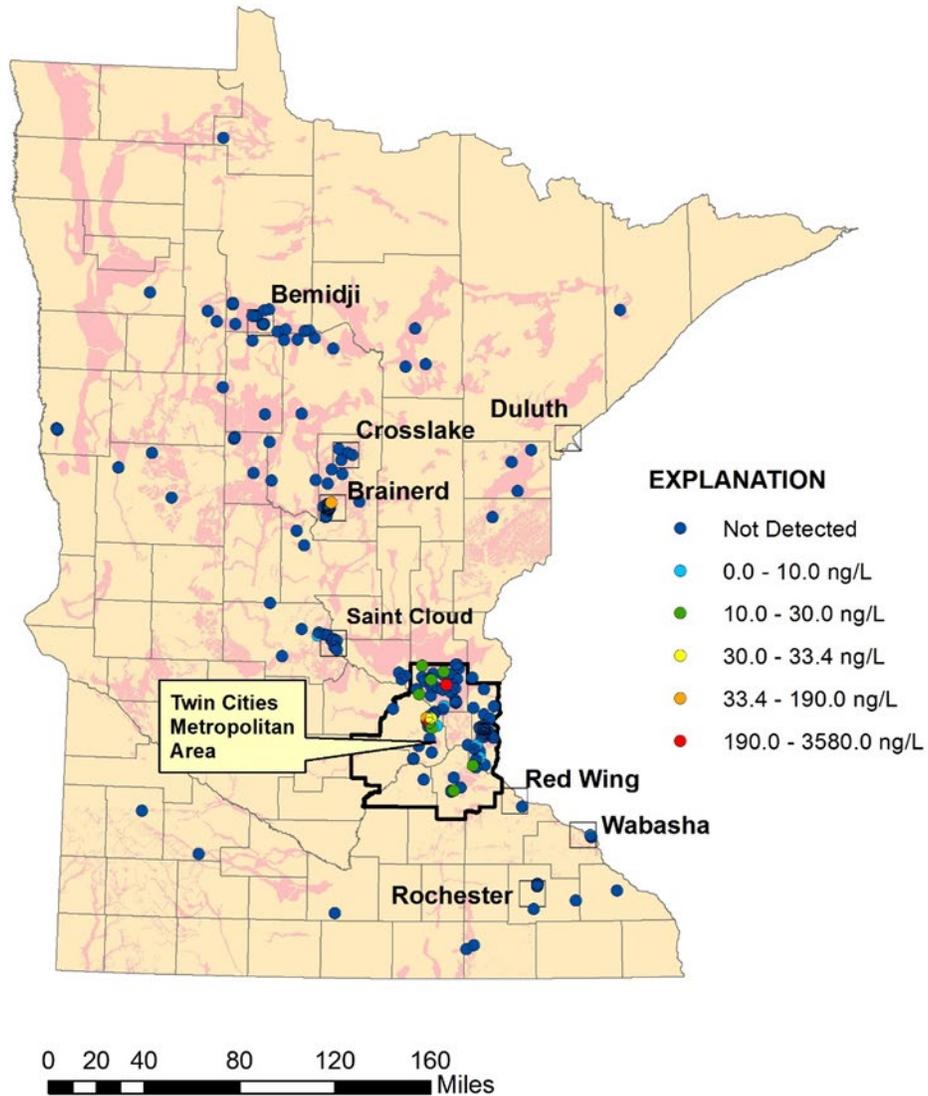


Figure 10. Perfluorohexanesulfonate (PFHxS) concentrations in Minnesota’s ambient groundwater, 2013.

The distribution of PFBS concentrations in the groundwater was similar to the results for PFHxS. PFBS concentrations ranged from below the laboratory method-reporting limit to 555 ng/L. The highest concentrations (88.4-555 ng/L) were measured in two wells in the central and northern TCMA and one well in the vicinity of Brainerd (Table 3, Figure 11). All of these are shallow monitoring wells, ranging from 15 to 44 deep, and are located in residential areas. The maximum PFBS concentration was measured in the well located in the northern TCMA.

