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Agency Name: Minnesota Pollution Control Agency

Title: Minnesota Pollution Control Agency's Statewide Water Quality Data in the National Groundwater Monitoring Network

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Overview of Work

The Minnesota Pollution Control Agency (MPCA) is a state agency that monitors environmental quality, offers technical and financial assistance, and enforces environmental regulations. The MPCA routinely monitors the state's groundwater to determine the kinds of pollution present, identify any emerging pollution trends, and evaluate whether any types of pollution controls are necessary. As part of its routine ambient groundwater monitoring activities, the MPCA currently samples a network about 270 wells across the state in three principal aquifers of national interest: 1) sand and gravel aquifers of glacial origin, 2) the Cambrian-Ordovician Aquifer System, and 3) the Upper Carbonate Aquifer. The majority of the agency's network wells are installed in the sand and gravel aquifers of glacial origin, and all of them are scheduled for annual sampling and tested for over 100 constituents in both the field and laboratory.

For this project, the MPCA maintained and updated its information in the National Groundwater Monitoirng Network (NGWMN) and prepared required reports documenting its standard operating procedures. The MPCA originally provided groundwater quality information from the Cambrian-Ordovician Aquifer system to the NGWMN in 2010 as part of a pilot project conducted cooperatively with the Minnesota Department of Natural Resources. The connection between the agency's data and the NGWMN data portal were severed a few years later because the MPCA switched data management systems and also changed its procedure for providing its ambient groundwater quality data to the U.S. Environmental Protection Agency (USEPA)'s Water Quality Exchange (WQX) which was used to provide data to the NGWMN.

This project reestablished the connection between the NGWMN Data Portal and the MPCA's water-quality data stored in WQX and also provided information from MPCA ambient network wells that were installed in two other principal aquifers of national interest: 1) Upper Carbonate Aquifer and 2) surficial sand and gravel aquifers of glacial origin. Finally, the NGWMN requires documentation of each participant's standard operating procedures for groundwater quality sampling, site selection for the network, and data management procedures. These documents also were produced as part of this project.

Description of the MPCA's Existing Water-Quality Network

The MPCA's Ambient Groundwater Monitoring Network (Figure 1) was put in place in 2004 to evaluate groundwater quality conditions in Minnesota and provide information on any changes in water quality. This monitoring is required by the state's Groundwater Protection Act which charges the MPCA to evaluate the presence and distribution of non-agricultural chemicals in the groundwater, such as solvents and metals. To meet its monitoring objectives, the MPCA's Ambient Groundwater Monitoring Network primarily samples shallow wells that underlie the urban parts of the state, where non-agricultural chemicals most likely are used and disposed. The wells sampled by the network typically are installed in the sand and gravel aquifer of glacial origin, the Upper Carbonate Aquifer, and Cambrian-Ordovician Aquifer systems (Table 1). The network wells are not evenly distributed throughout these aquifers but are concentrated in the parts of them that are

vulnerable to contamination. Aquifers that are not expected to contain human-caused pollution, such as the state's deep aquifers, typically are not sampled by this monitoring network.

There are two components to the MPCA's Ambient Groundwater Monitoring Network. Most of network wells intersect the water table of the surficial sand and gravel aquifers and serve as an early warning system. The remainder of the network primarily monitors the Cambrian-Ordovician Aquifer system and deep parts of the sand and gravel aquifers, although it does contain a couple of wells that are installed in the Upper Carbonate Aquifer. Most of the sampled Cambrian-Ordovician aquifer system wells are installed in the Prairie du Chien-Jordan aquifer because of its considerable use for public and domestic water supplies.

The early warning system wells in the MPCA's groundwater network are used to discern the effect of various urban land uses on groundwater quality and provide information on emerging trends. These wells are distributed among four different land use settings: 1) sewered 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, which mainly are forested areas in the Northern Minnesota, provides a baseline to assess the extent of any pollution from all other land use settings. Most of the wells in the early warning system component of the network contain young water that was recently recharged into the groundwater. The results of testing to determine the age of the water extracted from the wells in the early warning network has found that it is less than one year old in over 80% of the tested wells.

