

2018 Project Abstract

For the Period Ending June 30, 2022

PROJECT TITLE: Characterize Unregulated Contaminants in Source Water and Drinking Water

PROJECT MANAGER: Stephen Robertson

AFFILIATION: Minnesota Department of Health

MAILING ADDRESS: 625 Robert Street N

CITY/STATE/ZIP: Saint Paul, Minnesota, 55164-0975

PHONE: 651-201-4648

E-MAIL: steve.robertson@state.mn.us

WEBSITE: www.health.state.mn.us

FUNDING SOURCE: Environment and Natural Resources Trust Fund

LEGAL CITATION: M.L. 2018, Chp. 214, Art. 4, Sec. 02, Subd. 04g

APPROPRIATION AMOUNT: \$1,000,000

AMOUNT SPENT: \$966,516

AMOUNT REMAINING: \$33,483

Sound bite of Project Outcomes and Results

Analysis of drinking water resources reveals the presence of a range of unregulated contaminants at low levels. Most of these levels are below health-based guidance, if available. Results are being used to inform development of new health-based guidance and to perpetuate drinking water ambient monitoring.

Overall Project Outcome and Results

This project sampled water from 105 public water systems statewide for a wide spectrum of drinking water contaminants. Participating public water systems were organized into three groups: systems that use surface water, systems that use groundwater potentially influenced by wastewater, and systems that use groundwater potentially affected by agricultural land uses. Depending on the group, samples were analyzed for as many as 600 different contaminants, including pharmaceuticals, per- and polyfluoroalkyl substances (PFAS), organic wastewater indicators, and pesticides.

Results for individual systems showed that most contaminants analyzed were not detected in drinking water, but some contaminants were present at low levels. The detections included 84 pesticides, 51 pharmaceuticals, 43 wastewater indicators, 15 PFAS, eight benzotriazoles, and one inorganic compound. Some contaminants were detected at multiple systems. Results were compared against health-based guidance values, if available, although most contaminants analyzed lack health-based guidance values. A few results exceeded available guidance values. In those instances, MDH staff coordinated with the public water system to validate results and take action where appropriate.

There were detections of contaminants from most classes analyzed, but pesticides and PFAS were the most commonly detected. The most frequently detected contaminants across the study included lithium, pesticides (metolachlor, atrazine, deethylatrazine), PFAS (PFBA, PFHxS, PFOS, PFOA), and tribromomethane. Differences in occurrence or 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 contaminant concentrations than those collected from non-vulnerable sites.

Results have been used to prioritize and nominate contaminants for the development of health-based guidance. Also, the project has led to creation of a permanent drinking water ambient monitoring program. This ongoing work will help mitigate and manage the exposure to unregulated contaminants through Minnesota's drinking water.

Project Results Use and Dissemination

The project and associated materials are described on the MDH website. This project has spurred creation of risk communication resources for public water systems and MDH staff.

A project summary report has been prepared and will be available on the MDH website by October 2022.

Preliminary results from the project have been presented at the University of Minnesota's Water Resource Conference (October 2020). A complete analysis of the results is forthcoming and will be prepared for publication.

A professional paper describing the ELISA methodology used in this project is in press for publication. (Krall, Aliesha L., et al, 2022)



Environment and Natural Resources Trust Fund (ENRTF)

M.L. 2018 ENRTF Work Plan Final Report (Main Document)

Today's Date: August 15, 2022

Final Report

Date of Work Plan Approval: 06/05/2018

Project Completion Date: June 30, 2022

PROJECT TITLE: Characterize Unregulated Contaminants in Source Water and Drinking Water

Project Manager: Steve Robertson

Organization: Minnesota Department of Health

College/Department/Division: Environmental Health Division

Mailing Address: 625 Robert Street North

City/State/Zip Code: Saint Paul, MN 55164-0975

Telephone Number: 651-201-4648

Email Address: steve.robertson@state.mn.us

Web Address: www.health.state.mn

Location: Statewide

Total Project Budget: \$1,000,000

Amount Spent: \$966,516.58

Balance: \$33,483.42

Legal Citation: M.L. 2018, Chp. 214, Art. 4, Sec. 02, Subd. 04g

Appropriation Language: \$1,000,000 the second year is from the trust fund to the commissioner of health to establish monitoring networks of public water-system wells and surface-water intakes to determine if contaminants persist after standard public water treatment. This appropriation is available until June 30, 2022, by which time the project must be completed and final products delivered.