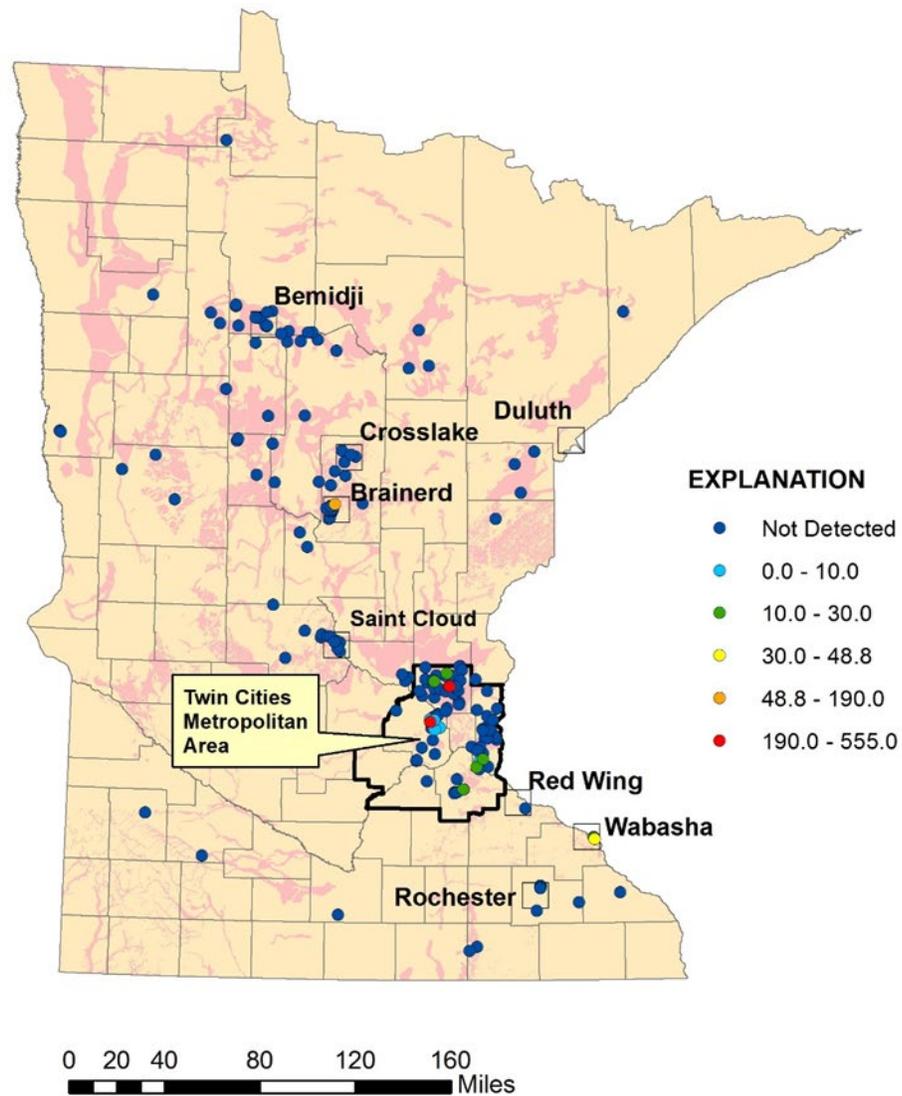


Figure 11. Perfluorobutanesulfonate (PFBS) concentrations in Minnesota’s ambient groundwater, 2013.

The highest perfluoroheptanoic acid (PFHpA) concentrations were measured in a shallow monitoring well located in a residential area in the vicinity of Brainerd (Table 3, Figure 12). This well had a PFHpA concentration of 123 ng/L and was located in a residential area that used SSTS for wastewater disposal. The detected PFHpA concentrations in the other wells sampled in this study were lower than these and ranged from 1.5 to 29.1 ng/L.