The early warning system component of the MPCA's network initially was developed in 2004. To save costs, existing shallow monitoring wells were used. Most of these were constructed as part of the MPCA's ambient groundwater monitoring activities during the 1990s, US Geological Survey (USGS) projects, or the USGS's National Water-Quality Assessment. However, the existing wells were not located in all of the settings of interest to the MPCA, and monitoring wells needed to be installed to fill this gap. This occurred primarily from 2010-2016 and approximately 150 monitoring wells were installed for this network during this period.

The remainder of the wells in the MPCA's network are used to assess water-quality conditions at depth in places that are vulnerable to contamination. Most of the Cambrian-Ordovician Aquifer System wells are located in the eastern Twin Cities Metropolitan Area (TCMA). The deep sand and gravel aquifer wells sampled by the network are located throughout the state.

Table 1. Number of wells monitored by the MPCA's Groundwater Monitoring Network by U.S. Geological Survey Principal Aquifer

Principal Aquifer	Number of Sites Monitored
Surficial Aquifer System	198
Cambrian-Ordovician Aquifer System	38
Upper Carbonate Aquifer	5
Cretaceous Aquifer	0
Crystalline-Rock Aquifer	0

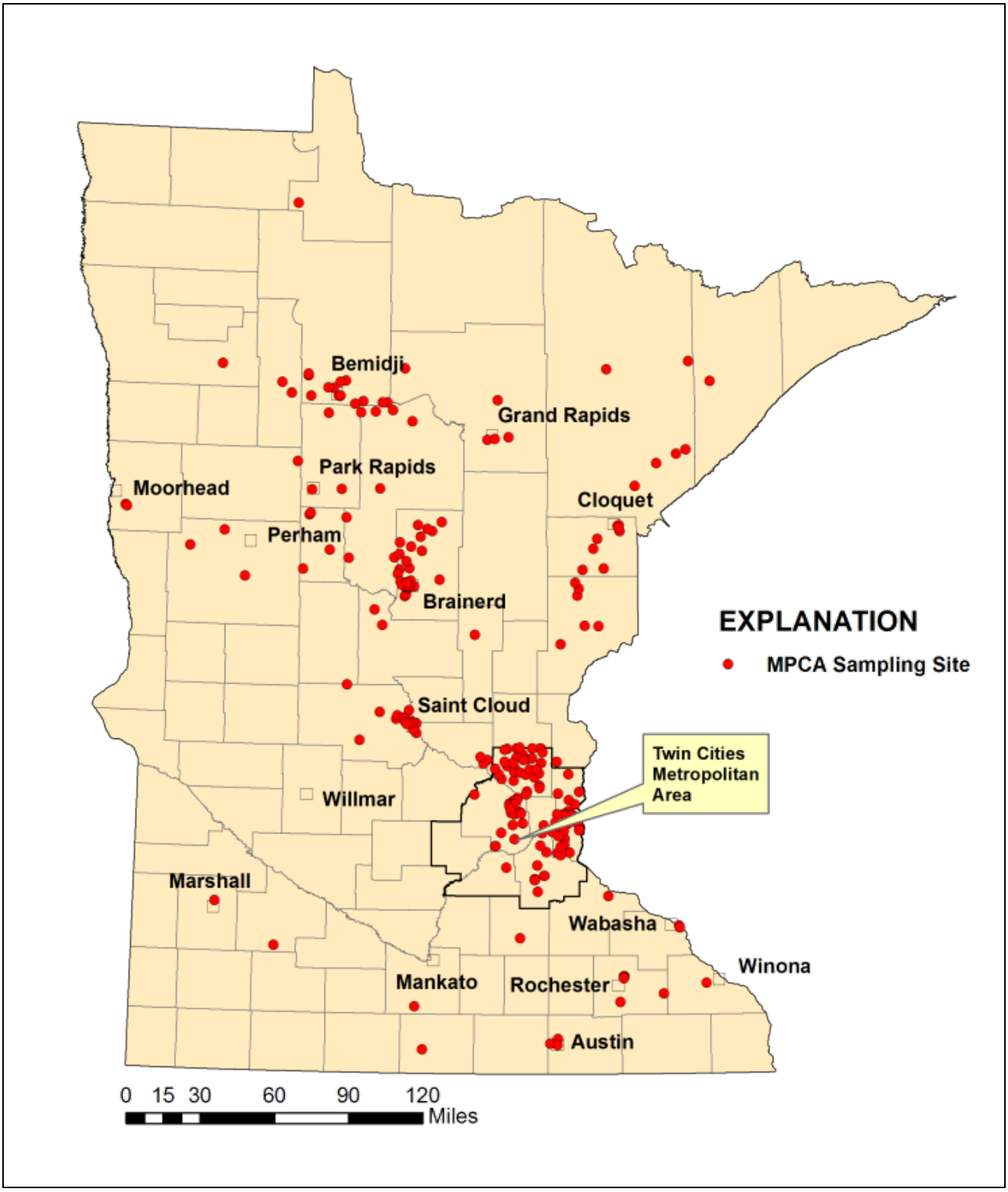

Figure 1. The MPCA's Ambient Groundwater Monitoring Network, 2016.

Site Selection Process

The process used to select MPCA Ambient Groundwater Monitoring Network wells for the NGWMN closely followed the requirements specified in the Framework document (Subcommittee on Ground Water, 2013) and the associated tip sheets (National Ground-Water Monitoring Network Resources for Data Providers, 2018). The two main considerations when selecting sites for the NGWMN were that: 1) the well was installed in an aquifer of national interest and 2) the site met the network's requirements.

MPCA network wells were selected from three principal aquifers that were of interest to the NGWMN. These included the sand and gravel aquifers of glacial origin, the Cambrian-Ordovician system, and the Upper Carbonate aquifer. When selecting MPCA sites for the NGWMN, it was recognized that the individual aquifers that comprise the Cambrian-Ordovician aquifer system are very productive, and the major aquifers within the Cambrian-Ordovician aquifer system (the St. Peter, Prairie du Chien-Jordan, Tunnel City/Wonewoc, and Mount Simon-Hinckley aquifers) were considered separately when determining the number of MPCA well sites to select for the NGWMN.

