



## Data Summary Report: Unregulated Contaminants Monitoring Project

FINAL REPORT (FEBRUARY 2023)

## **Unregulated Contaminants Monitoring Project**

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## Acronyms

CEC: Contaminant of emerging concern CWS: Community water system EPA: Environmental Protection Agency L: Liter MDA: Minnesota Department of Agriculture MDH: Minnesota Department of Health mg: Milligram MNDNR: Minnesota Department of Natural Resources NWQL: National Water Quality Laboratory (USGS) ng: Nanogram ORP: Oxidative reduction potential UCMR: Unregulated Contaminant Monitoring Rule USGS: U.S. Geological Survey

## Acronyms used for contaminants

6:2 FTS: 6:2 Fluorotelomersulfonate BTZs: Benzotriazoles CIAT: Deethylatrazine CEAT: Deisopropylatrazine DEET: N,N-diethyl-meta-toluamide EtFOSAA: N-ethyl-perfluorooctane sulfonamido acetic acid MDMA: 3,4-methylenedioxy-methamphetamine MeFOSAA: N-Methylperfluorooctanesulfonamidoacetic acid OA: Oxanilic acid OIAT: 2-hydroxy-4-isopropylamino-6-amino-s-triazine OIET: 2-hydroxyatrazine PFAS: Per- and polyfluoroalkyl substances PFBA: Perfluorobutanoate PFBS: Perfluorobutanesulfonate PFHpA: Perfluoroheptanoate

PFHxA: Perfluorohexanoate

PFHxS: Perfluorohexanesulfonate

PFNA: Perfluorononanoate

PFOA: Perfluorooctanoate

PFOS: Perfluorooctanesulfonate

PFOSA: Perfluorooctanesulfonamide

PFPeA: Perfluoropentanoate

SA: Ethanesulfonic acid

## **Executive Summary**

The Drinking Water Protection Section of the Minnesota Department of Health conducted reconnaissance monitoring of selected public water systems in Minnesota. Funding was obtained primarily from the Environment and Natural Resources Trust Fund. Sampling was conducted in 2019 and 2021. Laboratory analysis of samples was conducted for a variety of different contaminants of emerging concern (CECs), including selected pharmaceuticals, pesticides, PFAS, wastewater indicators and other parameters chosen for the physical and land use setting surrounding the sampling points.

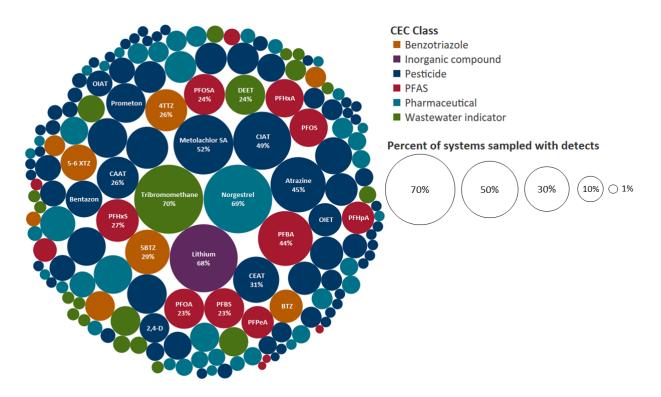
Sampling site and parameter selection were designed with several goals, as follows:

- Characterize occurrence and distribution of selected CECs in settings where such chemicals are most likely to be present;
- Determine if any such occurrences represent a public health concern;
- Compare results from coupled source water and finished (i.e., treated) water samples at public water system sites where such sampling is feasible;
- Assess if results from geologically vulnerable (sensitive subject to rapid recharge) and geologically non-vulnerable settings differ significantly.

306 samples were collected as part of the study, from three networks of public water systems differentiated on the basis of source water type (i.e., surface water or groundwater) and land use environment (agricultural and wastewater influenced).

This report provides a preliminary, qualitative evaluation of the results. Additionally, more rigorous research will be conducted on these water quality data to evaluate the below findings in more detail. High-level findings from this assessment include the following:

- Very few samples exceeded health-based guidance for CECs;
  - When this occurred, MDH staff conducted follow up sampling at the system and provided technical advice about managing the situation.
- Only a fraction of the CECs analyzed were detected;
  - Of the 522 different CECs analyzed in the water samples, 161 were detected in one or more samples;
  - Additionally, most detections were at low levels;
- Among the CEC classes included in the analytical work, pesticides and PFAS were generally detected at a greater frequency than other CECs;
  - See Executive Summary Figure 1.



# Executive Summary Figure 1. Summary of CECs detected at all sites (N = 107) by class and relative frequency of detection.

Each dot represents an individual contaminant within a class. The size of the dot represents the percentage of sites at which the contaminant was detected, based on the number of sites at which it was analyzed.

- The ten most commonly detected individual compounds include:
  - Tribromomethane, or bromoform, (a disinfection by-product) (70% of sites where analyzed);
  - o norgestrel (a pharmaceutical) (69% of sites where analyzed);
  - lithium (68% of sites where analyzed);
  - Metolachlor SA (52%), Deethylatrazine (49%), atrazine (45%), and deisopropylatrazine (31%) (pesticides);
  - PFBA (44%) and PFHxS (27%) (PFAS compounds); and
  - 5-methyl benzotriazole (29%) (a benzotriazole).
- Some CECs were detected more frequently in samples collected from surface waters than those collected from groundwater sources;
- CEC concentrations were generally higher in vulnerable settings compared to nonvulnerable settings;

- Whether CECs were detected more frequently in the source water or finished water varied by CEC class. For example,
  - Benzotriazoles and pharmaceuticals were more frequently detected in source water samples than finished water samples; and
  - Tribromomethane, or bromoform, a common disinfection by-product, was more frequently found in finished water samples than in source water samples.

This work prompted a series of programmatic changes and innovations:

- A response framework was established for helping the program and public water systems manage detections of unregulated CECs in drinking water;
- Results were forwarded to the program within MDH responsible for developing healthbased guidance in order to nominate specific compounds found in drinking water but for which limited or no risk advice is available;
- MDH is seeking support from the Clean Water Council to support the establishment of permanent capacity within the Drinking Water Protection Section to continue sampling efforts of this type.

## Introduction

Over a decade of research has demonstrated that unregulated contaminants, also known as contaminants of emerging concern<sup>1</sup> (CECs), are often present in Minnesota waters, usually at low levels (Lee et al. 2011; Kroening, 2012; Ferrey, 2013; Ferrey et al. 2013; Ferrey, 2015; Ferrey et al., 2017; Kroening and Vaughan, 2019). While monitoring of rivers, lakes, and groundwater in aquifers provides useful information about what might be found in drinking water sources and the broader environment, without sampling at wells or intakes used for drinking water supply, it generally does not provide the specificity needed to evaluate contaminants in drinking water. The monitoring data collected for this study specifically addresses CECs in source and finished drinking water.

The occurrence and fate of CECs can be affected by the different processes used to supply, treat, and deliver drinking water. Intakes and wells are typically constructed following certain guidelines or regulations to isolate them from known sources of contamination. Engineering design specifications help to prevent contamination and achieve public health goals. Drinking water treatment subjects the water to a variety of processes and controls, generally with the aim of improving the aesthetic quality (*i.e.*, taste, odor, appearance) and meeting water quality standards. Standard treatment at drinking water systems varies widely but is seldom designed for removal of CECs. Research has shown that certain CEC classes are associated with specific waste streams or land uses that may be upgradient or upstream of drinking water intakes (Lee et al., 2011; Fairbairn et al; 2016; Lenka et al., 2021). For example, wastewater reclamation facility (WRF) effluent often contains pharmaceuticals, personal care product ingredients, and per- and polyfluoroalkyl substances (PFAS), among other CECs (Lee et al., 2011; Lenka et al., 2021). Likewise, pesticides are used in many settings, with more concentrated applications in agricultural areas (Nicolopoulou-Stamati et al., 2016). Glassmeyer et al. (2017) summarizes a study of CEC occurrence in drinking water sources and associated finished drinking water–work that is described in more detail by Boone et al., 2019 and Furlong et al., 2017.

Concern over CEC contamination led to the present study, which focuses on the occurrence and fate of a wide range of CECs in Minnesota drinking water. Monitoring studies such as this one, provide information on potential exposures to CECs and may lend insight on public health concerns, drinking water management, and future monitoring needs.

<sup>&</sup>lt;sup>1</sup> For this report we are adopting the following definition of CECs: "CECs can be a contaminant that has been newly discovered in the environment (e.g., per- and polyfluoroalkyl substances). A CEC may also be a contaminant that has been known for a long time but is generating increased interest in the scientific community due to new scientific information about its impacts on public health or the environment. These contaminants are often unregulated or are regulated at a level that may no longer be considered adequately protective of human and ecological health" (ASDWA and ACWA, 2019).

## CECs and drinking water in Minnesota

Three principal factors drive the monitoring of drinking water for CECs in Minnesota. The first is ever-improving laboratory analytical capabilities. Such advances allow the identification of more chemicals at lower concentrations. Second, as new toxicity information becomes available, health-based guidance is developed to evaluate potential human health risks from exposures to CECs in water. Third, the public is increasingly concerned about water quality in Minnesota<sup>2</sup>.

Prior CEC occurrence studies in Minnesota drinking water have been conducted for federally mandated monitoring (e.g., US EPA, 2021) or as part of episodic, project-based monitoring (e.g., MDA, MDH, 2016). The federally mandated Unregulated Contaminants Monitoring Rule (UCMR; Monitoring Unregulated Contaminants in Drinking Water) occurs approximately every five years. It requires medium and large community public water systems, as well as a randomized selection of small community and noncommunity systems, to conduct monitoring for priority contaminants, which are selected by the U.S. Environmental Protection Agency (EPA) based on expected occurrence in drinking water, availability of health assessments or health-effects information, active use, and persistence and mobility data. The federal UCMR sampling covers a list of target chemicals. The monitoring data are used to inform development of future water quality standards. Other assessments of Minnesota's drinking water have been conducted by the Minnesota Department of Health (MDH) in conjunction with various partners, based on specific questions or needs. These assessments have included surveys for pesticides (Johnson et al., 2016), general water chemistry, manganese, and viruses and pathogens (Stokdyk et al., 2019, 2020). Local assessments also occur in response to spills or in relation to known contamination, but historically have not been statewide in scope.

## **Problem statement**

Prior monitoring efforts in Minnesota have left an incomplete picture regarding occurrence and distribution of the many classes of CECs in drinking water. National studies have emerged that characterize the presence of CECs in paired source and finished water samples at select public water systems nationwide, demonstrating that although some contaminants are removed during the treatment process, others are not (Glassmeyer, et al, 2017). A better understanding of occurrence can inform future water regulation, management, and potential treatment options.

<sup>&</sup>lt;sup>2</sup> We know this from national Gallup polls that show drinking water contamination is the top public environmental health concern (see <u>A Seven-Year Stretch of Elevated Environmental Concern</u>). Priority identification efforts conducted as part of local comprehensive watershed planning in Minnesota commonly rank drinking water protection and quality at the top of the list.

The primary goal of this project is to characterize the presence of select CECs in both drinking water sources and corresponding finished drinking water in Minnesota. Three distinct monitoring networks were established as part of this work, allowing results to be evaluated in terms of land use, geologic vulnerability, and type of water resource used for drinking water supply (i.e., surface water or groundwater).

This report summarizes the results of this project in a high-level overview. A more rigorous quantitative assessment is under development.

## Methodology

This section describes the public water systems selected for inclusion in the study and the parameters chosen for laboratory analysis. While the overall objective of the study is to evaluate the occurrence and distribution of CECs in drinking water, the specific approaches were designed to evaluate the following: 1) if CEC concentrations differ between samples collected at the source (e.g. pre-treatment) from those collected at the entry point (e.g., post-treatment<sup>3</sup>), at both groundwater and surface water-sourced systems, 2) if geologic conditions influence the observed levels of CECs, and 3) the effect of land use on CEC presence in groundwater systems. There are roughly 960 community public water systems in Minnesota and there were insufficient resources to sample them all. Accordingly, MDH created a Technical Advisory Team to advise on site selection and on an appropriate laboratory analysis plan. These selections were made strategically to identify sites most likely to be affected by CECs. Additionally, samples from those sites were analyzed for CECs most likely to be present in the water from the environments from which they were collected.

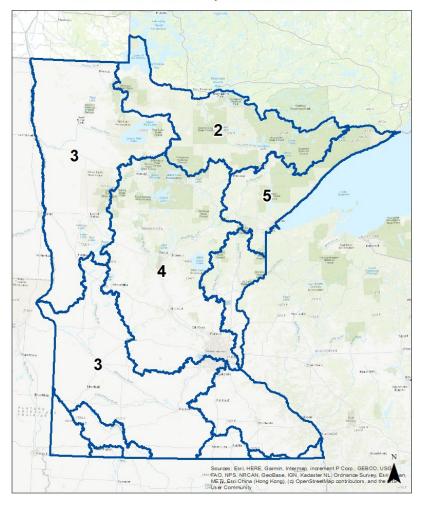
## Site selection

To optimize available resources, three networks of drinking water sources were established. The CECs analyzed were tailored for each network. Waters that constitute drinking water sources in Minnesota are widely variable. Creating three different networks provided a means of evaluating the different kinds of drinking water sources (e.g., surface water and groundwater) as well as the effects of settings that vary in different parts of the state.

*Surface Water Systems.* The first network (Figure 1) is comprised of 17 public water system sites that use surface water as a source of supply. The surface water sites included in the study were not differentiated by land use type given the wide range of land use types and inherent vulnerability of surface water bodies and the small number of such systems statewide. There are only 23 community public water systems in Minnesota that rely on surface water, so the inclusion of most of these in the network did not strain analytical resources.

<sup>&</sup>lt;sup>3</sup> None of the sampled systems use treatment specifically designed for CEC removal. Previous work had established that standard treatment might provide unintentional, incidental removal in some circumstances (cf., Glassmeyer et al, 2017).

Several of the systems that use Lake Superior and the Red Lake River as a source were not sampled because they share a common source with another system that was sampled. This eliminated some redundancy in the sampling and maximized efficient use of resources.



Surface Water Sites by Surface Watersheds

# Figure 1. Number of surface water network sites by Hydrologic Unit Code 4 watershed (MNDNR, 2019).

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*Groundwater systems.* Two separate networks, each comprised of 45 public water systems (Figures 2 and 3), were established to evaluate the water quality of systems that rely on groundwater – one for sites located in predominantly agricultural settings and one for sites located in settings potentially influenced by wastewater discharge. These two land use environments are common in and around the Drinking Water Supply Management Areas

(DWSMAs) statewide and provide challenges relative to land management within DWSMAs. There are hundreds of public water systems in Minnesota in each of these settings. To determine the most vulnerable wells to include in the project, all public water systems in the state were evaluated relative to criteria designed to identify those most likely to be affected by CECs. Two principal factors drove this evaluation: geologic vulnerability (sensitivity) (MDH, 2019) and land use activities (MPCA, 2018; Metropolitan Council, 2020).

The Drinking Water Program at MDH has long used geologic vulnerability as a high-level screening criterion to evaluate the likelihood of contamination from nearby land uses, to set sampling schedules under Safe Drinking Water Act (SDWA) compliance monitoring, to evaluate waivers of SDWA sampling requirements, and to phase public water systems into the wellhead protection program. Similar criteria are used elsewhere in Minnesota to assess environments susceptible to near surface contamination (MNDNR, 2016). MDH uses a series of factors to assess the vulnerability of a well. The principal factors are the following: 1) geologic material through which a well is constructed, 2) chemical and isotopic composition of the well water as evidence of recent recharge, 3) well construction, and 4) well pumping (MDH, 1997, 2018, 2019). Public water systems with vulnerable wells are subject to recent recharge and the potential effect of land uses in proximity of the well. In contrast, non-vulnerable wells are often isolated from nearby land uses by geologic conditions that limit recharge. In Minnesota we commonly find that water samples from vulnerable wells contain more contaminants (e.g., nitrate, chloride) than non-vulnerable ones.