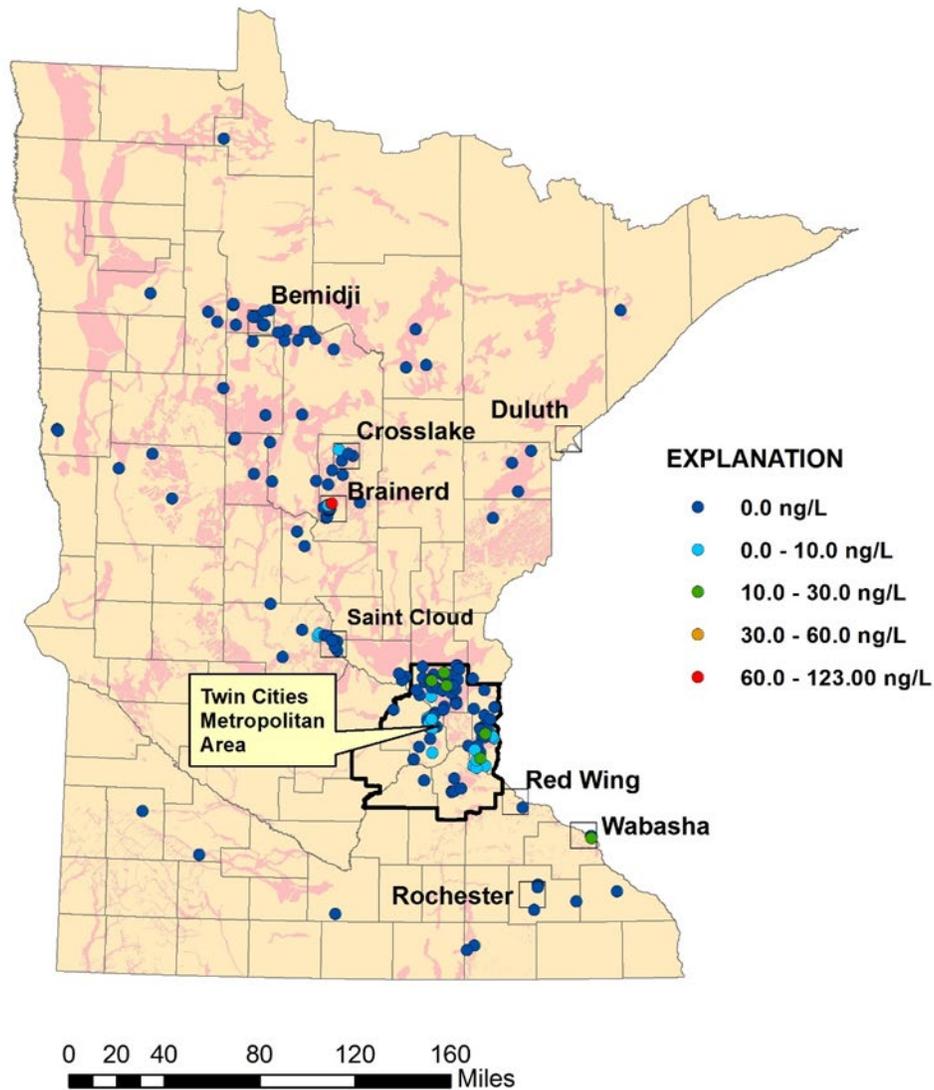


Figure 12. Perfluoroheptanoic acid (PFHpA) concentrations in Minnesota’s ambient groundwater, 2013.

All 13 of the PFCs analyzed in the study were measured in one shallow monitoring well located in a residential area near Brainerd. This was a 44-foot-deep well and contained the only water where perfluorooctanesulfonamide (PFOSA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorododecanoic acid (PFDoA) concentrations were measured. The measured concentrations of these five PFCs ranged from 17.1 to 41.8 ng/L (table 3). This same well also had some of the highest PFC concentrations measured in this study, including the

maximum PFPeA and PFHpA concentrations and some of the highest PFOA, PFHxA, PFOS, PFHxS, and PFBS concentrations.

Overall, PFOA and PFOS concentrations in 3.7% of the sampled wells exceeded the EPA health advisory set in May 2016. Table 3 lists the maximum concentrations of all of the thirteen PFCs measured as part of this study. Seven of the sampled wells had PFC concentrations that exceeded the EPA health advisory. Three of the seven wells had PFOA concentrations that exceeded 70 ng/L, with concentrations ranging from 73.8 to 149 ng/L. The PFOS concentrations in two of the seven wells exceeded 70 ng/L; the concentrations in these wells were 98 and 98.8 ng/L. Finally, the combined PFOA and PFOS concentrations in six of the seven wells exceeded 70 ng/L, ranging from 70.9 to 162.6 ng/L.

The seven wells with concentrations exceeding the EPA's health advisory generally were shallow monitoring wells located in residential areas. None of these wells were affected by the known industrial PFC contamination in Washington County. Five of the wells with concentrations exceeding the health advisory were located in residential areas where municipal wastewater was either disposed through a centralized sewer system or using subsurface sewage treatment systems. The remaining two wells that had concentrations exceeding the health advisory were installed to monitor the leachate emanating from two old landfills. Most of these wells generally were shallow and specifically were constructed for monitoring purposes; the depths of these wells ranged from 15 to 44 feet deep. However, the PFOA concentration in one 58-foot-deep domestic drinking water well did exceed the health advisory.