Any groundwater monitoring site considered for the NGWMN was required to be an actively-monitored MPCA network well that contained the minimum data elements specified in the Framework document and tip sheets. The preferred sites considered for the NGWMN met the baseline requirement of at least five years of data. The number of selected wells was based on the NGWMN's trend site density since all of the sites in the MPCA's network are scheduled for annual sampling. The NGWMN trend network density of 1-5 wells for every thousand square miles and the extent of each of the major aquifers in the state was used to determine the proposed number of sites for each aquifer. The statewide quaternary geology map produced by the Minnesota Geological Survey (Hobbs and Goebel, 1982) along with the suggested NGWMN trend network density was the initial basis for selecting this number of MPCA sites for the NGWMN. A similar statewide map showing the entire extent of the bedrock aquifers in the state was not available. The only statewide map (Jirsa et al 2011) showed the area where each of the state's bedrock aquifers are the first bedrock aquifer. The total extent of each of the bedrock aquifers in the Cambrian-Ordovician system and the Galena aquifer was estimated by mapping the locations of wells installed in each of these aquifers. Only wells from the County Well Index (CWI) whose stratigraphy was reviewed by a geologist from the Minnesota Geological Survey (MGS) were used for this analysis. The interpolated aquifer extent from this analysis was then overlain with the limits of each aquifer defined by Jirsa et al (2011) to estimate the total extent of each aquifer.

Ninety-four wells installed in the sand and gravel aquifers were selected for the NGWMN. The selected wells represented the variety of urban land use settings and deep parts of these aquifers that are sampled by the MPCA's Ambient Groundwater Monitoring Network. Eighty of the selected wells intersected the water table underlying urban and undeveloped land. Fifteen of the selected wells were installed in commercial/industrial areas. Eighteen wells were selected in residential areas that use centralized sewer systems for wastewater treatment and disposal, and an additional eighteen wells were located in residential areas that use SSTS. Twenty-eight of the selected wells were located in undeveloped areas. The remaining wells primarily were

installed in deep parts of the sand and gravel aquifers, and the depth of these wells ranged from 52 to 112 feet. The aquifer type also was consistent with the MPCA Ambient Groundwater Monitoring Network's design. Most of the wells selected for the NGWMN represented unconfined aquifers which is consistent with the MPCA's monitoring network design; however, one-half of the selected deep sand and gravel wells represented confined aquifers.