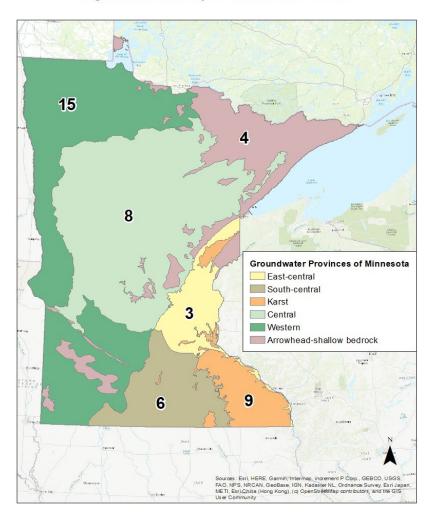
For this study, 30 vulnerable wells and 15 non vulnerable wells were selected to be part of each groundwater network. These wells were ranked based on land use evaluations (described below) and were sorted based on vulnerability. Inclusion of vulnerable wells was the priority, so these wells were sampled as part of the Phase 1 monitoring (2019). Concurrent MDH research on pathogen occurrence (Stokdyk, 2019, 2020) demonstrated pathogen presence in settings previously determined to be non-vulnerable. Hence 15 non-vulnerable wells were identified using similar land use criteria (agricultural and wastewater) and sampled as part of the Phase 2 monitoring (2021) to determine if similar results might be obtained for CEC occurrence.

Land use conditions assessed as part of the site selection process for agricultural settings differed from those assessing the potential of wastewater influence. In each case, though, land use and inventories of potential sources of contamination were used. The following considerations were used to select sample sites for the agriculture network (Figure 2):

- Prior detections of key water quality parameters, such as:
  - elevated nitrate (exceeding 3 mg/L),
  - o pesticides, and
  - o pathogens associated with livestock or manure
- Proportion of agricultural land uses within the drinking water supply management area (DWSMA) for the well;

• Measures in the wellhead protection plan directed at agricultural land uses.

Sites that met one or more of these criteria were ranked and prioritized. Additionally, sites were sorted by location within the state. Spatial variation was important to include because of the reconnaissance nature of this study and because crop production, associated agricultural practices, and geologic settings change regionally in the state. Figure 2 shows how many selected sites correspond to groundwater provinces mapped by MNDNR (2021).



Agriculture Sites by Groundwater Province

# Figure 2. Number of agriculture network sites by groundwater province (MNDNR, 2021).

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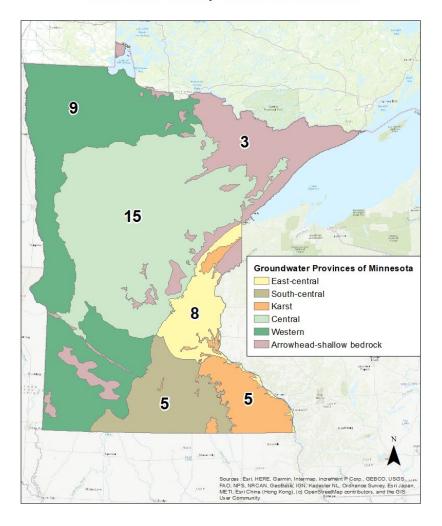
The following considerations were used to select sample sites for the wastewater network (Figure 3):

- Previous water quality monitoring results indicative of wastewater influence, such as:
  - A chloride:bromide ratio between 500 and 800 (Davis, et al, 2005)
  - Chloride results between 40-100 mg/L
  - Past microbial detections
  - Prior pharmaceutical or artificial sweetener detection (*cf.*, Van Stempvoort et al, 2011, Wolf, et al, 2012, and Stokdyk et al, 2020.)
- Presence of known wastewater sources including wastewater treatment plants, assessed within the DWSMA and within a 1-mile radius;
- Presence of subsurface sewage treatment systems (SSTS) (MPCA What's in my Neighborhood (WIMN), 2019) and residential septic as obtained from well construction logs (MDH, 2019);
- Existence of discharges permitted under the National Pollutant Discharge Elimination System (NPDES); and
- Sewer infrastructure within the drinking water supply management area for the well.

Sites that met one or more of these criteria were ranked and prioritized. Sites that met several of the above criteria were considered higher risks for CEC occurrence from wastewater than sites that triggered few or none of the criteria. Additionally, sites were sorted by location within the state. Spatial variation was important to include due to the reconnaissance nature of this study and because crop production (associated agricultural practices) and geologic settings change regionally in the state. Figure 3 shows how many selected sites correspond to groundwater provinces mapped by MNDNR (2021).

Data sources used in the assessment process are from Minnesota SDWA compliance data, publicly available data sources (e.g., MPCA WIMN 2019), surveys of potential sources of contamination from Minnesota Source Water Protection program activities, and past monitoring projects (Stokdyk, et al, 2019, 2020). Criteria involving land use generally focused on spatial areas approved as DWSMAs in Minnesota.

A small number of sampling sites (8) met the selection criteria for both the agricultural and the wastewater networks.



Wastewater Sites by Groundwater Province

# Figure 3. Number of wastewater network sites by groundwater province (MNDNR, 2021).

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*Source (raw) and finished (treated) samples.* At each groundwater or surface water sampling site, water samples were collected from both the source (i.e., the well or the surface water intake) and from the entry point at which finished drinking water enters the distribution system. These sites were defined by the community water system (CWS). Entry points are the sampling sites at which most SDWA compliance sampling is conducted. Sample collection at these sites occurred on the same day but no effort was made to align sample collection times to assure the same parcel of water was being sampled at each sampling site.

186 samples were collected and analyzed during Phase 1 of this study and 120 samples were collected and analyzed during Phase 2.

## Selection of CECs for analysis

While the number of chemicals for which drinking water standards exist in the U.S is about 100, CECs in use may be over 80,000 (U.S. EPA, 2023). The large number of CECs assessed in this study made it expedient to create groups of compounds based on like usage, class, or chemical structure. CECs were categorized into the following general classes: pesticides, wastewater indicators, benzotriazoles (including benzothiazoles), pharmaceuticals (including hormones, personal care products, and illicit drugs), inorganic compounds, and PFAS. Some CECs are regulated under the Safe Water Drinking Act, but their degradates are not (e.g., atrazine), despite frequent occurrence in the environment. Inclusion of parent and degradate CECs increases the amount of data that can be used to inform decisions regarding monitoring and regulations.

Because available resources for laboratory analytical work were limited and information from prior work on CECs in Minnesota waters was used to guide CEC selection (e.g., Lee, et al 2011; Kroening, 2012; Ferrey, 2013, 2015, 2017), we elected to customize the parameter list for each of the unique networks. For example, a broad array of pesticides was selected for sampling sites from the agricultural network.

CEC groups were matched to one of the three networks using the following general conditions:

- 1. Association of CECs with wastewater disposal or agricultural land use activities (*cf.*, Vidal-Dorsch, et al, 2012; Elliot, et al, 2018).
- Results from prior monitoring studies. Preference was given to CECs that have been found in previous work in groundwater or surface water in Minnesota, or nationally (*cf.*, Ferrey, et al, 2013, 2015, 2017; Hruby, et al 2015; Johnson et al., 2016; MDA, 2021, 2022; Roberson and Eaton, 2014).
- 3. Balancing laboratory analytical limitations. These included:
  - a. Cost associated with laboratory analysis.
  - b. Method detection limits and method reporting limits state of the art analytical methods were sought to correspond with new health-based guidance.
  - c. Schedules of contaminants offered by available labs. Most available schedules of parameters included many, but not all the desired CECs.
- 4. CECs that are of public health interest<sup>4</sup>.

<sup>&</sup>lt;sup>4</sup> MDH staff regularly review its health-based guidance, usually based on new or updated toxicological information. As new understandings emerge about chemicals, especially if this results in lowering health-based guidance values, new occurrence and distribution information is needed to assess public health impact. Examples of changes in this area include new values for various PFAS contaminants, and for manganese, for which a federal secondary maximum contaminant level exists.

Table 1 shows the monitoring networks and the associated CEC lists. Explanation of these selections is explained below.

*Agricultural network.* CEC groups chosen for the agriculture network were selected, in addition to the considerations listed above, based on their association with agricultural land use (Tables 1-2). Detection of CECs prioritized for the agricultural network provides information about general occurrence in high-risk settings. The CECs analyzed for Phase 1 monitoring primarily included pesticides and pesticide degradates. PFAS were added in Phase 2 due to general concern about PFAS occurrence in the environment and because of known associations of PFAS with certain agricultural chemicals (Lasee, et al, 2022).

*Wastewater network*. CEC groups chosen for the wastewater network were selected, in addition to the considerations listed above, based on their association with wastewater disposal (Tables 1-2). Detection of these CECs in drinking water indicates that contaminants in human waste and wastewater are reaching aquifers and impacting public water supply wells. These CECs include pharmaceuticals, personal care products, specific wastewater indicators, and PFAS.

*Surface water network.* The surface water sites are the most vulnerable water supplies of the three sampling networks included in this study based on known wastewater discharges to Class 1 waters (drinking water sources), prior monitoring work in Minnesota (Ferrey, 2013, 2017) and the residence time and flux rates of streams and rivers. Some of the surface water sources of drinking water in Minnesota also drain agricultural areas of the state, in which a range of different crops are grown. Accordingly, the CECs selected for the surface water network consist of those selected for the agriculture and wastewater networks, as well as additional CECs (Tables 1-2). These additional CECs include benzotriazoles, illicit drugs, alkylphenols and alkylphenol ethoxylates, hormones, and an expanded array of pharmaceuticals and personal care products that are more broadly detected in surface waters<sup>5</sup>.

Water samples were analyzed at either the MDH Public Health Laboratory (MDH; St. Paul, MN), the USGS National Water Quality Laboratory (USGS NWQL; Denver, CO), SGS AXYS Analytical, Ltd. (AXYS; Sidney, British Columbia, Canada), or Eurofins Eaton Analytical, LLC. (Eurofins; South Bend, IN).

A complete list of analytes is included in Appendix A: Complete List of Parameters.

<sup>&</sup>lt;sup>5</sup> Note that some CECs were included in multiple laboratory analytical schedules, so results for specific networks may include unexpected CECs, based on the above explanation of which CECs were analyzed at which networks. For example, several pesticides (e.g., atrazine, metolachlor) are included in the wastewater indicator schedule, providing information for select pesticides at wastewater sites even though pesticides were not a targeted CEC class. In instances when results for a given CEC were obtained from multiple analytical schedules in the same sample, the results associated with the lowest method reporting limit were used to create summaries.

## Table 1. CECs sampled by network in Phase 1 of the project during 2019.

MDH, Minnesota Department of Health; USGS NWQL, U.S. Geological Survey National Water Quality Laboratory; AXYS, SGS AXYS Analytical, Ltd.

Parameter Group	Laboratory	Agriculture Network	Wastewater Network	Surface Water Network
Lithium	MDH	х	х	x
Wastewater indicators	USGS NWQL		х	х
Pharmaceuticals	USGS NWQL		х	x
PFAS	AXYS		х	x
Benzotriazoles/benzothiazoles	MDH			x
Illicit Drugs	MDH			х
Pharmaceuticals and Personal Care Products (limited list, lists 1 & 6 defined in appendix)	AXYS		х	
Pharmaceuticals and Personal Care Products (extensive list, lists 1, 3 & 6 defined in appendix)	AXYS			х
Alkylphenols and Alkylphenol Ethoxylates	AXYS			х
Hormones	AXYS			х
Pesticides/pesticide degradates	USGS NWQL	х		х

## Table 2. CECs sampled by network in Phase 2 of the project during 2021.

MDH, Minnesota Department of Health; AXYS, SGS AXYS Analytical, Ltd.; USGS NWQL, U.S. Geological Survey National Water Quality Laboratory

Parameter Group	Laboratory	Phase 1 Agriculture Network	Non-vulnerable Agriculture Network	Non-vulnerable Wastewater Network
PFAS	AXYS	х	x	x
Pharmaceuticals and Personal Care Products (limited list, lists 1 & 6 defined in appendix)	AXYS			x
Benzotriazoles/benzothiazoles	MDH			x
Pesticides (except cyanazine degradates)	USGS NWQL	x	x	
Cyanazine degradates	Eurofins	Х	x	

## Sample collection

## General procedures.

At each site, the source (raw) water was sampled first, if possible. The source water taps were flushed by filling several five-gallon buckets. Field measurements were taken at 3-minute intervals until they stabilized, or until 15 minutes had passed. The field parameters recorded at each source water tap included temperature, pH, specific conductance, dissolved oxygen, and oxidative reduction potential.

Field personnel wore nitrile gloves to collect all water samples, and sample bottles were kept inside individual plastic storage bags. Water samples were immediately placed on ice and kept refrigerated or frozen (as appropriate and per standard method protocols) until time of shipment to the laboratory.

It is important to note that the same parcel of water was not sampled at both the source and finished water sampling points. We did not calculate the time it would take for water to move from the well or intake through the treatment plant or system of pipes to reach the entry point, or finished water tap; therefore, any difference observed between the source and finished water samples may be due to different CECs moving through each system at varying intervals. Despite this, results provide an overall indication of what CECs may be present at any given time, and at what concentrations. The study design also did not account for treatment type as a part of the selection criteria for public water systems. Any removal of CECs observed in finished water samples is incidental.

*Phase 1 sample collection.* Phase 1 of the Unregulated Contaminants Monitoring Project refers to sample collection that occurred between August 2019 and November 2019 at vulnerable wells and at surface water systems. Sites in the wastewater and agriculture networks were each sampled once. Surface water sites were sampled twice to account for the greater degree of seasonal variability that is expected in surface water settings.

*Phase 2 sample collection.* Sampling for Phase 2 began in August 2021 and was completed in November 2021. The Phase 1 agriculture network sites were revisited and sampled for PFAS and atrazine and cyanazine degradates (Appendix A). Additional sampling sites were added to the existing agriculture and wastewater networks. The new sites consisted of geologically 'non-vulnerable' wells, 15 in land use settings associated with agriculture and 15 in land use settings associated with wastewater discharge. The addition of these sites allowed us to compare how geologic vulnerability influences the presence and concentrations of CECs in groundwater and drinking water. These sites were selected using similar land use criteria established in Phase 1 of the project.

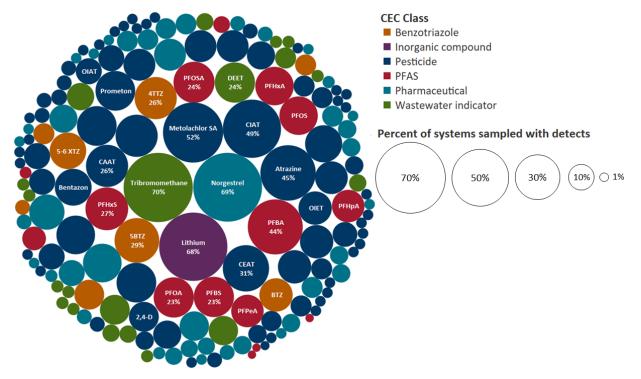
QA/QC. Quality control samples were collected at 10 percent of sites from each network and were randomly selected. Several quality control samples were collected during both phases, including field replicate and field blank samples to assess potential variability and contamination associated with sample collection and handling. A total of four field replicate samples were collected during Phase 1, and three were collected during Phase 2. A total of 89 comparisons could be made between environmental and replicate sample concentrations (i.e., a contaminant was detected in the environmental sample, replicate sample, or both); of those comparisons, relative percent difference could be calculated for 71 (80%) because the CEC was detected in both samples. Relative percent difference ranged from 0 to 67, with a majority below 30%, indicating good repeatability. A total of nine field blanks were collected. Three different CECs were detected between two of the field blanks: norgestrel, nicosulfuron, and tri(2-butoxyethyl) phosphate. To reduce uncertainty associated with potential contamination, environmental concentrations of these three CECs were considered non-detects if they were <10 times the maximum concentration in blank samples. Additionally, laboratory quality issues associated with the mestranol results were identified, and mestranol concentrations were removed.