Eight percent of the sampled wells had PFOA, PFOS, or PFHxS concentrations that exceeded the MDH's updated HBVs or surrogate value. These fifteen wells were located in five different counties: 1) Anoka, 2) Crow Wing, 3) Hennepin, 4) Wabasha, and 5) Washington. Eight of the wells had PFOA concentrations that exceeded the updated MDH HBV, with concentrations ranging from 37.7 to 149 ng/L. Six wells had PFOS concentrations that exceeded the updated MDH HBV, with concentrations ranging from 31.4 to 98.8 ng/L. Six wells also had PFHxS concentrations exceeding the surrogate value of 27 ng/L, with concentrations ranging from 27.8 to 3,580 ng/L. The water in four wells contained concentrations of two or more PFCs that exceeded MDH's updated HBVs or surrogate value. Two wells had both PFOS and PFHxS concentrations that exceeded the updated HBV and surrogate value. One well contained water with concentrations of PFOA and PFHxS that exceeded the MDH's updated HBV or surrogate values, and another well contained water with concentrations of PFOA, PFOS, and PFHxS concentrations that exceeded these values.

Seventy-three percent of the wells with concentrations exceeding the updated MDH HBVs or surrogate value were shallow monitoring wells that do not provide drinking water to people. These wells generally intersected the water table and generally were split between sewered and unsewered residential areas. Four of these wells were located in sewered residential areas in Hennepin and Washington Counties, and another three of the wells were located in residential areas that treat their wastewater using subsurface sewage treatment systems in Anoka and Washington Counties. The remaining wells were located in commercial areas or downgradient of two closed landfills.

Four of the fifty sampled water supply wells (8%) had PFOA or PFOS concentrations that exceeded the updated MDH HBVs. Two of these domestic wells were located within the area affected by known industrial PFC contamination in Washington County. The other two domestic wells with concentrations exceeding the HBVs were located in Wabasha County. Both of these wells were installed in the sand and gravel aquifers, ranging from 58 to 66 feet deep.

Discussion

These results indicate that PFCs generally are not present in Minnesota's ambient groundwater at concentrations that are harmful to human health. Eight percent of the sampled wells (15 out of the 187

wells) had PFOA, PFOS, or PFHxS concentrations that exceeded the updated HBVs or surrogate value set by the MDH for drinking water in May 2017. Most of the wells with elevated PFOA, PFOS, or PFHxS concentrations were shallow wells constructed to monitor the groundwater underlying residential areas or emanating from old landfills. These wells do not supply drinking water. Only 4 out of the 50 sampled water-supply wells contained PFC concentrations that exceeded the MDH's updated HBVs, even when the sampling focused on areas where the groundwater naturally is vulnerable to contamination. PFC concentrations that exceeded the updated MDH HBVs or surrogate values for PFHxS were not completely unexpected in two of the water-supply wells since they were located within the 100+ square mile plume of PFC contamination in Washington County.

As expected, the measured PFC concentrations in the ambient groundwater were much lower than those found in wells directly affected by the former 3M fluorochemical industrial waste disposal sites. The highest concentration of any individual PFC measured in this study was 3,580 ng/L, and the highest measured PFOA and PFOS concentrations were 149 and 98.8 ng/L, respectively. These concentrations are much lower compared to those reported in the groundwater at 3M's Cottage Grove manufacturing facility or the 3M fluorochemical industrial waste disposal sites (Minnesota Pollution Control Agency, 2008). For example, in one well at the 3M manufacturing facility, PFOS concentrations were reported as high as 346,000 ng/L and PFOA concentrations were reported as high as 846,000 ng/L (U.S. Department of Health and Human Services, 2005). These concentrations are over 2,000 times greater than the concentrations measured in this study. Similarly high PFOA and PFOS concentrations also are in the groundwater immediately adjacent to the PFC industrial waste disposal sites. At the former waste disposal sites in Lake Elmo and Oakdale, PFOS concentrations in the groundwater ranged from 2,690 to 30,100 ng/L, and the PFOA concentrations ranged from 42,000 to 66,100 ng/L (U.S. Department of Health and Human Services, 2008). These concentrations are about 30 to 700 times higher than those detected by this investigation of the state's ambient groundwater.