Most of the Upper Carbonate Aquifer and Cambrian-Ordovician system wells in the MPCA's Ambient Groundwater Monitoring Network were selected for inclusion in the NGWMN. The only well that was not selected had an unknown depth and no corresponding lithology information.

Four Upper Carbonate Aquifer wells were selected for the NGWMN. These were the same wells that were offered to the network in 2011 pilot study, and all of them were installed in the Galena aquifer. One well that originally was included in the pilot study, W0000143, was dropped from the NGWMN because there is no driller's log available for this well. The depths of these wells ranged from 52 to 340 feet below the land surface. Two of the wells represented confined conditions in the aquifer, and the other two wells represented unconfined conditions.

Thirty-three Cambrian-Ordovician aquifer system wells in the MPCA's Ambient Groundwater Monitoring Network were selected for the NGWMN. Three of these wells were from the St. Peter aquifer. The depths of these wells ranged from 49 to 172 feet below the land surface and primarily represented unconfined conditions. Twenty-five wells from the Prairie du Chien-Jordan aquifer were selected for the NGWMN and mainly were the same wells selected for the network during the 2011 pilot study. The depth of these wells ranged from 75 to 350 feet below the land surface. Sixteen of them were installed in the Prairie du Chien Group, and the remaining nine wells were installed in the Jordan sandstone. The wells also represented a mix of aquifer types. Eighteen of the wells represented confined conditions, and the remaining seven wells represented unconfined conditions. Five wells of the selected wells were installed in the Tunnel City, Wonewoc, or Mount Simon aquifers. The depth of these wells ranged from 125 to 940 feet below the land surface and all of them represented confined conditions. Three of the wells were installed in the Tunnel City Group, and the remaining two wells were installed in the Wonewoc and Mount Simon sandstones. The Mount Simon aquifer well was nested with one of the Tunnel City wells. The Wonewoc well, site identifier 453790, is slated for sampling in 2018.

Assigning Subnetworks and Monitoring Categories

All wells selected for the NGWMN that had sufficient water-quality data were assigned to the Background, Suspected Changes, or Documented Changes subnetworks. The Background Subnetwork contains wells located in areas where the water-quality represents the natural conditions. The Suspected Changes Subnetwork contains wells located in areas where the land use has changed resulting in subsequent or anticipated water quality changes. The Documented Changes Subnetwork contains wells located in areas where the groundwater quality is known to be degraded. The NGWMN requires that each well in the NGWMN undergoes a baseline process of five years of data collection in order to properly classify the well into each of these subnetworks.

The available nitrate and chloride data collected from each well were used to classify each well into the three subnetworks. This is very similar to the procedure used as part of the 2011 pilot study. In order for a well to be assigned to the Background Subnetwork, the reported chloride concentrations were required to be less than 35 mg/L or the measured nitrate concentrations were required to be less than 1. In addition, the chloride to bromide ratio of the well water was required to be less than 200, which represents background conditions. The criteria used to assign sites to the Documented Changes Subnetwork were that the nitrate concentrations exceeded 1 mg/L or the chloride concentrations were greater than 35 mg/L. The sites that were not assigned to the Background or Documented Changes Subnetwork were assigned to the Suspected Changes Subnetwork. This would include wells where the chloride/bromide ratios were greater than 200 and indicated a wastewater or water softener or deicing chemical source but had a chloride concentrations that was less than 35 mg/L.

For most of the wells selected for the NGWMN, the land use settings corresponded to the NGWMN subnetwork assignment. Over 80 percent of the shallow sand and gravel aquifer wells located in the various urban land use settings were assigned to the Documented Changes Subnetwork, and the remainder were assigned to the Suspected Changes Subnetwork. In contrast, over 85 percent of the shallow sand and gravel aquifer wells assigned to the Background Subnetwork were located in undeveloped areas.