## Results

The charts and tables below aim to highlight the most frequently detected CECs in each network and within each contaminant group and are not comprehensive. The complete dataset for this project is available in a USGS data release (Elliott, 2023).

## All sites

Of the 522 distinct CECs analyzed (Appendix A) in samples collected during Phase 1 and Phase 2, 161 (32%) unique chemicals were detected<sup>6</sup>. The CEC detections included 76 pesticides (or pesticide degradates), 41 pharmaceuticals, 20 wastewater indicators, 15 PFAS, 8 benzotriazoles, and lithium (Figure 4). Table 3 summarizes key results and Figure 4 provides an overall qualitative depiction of study results. Wastewater indicators and pharmaceuticals were generally detected less frequently than pesticides and PFAS, although some wastewater indicators and pharmaceuticals were detected frequently (e.g., tribromomethane, or bromoform, and norgestrel).



# Figure 4. Summary of CECs detected at all sites (N = 107) by class and relative frequency of detection.

Each dot represents an individual contaminant within a class. The size of the dot represents the percentage of sites at which the contaminant was detected, based on the number of sites at which it was analyzed. Five frequently detected contaminants across all sites include: tribromomethane (70%), norgestrel (68%), lithium (68%), metolachlor SA (52%), and CIAT (49%).

<sup>&</sup>lt;sup>6</sup> Detections include 1) results quantified above the method reporting limit and 2) results estimated below the method reporting limit and above the method detection limit.

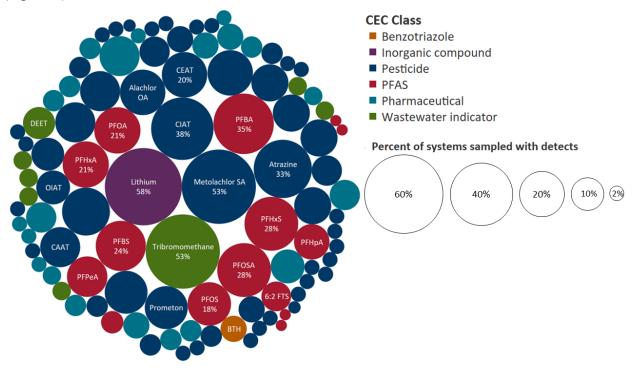
## Table 3. Overall summary of results.

Contaminant of Emerging Concern (CEC) class	Total number detected	Percent of sites with ≥1 detection (%)	Maximum number detected in a sample	Most frequently detected CEC			
Vulnerable agriculture sites (n=30)							
Pesticides	48	95	10	Metolachlor SA			
PFAS	11	73	11	PFBA			
	Non-vi	ulnerable agricultu	re sites (n=15)				
Pesticides	16	47	6	Deethylcyanazine acid			
PFAS	9	67	7	PFOSA			
	Vuln	erable wastewater	sites (n=30)				
Wastewater indicators	20	95	10	Bromoform			
Pharmaceuticals	17	68	6	Sulfamethoxazole			
PFAS	11	64	9	PFBA			
	Non-vu	Inerable wastewat	ter sites (n=15)				
Pharmaceuticals	1	7	1	Diphenhydramine			
PFAS	3	40	2	PFOSA			
	Vulnerable	e agriculture/waste	ewater sites (n=8)				
Pesticides	17	75	9	Metolachlor SA			
PFAS	11	63	10	PFBA			
Pharmaceuticals	13	50	9	Sulfamethizole Carbamazepine			
Wastewater indicators	5	88	4	Bromoform			

Contaminant of Emerging Concern (CEC) class	Total number detected	Percent of sites with ≥1 detection (%)	Maximum number detected in a sample	Most frequently detected CEC
		Surface water sites	; (n=17)	
Pesticides	55	94	35	Atrazine
PFAS	11	94	8	PFBA
Pharmaceuticals	30	94	7	Metformin
Wastewater indicators	18	100	10	Bromoform
Benzotriazoles/ benzothiazoles	8	69	6	4-methyl benzotriazole
Hormones	4	19	2	Androsterone
Illicit drugs	1	6	1	MDMA

## Groundwater sites (agriculture and wastewater networks)

A total of 100 CECs were detected across all 90 groundwater sites. One wastewater indicator, lithium, 14 pesticides and degradates, 1 pharmaceutical, and 9 PFAS were detected in more than 20% of samples collected from all groundwater sites (Figure 5). Generally, pesticides and pharmaceuticals were less frequently detected at groundwater sites when compared with surface water sites. Only one benzotriazole/benzothiazole was detected at a groundwater site (Figure 5).



# Figure 5. Summary of CECs detected at groundwater sites (N = 90) by class and relative frequency of detection.

Each of dot represents an individual contaminant within a class. The size of the dot represents the percentage of sites at which the contaminant was detected, based on the number of sites at which it was analyzed. Five frequently detected contaminants across groundwater sites include: lithium (58%), tribromomethane (53%), metolachlor SA (53%), CIAT (38%), and PFBA (35%).

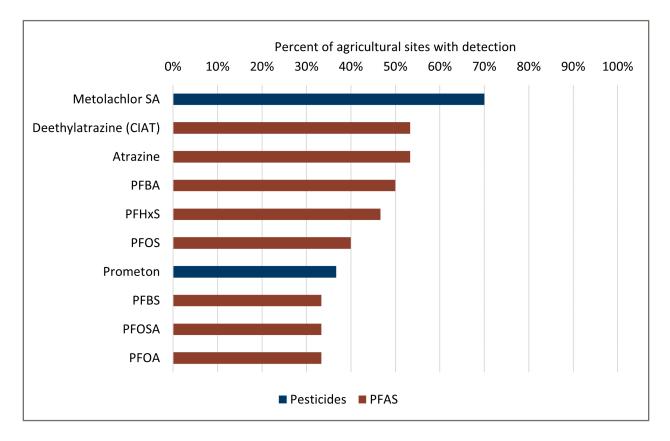
The detailed analytical results by monitoring network are presented in the following sections. Results from the agriculture sites are presented first, followed by results from the wastewater, agriculture/wastewater, and surface water sites.

## Agriculture network sites

## **Results summary**

- No pesticides or pesticide degradates detected in agricultural network samples exceeded available drinking water guidance values. Additionally, no PFAS compound exceeded available drinking water guidance values.
- Pesticides were more frequently detected in samples from source and finished waters collected from sites located within vulnerable geologic settings (2019) than in samples from sites located in non-vulnerable settings (2021).
- The most frequently detected pesticide was metolachlor SA.
- Pesticide degradates were detected more frequently in finished water samples than in source water samples. These results will be evaluated more rigorously to determine if it is a statistically significant difference.
- Similar numbers of individual PFAS were detected at both vulnerable and nonvulnerable sites.
- The most frequently detected PFAS compounds were PFBA, PFHxS, and PFOSA.
- Concentrations of PFAS were similar in source and finished water samples, but higher concentrations were generally observed in water samples collected from vulnerable sites than the concentrations at non-vulnerable sites.

Pesticides, pesticide degradates, and PFAS comprised the majority of CECs analyzed at agriculture sites. Figure 6 displays the ten CECs that were most frequently detected at geologically vulnerable agriculture sites. Three pesticides, including pesticide degradates, were detected at more than 50% of the sites sampled: metolachlor ethanesulfonic acid (SA), deethylatrazine (CIAT), and atrazine. Total atrazine represents the combined concentration of atrazine and its degradates analyzed by Eurofins Eaton Analytical. Three PFAS were also commonly detected in at least 40% of vulnerable sites: PFBA, PFHxS, and PFOS.



# Figure 6. Ten most frequently detected CECs at vulnerable agriculture sites (N = 30).

The remainder of this section presents information about the vulnerable network sites, the non-vulnerable network sites, and the spatial distribution of the detections for samples collected from groundwater agricultural network wells. See 'Site Selection' subsection in 'Methodology' for description of how sites were identified as vulnerable or non-vulnerable.

## Vulnerable agricultural sites

Thirty vulnerable agricultural sites were first sampled in 2019. Source and finished water samples were analyzed for the presence of up to 230 pesticides and pesticide degradates, and up to 40 PFAS (Table 4).

Pesticides and/or pesticide degradates were detected at all but three sites. Eleven pesticides and/or pesticide degradates were detected in more than 20% of samples collected from vulnerable agriculture sites (Table 4). A total of 40 pesticides and/or pesticide degradates were detected in at least one sample, with 37 detected in source water samples and 33 detected in finished water samples. The maximum number of pesticides and pesticide degradates detected in a sample was 13.

# Table 4. Pesticides and pesticide degradates detected in >20% of source andfinished water samples collected from vulnerable agriculture sites.

Dash (--) indicates no available guidance value.

Pesticide	Source water detection frequency (%)	Source water maximum concentration (ng/L)	Finished water detection frequency (%)	Finished water maximum concentration (ng/L)	Lowest drinking water guidance value <sup>a</sup> (ng/L)
Metolachlor SA	57	4,910	71	2,470	800,000 <sup>b</sup>
Atrazine	50	94.3	46	80.9	3,000 <sup>b</sup>
Deethylatrazi ne (CIAT)	43	111	36	108	3,000 <sup>b</sup>
N,N-diethyl- meta- toluamide (DEET)	38	17.3	38	120	200,000 <sup>b</sup>
Metolachlor oxanilic acid (OA)	33	1,130	25	1,200	800,000 <sup>c</sup>
Prometon	33	31.9	36	11.3	100,000°
Alachlor oxanilic acid (OA)	30	98.5	36	106	50,000 <sup>d</sup>
Deethylcyanaz ine acid	27	160	30	160	1,000 <sup>d</sup>
Hydroxydeeth yl atrazine (OIAT)	27	29.1	18	18.4	
2- hydroxyatrazi ne (OIET)	23	120	29	44.3	
Cyanazine acid	21	65	12	63	1,000 <sup>b</sup>

<sup>a</sup> Minnesota Department of Health <u>Human Health-Based Water Guidance Table</u>

- <sup>b</sup> Health risk limit
- <sup>c</sup> Health based value
- <sup>d</sup> Risk assessment advice

Metolachlor SA was the most frequently detected pesticide degradate in source water and finished water samples. It was detected in 57% of source water samples and 71% of finished water samples. It is not known why frequency of occurrence is different between source and finished samples. Future analysis will evaluate the statistical significance of results. Individual pesticide and pesticide degradate concentrations range from 1.0 to 4.910 ng/L in source water samples, and from 1.04 to 2,510 ng/L in finished water samples (Table 5). Our findings generally align with the MDA's private well and ambient groundwater monitoring program (MDA, 2022), in which similar types of pesticides were detected frequently and maximum concentrations were within similar ranges.

In 2021, cyanazine and cyanazine degradates were analyzed at vulnerable and non-vulnerable agriculture sites. Total cyanazine<sup>7</sup> (the sum of cyanazine and cyanazine degradate concentrations) is used for determining the health risk associated with drinking water that may contain cyanazine and its degradates. Maximum concentrations of total cyanazine were 288 ng/L and 284 ng/L in source and finished waters collected from vulnerable agriculture sites, respectively. Maximum concentrations in source and finished waters collected from non-vulnerable sites were 26 ng/L and 7.3 ng/L, respectively. There were no exceedances of the 1,000 ng/L cumulative drinking water guidance value.

At least one PFAS was detected at 70% of sampled sites. A total of 8 PFAS were detected in >20% of sites collected from the agriculture sites (Table 5). One sample contained 14 different PFAS contaminants. Source water samples contained 12 distinct PFAS and finished water samples contained 14. The maximum number of PFAS detected in any sample was 11.

<sup>&</sup>lt;sup>7</sup> For this study, total cyanazine represents the sum of cyanazine, cyanazine acid, cyanazine amide, deethylcyanazine, deethylcyanazine acid, and deethylcyanazine amide.

# Table 5. PFAS detected in >20% of source and finished water samples collected from vulnerable agriculture sites.

PFAS	Source water detection frequency (%)	Source water maximum concentration (ng/L)	Finished water detection frequency (%)	Finished water maximum concentration (ng/L)	Lowest drinking water guidance value <sup>a</sup> (ng/L)
PFBA	42	436	46	368	7,000 <sup>b</sup>
PFHxS	39	5.74	38	6.81	47 <sup>c</sup>
PFOS	35	8.58	31	8.27	15 <sup>c</sup>
PFOA	32	19.9	27	18	35 <sup>b</sup>
PFBS	32	4.76	31	5.02	100 <sup>c</sup>
PFHxA	29	14.7	31	14.7	200 <sup>c</sup>
PFPeA	26	24.1	27	20.5	
РҒНрА	23	3.79	23	3.93	

<sup>a</sup> Minnesota Department of Health <u>Human Health-Based Water Guidance Table</u>

<sup>b</sup> Health risk limit

<sup>c</sup> Health based value

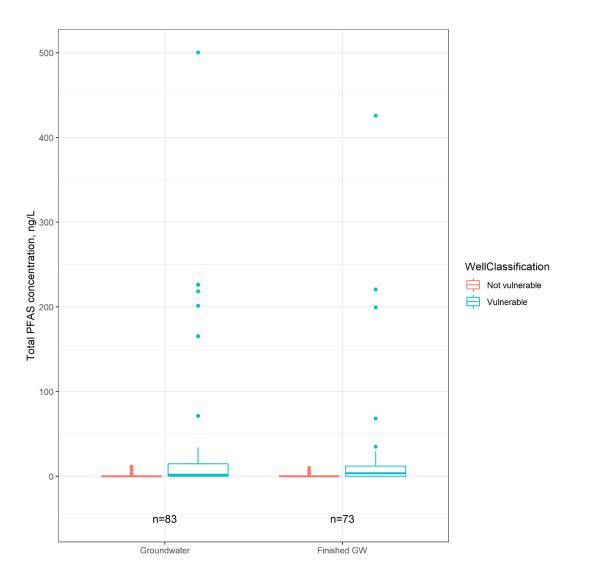
PFBA was the most frequently detected PFAS in source water and finished water samples. PFBA was detected in 42% of source water samples and 46% of finished water samples. Except for PFOSA, which was detected more frequently in finished water compared to source water samples, the relative order of PFAS by detection frequency was similar in source and finished water samples. Most concentrations of individual PFAS were below 25 ng/L. The maximum total PFAS sample concentration (sum of all detected PFAS within a sample) was 500 ng/L, with generally similar total sample concentrations in source and finished water samples.

## Non-vulnerable agricultural sites

A total of 15 groundwater sites categorized as being in a non-vulnerable geologic setting and predominantly agricultural landscape were sampled during 2021. Source and finished water samples were characterized for the presence of up to 230 pesticides and pesticide degradates, and up to 40 PFAS.

A total of 16 different pesticides and pesticide degradates were detected in at least one water sample, with four detected in source water samples and 12 detected in finished water samples. At least one pesticide or pesticide degradate was detected at 47% of sampled sites. The number of pesticides and pesticide degradates detected in water samples ranged from zero to six. Detected pesticides and pesticide degradates in source water samples were found in <10% of samples; three pesticides and pesticide degradates were detected in ≥15% of finished water samples. Deethylcyanazine acid was the most frequently (33%) detected pesticide degradate in finished water samples. Concentrations ranged from 1.2 (fenamiphos; insecticide) to 6.2 ng/L (hexazinone transformation product G; herbicide degradate) in source waters and from 0.86 (prometryn; herbicide) to 1,340 ng/L (alachlor ethanesulfonic acid; herbicide degradate) in finished waters.

At least one PFAS was detected at 67% of sampled sites. A total of nine PFAS were detected in at least one water sample, with two detected in source water samples and nine detected in finished water samples. The maximum number of PFAS that were detected in any sample was seven. One PFAS was detected in >15% of source water (6:2 FTS at 20%) and finished water (PFOSA at 36%) samples. Concentrations ranged from 0.478 (PFOSA) to 11.2 (6:2 FTS) ng/L in source waters and 0.39 (PFHxA) to 6.63 (6:2 FTS) ng/L in finished waters. The number of PFAS detected and total PFAS concentrations were similar between source and finished water samples at any given site. Generally, concentrations were less than those detected at vulnerable sites (Figure 7). For example, the maximum total PFAS sample concentration was 11.2 ng/L, 40 times lower than that observed at vulnerable sites.