This study also found that the concentrations of many of the PFCs were significantly higher in wells that were located within the 100+ square mile plume of PFC contamination in Washington County or immediately downgradient of two old landfills in Anoka County compared to those in other parts of the state (Table 4). The estimated median PFC concentrations ranged from 0.7 to 227 ng/L in the vicinity of the 100+ square mile PFC contamination plume in Washington County or downgradient of the two old landfills; the estimated median PFC concentrations in all other monitored parts of the state were at least an order of magnitude lower and ranged from 0.002 to 6.9 ng/L. PFBA showed the greatest variation in concentrations. The median PFBA concentration in wells that were located near former 3M fluorochemical industrial waste disposal sites in Washington County or old landfills in Anoka County was 227 ng/L, but the estimated median concentrations were more than 30 times lower, 6.9 ng/L, in other parts of the state.

Table 4. Estimated median concentrations of the most commonly detected perfluorochemicals in Minnesota's groundwater areas with known or suspected contamination compared to levels in the ambient groundwater in the other monitored parts of the state.

Chemical	Median concentrations		p-value
	Areas with known or suspected contamination	Ambient groundwater in all other parts of Minnesota	
Perfluorobutanoic acid (PFBA)	227 ng/L	6.9 ng/L	0
Perfluoropentanoic acid (PFPeA)	6.8 ng/L	0.8 ng/L*	0
Perfluorohexanoic acid (PFHxA)	5.5 ng/L	0.2 ng/L*	0
Perfluoroheptanoic acid (PFHpA)	0.7 ng/L	0.1 ng/L*	0.008
Perfluorooctanoic acid (PFOA)	7.9 ng/L	0.4 ng/L	0
Perfluorooctane sulfonate (PFOS)	1.7 ng/L	0.1 ng/L*	0.019
Perfluorobutane sulfonate (PFBS)	1.8 ng/L*	0.002 ng/L*	0.057
Perfluorohexanesulfonate (PFHxS)	0.8 ng/L	0.002 ng/L*	0.082

*Median concentration estimate is tenuous due to greater than 80% censored data.

Similar results were found in other published studies that investigated sites affected by discharges or waste disposal from fluorochemical manufacturing facilities. An investigation of PFCs in the Tennessee River (Hansen, Johnson, Eldridge, Butenhoff, & Dick, 2002) showed that PFOS concentrations in the river tripled to 114 ng/L at a sampling site that was downstream of a fluorochemical-manufacturing facility. The PFOA concentration in the Tennessee River showed a similar increase. In West Virginia, PFOA was released to the air and the Ohio River from a fluorochemical manufacturing facility from the 1950s until the early 2000s (C8 Science Panel, 2015; Shinn et al., 2011). Within one mile of the fluorochemical manufacturing facility in West Virginia, the maximum PFOA concentration in drinking water wells was 2,800 ng/L, and concentrations as high as 14,300 ng/L were measured in monitoring wells (C-8 Groundwater Investigation Steering Team, 2003). PFC concentrations as high as 4,385 ng/L were found in surface and drinking waters in northwestern Germany (Skutlarek, Exner, & Farber, 2006); the main source of these high concentrations was PFC-containing industrial waste that was applied as a soil improver on the farmland. In England, PFOS concentrations as high as 5,910 ng/L were measured in the groundwater underlying an oil depot explosion site; these high concentrations resulted from using PFOS-containing fire-fighting foam to extinguish the fire (Rumsby et al., 2010).

This study found that the PFC expected to be the most soluble and mobile in the groundwater, PFBA, generally was measured at the highest concentrations of all the PFCs analyzed in this study. PFBA has several sources in the environment. It is formed by the degradation of some fluorochemicals (Liu et al., 2010; Zhao et al., 2013). This chemical also was formerly used to manufacture photographic film (3M Company, 2008) and is an impurity formed during PFC manufacturing. The short four-carbon chain on this PFC combined with the carboxylate functional group allows this chemical to move more readily in the groundwater compared to the other PFCs that were analyzed. The median PFBA concentration measured in this study was 10.2 ng/L. In contrast, the median concentrations of all the other analyzed PFCs were less than 1 ng/L. Similarly, the maximum PFBA concentration measured in this study was 1,680 ng/L, which is about three times greater than the maximum concentrations of all the other analyzed PFCs except PFHxS. The highest PFBA concentrations generally were measured in wells in urban areas, especially within the 100+ square mile PFC contamination plume in Washington County.