Similarly, most of the bedrock and deep sand and gravel aquifer wells selected for the NGWMN also were assigned to the Documented Changes Subnetwork. Seventy-one percent of the deep sand and gravel aquifer wells, and 78 percent of the bedrock aquifer wells selected for the NGWMN were assigned to this subnetwork. Only one of the deep sand and gravel aquifer wells and eight of the bedrock aquifer wells were assigned to the Background Subnetwork. There were fewer Background Subnetwork wells selected for the NGWMN compared to Documented Changes Subnetwork wells because the MPCA's monitoring network primarily focuses on monitoring groundwater-quality conditions in areas that are most likely to be impacted by urban contamination sources.

Minimum Data Elements

The required information for the NGWMN were provided as recommended in the Framework Document and the associated tip sheets. All NGWMN wells were assigned a site number that corresponds to the "Minnesota Unique Well Number." This is a well identifier that is unique within the State of Minnesota and issued by the Minnesota Department of Health (MDH) when a well installation permit is received. The data elements associated with describing the well location were provided as suggested in the well registry. This included the horizontal coordinates, national and local aquifer codes, and confinement status. The well construction and lithology information was provided to the NGWMN using web services developed by the MGS for the County Well Index (CWI). The CWI is the water well database for the State of Minnesota and contains information both raw and interpreted data derived from driller's logs. The water-quality data were provided to the NGWMN from the EPA's Water-Quality Exchange or WQX. This project did not provide any groundwater level data to the national network.

The MPCA wells that were selected for the NGWMN contained most of the minimum data elements that were specified in the Framework Document and associated tip sheets. The only data elements that were missing for many of the sites were the accuracy associated with the horizontal coordinates and land surface altitude.

Field Techniques and Data Management

The NGWMN requires that each participant provide documentation of its standard operating procedures. As part of this project, the MPCA updated and officially published a report describing its field data collection procedure as well as its data management procedure. The references for these two documents are:

Samuelson, A. and S. Kroening, 2017, Data Management Protocol for the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network: Minnesota Pollution Control Agency Report wq-am1-08.

Kroening, S., and A. Samuelson, 2017, Field Guidance Manual for the Minnesota Pollution Control Agency's Ambient Groundwater Monitoring Network: Minnesota Pollution Control Agency Report wq-am1-09.

The sampling process used by the MPCA generally is consistent with the Framework Document for the NGWMN. Briefly, the field staff uses standard groundwater sampling procedures to collect water from each well. Prior to sample collection, each monitoring well is purged using a submersible pump outfitted with new polyethylene tubing. While the well is purged of any stagnant water in the casing, field measurements of water temperature, specific conductance, pH, and the dissolved oxygen concentration in the water are made using a calibrated multiparameter meter. Water samples are drawn from each well for laboratory analysis only after these field measurements have stabilized. Water samples are collected to determine over 100 field and laboratory parameters (Appendix 1). Each well is tested for field parameters, general chemistry, major cations, trace elements, and volatile organic compounds. These analyses either are conducted in the field by trained MPCA staff or sent to the MDH Environmental Laboratory. Each year, contaminants of emerging concern (CEC)

samples also are analyzed in a subset of 40 wells from the network. The CEC samples currently are sent to SGS AXYS Analytical Services in Vancouver, Canada for analysis.

Laboratory Analytes and Accreditation

Water samples are collected from the wells in the MPCA's Ambient Groundwater Monitoring Network for the most of the chemicals on the NGWMN's standard, extended, and supplemental analyte lists (Appendix 1). All field parameters are measured by MPCA staff using calibrated meters according to the standard operating procedure. The general chemistry, cation, trace element, and volatile organic chemical analyses are performed by the MDH Environmental Laboratory which is accredited by the US Environmental Protection Agency (Appendix 2). All samples for chemicals of emerging concern, which are collected from 40 MPCA network wells each year, are analyzed by SGS AXYS Analytical Services, which is accredited for pharmaceutical and personal care product and triclosan analyses in water by the Canadian Association for Laboratory Accreditation and the Maine Center for Disease Control and Prevention, Department of Health and Human Services. The only constituents listed in the Framework Document that are not routinely analyzed by the MPCA's network are oxygen reduction potential and isotopes.