# Figure 7. Boxplot summary of total PFAS sample concentrations in samples collected from agriculture sites.

The median value is represented by the line within the boxes; interquartile range is represented by the box. Whiskers extend to minimum and maximum values excluding outliers. Individual dots represent outliers.

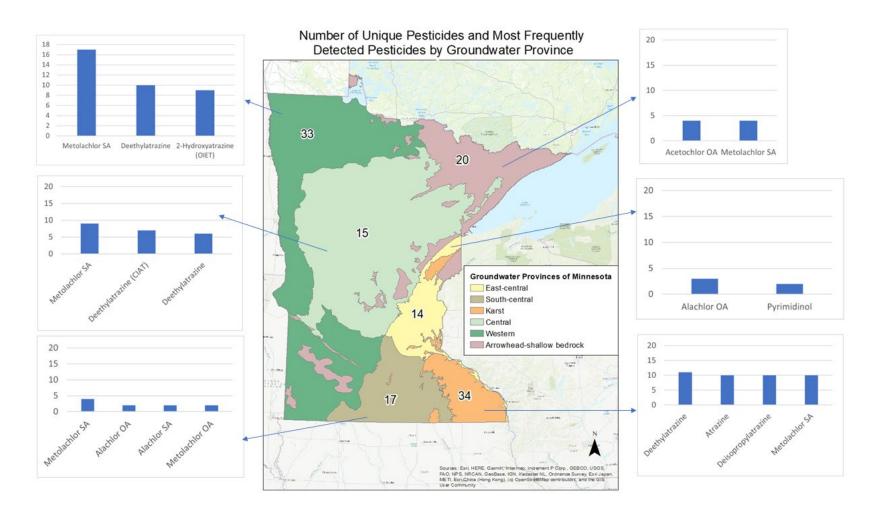
## **Spatial distribution**

Figure 8 shows the spatial distribution of pesticides detected at public water systems sampled for this project. Sampling sites were categorized according to their presence in one of the six groundwater provinces identified in the state. Geologic and hydrogeologic conditions tend to be similar within each province but differ from one province to another. For example, karst conditions are much more likely to occur in the southeast portion of the state than elsewhere

in the state. Likewise, shallow crystalline bedrock is more common in the northeast portion of the state (and a few other spotty areas) than elsewhere.

Land use also varies across the state. In areas in which agriculture dominates local land use, the crops and agricultural practices vary. For example, sugar beets are the dominant crop in the lake deposits of the former Lake Agassiz basin, whereas corn and soybeans dominate in much of the rest of the southern agricultural areas. Potatoes are a common crop in the central sands. Agriculture management (including the type and amount of pesticides used and the timing of application) approaches may vary because of setting and crop type, so it is reasonable to expect water quality to vary in different regions.

Figure 8 shows the number of pesticides and most frequently detected pesticides by groundwater province. Pesticide occurrence is similar throughout the different regions of the state, but numbers of pesticides detected and specific pesticides detected does vary (Figure 8). For example, metolachlor SA had the highest or second highest detection frequency in four out of the six groundwater provinces.



# Figure 8. Number of pesticides and pesticide degradates detected in all samples (source and finished) collected from agriculture sites (vulnerable and non-vulnerable) by groundwater province (map; MNDNR, 2021), and the most frequently detected pesticides and pesticide degradates by groundwater province.

Bar charts; y-axis is detection frequency, in percent. Map image is the intellectual property of ESRI and is used herein under license. Copyright ©2019 ESRI and its licensors. All rights reserved.

### Wastewater sites

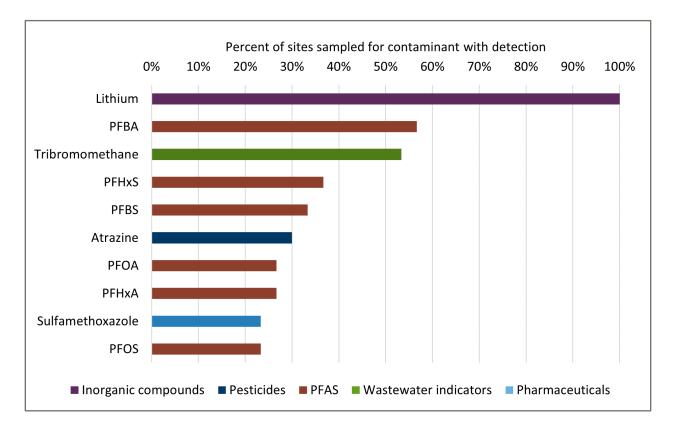
### **Results summary**

- The lowest drinking water guidance value for bromoform was exceeded at one site. Another site exceeded available drinking water guidance values for PFAS. Two sites exceeded the drinking water guidance value for pentachlorophenol.
- Few wastewater indicators and pharmaceuticals were present in >15% of water samples from both vulnerable (2019) and non-vulnerable (2021) sites.
- Bromoform (disinfection byproduct) was frequently detected in finished water samples collected from vulnerable sites (no data for non-vulnerable), and at a higher rate compared to source water samples.
- PFAS were detected less frequently and at lower concentrations in water samples collected from non-vulnerable sites, compared to vulnerable sites.
- The most frequently detected PFAS at vulnerable sites was PFBA.

### **All wastewater sites**

The water samples from 45 sites in the wastewater network were analyzed for hundreds of CECs, including PFAS, wastewater indicators, and pharmaceuticals. The ten most frequently detected CECs are presented in Figure 9. All samples contained detectable lithium<sup>8</sup>, which is likely geogenic in Minnesota waters (Hem, 2005; Lindsay, et al, 2021), although there are possible anthropogenic sources as well. Tribromomethane, or bromoform, a disinfection by-product, was detected at 21 of the 30 vulnerable sites (70%). Six of the 10 most frequently detected CECs were PFAS, detected at eight or more sites: PFBA, PFHxS, PFOS, PFBS, PFOA, and PFHxA. Atrazine was also widely detected, present at 11 of the 30 vulnerable sites (37%). Although pesticides were not analyzed at wastewater sites, atrazine was also included in the wastewater indicators from one of the analytical laboratories.

<sup>&</sup>lt;sup>8</sup> Concern about lithium in natural waters, especially drinking water sources is increasing because of its use as a human therapeutic (Sharma, et al, 2022), its reported linkage to thyroid functions (Broberg, et al, 2011), and because of its increased use in battery production (Lindsay, et al, 2021; Sharma, et al, 2022). Consequently, US EPA includes lithium in the fifth UCMR (UCMR5) (US EPA, 2021).



### Figure 9. Ten most frequently detected CECs at vulnerable wastewater sites (N=30).

The remainder of this section regarding results from the wastewater network will separately present the results from the vulnerable sites and the non-vulnerable sites.

### **Vulnerable wastewater sites**

A total of 30 groundwater public water systems categorized as being in a vulnerable geologic setting and predominately urban (including suburban and exurban) landscape were sampled during 2019. Source and finished water samples were analyzed for the presence of up to 61 wastewater indicators, 110 pharmaceuticals, 33 PFAS, and lithium.

At least one wastewater indicator was detected at all but three sites. A total of 23 wastewater indicators were detected in at least one sample, with 17 detected in source water samples and 14 detected in finished water samples. The maximum number of wastewater indicators detected in any sample was ten. A total of six wastewater indicators were detected in >10% of samples (Table 6).

## Table 6. Wastewater indicators detected in >10% of source and/or finishedwater samples collected from vulnerable wastewater sites.

Wastewater indicator	Source water detection frequency (%)	Source water maximum concentration (ng/L)	Finished water detection frequency (%)	Finished water maximum concentration (ng/L)	Lowest drinking water guidance value <sup>a</sup> (ng/L)
Atrazine	32	37.4	22	38.3	3,000 <sup>b</sup>
Prometon	14	20	17	10	100,000°
Bromoform	13	6,300	77	40,900	40,000 <sup>b</sup>
Nicotine	13	39	0		
DEET	9	30	11	30	200,000 <sup>b</sup>
Bromacil	5	10	11	20	70,000 <sup>d</sup>

Dash (--) indicates no available guidance value.

<sup>a</sup> Minnesota Department of Health <u>Human Health-Based Water Guidance Table</u>

<sup>b</sup> Health risk limit

<sup>c</sup> Health based value

<sup>d</sup> EPA health advisory

The most frequently detected wastewater indicators were atrazine (32%) in source water and bromoform (77%) in finished water samples. Concentrations of wastewater indicators ranged from 6.7 to 6,300 ng/L in source water samples, and from 4 to 40,900 ng/L in finished water samples.

At least one pharmaceutical was detected at 63% of sampled sites. A total of 22 distinct pharmaceuticals were detected in at least one sample, with 18 detected in source water samples and 16 detected in finished water samples. The maximum number of pharmaceuticals detected in any one sample was nine. Sulfamethoxazole was detected in >20% of source water samples and acetaminophen was detected in 15% of finished water samples. Generally, fewer numbers of pharmaceuticals and total pharmaceutical concentrations were lower in finished water samples, compared to source water.

At least one PFAS was detected at 63% of sampled sites. A total of 13 PFAS were detected in at least one sample, with 12 detected in source water samples and 11 detected in finished water samples. The maximum number of PFAS detected in any sample was nine. Table 7 summarizes the PFAS detection frequency and maximum observed concentrations for PFAS detected in ≥15% of samples.

## Table 7. PFAS detected in ≥15% of source and finished water samples collected from vulnerable wastewater sites.

Dash (--) indicates no available guidance value.

PFAS Contaminant	Source water detection frequency (%)	Source water maximum concentration (ng/L)	Finished water detection frequency (%)	Finished water maximum concentration (ng/L)	Lowest drinking water guidance value <sup>a</sup> (ng/L)
PFBA	45	190	54	175	7,000 <sup>b</sup>
PFHxS	32	5.74	31	5.34	47 <sup>c</sup>
PFBS	26	3.72	35	3.04	100 <sup>c</sup>
PFHxA	23	14.7	23	14.7	200 <sup>c</sup>
PFOA	19	19.9	23	18	35 <sup>b</sup>
PFPeA	19	11.2	15	8.12	

<sup>a</sup> Minnesota Department of Health <u>Human Health-Based Water Guidance Table</u>

<sup>b</sup> Health risk limit

<sup>c</sup> Health based value

PFBA was detected in 54% of finished water samples and 45% of source water samples. Generally, the order of PFAS from greatest to least detected was similar for source and finished water samples; maximum concentrations were generally similar between source and finished water samples as well. By site, the number of PFAS detected and total PFAS concentrations were similar between source and finished water samples.

Lithium was detected in every source and finished water sample. Concentrations ranged from 2,790 to 109,000 ng/L in source water samples and from 2,820 to 77,600 ng/L in finished water samples. Generally, concentrations were similar in source and finished water samples.

### Non-vulnerable sites

A total of 15 groundwater public water system sites categorized as being in a non-vulnerable geologic setting and predominately urban (including suburban and exurban) landscape were sampled during 2021 in Phase 2 of the project. Source and finished water samples were characterized for the presence of up to 110 pharmaceuticals, up to 40 PFAS, and 9 benzotriazoles and benzothiazoles.

One pharmaceutical (diphenhydramine, an antihistamine) was detected in one source water sample at a concentration of 0.69 ng/L. This is a lower proportion of sites with a detection in

either source or finished water, compared to vulnerable sites (7% of non-vulnerable sites versus 68% of vulnerable sites).

At least one PFAS was detected at 40% of sampled sites. A total of three PFAS were detected in at least one sample, with two unique PFAS detected in both source and finished water samples. The maximum number of PFAS detected in any sample was two. PFOSA was detected in 20% of source samples and 33% of finished water samples. Total PFAS concentrations in individual samples was substantially lower in samples collected from non-vulnerable wastewater sites, compared to vulnerable wastewater sites.

While incidence and concentrations of some pharmaceuticals and PFAS in samples from nonvulnerable geologic settings appear to be lower than from vulnerable environments, this finding will be more fully evaluated in future assessments of data from this study. For PFAS, additional efforts to more fully represent PFAS occurrence and distribution in Minnesota drinking water is currently underway as part of the Statewide PFAS Initiative (see <u>PFAS Testing in Public Water</u> <u>Systems</u>).

One benzotriazole (benzothiazole; multiple uses including corrosion inhibitor and ultraviolet light stabilizer) was detected in one finished water sample at a concentration of 180 ng/L. Benzotriazoles and benzothiazoles were not characterized at vulnerable wastewater sites. Thus, no comparisons between the two vulnerable classifications could be made.

### **Spatial Distribution**

Figure 10 shows the observed water quality measured by numbers of unique wastewater indicators detected by groundwater province and by the specific contaminants detected by region. Lithium was frequently detected in each region; atrazine and tribromomethane, or bromoform, were each frequently detected in four of the six groundwater provinces.

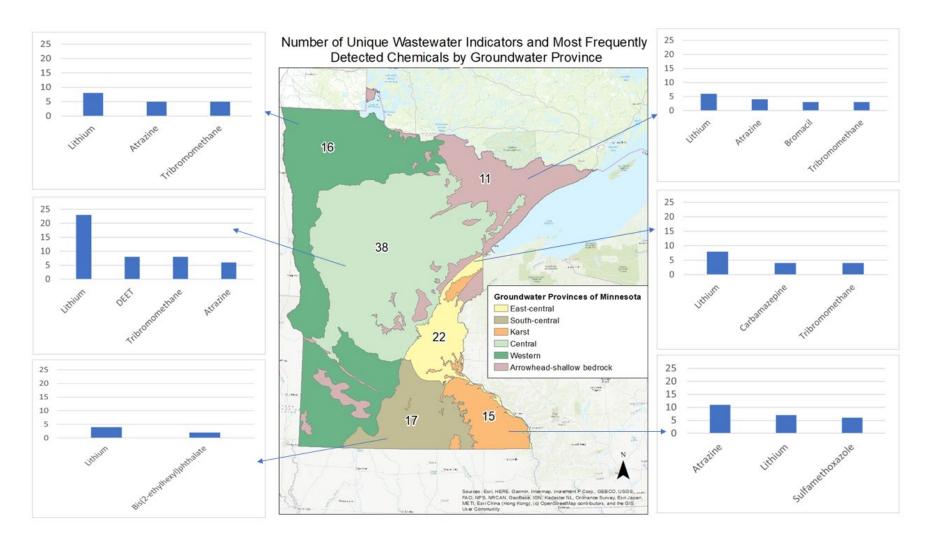


Figure 10. Number of unique wastewater indicators detected in all samples (source and finished) collected from wastewater sites (vulnerable and non-vulnerable) by groundwater province (map; MNDNR, 2021) and the most frequently detected wastewater indicators by groundwater province (bar charts; y-axis is detection frequency, in percent).

Map image is the intellectual property of ESRI and is used herein under license. Copyright ©2019 ESRI and its licensors. All rights reserved.

### Agriculture/wastewater sites

Eight groundwater public water system sampling sites are part of both the agriculture and wastewater networks. Although results were incorporated into the separate agriculture and wastewater network summaries, they are also presented here. Future assessment will attempt to determine if this set of results is quantitatively different for any of the parameters analyzed from the results from either the agricultural or the wastewater networks.

### Agriculture/wastewater results summary

- The most frequently detected pesticides and pesticide degradates were herbicide degradates.
- No pesticides or pesticide degradate concentrations exceeded available drinking water guidance values.
- More than half of the detected PFAS were present in >15% of samples.
- No PFAS concentrations exceeded available drinking water guidance values.
- Sulfamethizole and carbamazepine were the most frequently detected pharmaceuticals.
- Fewer wastewater indicators were detected in source and finished water samples collected from agriculture/wastewater sites, compared to all other water samples where OWCs were measured.

### **Vulnerable sites**

A total of eight groundwater public water systems categorized as being in a vulnerable geologic setting and mixed agriculture/urban landscape were sampled during 2019. Source and finished waters were characterized for the presence of up to 230 pesticides, up to 40 PFAS, up to 110 pharmaceuticals, lithium, and up to 61 wastewater indicators.