Shallow monitoring wells located in residential areas without any known contamination attributed to the 3M fluorochemical industrial waste disposal or old landfills contained the highest concentrations of

many of the PFCs analyzed in this study of Minnesota's ambient groundwater. The highest concentrations of PFHxA (110 and 124 ng/L) were measured in monitoring wells in residential areas that use SSTS for wastewater disposal. In contrast, in this study this chemical generally was measured at moderate concentrations (about 14-68 ng/L) in the groundwater affected by old landfills or the groundwater in the 100+ square mile PFC contamination plume in Washington County. Elevated PFHpA concentrations were measured in wells located in several areas outside of Washington County: Brainerd, Wabasha, and the northern TCMA. Similar to the results for PFHxA, the maximum PFHpA concentration measured in this study (123 ng/L) was from a monitoring well located in a residential area that uses SSTS for wastewater disposal in the vicinity of Brainerd. Similarly, the highest PFOS concentrations in this study generally were measured in monitoring wells located in residential areas in the northern and central TCMA. The highest PFBS and PFHxS concentrations were measured in a monitoring well in a residential area in the northern TCMA. The chemicals PFOSA, PFNA, PFDA, PFUnA, and PFDoA only were measured once, in a monitoring well in a residential area in the vicinity of Brainerd.

The specific cause for the high perfluorochemical concentrations in these wells was not identified as part of this investigation; however, several possible sources could have contributed these chemicals to the groundwater. These sources may include municipal and industrial wastes, wastewater biosolids, fire-fighting foams that contain fluorinated surfactants, and atmospheric deposition.

Wastewater is a well-documented source of PFC contamination that may have contributed to the presence of PFCs in some of the wells. These wastes usually contain PFCs because fluorochemicals are incorporated in a wide variety of products, including water repellent coatings on apparel and carpets, cleaners, shampoos, and polishes. Any PFCs or any fluorochemicals that break down to form PFCs present in these items may be released into wastewater through their use and disposal. Numerous studies in Minnesota and across the nation have found PFCs in wastewater treatment plant effluent. The MPCA sampled the effluent from over 50 wastewater treatment plants across the state for the same 13 PFCs analyzed in this study in 2007 and 2008 (Minnesota Pollution Control Agency, 2008). All 13 PFCs were detected in at least 1 of the samples collected in the study. The most commonly detected PFCs in the wastewater effluent (listed in order from highest to lowest detection frequency) were the perfluorinated carboxylates that contain eight carbon atoms or fewer: PFOA, PFHxA, PFBA, PFHpA, and PFPeA. Perfluorinated sulfonates that contain eight or fewer carbons (PFOS, PFBS, and PFHxS) were detected in about 40 to 50% of the samples collected in the wastewater study. Other researchers also found PFCs in wastewater effluent. PFOA and PFOS were found in the effluents from six wastewater treatment plants in various places in the U.S. (Schultz et al., 2006). Sinclair and Kannan (2007) measured up to eight different PFCs and fluorotelomer alcohol degradates, including PFOA and PFOS, in the effluent from six wastewater treatment plants in New York. Boulanger et al. (2005) found PFOA, PFOS, and a degradation product of N-EtFOSE in the effluent from a wastewater treatment facility in Iowa that has no known fluorochemical manufacturing and production.

The solid waste generated by both industrial and municipal wastewater treatment may also contribute PFCs to the groundwater. Several investigators have detected PFCs in wastewater biosolids (Higgins, Field, Criddle, & R.G., 2005; Lindstrom et al., 2011; Loganathan, Sajwan, Sinclair, Kumar, & Kannan, 2007; Minnesota Pollution Control Agency, 2008; Schultz et al., 2006; Sinclair & Kannan, 2007), and several studies have documented that the PFCs present in these biosolids can be transported to both surface and groundwater. Skutlarek et al. (2006) attributed the high PFC concentrations in rivers in northwestern Germany to the application of fluorochemical-containing biosolids. Lindstrom et al. (2011) found that the PFC concentrations were above the limits set to protect human health in the groundwater underlying areas that received applications of biosolids produced from the treatment of wastewater containing fluorochemical manufacturing wastes.

None of the wells sampled as part of this study were located near a wastewater treatment facility or an area that was known to receive biosolids applications. However, the presence of contaminants of emerging concern (CECs) in about 35% of the MPCA's network wells (Erickson, Langer, Roth, & Kroening, 2014) suggests that some of the groundwater sampled in this study may have been affected by wastewater. While Erickson et al did not explicitly determine how the wastewater reached the study wells in her study; possible sources include SSTS, leaking sewer lines, or unknown old landfills. It is possible that these same sources of CECs could have contributed the PFCs that were measured in the groundwater in this investigation.