Lithology and Well Construction Web Services

For this project, the MPCA coordinated with the MGS to develop web services to the lithology and well construction data associated with the wells selected for the NGWMN. In the state of Minnesota, this information is stored in the CWI database which is jointly managed by the MGS and MDH. CWI contains the construction and lithology information reported by the well driller as well as stratigraphy and lithology that were interpreted by the MGS as part of their investigations. The web service developed for the NGWMN contains the well construction information reported on the driller's logs and the MGS-interpreted stratigraphy and lithology. Some of the wells in the web service are missing stratigraphic or lithologic information because the MGS has not reviewed the driller's logs for all of the wells in the MPCA's Ambient Groundwater Monitoring Network.

Other Work Done to Support the NGWMN

This project reconnected the MPCA's Ambient Groundwater Monitoring Network data with the NGWMN Data Portal. This reconnection was needed because the MPCA was in the process of switching data management systems during the 2011 pilot study. As part of this system change, the MPCA also changed its well identifiers from an arbitrarily selected four or five digit number to the Minnesota Unique Well Number. In addition, the MPCA changed the agency code where its ambient groundwater quality data are stored in the US EPA's WQX to MNPCA_AGW. No other changes to the MPCA's water-quality data management activities are anticipated in the near future which would impact the water-quality web services to the NGWMN data portal.

Other work done as part of this project included updating the MPCA information contained in the NGWMN well registry. This was necessary because the NGWMN now (2018) requires more sampling site information compared to when the pilot studies were conducted in 2010-2011.

References

Hobbs, H.C.; Goebel, J.E.. (1982). S-01 Geologic map of Minnesota, Quaternary geology. Minnesota Geological Survey. Retrieved from the University of Minnesota Digital Conservancy, http://hdl.handle.net/11299/60085.

Jirsa, Mark A.; Boerboom, Terrence J.; Chandler, V.W.; Mossler, John H.; Runkel, Anthony C.; Setterholm, Dale R.. (2011). S-21 Geologic Map of Minnesota-Bedrock Geology. Minnesota Geological Survey. Retrieved from the University of Minnesota Digital Conservancy, http://hdl.handle.net/11299/101466.

National Ground-Water Monitoring Network Resources for Data Providers, 2018, https://cida.usgs.gov/ngwmn/learnmore.jsp

Subcommittee on Ground Water of the Advisory Committee of Water Information, 2013, A National Framework for Ground-Water Monitoring in the United States, https://acwi.gov/sogw/ngwmn_framework_report_july2013.pdf

Appendix 1

Field parameters and chemical constituents analyzed by the MPCA's Ambient Groundwater Monitoring Network

Table 2. Field parameters, general chemistry constituents, major cations, and trace elements analyzed by the MPCA's Ambient Groundwater Monitoring Network

FIELD PARAMETERS	**TRACE ELEMENTS**
Oxygen	Aluminum
pH	Arsenic
Specific conductance	Barium
Water Temperature	Beryllium
GENERAL CHEMISTRY	Cadmium
Alkalinity	Chromium
Ammonia nitrogen	Cobalt
Nitrate plus nitrite nitrogen	Copper
Organic plus ammonia nitrogen	Lead
Phosphorus	Lithium
Bromide	Manganese
Chloride	Molybdenum
Sulfate	Nickel
Organic carbon	Silver
MAJOR CATIONS	Strontium
Boron	Titanium
Calcium	Vanadium
Iron	Zinc
Magnesium	
Potassium	
Sodium	

Table 3. Volatile Organic Compounds Analyzed by the MPCA's Ambient Groundwater Monitoring Network