At least one pesticide or pesticide degradate was detected at 75% of sampled sites. A total of 17 pesticides and pesticide degradates were detected in at least one sample, with 13 detected in source water samples and 15 detected in finished water samples. The maximum number of pesticides and pesticide degradates detected in any one sample was nine. Table 8 lists the pesticides and pesticide degradates that were detected in ≥25% of samples collected from vulnerable agriculture/wastewater sites.

## Table 8. Pesticides and pesticide degradates detected in ≥25% of source and/or finished water samples collected from vulnerable agriculture/wastewater sites.

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Pesticide Contaminant	Source water detection frequency (%)	Source water maximum concentration (ng/L)	Finished water detection frequency (%)	Finished water maximum concentration (ng/L)	Lowest drinking water guidance value <sup>a</sup> (ng/L)
Deethylatrazine	38	16.2	0		3,000 <sup>b</sup>
Metolachlor SA	38	486	50	515	800,000 <sup>c</sup>
DEET	38	100	38	120	200,000 <sup>c</sup>
Alachlor OA	38	37.1	38	31.1	50,000 <sup>b</sup>
Hydroxyatrazine	38	21.9	38	14.4	
Prometon	38	21.7	38	10.7	100,000 <sup>d</sup>
Atrazine	38	8.26	25	6.85	3,000 <sup>c</sup>
Metolachlor OA	25	111	25	72	800,000 <sup>d</sup>
Metolachlor	25	41.4	29	21.7	300,000°
Dechlorometolachlor	25	12.4	13	12.4	

<sup>a</sup> Minnesota Department of Health <u>Human Health-Based Water Guidance Table</u>

<sup>b</sup> Risk assessment advice

<sup>c</sup> Health risk limit

<sup>d</sup> Health based value

Four different pesticides and pesticide degradates were detected in 38% of source water samples, and three of those also were detected at the greatest frequency in the finished water samples. Dethylatrazine was most commonly detected in source water samples at 38%. Metolachlor SA was most frequently detected in finished water samples at 50% (Table 8). Concentrations of pesticide and pesticide degradates ranged from 1.6 to 486 ng/L in source water samples, and from 1.3 to 515 ng/L in finished water samples. Generally, the number of pesticides detected was similar between source and finished water samples at any given site.

At least one PFAS was detected at 63% of sampled sites. A total of 11 PFAS were detected in at least 1 sample, with 10 distinct compounds detected in source water samples and 10 distinct

compounds detected in finished water samples. The maximum number of PFAS detected in any one sample was 10. PFAS detected in more than 10% of samples collected from vulnerable agriculture/wastewater sites are summarized in Table 9.

### Table 9. PFAS detected in >10% of source and finished water samples collected from vulnerable agriculture/wastewater sites.

PFAS Contaminant	Source water detection frequency (%)	Source water maximum concentration (ng/L)	Finished water detection frequency (%)	Finished water maximum concentration (ng/L)	Lowest drinking water guidance value <sup>a</sup> (ng/L)
PFOS	33	8.58	38	8.27	15 <sup>b</sup>
PFHxS	33	5.74	25	5.34	47 <sup>c</sup>
PFOA	22	19.9	13	18	35 <sup>b</sup>
PFHxA	22	14.7	25	14.7	200 <sup>c</sup>
PFBA	22	9.71	50	9.44	7,000 <sup>b</sup>
PFPeA	22	6.22	25	5.78	
PFBS	22	1.55	25	1.24	100 <sup>c</sup>
РҒНрА	11	3.79	13	3.93	
PFNA	11	1.21	13	.891	

Dash (--) indicates no available guidance value.

<sup>a</sup> Minnesota Department of Health <u>Human Health-Based Water Guidance Table</u>

<sup>b</sup> Health risk limit

<sup>c</sup> Health based value

PFOS and PFHxS were the most frequently detected PFAS in source water samples at 33%, while PFBA was most frequently detected in finished water samples at 50%. Total PFAS sample concentrations were <100 ng/L. Generally, similar numbers of PFAS and total sample concentrations were similar between source and finished water samples.

At least one pharmaceutical was detected at 50% of sampled sites. A total of 13 pharmaceuticals were detected in at least 1 sample, with 11 detected in source water samples and 8 detected in finished water samples. The maximum number of pharmaceuticals detected in a sample was nine.

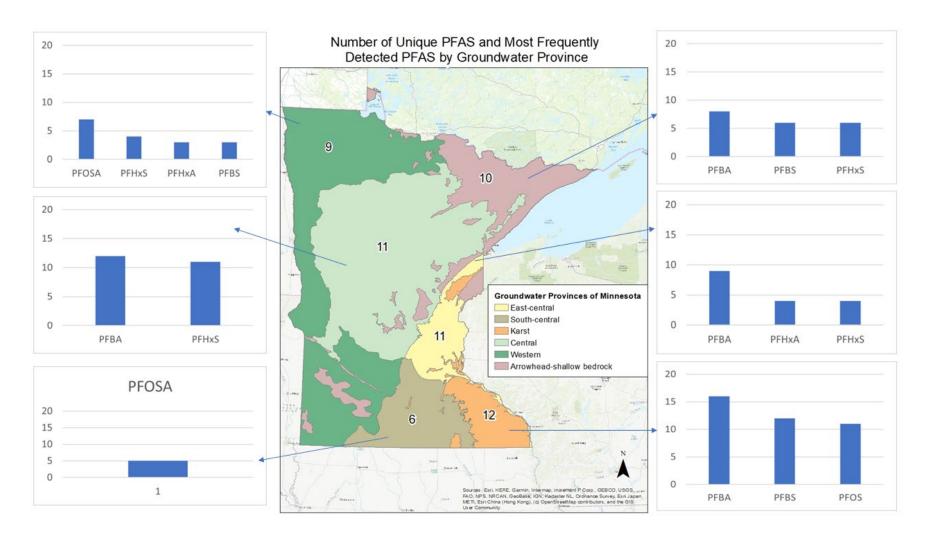
One pharmaceutical was detected in ≥15% of source water samples (sulfamethizole at 25%) and finished water samples (carbamazepine at 25%). Concentrations of individual pharmaceuticals ranged from 0.73 to 2,040 ng/L in source water samples, and from 1.5 to 76.2 ng/L in finished water samples. When comparisons could be made, individual pharmaceuticals had similar detection frequencies and maximum concentrations between source and finished water samples.

Lithium was detected in every source and finished water sample. Concentrations ranged from 1,620 to 60,500 ng/L in source water samples and from 1,700 to 34,000 ng/L in finished water samples. Generally, concentrations were similar in source and finished water samples collected from any given site.

At least one wastewater indicator was detected at every site, except one. A total of five wastewater indicators were detected in at least one sample, with five detected in source water samples and three detected in finished water samples. The maximum number of wastewater indicators detected in a sample was four. All wastewater indicators detected in source water samples were detected in <15% of samples. Bromoform and isophorone (industrial compound) were detected in 50% and 25% of finished water samples, respectively. Concentrations of individual wastewater indicators ranged from 14 to 6,300 ng/L in source water samples, and from 4 to 22,500 ng/L in finished water samples. Detection frequencies of individual wastewater indicators and maximum concentrations were generally similar between source and finished waters.

### **Spatial Distribution**

Figure 11 below shows the observed water quality measured by numbers of unique PFAS detected by groundwater province and by the specific PFAS detected by region. PFBA was the most frequently detected PFAS in the arrowhead, east-central, karst, and central groundwater provinces (Figure 11); PFOSA was the most frequently detected PFAS in the western and south-central provinces. PFHxS was also frequently detected across different regions of the state (four out of the six groundwater provinces).



# Figure 11. Number of unique PFAS detected in all samples (source and finished) collected from vulnerable groundwater sites by groundwater province (map; MNDNR, 2021) and the most frequently detected PFAS by groundwater province (bar charts; y-axis is detection frequency, in percent).

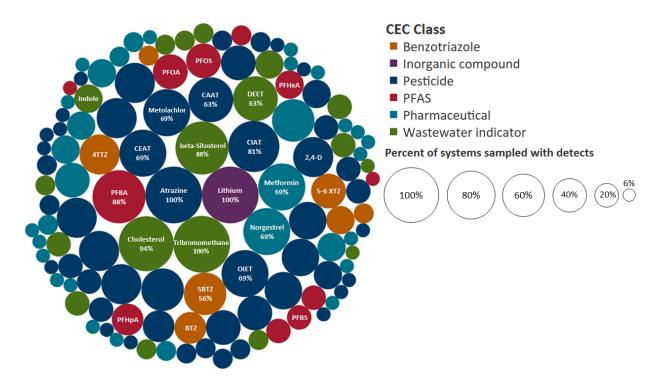
Map image is the intellectual property of ESRI and is used herein under license. Copyright ©2019 ESRI and its licensors. All rights reserved

### Surface water sites

### **Results summary**

- More pesticides and pesticide degradates were present in water samples collected from surface water sourced sites, compared to groundwater sourced sites.
- Atrazine was the most frequently detected pesticide.
- No pesticides or pesticide degradate concentrations exceeded available drinking water guidance values.
- Similar numbers of PFAS were detected in samples collected from surface water sites, compared to groundwater sites, but total PFAS sample concentrations were lower.
- No PFAS concentrations exceeded available drinking water guidance values. Drinking water guidance values for pentachlorophenol were exceed at four sites. Guidance values for bromoform were exceeded at one site.
- Metformin was the most frequently detected pharmaceutical.
- A plant sterol and an animal sterol were the most frequently detected wastewater indicators.
- Hormones were detected in <10% of samples.

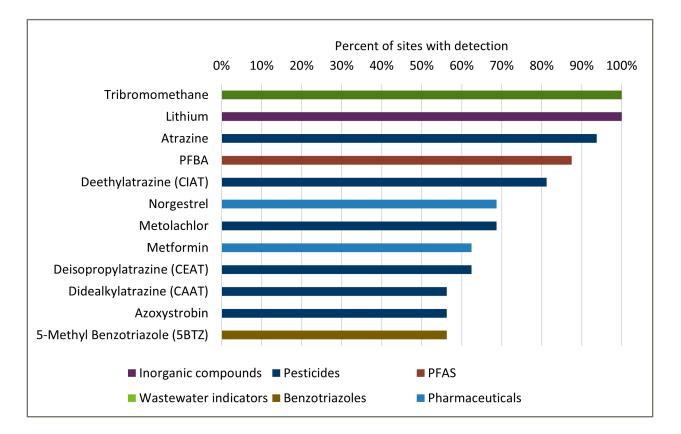
Across the 17 surface water sites, 115 CECs were detected in both source and finished drinking water. There was wide representation of the major CEC classes in the surface water network (Figure 12). Twenty pesticides and three wastewater indicators were detected in  $\geq$ 20% of source and finished water samples across sites. Eleven PFAS were detected, though they were not as dominant compared to the groundwater sites (Figure 12; Figure 5). One inorganic compound, lithium, was detected at all sites. More pharmaceuticals were detected than at the groundwater sites (Figure 12; Figure 5), and at a higher relative frequency. Seven benzotriazoles and benzothiazoles were detected in surface water sites, compared to one across groundwater sites (Figure 12; Figure 5).



## Figure 12. Summary of CECs detected at surface water sites (N = 17) by class and relative frequency of detection.

Each dot represents an individual contaminant within a class. The size of the dot represents the percentage of sties at which the contaminant was detected, based on the number of sites at which it was analyzed. Frequently detected contaminants across surface water sites include: lithium (100%), atrazine (100%), tribromomethane (100%), cholesterol (94%), PFBA (88%), and beta-Sitosterol (88%).

Three CECs were detected at all 17 surface water sites: tribromomethane, or bromoform, lithium, and atrazine (Figure 13). Cholesterol and beta-sitosterol were commonly detected wastewater indicators, at 15 and 14 sites, respectively. PFBA was the most frequently detected PFAS, at 14 of the sites (88%). Deethylatrazine (CIAT), metolachlor, deisopropylatrazine (CEAT), and 2-hydroxyatrazine (OIET) were the most frequently pesticides and pesticide degradates, detected at 69% or more of the sites. Two pharmaceuticals, norgestrel and metformin, were detected at 11 sites (69%).



### Figure 13. Most frequently detected CECs at surface water sites (N=34).

### Selection of 10 most frequently detected CECs from network; 13 shown due to same detection frequencies.

A total of 17 surface water public water system sites were sampled twice in 2019 during the period of August to November. The following summary accounts for both water samples related to number of detections in individual samples and total sample concentrations, but detection frequencies and concentrations of individual CECs reflect results from all samples. Source and finished waters were characterized for the presence of 230 pesticides, 33 PFAS, 110 pharmaceuticals, 61 wastewater indicators, benzotriazoles and benzothiazoles, 17 hormones, 4 illicit drugs, and lithium.

At least one pesticide or pesticide degradate was detected at all sites except one, for both sample events. A total of 55 pesticides and pesticide degradates were detected in at least one sample, with 53 detected in source water samples and 33 detected in finished water samples. The maximum number of pesticides and pesticide degradates detected in a sample was 35. Atrazine was the most frequently detected pesticide in both source and finished waters (Table 10). Furthermore, several atrazine degradates were detected in >30% of source water and/or finished water samples.

## Table 10. Pesticides and pesticide degradates detected in >40% of source and/or finished water samples collected from surface water sites.

Dash (--) indicates no available guidance value.

Pesticide Contaminant	Source water detection frequency (%)	Source water maximum concentratio n (ng/L)	Finished water detection frequency (%)	Finished water maximum concentratio n (ng/L)	Lowest drinking water guidance value <sup>a</sup> (ng/L)
Atrazine	88	363	84	160	3,000 <sup>b</sup>
Metolachlor	62	211	48	214	300,000 <sup>b</sup>
Deethylatrazine	62	84.6	45	64.8	3,000 <sup>b</sup>
Metolachlor SA	50	1,210	45	772	800,000 <sup>b</sup>
Dechlorometolachlor	50	42.1	26	20.7	
Didealkylatrazine	50	101	14	89	1,000 <sup>c</sup>
Desamino metribuzin	47	109	0		10,000 <sup>c</sup>
Acetochlor OA	44	1,520	39	882	
Hydroxyatrazine	44	176	35	86.3	
2,4-D	44	141	16	97.2	30,000 <sup>b</sup>

<sup>a</sup> Minnesota Department of Health <u>Human Health-Based Water Guidance Table</u>

<sup>b</sup> Health risk limit

<sup>c</sup> Risk assessment advice

Concentration of individual pesticides and pesticide degradates ranged from 0.81 to 1,520 ng/L in source water samples, and from 1 to 882 ng/L in finished water samples. Generally, the number of pesticides and pesticide degradates in finished water samples were similar to or less than those in source water samples. Atrazine was the most frequently detected pesticide in source water samples (88%) and finished water samples (84%).

PFAS were detected in samples from all sites, except one during the first sample event and seven during the second. A total of 11 PFAS were detected in at least one sample, with 10 detected in source water samples and 9 detected in finished water samples. The maximum number of PFAS detected in a sample was eight. PFBA was the most frequently detected PFAS in both types of samples (Table 11). PFBA was detected in 62% of source water samples and

72% of finished water samples. Concentrations of individual PFAS ranged from 0.762 to 32.9 ng/L in source water samples, and from 0.768 to 33.2 ng/L in finished water samples.

## Table 11. PFAS detected in >15% of source and finished water samples collected from surface water sites.

PFAS Contaminant	Source water detection frequency (%)	Source water maximum concentration (ng/L)	Finished water detection frequency (%)	Finished water maximum concentration (ng/L)	Lowest drinking water guidance value <sup>a</sup> (ng/L)
PFBA	62	32.9	72	33.2	7,000 <sup>b</sup>
PFOA	26	1.95	22	2.04	35 <sup>⊳</sup>
PFOS	24	2.96	16	1.15	15 <sup>c</sup>
PFHxA	24	3.26	19	2.79	200 <sup>c</sup>
РҒНрА	21	1.22	16	1.25	

Dash (--) indicates no available guidance value.