I. PROJECT STATEMENT:

Unregulated contaminants are one of the 21st century threats to drinking water for which existing resources and regulatory approaches are insufficient. The Minnesota Department of Health (MDH) monitors all public water systems (approximately 7000 statewide) for conformance with federal monitoring requirements and water quality standards. EPA has established about 100 water quality standards for drinking water. Federal regulation requires that these standards be met in finished water – the product that a public water system delivers to its customers. For thousands of chemicals in use in modern society, little or no monitoring of drinking water is done because there is neither a federal regulatory mandate nor resources to test for them in drinking water sources. Some of our agency partners (MPCA, MDA, USGS, EPA) have conducted monitoring of lakes, rivers or ambient groundwater to better understand water quality conditions, but none of these efforts have been focused on drinking water sources.

Drinking water sources vary across the state of Minnesota. While most of the state's residents drink groundwater (mostly from wells), many of the largest public water systems in the state (serving about 20 percent of the population), rely on rivers, lakes or other surface water. Land use is a factor that determines groundwater and surface water quality where precipitation onto contaminant sources soaks into the ground or runs off into streams or lakes. Prior work established that land uses involving wastewater disposal and agricultural chemical storage/use on the land can cause unregulated contaminants to occur in water supplies. Industrial and municipal wastewater effluent contains pharmaceuticals, personal care products and other endocrine-active substances, while runoff and infiltration from agricultural lands can contain various types of pesticides, as well as nutrients. Additionally, natural events like algal blooms can produce cyanotoxins that are acutely toxic to human health.

In Minnesota, the distribution of drinking water is seldom directly from the source without some degree of handling and treatment. Sometimes this handling and treatment is to satisfy regulatory requirements that protect public health, and sometimes it is to provide some aesthetic value, like softening or removal of iron. Due to the cost and lack of a regulatory mandate, it is very unusual for public water systems to design for the removal of unregulated contaminants. However, research indicates that existing treatment processes sometimes provide incidental removal of some unregulated contaminants. Consequently, in addition to characterizing unregulated contaminants present in selected high risk drinking water sources, this project will evaluate the degree to which contaminants present in raw source water may persist to finished drinking water.

The goals of this project are to 1) characterize the presence of selected unregulated contaminants in drinking water sources and associated samples of treated drinking water in Minnesota, and 2) identify screening approaches to simplify and target future monitoring efforts. Also, the information will be of value in MDH efforts to assist public water systems statewide in the areas of source water protection, water treatment, health based guidance, and risk communication. Currently, the lack of data to drive these efforts undermines the integrity of future drinking water protection efforts. As a result, achieving project goals pertaining to drinking water source characterization will provide data and knowledge that state and local officials can use to prioritize future interventions in a way that minimizes risk and maximizes public health benefits.

II. OVERALL PROJECT STATUS UPDATES:

First Update January 31, 2019

MDH created an internal working team for the project. Additionally, MDH created a technical advisory team (TAT) comprised of internal and external stakeholders. This team has met four times since project inception to discuss project goals, interim work products and to advise the MDH working team on the development of the overall monitoring plan for the project. Much of the analytical work will be done by USGS under the auspices of a work order as part of an existing Joint Funding Arrangement (JFA), which has already been established with USGS. Execution of the work order is pending; USGS staff were affected by the partial federal government shutdown. If the shutdown resumes, schedules for this project may be affected.

Second Update June 30, 2019

Overall project work moved forward since January, 2019 in the following areas: 1) Activity 1 site and parameter selection were concluded and a monitoring plan finalized as described in the Activity 1 status update, 2) preparations were made to initiate Activity 2, as described below, and 3) communications materials were developed to describe project goals, objectives and outcomes to project participants, MDH staff, and partners.

Third Update January 31, 2020

Field staff were hired in July to conduct the statewide sampling per the monitoring plan (this plan is available here: <https://www.health.state.mn.us/communities/environment/water/unregcontam.html>). Coordination and training with USGS staff were conducted in July and early August. 30 PWS wells were sampled in agriculturally sensitive areas, 30 PWS wells vulnerable to wastewater were sampled, and 16 surface water systems were sampled twice. All site visits included a sample at both the source and entry point. Sampling was conducted between August-November 2019.

In total samples are being analyzed for about 12 different parameter groups, including pesticides, pharmaceuticals personal care products, and PFAS. The capabilities of three separate contracted laboratories were enlisted to conduct the analytical work. All results will not be received by MDH until about May, 2020.