Class B fire-fighting foams are another source of PFCs that could have affected the groundwater sampled in this study. These foams were developed in the 1960s to extinguish liquid fuel fires, such as gasoline or kerosene fires. The PFC-bearing Class B foams are proprietary mixtures that include a fluorocarbon surfactant, hydrocarbon-based surfactant, and a solvent. The fluorocarbon surfactant is the primary fire-extinguishing chemical in the foam and also serves as a vapor sealant that prevents the re-ignition of the fire (Moody & Field, 2000). As part of emergency preparedness plans, Class B foams were used in firefighting training exercises. The wastewater generated as part of these exercises was typically disposed into a wastewater treatment facility, into a nearby surface water via storm sewers, or directly onto the land adjacent to the training facility. These disposal practices have resulted in the groundwater and surface water contamination from fluorinated surfactants, fuels, and solvents at several military bases across the United States (Moody & Field, 2000).

Similar PFC contamination from fire-fighting foams also has occurred in Minnesota. The MPCA and MDH investigated areas where PFC-bearing Class B foams were used from 2008 to 2011. The MPCA evaluated PFCs in the groundwater, surface water, and soil at about 20 fire-fighting training sites where Class B foams were deployed to fight large fires (Delta Consultants, 2010). PFCs were detected in most of the collected groundwater and surface water samples. The most-frequently detected PFCs in the water samples were PFOA, PFBA, PFHxA, and PFPeA. PFOA and PFOS concentrations in the groundwater exceeded the HRLs set by the MDH in 2009 for drinking water in monitoring wells at about 35% of the assessed sites. The MDH sampled water-supply wells near identified firefighting training sites in 2009 (Minnesota Department of Health, 2016a). These included municipal wells in 17 communities and 16 water-supply wells that provide water to places such as businesses, schools, and churches. Low concentrations of PFCs were detected in seven of the municipal water-supply wells, and none were detected in the other sampled wells. It was beyond the scope of this study to perform a detailed assessment to determine whether Class B foams historically were used in the vicinity of each of the 187 wells that were sampled as part of this study; however, these foams are a potential source of some of the measured PFC groundwater contamination.

Atmospheric deposition is another source that also may have contributed to the PFC detections in this study of Minnesota's ambient groundwater. Some PFC-containing chemicals, such as mist suppressants used in chrome plating, have been vented to the atmosphere. Several researchers (Ellis et al., 2004; Giesy & Kannan, 2002) have hypothesized that atmospheric transport and deposition is the reason for the presence of PFCs, such as PFOA and PFOS, in the blood of animals in very remote regions throughout the world like the Arctic that lack any urban or industrial sources of these chemicals. PFOA and PFOS are not directly transported through the atmosphere since these chemicals exist in an ionic form and are not volatile. However, most scientists believe that volatile fluorinated chemicals, often called PFC precursors, such as fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamide ethanols, and perfluorooctane sulfonamides (FOSAs), undergo atmospheric transport (Ahrens et al., 2011; D'Eon, Hurley, Wallington, & Mabury, 2006; Shoeib, Harner, & Vlahos, 2006) and are ultimately degraded to PFCs such as PFOA and PFOS. Many researchers have documented the presence of PFC precursor chemicals in the air (Jahnke, Ahrens, Ebinghaus, & Temme, 2007; Martin et al., 2002; Shoeib et al., 2006;

Stock, Lau, Ellis, Muir, & Mabury, 2004), and research into the fate of these chemicals in the air found that both the FTOHs (Ellis et al., 2004) and FOSAs (Martin, Ellis, Mabury, Hurley, & Wallington, 2006) degrade to form perfluoroalkyl carboxylates in the air.

The PFCs detected in this investigation of ambient Minnesota's groundwater will remain in the environment for a long time. These compounds are extremely stable and do not break down in either soil or water (Ferrey et al., 2012; Rumsby et al., 2010; U.S. Environmental Protection Agency, 2016a, 2016b). As a result, any PFCs transported to the groundwater will remain there until they are naturally transported to streams and lakes by groundwater inflow or pumped up to the land surface. These chemicals also pose a problem if they are transported to streams and lakes because some PFCs such as PFOS bioaccumulate in fish.

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