<sup>a</sup> Minnesota Department of Health <u>Human Health-Based Water Guidance Table</u>

<sup>b</sup> Health risk limit

<sup>c</sup> Health based value

The maximum total sample PFAS concentration in samples was 50.8 ng/L. The number of PFAS detected in finished water samples was generally similar to source water samples at any given site (Figure 14); where comparisons could be made, total PFAS concentrations in finished water samples were generally slightly lower.

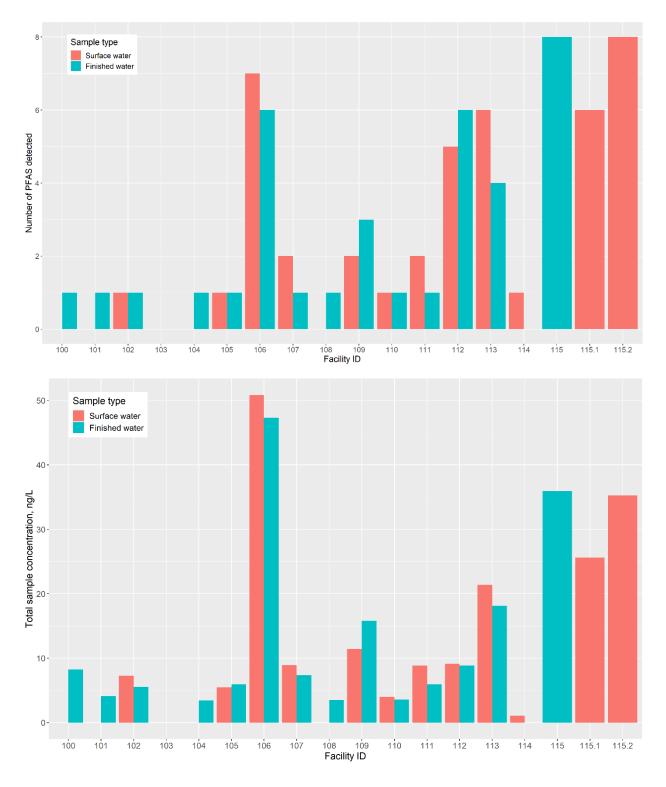


Figure 14. Number of PFAS detected (top graph) and total PFAS sample concentrations (sum of all detected PFAS within a sample; bottom graph) in source and finished water samples collected from surface water sourced sites.

Pharmaceuticals were detected at all but five sites during the first sample event and all but one during the second. A total of 30 pharmaceuticals were detected in at least 1 sample, with 23 detected in source water samples and 11 detected in finished water samples. The number of pharmaceuticals detected in samples ranged from zero to seven. Concentrations of individual pharmaceuticals ranged from 0.461 to 92.2 ng/L in source water samples, and from 0.502 to 86.2 ng/L in finished water samples. Metformin was the most frequently detected pharmaceutical with concentration ranges from 8.96 to 27.7 in both source and finished water samples. Metformin was detected in 41% of source water samples and 40% of finished water samples. During the first sample event, the number of pharmaceuticals was generally lower in finished water samples compared to source water samples. However, the opposite was true for the second sample event where more pharmaceuticals were often observed in finished water samples.

At least one wastewater indicator was detected in every sample collected from surface water sites. A total of 18 wastewater indicators were detected in at least 1 sample, with 17 detected in source water samples and 10 detected in finished water samples. The maximum number of wastewater indicators detected in any sample was ten. The most frequently detected wastewater indicator was *beta*-Sitosterol in source waters (59%) and bromoform in finished water samples (100%). Concentrations of individual wastewater indicators ranged from 2.46 to 5,400 ng/L in source water samples, and from 4.63 to 47,500 ng/L in finished water samples.

Benzotriazoles were detected at all but six sites during the first sample event and all but five sites during the second sample event. A total of eight benzotriazoles were detected in at least one sample, with eight detected in source water samples and five detected in finished water samples. The maximum number of benzotriazoles detected in any sample was six. Furthermore, benzotriazoles were not detected in any samples collected from five sites. The most frequently detected benzotriazole was 4-methyl benzotriazole in both source and finished water samples. It was detected in 53% of source water samples and 19% of finished water samples. Except for one instance, the number of benzotriazoles detected was lower in finished compared to source water samples.

Hormones were detected at three different sites; hormones were detected at one of the sites during both sample events. A total of four hormones were detected in at least one sample, with three detected in source water samples and two detected in finished water samples. The maximum number of hormones detected in any sample was two. Concentrations ranged from 0.384 ng/L (progesterone) to 73.3 ng/L (androsterone) in source water samples and from 2.67 ng/L (androstenedione) to 57.3 ng/L (androsterone) in finished water samples. One hormone was detected in a finished water sample when there were no hormones detected in the corresponding source water sample.

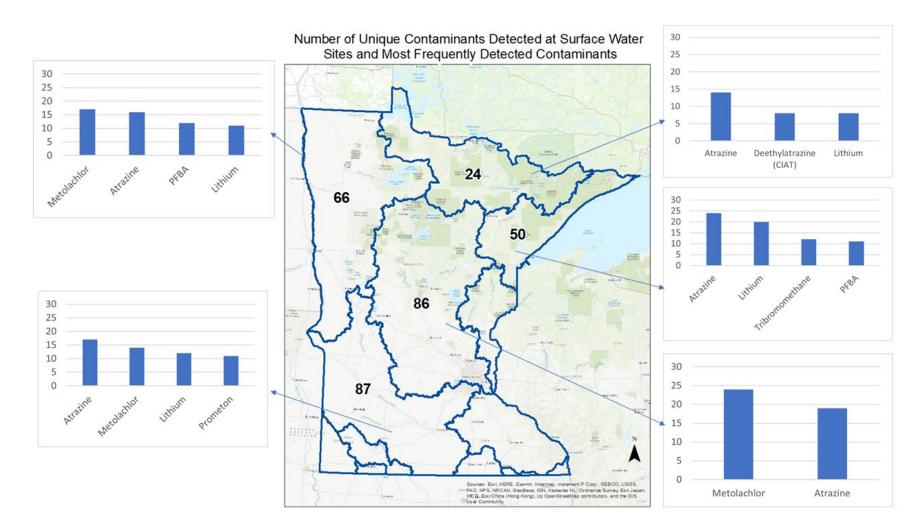
Only one illicit drug was detected. MDMA (3,4-Methylenedioxymethamphetamine, or commonly known as ecstasy) was detected in one finished water sample at a concentration of 0.95 ng/L.

Lithium was detected in all source and finished water samples. Concentrations ranged from 600 to 120,000 ng/L in source water samples and from 570 to 77,700 ng/L in finished water samples. Lithium concentrations were generally similar in both source and finished water samples.

### Spatial Distribution

Figure 15 below shows the spatial distribution of CECs detected in this study, as observed at surface water supplied public water systems. Sampling sites were categorized according to their presence in a Hydrologic Unit Code-4 surface watershed, as defined by the MNDNR (2021). A watershed is an area of land within which all water on the ground surface generally flows to the same drainage point, therefore, it's feasible that similar CECs may be detected at multiple sites within the same watershed boundary.

Figure 15 shows the observed water quality results measured by the unique number of contaminants detected at surface water sites by watershed. Atrazine was frequently detected in all watersheds; metolachlor, PFBA, and lithium were also frequently detected.

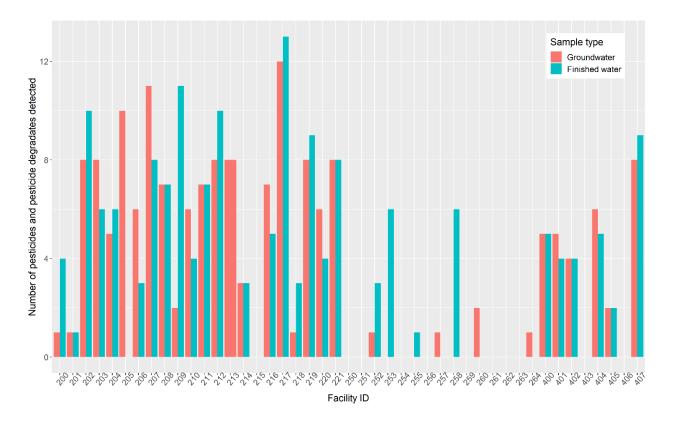


### Figure 15. Numbers of unique CECs detected in all samples (source and finished) collected from surface water sites by Hydrologic Unit Code-4 (map; MNDNR, 2019) and the most frequently detected CECs by watershed.

Bar charts; y-axis is detection frequency, in percent. Map image is the intellectual property of ESRI and is used herein under license. Copyright ©2019 ESRI and its licensors. All rights reserved.

### Source and finished water comparison

Overall, fewer unique CECs were detected in finished waters, compared to source waters, but patterns varied by CEC class and site network. Fewer distinct pesticides and pesticide degradates were detected in finished waters compared to source waters collected from vulnerable agriculture and surface water sites; more distinct pesticides and pesticide degradates were detected in finished waters at non-vulnerable agriculture and agriculture/wastewater sites (Figure 16). Within each network, the maximum concentration of pesticides and pesticide degradates in source water samples was greater than the maximum concentration in finished water samples. For example, the maximum concentration in source water samples collected from vulnerable agriculture sites was 4,910 ng/L (metolachlor SA), and the maximum concentration in finished water samples was 2,510 ng/L (alachlor SA).

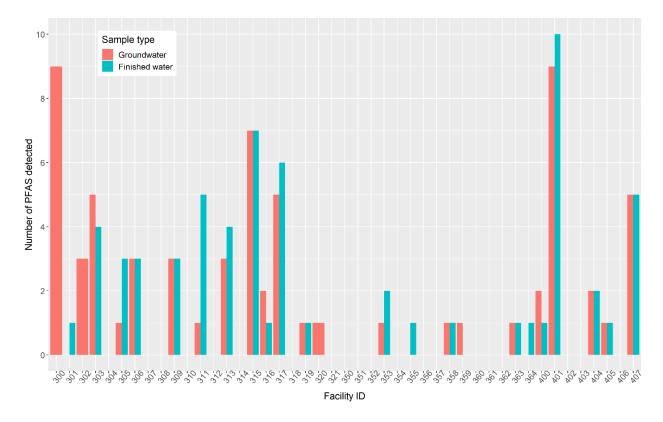


# Figure 16. Number of pesticides and pesticide degradates detected in groundwater (source water) and finished water samples collected from agriculture sites.

### Missing bars indicate that no pesticide or pesticide degradates were detected.

More distinct PFAS compounds were detected in finished waters collected from vulnerable and non-vulnerable agriculture sites; similar numbers of distinct PFAS were detected at all other sites. Although more PFAS were detected in some finished water samples, compared to the

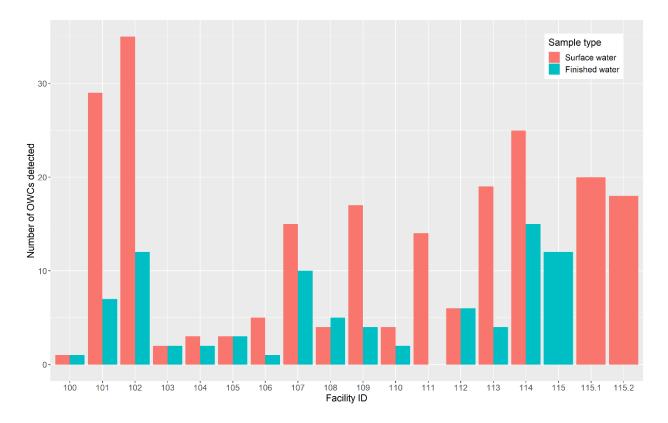
associated source water samples (e.g., Figure 17), total PFAS concentrations were similar between the two sample types (range from 0.418 to 500.26 ng/L in source water samples and from 0.419 to 425.71 ng/L in finished water samples).



### Figure 17. Number of PFAS detected in groundwater (source water) and finished water samples in the wastewater network.

Missing bars indicate that no PFAS were detected.

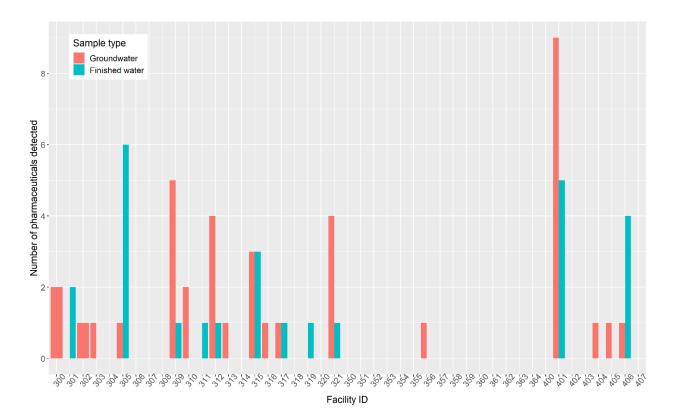
Fewer distinct wastewater indicators were detected in finished waters compared to source samples (see Figure 18 for surface water network example). This is largely an artifact of the presence of the disinfection byproduct, tribromomethane, or bromoform, in finished water samples.



# Figure 18. Number of OWCs detected in surface water (source water) and finished water samples collected from surface water sites during the first sample event.

Missing bars indicate that no OWCs were detected.

Fewer distinct pharmaceuticals were detected in finished waters, compared to source waters, at all sites. The number of pharmaceuticals detected in finished water samples was typically similar or lower than the number detected in source water samples (see Figure 19 for wastewater network example). Surface water sites were an exception, where variable results were observed.



### Figure 19. Number of pharmaceuticals detected in groundwater (source water) and finished water samples in the wastewater network.

Missing bars indicate that no pharmaceuticals were detected.

Similar numbers of benzotriazoles and benzothiazoles were observed between source and finished waters collected from surface water sites, but total concentrations were generally lower in finished waters. Total benzotriazole and benzothiazole concentrations in source water samples ranged from 1.2 to 164.1 ng/L, whereas total concentrations in paired finished water samples were often 0 or <10 ng/L.

Lithium was detected in all source and finished water samples. Furthermore, concentrations were similar between paired samples collected from a given site.

### Assessment of results against health-based guidance values

Results were compared against available MDH health-based guidance values, although most CECs analyzed lack published guidance values. A small number of results (n=9) exceeded available health-based guidance values. In those instances, MDH staff coordinated with public water systems to validate results by collecting additional samples that were analyzed for the CECs of interest and to take action, if appropriate.

One public water system exceeded the Health Risk Index (HRI) for PFAS. MDH worked with this system to remove the affected well from service. This system now provides drinking water below the HRI for PFAS.

Six samples exceeded the health risk limit (HRL) of 0.3  $\mu$ g/L for pentachlorophenol (PCP). These public water systems were resampled for this compound and all subsequent results, as well as historical samples, were found to be below the laboratory detection limit for PCP.

Two samples exceeded the HRL of 40  $\mu$ g/L for tribromomethane, or bromoform, which is a disinfection byproduct (DBP)<sup>9</sup>. Results for these systems meet standards set by the Safe Drinking Water Act (SDWA; USEPA, 2004). Based on guidance provided in MDH's CEC Framework, these systems were not resampled.

As a result of the occurrence data obtained through this study, several new contaminants have been nominated to the MDH CEC Initiative. These contaminants include impazethapyr, hydroxymetolachlor, dechlorometolachlor, 5-6-dimethyl benzotriazole, and 2-hydroxyatrazine. Dechlorometolachlor, hydroxymetolachlor, and 2-hydroxyatrazine are currently on the workplan of the Health Risk Limit (HRL) program. These contaminants may be reviewed by MDH scientists and considered for development of health-based guidance values.

### **Conclusions**

Through this project, water was sampled from over 100 public water systems statewide and analyzed for a wide spectrum of CECs. Depending on the network, samples were analyzed for as many as 600 different CECs, including various numbers of pharmaceuticals, PFAS, wastewater indicators, and pesticides.