Fourth Update June 30, 2020 (July 17, 2020)

After the conclusion of field activities late in the fall of 2019, most of the time period associated with this update has been spent awaiting the delivery of results from the analytical laboratories. As of the time of this update, we are in receipt of all results from AXYS Analytical, and the MDH public health lab. We have partial results from the USGS. Their analytical capabilities have been significantly impacted by the COVID pandemic. Results from USGS are expected in the next update period for this grant. MDH staff are preparing interim results memos that will be sent to participating public water systems in August.

Fifth Update January 31, 2021

All results from the MDH, AXYS Analytical and USGS laboratory analytical work has been received. Data have been compiled and preliminary assessments made relative to known public health protection criteria. Interim results reports have been distributed to participating public water systems. MDH and USGS staff presented early results assessments to Water Resources Conference. Budgets have been updated and evaluated. Sufficient budget remains to plan additional field activities to provide additional insight within bounds of overall study design.

AMENDMENT REQUEST March 10, 2021 (Approved by LCCMR 3/15/2021)

We are requesting a shift from the personnel budget to Professional/Technical/Service Contracts. Specifically, this transfer will address a negative balance on the line item for MDH Public Health Laboratory.

- Personnel budget will be reduced by \$5165 to a revised budget of \$47,235 (\$7797 remaining balance).
- Professional/Technical/Service Contracts will increase by \$5165 to \$26,400 (\$0 remaining balance).

This change is being requested because the actual costs charged to MDH for laboratory analysis differed from those estimated at project outset. To offset this change, MDH will cover personnel costs as an additional in-kind contribution to the project.

Sixth Update June 30, 2021

Preliminary data compilation and assessments complete. Professional paper prepared describing subset of monitoring work. Review of budget revealed first phase of field activities was completed below forecasted cost estimates. Supplemental monitoring plans created for second phase of monitoring.

Amendment Request (Approved by LCCMR 10/5/2021)

1. Extend project end date to June 30, 2022 from December 31, 2021. This will allow phase two follow sampling as described in Activity 1, Task 4 and Activity 2, Task 3.
2. Adjust budget to direct remaining funds for phase two sample analysis and ongoing USGS professional/technical services. Specifically, re-allocate funds originally designated for MDH payroll (\$7797), travel (\$15,123), USGS professional/technical services (\$24,993) and supply expenses (\$3941) to analytical laboratory. This action will zero out budget in the MDG personnel, travel, and expenses

categories. Remaining project expenditures will be in the following categories: private analytical laboratory (approx. \$193,000) and USGS professional/technical services (approx. \$44,802).

Final Update January 31, 2022

Phase 2 of sampling is complete. Laboratory analysis pending. Data analysis plan is under development and is being reviewed by project partners.

Overall Project Outcomes and Results

This project sampled water from 105 public water systems statewide for a wide spectrum of drinking water contaminants. Participating public water systems were organized into three groups: systems that use surface water, systems that use groundwater potentially influenced by wastewater, and systems that use groundwater potentially affected by agricultural land uses. Depending on the group, samples were analyzed for as many as 600 different contaminants, including pharmaceuticals, per- and polyfluoroalkyl substances (PFAS), organic wastewater indicators, and pesticides.

Results for individual systems showed that most contaminants analyzed were not detected in drinking water, but some contaminants were present at low levels. The detections included 84 pesticides, 51 pharmaceuticals, 43 wastewater indicators, 15 PFAS, eight benzotriazoles, and one inorganic compound. Some contaminants were detected at multiple systems. Results were compared against health-based guidance values for contaminants for which that information is available, although most contaminants analyzed lack health-based guidance values. A few results exceeded available guidance values. In those instances, MDH staff coordinated with the public water system to validate results and take action where appropriate.

There were detections of contaminants from most classes analyzed, but pesticides and PFAS were the most commonly detected. The most frequently detected contaminants across the study included lithium, pesticides (metolachlor, atrazine, deethylatrazine), PFAS (PFBA, PFHxS, PFOS, PFOA), and tribromomethane. Differences in occurrence or 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 contaminant concentrations than those collected from non-vulnerable sites.

Results have been used to prioritize and nominate contaminants for the development of health-based guidance. Also, the project has led to creation of a permanent drinking water ambient monitoring program. This ongoing work will help mitigate and manage the exposure to unregulated contaminants through Minnesota's drinking water.

III. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Develop detailed monitoring plan

Description: Analyze land use adjacent to public water system wells and upstream of intakes. Identify wells and intakes at risk from wastewater disposal and agricultural chemicals. Develop monitoring networks comprised of public water system wells and intakes at which the water quality effects of wastewater and agricultural chemicals can be sampled and evaluated.