1,1,1,2-Tetrachloroethane	2-Chlorotoluene	Hexachlorobutadiene
1,1,1-Trichloroethane	4-Chlorotoluene	Isopropylbenzene
1,1,2,2-Tetrachloroethane	Acetone	Methyl ethyl ketone (MEK)
1,1,2-Trichloroethane	Allyl chloride	Methyl isobutyl ketone (MIBK)
1,1,2-Trichlorotrifluoroethane	Benzene	Methyl tertiary butyl ether (MTBE)
1,1-Dichloroethane	Bromobenzene	Methylene chloride
1,1-Dichloroethene	Bromochloromethane	Naphthalene
1,1-Dichloropropene	Bromodichloromethane	n-Butylbenzene
1,2,3-Trichlorobenzene	Bromoform	n-Propylbenzene
1,2,3-Trichloropropane	Bromomethane	o-Xylene
1,2,4-Trichlorobenzene	Carbon tetrachloride	p&m-Xylene
1,2,4-Trimethylbenzene	Chlorobenzene	p-Isopropyltoluene
1,2-Dibromo-3-chloropropane (DBCP)	Chlorodibromomethane	sec-Butylbenzene
1,2-Dibromoethane (EDB)	Chloroethane	Styrene
1,2-Dichlorobenzene	Chloroform	tert-Butylbenzene
1,2-Dichloroethane	Chloromethane	Tetrachloroethene
1,2-Dichloropropane	cis-1,2-Dichloroethene	Tetrahydrofuran (THF)
1,3,5-Trimethylbenzene	cis-1,3-Dichloropropene	Toluene
1,3-Dichlorobenzene	Dibromomethane	trans-1,2-Dichloroethene
1,3-Dichloropropane	Dichlorodifluoromethane	trans-1,3-Dichloropropene
1,4-Dichlorobenzene	Dichlorofluoromethane	Trichloroethene (TCE)
2,2-Dichloropropane	Ethyl ether	Trichlorofluoromethane
2,2-Dichloropropane	Ethylbenzene	

Table 4. Contaminants of Emerging Concern analyzed by the MPCA's network

1,7-Dimethylxanthine	Cyclophosphamide	Miconazole
10-hydroxy-amitriptyline	Daunorubicin	Moxifloxacin
2-Hydroxy-ibuprofen	DEET	Naproxen
4-n-Octylphenol	Dehydronifedipine	Norfloxacin
4-Nonylphenol diethoxylates	Desmethyldiltiazem	Norfluoxetine
4-Nonylphenol monoethoxylates	Diatrizoic acid	Norgestimate
4-Nonylphenols	Diazepam	Norverapamil
Acetaminophen	Digoxigenin	Ofloxacin
Albuterol	Digoxin	Ormetoprim
Alprazolam	Diltiazem	Paroxetine
Amitriptyline	Diphenhydramine	Penicillin G
Amlodipine	Doxorubicin	Penicillin V
Amphetamine	Drospirenone	Prednisolone
Amsacrine	Enalapril	Prednisone
Atenolol	Enrofloxacin	Promethazine
Atorvastatin	Erythromycin-H2O	Propoxyphene
Azathioprine	Etoposide	Propranolol
Azithromycin	Flumequine	Ranitidine
Benzoylecgonine	Fluocinonide	Rosuvastatin
Benztropine	Fluoxetine	Roxithromycin
Betamethasone	Fluticasone propionate	Sarafloxacin
Bisphenol A	Furosemide	Sertraline
Busulfan	Gemfibrozil	Simvastatin
Caffeine	Glipizide	Sulfachloropyridazine
Carbadox	Glyburide	Sulfadiazine
Carbamazepine	Hydrochlorothiazide	Sulfadimethoxine
Cefotaxime	Hydrocodone	Sulfamerazine
Cimetidine	Hydrocortisone	Sulfamethazine
Ciprofloxacin	Ibuprofen	Oxacillin
Citalopram	Iopamidol	Oxazepam
Clarithromycin	Lincomycin	Oxolinic Acid
Clinafloxacin	Lomefloxacin	Oxycodone
Clonidine	Medroxyprogesterone Acetate	Sulfamethizole
Clotrimazole	Melphalan	Sulfamethoxazole
Cloxacillin	Meprobamate	Sulfanilamide
Cocaine	Metformin	Sulfathiazole
Codeine	Methylprednisolone	Tamoxifen
Colchicine	Metoprolol	Teniposide
Cotinine	Metronidazole	

Table 4. Contaminants of Emerging Concern analyzed by the MPCA's network (continued)

Theophylline	Triclocarban	Verapamil
Thiabendazole	Triclosan	Virginiamycin M1
Trenbolone	Trimethoprim	Valsartan
Trenbolone acetate	Tylosin	Warfarin
Triamterene	Venlafaxine	Zidovudine