Results showed that most CECs analyzed were not detected in drinking water, but some CECs were present at low concentrations. The detections included 84 pesticide compounds, 51 pharmaceuticals, 43 wastewater indicators, 15 PFAS, 8 benzotriazoles, and 1 inorganic

<sup>&</sup>lt;sup>9</sup> Disinfection is necessary to reduce the risk of pathogen exposure in finished drinking water. The benefits of disinfection outweigh the risks of DPBs if systems monitor and manage the process appropriately. The World Health Organization states, "in all circumstances, disinfection efficiency should not be compromised in trying to meet guidelines for DBPs, including chlorination byproducts, or in trying to reduce concentrations of these substances" (Centers for Disease Control and Prevention (CDC), 2022).

compound. Results assessments at individual sites revealed nine instances of potential public health concern. The results from these sites were reviewed and follow up samples were collected, where applicable. Response actions were implemented at one site, where system-level changes minimized or removed the public health risk.

Pesticides and PFAS showed the most widespread occurrence in water samples. Outside of lithium, which was detected in all samples, differences in occurrence and concentration were observed in source versus finished water samples for some groups (e.g., pharmaceuticals, benzotriazoles) but not for others (e.g., PFAS, pesticides). Samples collected in geologically vulnerable settings generally showed higher CEC concentrations than those collected from non-vulnerable sites.

This project has had a transformative effect on the approach to monitoring and managing risks from CECs in drinking water in Minnesota. Whereas prior work on characterizing drinking water focused on individual CECs, or was required by EPA, the work undertaken as part of this project has been voluntary and more comprehensive. Sampling relied on voluntary participation of public water systems. Most invited systems elected to participate, understanding the value of improving our understanding of CECs in drinking water, despite a concomitant risk of public alarm over detections in drinking water. MDH supported participants by providing risk communication materials and technical assistance to investigate and manage any detections of potential concern. Because the water samples were subjected to analyses for so many CECs, it was understood from prior work on the national scale that the sampling would likely result in detections at most sites. Such broad-based studies are useful to reveal the types of CECs that may be present in drinking water sources and in finished water. The broad assessment across CEC classes also leads to a better understanding of land use effects on source water quality. Results from this project can be applied to target future monitoring based on land use, geology, and potential threats to drinking water sources and public health.

Recognition of the value of monitoring drinking water (both source and finished water) for CECs has been cemented within MDH. Results from this study have been used to screen for potential health risks, as data to provide urgency to the development of new health-based guidance, and as a foundation to structure future work. MDH has used data from this project to identify frequently detected CECs across public water systems and nominate these CECs for development of new health-based guidance. These guidance values are used by MDH, its partners, and the general public to assess, manage, and communicate potential health risks from CEC exposure through drinking water. Monitoring data and guidance values can be used in conjunction to make informed, science-based decisions about future monitoring needs, activities to manage potential threats to the drinking water source, and consumer behavior around drinking water consumption and treatment.

This report provides a summary and overview of the sampling results across study sites and networks. Future analysis of the data will include in-depth assessment of CEC patterns observed in source and finished water, vulnerable and non-vulnerable geology, and land use effects.

MDH is in the process of establishing a formal program to continue and build upon this work, the Drinking Water Ambient Monitoring Program. As of the preparation of this report, funding for this work is being sought through Minnesota's Clean Water Fund. The Drinking Water

Ambient Monitoring Program will provide greater flexibility to MDH to readily collect and analyze data based on exposure and human health concerns, rather than relying on monitoring data from partner agencies and organizations, which may not be inclusive of (or generalizable to) drinking water sources and may rather target parameters based on ecological or environmental effects. These data allow MDH to be proactive and nimble in identifying and nominating CECs for health-based guidance and responding to potential concerns for the health of all Minnesotans.

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### **Appendix A: Complete list of parameters**

### Inorganic compound

Lithium

# Field Parameters (samples were collected and analyzed but results are not assessed in this document)

Dissolved oxygen

рΗ

Specific conductance

Water temperature

# USGS Pesticides and Pesticide Degradates Analyzed at the National Water Quality Laboratory

USGS pesticides and pesticide degradates	Chemical abstracts service registry number (CASRN)	Minimum reporting level (ng/L)
1H-1-2-4-Triazole	288-88-0	22
2-(1-Hydroxyethyl)-6-methylaniline (HEMA)	196611-19-5	54
2-[(2-Ethyl-6-methylphenyl)amino]-1-propanol	61520-53-4	5
2-4-D	94-75-7	62
2-Aminobenzimidazole	934-32-7	9
2-Amino-N-isopropylbenzamide	30391-89-0	4
2-Chloro-2'-6'-diethylacetanilide	6967-29-9	5
2-Chloro-N-(2-ethyl-6-methylphenyl)acetamide	32428-71-0	5
2-Hydroxy-4-isopropylamino-6-amino-s-triazine OIAT	19988-24-0	4
2-Hydroxy-6-ethylamino-4-amino-s-triazine (OEAT)	7313-54-4	100
2-Hydroxyatrazine (OIET)	2163-68-0	8
3-4-Dichlorophenylurea	2327-02-8	108
3-Hydroxycarbofuran	16655-82-6	16
3-Phenoxybenzoic acid	3739-38-6	61
4-(Hydroxymethyl)pendimethalin	56750-76-6	114
4-ChlorobenzylMethylSulfoxide	24176-68-9	3.2
4-Hydroxychlorothalonil	28343-61-5	42
4-Hydroxyhexazinone A	72576-13-7	3
Acephate	30560-19-1	10
Acetochlor	34256-82-1	10
Acetochlor OA	194992-44-4	65

#### **USGS pesticides and pesticide degradates Chemical abstracts** Minimum reporting service registry level (ng/L) number (CASRN) **Acetochlor SA** 187022-11-3 320 Acetochlor SAA 176 618113-86-3 Alachlor 27 15972-60-8 Alachlor OA 171262-17-2 60 **Alachlor SA** 360 142363-53-9 Alachlor SAA 494847-39-1 128 Aldicarb 8 116-06-3 20 Aldicarb sulfone 1646-88-4 Aldicarb sulfoxide 1646-87-3 2.2 834-12-8 2.6 Ametryn Asulam 3337-71-1 24 Atrazine 1912-24-9 6.8 Azinphos-methyl 8 86-50-0 **Azinphos-methyl oxon** 15 961-22-8 3 Azoxystrobin 131860-33-8 Bentazon 25057-89-0 9 Bifenthrin 82657-04-3 19 Bromacil 314-40-9 5.6 Bromoxynil 1689-84-5 60 5 33629-47-9 **Butralin** 10 Butylate 2008-41-5 5.6 Carbaryl 63-25-2 Carbendazim 10605-21-7 10 Carbofuran 5 1563-66-2 90982-32-4 8.8 Chlorimuron-ethyl **Chlorpyrifos** 2921-88-2 3 4.4 **Chlorpyrifos oxon** 2921-89-2 Chlorsulfuron 50 64902-72-3 105 cis-Cyhalothric acid 68127-59-3 cis-Permethrin 61949-76-6 4.2 Cyanazine 21725-46-2 50 DCPA monoacid 887-54-7 700 Dechlorofipronil 3.8 ---2 Dechlorometolachlor 126605-22-9 **Deethylatrazine (CIAT)** 6190-65-4 11 Deiodo flubendiamide 10 1016160-78-3 2.8 **Deisopropyl prometryn** 4147-57-3 1007-28-9 **Deisopropylatrazine (CEAT)** 20 **Demethyl fluometuron** 3032-40-4 3.6

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USGS pesticides and pesticide degradates	Chemical abstracts service registry number (CASRN)	Minimum reporting level (ng/L)
Demethyl hexazinone B	56611-54-2	3
Demethyl norflurazon	23576-24-1	4
Desamino-diketo metribuzin	52236-30-3	200
Desamino Metribuzin	35045-02-4	9
Desulfinylfipronil	205650-65-3	3.8
Desulfinylfipronil amide	1115248-09-3	10
Diazinon	333-41-5	6.4
Diazoxon	962-58-3	4
Dicamba	1918-00-9	800
Dichlorvos	62-73-7	52
Dicrotophos	141-66-2	4
Didealkylatrazine (CAAT)	3397-62-4	24
Didemethyl hexazinone F	56611-55-3	10
Diflubenzuron	35367-38-5	6
Diflufenzopyr	109293-97-2	72
Diketonitrile-isoxaflutole	143701-75-1	10
Dimethenamid	87674-68-8	3
Dimethenamid OA	380412-59-9	85
Dimethenamid SA	205939-58-8	79
Dimethenamid SAA		189
Dimethoate	60-51-5	4.6
Disulfoton	298-04-4	11
Disulfoton oxon	126-75-0	2
Disulfoton oxon sulfone	2496-91-5	6
Disulfoton oxon sulfoxide	2496-92-6	6
Disulfoton sulfone	2497-06-5	9
Disulfoton sulfoxide	2497-07-6	4
Diuron	330-54-1	5
EPTC	759-94-4	206
EPTC R248722	65109-69-5	4
Ethoprop	13194-48-4	5
Etoxazole	153233-91-1	4.2
Fenamiphos	22224-92-6	4.6
Fenamiphos sulfone	31972-44-8	5
Fenamiphos sulfoxide	31972-43-7	5
Fenbutatin oxide	13356-08-6	120
Fentin	668-34-8	30
Fipronil	120068-37-3	4
Fipronil amide	205650-69-7	9.2

### USGS pesticides and pesticide degradates Minimum reporting Chemical abstracts service registry level (ng/L) number (CASRN) **Fipronil sulfide** 120067-83-6 4.2 **Fipronil sulfonate** 209248-72-6 44 **Fipronil sulfone** 120068-36-2 5.6 Flubendiamide 4.4 272451-65-7 Flumetsulam 98967-40-9 17 Fluometuron 2164-17-2 10

Fonofos	944-22-9	11
Halosulfuron methyl	100784-20-1	12
Hexazinone	51235-04-2	3.6
Hexazinone TP C	72585-88-7	2
Hexazinone TP D	30243-77-7	294
Hexazinone TP E	72576-14-8	76
Hexazinone TP G		22
Hydroxyacetochlor	60090-47-3	20
Hydroxyalachlor	56681-55-1	6
Hydroxydiazinon	29820-16-4	11
HydroxyDidemethylFluometuron		50
Hydroxymetolachlor	131068-72-9	2.4
HydroxyMonodemethylFluometuron		12
Hydroxyphthalazinone		28
Hydroxysimazine	2599-11-3	120
Imazamox	114311-32-9	30
Imazaquin	81335-37-7	10
Imazethapyr	81335-77-5	8
Imidacloprid	138261-41-3	16
Indoxacarb	173584-44-6	5.2
Isoxaflutole	141112-29-0	18
Isoxaflutole Acid RPA 203328	142994-06-7	9.2
Kresoxim-methyl	143390-89-0	5
Lactofen	77501-63-4	10
Linuron	330-55-2	5.6
Malaoxon	1634-78-2	2.4
Malathion	121-75-5	5.4
МСРА	94-74-6	95
Metalaxyl	57837-19-1	6
Metconazole	125116-23-6	5
Methamidophos	10265-92-6	10
Methidathion	950-37-8	8.4
Methomyl	16752-77-5	3

#### **USGS pesticides and pesticide degradates Chemical abstracts** Minimum reporting service registry level (ng/L) number (CASRN) **Methomyl oxime** 13749-94-5 8000 Methoxyfenozide 161050-58-4 2.2 Methyl paraoxon 19 950-35-6 Metolachlor 3.2 51218-45-2 **Metolachlor OA** 152019-73-3 149 68 **Metolachlor SA** 171118-09-5 **MetolachlorHydroxyMorpholinone** 61520-54-5 10 Metribuzin 21087-64-9 20 **Metribuzin DK** 56507-37-0 236 Molinate 2212-67-1 28 7 Myclobutanil 88671-89-0 5 N-(3-4-Dichlorophenyl)-N-methylurea (DCPMU) 3567-62-2 Naled 300-76-5 56 Nicosulfuron 12 111991-09-4 Norflurazon 3.4 27314-13-2 Novaluron 116714-46-6 50 **O-Ethyl O-methyl S-propyl phosphorothioate** 76960-87-7 5 **O-Ethyl S-methyl S-propyl phosphorodithioate** 76936-72-6 3 64 O-Ethyl-S-propyl-phosphorothioate 31110-62-0 Omethoate 2 1113-02-6 6 Orthosulfamuron 213464-77-8 19044-88-3 12 Oryzalin Oxamyl 23135-22-0 2 **Oxamyl** oxime 30558-43-1 5 500 Oxyfluorfen 42874-03-3 Paraoxon 311-45-5 3.4 Pendimethalin 40487-42-1 10 Phorate 11 298-02-2 55 Phorate oxon 2600-69-3 Phorate oxon sulfone 2588-06-9 20 Phorate oxon sulfoxide 2588-05-8 20 Phorate sulfone 2588-04-7 36 Phorate sulfoxide 2588-03-6 4.6 Phthalazinone 90004-07-2 15 **Piperonyl butoxide** 25 51-03-6 3 Profenofos 41198-08-7 4 Prometon 1610-18-0 7287-19-6 4.2 Prometryn 709-98-8 12

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Propanil

USGS pesticides and pesticide degradates	Chemical abstracts service registry number (CASRN)	Minimum reporting level (ng/L)
Propargite	2312-35-8	2
Propazine	139-40-2	3.2
Propiconazole	60207-90-1	6
Propoxur	114-26-1	3.2
Propyzamide	23950-58-5	2.4
Prosulfuron	94125-34-5	10
Pyraclostrobin	175013-18-0	2.4
Pyridaben	96489-71-3	2.4
Pyrimidinol	2814-20-2	8
Pyriproxyfen	95737-68-1	3
sec-Acetochlor OA	152019-74-4	55
Siduron	1982-49-6	5
Simazine	122-34-9	7.2
Sulfentrazone	122836-35-5	18
Sulfometuron-methyl	74222-97-2	4
Sulfosulfuron	141776-32-1	11
Tebuconazole	107534-96-3	15
Tebufenozide	112410-23-8	2
Tebupirimfos	96182-53-5	2
Tebupirimfos oxon		2
Tebuthiuron	34014-18-1	3
Tebuthiuron TP 104	59962-53-7	5.6
Tebuthiuron TP 108	39222-73-6	10
Tebuthiuron TP 109	59962-54-8	11
Tebuthiuron TP 109 (OH)	139888-73-6	38
Terbacil	5902-51-2	21
Terbufos	13071-79-9	6.8
Terbufos oxon	56070-14-5	4
Terbufos oxon sulfone	56070-15-6	11
Terbufos oxon sulfoxide	56165-57-2	4
Terbufos sulfone	56070-16-7	11
Terbufos sulfoxide	10548-10-4	3
Terbuthylazine	5915-41-3	3.6
Tetraconazole	112281-77-3	7
Thiobencarb	28249-77-6	4.2
trans-Permethrin	61949-77-7	3.8
Triallate	2303-17-5	12
Tribufos	78-48-8	2
Triclopyr	55335-06-3	88

USGS pesticides and pesticide degradates	Chemical abstracts service registry number (CASRN)	Minimum reporting level (ng/L)
Trifloxystrobin	141517-21-7	2.8

## Eurofins Atrazine and Cyanazine Degradates

Eurofins cyanazine degradates	CASRN	Minimum reporting level (ng/L)
Atrazine	1912-24-9	5
Cyanazine	21725-46-2	5
Cyanazine acid	36576-43-9	5
Cyanazine amide	36576-42-8	5
Deethylatrazine		5
Deethylcyanazine	21725-40-6	5
Deethylcyanazine acid	36749-35-6	5
Deethylcyanazine amide	36556-77-1	5
Deisopropylatrazine	1007-28-9	5
Didealkylatrazine	3397-62-4	25
Hydroxyatrazine	2163-68-0	5
Total atrazine		
Total cyanazine		

## AXYS PFAS

AXYS PFAS parameters	CASRN	Minimum reporting level (ng/L)
11Cl-PF3OUdS	2196242-82-5	1.47
3:3 FTCA	1169706-83-5	1.47
4:2 FTS	414911-30-1	1.47
5:3 FTCA	1799325-94-2	9.2
6:2 FTS	425670-75-3	1.33
7:3 FTCA	1799325-95-3	9.2
8:2 FTS	481071-78-7	1.47
9CI-PF3ONS	1621485-21-9	1.48
ADONA	2127366-90-7	1.47
EtFOSAA	2991-50-6	0.368
HFPO-DA	122499-17-6	1.4
MeFOSAA	2355-31-9	0.368
N-EtFOSA	4151-50-2	0.92
N-EtFOSE	1691-99-2	2.75

AXYS PFAS parameters	CASRN	Minimum reporting level (ng/L)
NFDHA	39187-41-2	0.736
N-MeFOSA	31506-32-8	0.423
N-MeFOSE	24448-09-7	3.68
PFBA	45048-62-2	1.47
PFBS	45187-15-3	0.368
PFDA	73829-36-4	0.368
PFDoA	171978-95-3	0.368
PFDoS	343629-43-6	0.368
PFDS	126105-34-8	0.368
PFEESA	220689-13-4	0.368
РҒНрА	120885-29-2	0.368
PFHpS	146689-46-5	0.368
PFHxA	92612-52-7	0.368
PFHxS	108427-53-8	0.368
PFMBA	1432017-36-1	0.368
PFMPA		0.736
PFNA	72007-68-2	0.368
PFNS	474511-07-4	0.368
PFOA	45285-51-6	0.368
PFOS	45298-90-6	0.368
PFOSA	754-91-6	0.368
PFPeA	45167-47-3	0.736
PFPeS	175905-36-9	0.37
PFTeDA	365971-87-5	0.368
PFTrDA	862374-87-6	0.368
PFUnA	196859-54-8	0.368

## **AXYS Pharmaceuticals and Personal Care Products**

AXYS pharmaceuticals and personal care products	CASRN	Minimum reporting level (ng/L)
1-7-Dimethylxanthine	611-59-6	55
2-Hydroxy-ibuprofen	51146-55-5	3.83
Acetaminophen	103-90-2	13.8
Amsacrine	51264-14-3	0.0372
Azathioprine	446-86-6	0.93
Azithromycin	83905-01-5	1.38
Busulfan	55-98-1	1.86
Caffeine	58-08-2	13.8

AXYS pharmaceuticals and personal care products	CASRN	Minimum reporting level (ng/L)
Carbadox	6804-07-5	1.4
Carbamazepine	298-46-4	1.38
Cefotaxime	63527-52-6	5.58
Ciprofloxacin	85721-33-1	5.58
Citalopram	59729-33-8	0.367
Clarithromycin	81103-11-9	1.38
Clinafloxacin	105956-97-6	5.58
Clotrimazole	23593-75-1	0.367
Cloxacillin	61-72-3	2.75
Colchicine	64-86-8	0.744
Cyclophosphamide	50-18-0	0.372
Daunorubicin	20830-81-3	1.86
Dehydronifedipine	67035-22-7	0.55
Diatrizoic acid	117-96-4	11.2
Digoxigenin	1672-46-4	5.58
Digoxin	20830-75-5	5.58
Diltiazem	42399-41-7	0.275
Diphenhydramine	58-73-1	0.55
Doxorubicin	23214-92-8	5.58
Drospirenone	67392-87-4	7.34
Enrofloxacin	93106-60-6	2.75
Erythromycin-H2O	114-07-8	2.11
Etoposide	33419-42-0	0.93
Flumequine	42835-25-6	1.4
Fluoxetine	54910-89-3	1.38
Furosemide	54-31-9	3.83
Gemfibrozil	25812-30-0	0.766
Glipizide	29094-61-9	0.766
Glyburide	10238-21-8	0.766
Hydrochlorothiazide	58-93-5	8.43
Ibuprofen	15687-27-1	3.83
Iopamidol	60166-93-0	74.4
Lincomycin	154-21-2	2.75
Lomefloxacin	98079-51-7	2.79
Medroxyprogesterone Acetate	71-58-9	3.67
Melphalan	148-82-3	22.3
Metronidazole	443-48-1	1.86
Miconazole	22916-47-8	1.38
Moxifloxacin	151096-09-2	2.28

AXYS pharmaceuticals and personal care products	CASRN	Minimum reporting level (ng/L)
Naproxen	22204-53-1	1.92
Norfloxacin	70458-96-7	14
Norgestimate	35189-28-7	2.75
Ofloxacin	82419-36-1	1.4
Ormetoprim	6981-18-6	0.55
Oxacillin	66-79-5	2.75
Oxazepam	604-75-1	226
Oxolinic Acid	14698-29-4	0.558
Penicillin G	61-33-6	2.75
Penicillin V	87-08-1	2.75
Rosuvastatin	287714-41-4	3.67
Roxithromycin	80214-83-1	0.275
Sarafloxacin	98105-99-8	13.8
Sulfachloropyridazine	80-32-0	1.38
Sulfadiazine	68-35-9	1.38
Sulfadimethoxine	122-11-2	0.275
Sulfamerazine	127-79-7	0.558
Sulfamethazine	57-68-1	0.558
Sulfamethizole	144-82-1	0.55
Sulfamethoxazole	723-46-6	0.558
Sulfanilamide	63-74-1	13.8
Sulfathiazole	72-14-0	1.38
Tamoxifen	10540-29-1	0.367
Teniposide	29767-20-2	3.67
Thiabendazole	148-79-8	1.38
Trimethoprim	738-70-5	1.38
Tylosin	1401-69-0	5.5
Venlafaxine	93413-69-5	0.367
Virginiamycin M1	21411-53-0	2.75
Warfarin	81-81-2	0.383
Zidovudine	30516-87-1	5.58
Triclocarban	101-20-2	0.383
Triclosan	3380-34-5	5.75

# USGS Pharmaceuticals Analyzed at the National Water Quality Laboratory

USGS pharmaceutical parameters	CASRN	Minimum reporting level (ng/L)
10-Hydroxy-amitriptyline	64520-05-4	88

USGS pharmaceutical parameters	CASRN	Minimum reporting level (ng/L)
1-7-Dimethylxanthine	611-59-6	88
Abacavir	136470-78-5	2
Acetaminophen	103-90-2	20
Acyclovir	59277-89-3	22
Albuterol	18559-94-9	6.7
Alprazolam	28981-97-7	21
Amitriptyline	50-48-6	37
Amphetamine	300-62-9	4.4
Antipyrine	60-80-0	50
Atenolol	29122-68-7	13
Benztropine	86-13-5	44
Betamethasone	378-44-9	114
Bupropion	34911-55-2	18
Caffeine	58-08-2	13.8
Carbamazepine	298-46-4	11
Carisoprodol	78-44-4	20
Chlorpheniramine	132-22-9	54
Cimetidine	51481-61-9	140
Citalopram	59729-33-8	6.6
Clonidine	4205-90-7	61
Codeine	76-57-3	32
Dehydronifedipine	67035-22-7	20
Desmethyldiltiazem	85100-17-0	70
Desvenlafaxine	93413-62-8	84
Dextromethorphan	125-71-3	8.2
Diazepam	439-14-5	4
Diltiazem	42399-41-7	10
Diphenhydramine	147-24-0	48
Duloxetine	116539-59-4	37
Erythromycin	114-07-8	2.11
Ezetimibe	163222-33-1	205
Fadrozole	102676-47-1	13
Famotidine	76824-35-6	34
Fenofibrate	49562-28-9	6.4
Fexofenadine	83799-24-0	44
Fluconazole	86386-73-4	30
Fluoxetine	54910-89-3	26
FluticasonePropionate	80474-14-2	30
Fluvoxamine	54739-18-3	80
Gabapentin	60142-96-3	160

USGS pharmaceutical parameters	CASRN	Minimum reporting level (ng/L)
Glipizide	29094-61-9	0.766
Glyburide	10238-21-8	0.766
Guanylurea	141-83-3	140
Hexamethylenetetramine	100-97-0	110
Hydrocodone	125-29-1	40
Hydrocortisone	50-23-7	147
Hydroxyzine	68-88-2	7.4
Iminostilbene	256-96-2	145
Ketoconazole	65277-42-1	113
Lamivudine	134678-17-4	16
Lidocaine	137-58-6	8
Loperamide	53179-11-6	80
Loratadine	79794-75-5	7
Lorazepam	846-49-1	202
Meprobamate	57-53-4	12
Metaxalone	1665-48-1	16
Metformin	657-24-9	13
Methadone	76-99-3	7.6
Methocarbamol	532-03-6	11
Methotrexate	59-05-2	52
Methyl salicylate	119-36-8	80
Metoprolol	51384-51-1	10
Morphine	57-27-2	80
Nadolol	42200-33-9	20
Nevirapine	129618-40-2	46
Nizatidine	76963-41-2	80
Nordiazepam	1088-11-5	20
Norethindrone	68-22-4	20
Norfluoxetine	56161-73-0	80
Norsertraline	87857-41-8	80
Norverapamil	67018-85-3	8.6
Omeprazole+Esomeprazole		16
Oseltamivir	196618-13-0	15
Oxazepam	604-75-1	3.67
Oxycodone	76-42-6	25
Paroxetine	61869-08-7	72
Penciclovir	39809-25-1	80
Pentoxifylline	6493-05-6	16
Phenazopyridine	94-78-0	13
Phendimetrazine	634-03-7	20

USGS pharmaceutical parameters	CASRN	Minimum reporting level (ng/L)
Phenytoin	57-41-0	188
Piperonyl butoxide	51-03-6	25
Prednisolone	50-24-8	150
Prednisone	53-03-2	105
Promethazine	60-87-7	114
Propoxyphene	469-62-5	28
Propranolol	525-66-6	26
Pseudoephedrine+Ephedrine		6
Quinine	130-95-0	80
Ractopamine	97825-25-7	20
Raloxifene	84449-90-1	80
Ranitidine	66357-35-5	192
Sertraline	79617-96-2	16
Sitagliptin	486460-32-6	97
Sulfadimethoxine	122-11-2	30
Sulfamethizole	144-82-1	104
Sulfamethoxazole	723-46-6	20
Tamoxifen	10540-29-1	270
Temazepam	846-50-4	18
Theophylline	58-55-9	80
Thiabendazole	148-79-8	4
Tiotropium	186691-13-4	50
Tramadol	27203-92-5	7.4
Triamterene	396-01-0	5.2
Trimethoprim	738-70-5	20
Valacyclovir	124832-26-4	163
Venlafaxine	93413-69-5	5.2
Verapamil	52-53-9	140
Warfarin	81-81-2	6

## USGS Wastewater Indicators Analyzed at the National Water Quality Laboratory

USGS wastewater indicators	CASRN	Minimum reporting level (ng/L)
1-4-Dichlorobenzene	106-46-7	80
1-Methylnaphthalene	90-12-0	40
2-6-Dimethylnaphthalene	581-42-0	40
2-Methylnaphthalene	91-57-6	40
3-beta-Coprostanol	360-68-9	1600

USGS wastewater indicators	CASRN	Minimum reporting level (ng/L)
3-Methyl-1H-indole	83-34-1	40
4-Cumylphenol	599-64-4	40
4-Nonylphenol (all isomers)	84852-15-3	1600
4-tert-Octylphenol	140-66-9	400
5-Methyl-1H-benzotriazole	136-85-6	320
Acetophenone	98-86-2	400
Acetylhexamethyltetrahydronaphthalene	21145-77-7	40
Anthracene	120-12-7	20
Anthraquinone	84-65-1	40
Atrazine	1912-24-9	160
BDE47	5436-43-1	40
Benzo[a]pyrene	50-32-8	20
Benzophenone	119-61-9	80
beta-Sitosterol	83-46-5	4800
beta-Stigmastanol	19466-47-8	3400
Bis(2-ethylhexyl)phthalate	117-81-7	2000
Bromacil	314-40-9	160
Caffeine	58-08-2	80
Camphor	76-22-2	80
Carbaryl	63-25-2	60
Carbazole	86-74-8	20
Chlorpyrifos	2921-88-2	120
Cholesterol	57-88-5	1600
Cotinine	486-56-6	6.4
DEET	134-62-3	40
Diazinon	333-41-5	320
Dichlorvos	62-73-7	80
Diethyl phthalate	84-66-2	400
d-Limonene	5989-27-5	160
Fluoranthene	206-44-0	20
HexaHydrohexamethylCyclopentaBenzopyran	1222-05-5	40
Indole	120-72-9	40
Isoborneol	124-76-5	90
Isophorone	78-59-1	50
Isopropylbenzene	98-82-8	40
Isoquinoline	119-65-3	800
Menthol	89-78-1	320
Metalaxyl	57837-19-1	160
Metolachlor	51218-45-2	40
Metolachlor	51218-45-2	40

USGS wastewater indicators	CASRN	Minimum reporting level (ng/L)
Naphthalene	91-20-3	20
Nicotine	54-11-5	58
p-Cresol	106-44-5	80
Pentachlorophenol	87-86-5	1600
Phenanthrene	85-01-8	20
Phenol	108-95-2	160
Prometon	1610-18-0	160
Pyrene	129-00-0	20
Tetrachloroethene	127-18-4	160
Tri(2-butoxyethyl) phosphate	78-51-3	640
Tri(2-chloroethyl) phosphate	115-96-8	160
Tribromomethane	75-25-2	160
Tributyl phosphate	126-73-8	64
Triclosan	3380-34-5	320
Triethyl citrate	77-93-0	40
Triphenyl phosphate	115-86-6	80
Tris(dichloroisopropyl) phosphate	13674-87-8	320

## AXYS Alkylphenols

AXYS alkylphenol parameters	CASRN	Minimum reporting level (ng/L)
4-n-Octylphenol	1806-26-4	0.124
4-Nonylphenol diethoxylates	20427-84-3	0.987
4-Nonylphenol monoethoxylates	68412-54-4	1.13
4-Nonylphenols	84852-15-3	0.523

## MDH Benzotriazoles & Benzothiazoles

MDH benzotriazoles & benzothiazoles	CASRN	Minimum reporting level (ng/L)
2-Amino Benzothiazole (2AM-BTH)	136-95-8	0.6
2-Hydroxy Benzothiazole (2OH-BTH)	934-34-9	25
2-Methylthio Benzolthiazole (2MeS-BTH)	615-22-5	5
4-Methyl Benzotriazole (4TTZ)	29878-31-7	1
5-6-Dimethyl Benzotriazole (5-6 XTZ)	4184-79-6	0.75
5-Chloro Benzotriazole (5Cl-BTZ)	94-97-3	0.61
5-Methyl Benzotriazole (5BTZ)	136-85-6	1
Benzothiazole (BTH)	95-16-9	66
Benzotriazole (BTZ)	95-14-7	7.4

## **AXYS Hormones**

AXYS hormones	CASRN	Minimum reporting level (ng/L)
17 alpha-Dihydroequilin	651-55-8	1.92
17 alpha-Estradiol	57-91-0	3.67
17 alpha-Ethinyl-Estradiol	57-63-6	4.59
17 beta-Estradiol	50-28-2	3.67
17 beta-Estradiol 3-benzoate	50-50-0	0.375
Allyl Trenbolone	850-52-2	0.373
Androstenedione	63-05-8	0.951
Androsterone	53-41-8	19
Bisphenol A	80-05-7	5.75
Desogestrel	54024-22-5	39.8
Equilenin	517-09-9	0.383
Equilin	474-86-2	1.92
Estriol	50-27-1	7.66
Estrone	53-16-7	3.67
Mestranol	72-33-3	18.3
Norethindrone	68-22-4	0.951
Norgestrel	6533-00-2	0.951
Progesterone	57-83-0	0.381
Testosterone	58-22-0	0.381

## MDH Illicit Drugs

MDH illicit drug parameters	CASRN	Minimum reporting level (ng/L)
3-4-methylenedioxy-N-methylamphetamine (MDMA)	42542-10-9	0.5
Amphetamine	300-62-9	1
Benzoylecgonine (BZE)	519-09-5	0.5
Cocaine	50-36-2	0.8
Codeine	76-57-3	4
Methamphetamine	537-46-2	1
Morphine	57-27-2	4.5
Pseudoephedrine/Ephedrine		0.78