Review previous state and national water monitoring information to establish a list of laboratory analytical parameters (i.e., specific compounds) targeted to Minnesota conditions. Parameters will be grouped into classes (e.g., pharmaceuticals, personal care products, pesticides, wastewater indicators, etc.). Further analysis will establish specific indicators for each class for which semi-quantitative pre-screening may provide information to guide rigorous and quantitative laboratory analysis. Develop formal strategy to use combination of screening approach and laboratory analysis to maximize the information received on the presence of unregulated contaminants while minimizing costs.

Create statewide monitoring networks for public water systems at risk from the following land uses: 1) wastewater disposal and 2) agricultural chemical storage and uses. Networks will consist of systems using both groundwater and surface water. Establish sampling schedule.

ENRTF BUDGET: \$ 59,341

Outcome	Completion Date
<i>1. Analyze land uses near public water system wells and intakes. Identify separate ranked lists of vulnerable public water system wells ranked relative to the degree of exposure to wastewater disposal and agricultural chemicals. Prospective sites are expected all over the state.</i>	January 2019
<i>2. Develop targeted list of parameters of concern in Minnesota due to wastewater disposal and agricultural chemical use. Employ both screening tools and quantitative laboratory analysis to evaluate drinking water sources.</i>	January 2019
<i>3. Create specific monitoring plan that lists wells, parameters and sampling schedule for 2019 and 2020.</i>	March 2019
<i>4. Update monitoring plan to include sites and parameters not included in 2019 sampling due to budget concerns</i>	September 2021

First Update January 31, 2019

Outcome 1, developing lists of prospective sampling sites, is well underway. Three different sets of monitoring sites are under development. The first is comprised of public water systems that use surface water as a drinking water source. Surface water resources are among the most vulnerable in the state. There are 23 community systems that use surface water in Minnesota, and nearly all will be included (multiple systems use Lake Superior as a source of supply – due to cost concerns, some will not be sampled because the additional information provided by multiple sampling sites on the lake will likely be negligible). The second set of sampling sites consists of systems that use groundwater as a drinking water source and are located in areas that might make them vulnerable to wastewater discharges. Prospective sites are being evaluated based on some of the following criteria: vulnerable geologic setting, multiple water quality criteria (e.g., chloride/bromide ratios, general wastewater indicators), preliminary results from ongoing Virus Study, proximity to wastewater disposal or conveyance infrastructure, and other land use considerations. The third set of sampling sites is of systems that use groundwater as a drinking water source and are located in areas that are subject to agricultural land uses. Prospective sites are being evaluated based on some of the following criteria: vulnerable geologic setting, existing water quality indicators (e.g., nitrate-nitrogen, results from 2015 Pesticide Occurrence Study), biological indicators of agricultural impact from ongoing Virus Study, land use (e.g. number of acres of cultivated lands in drinking water supply management areas), identification of agricultural response actions in wellhead protection plans.

Outcome 2 relates to parameter selection. The principal drivers for parameter selection are prior results from sampling efforts in Minnesota, cost and availability of suitable analytical techniques, stakeholder nominations, association of specific parameters to land use target (i.e., pesticides for agricultural sites), and results from national studies. Selected parameters vary for each of the three sets of monitoring sites, as described above for Outcome 1, because the parameters of interest differ depending on land use and drinking water source.

Outcome 3, development of formal monitoring plan. Creating the three separate monitoring networks, identifying the sampling sites for each, and selecting relevant parameters will be a balancing act. The more sampling sites, the more geographic representation we can obtain with the results. The more parameter schedules we add will provide a more comprehensive assessment of unregulated contaminants. Increasing either sampling sites or parameter schedules will increase cost, so the final monitoring plan will necessarily represent a balancing act.

Second Update June 30, 2019

Technical advisory team (TAT) completed its activity 1 work regarding candidate site selection criteria and parameter selection criteria. These were used to identify sampling sites for each of three sampling networks. Approximately 30-35 candidate sites were identified for both of the groundwater networks – one network of wells in or near wastewater sources and the other near agricultural land uses. The third network is comprised of 17 sites representing surface water sites. The monitoring plan for the project describes the results of this work. It is not yet posted to the MDH web site describing the project, but will be soon.

Third Update January 31, 2020

Outcomes 1, 2 and 3 were completed as of the last update. Monitoring plan is available at:

<https://www.health.state.mn.us/communities/environment/water/unregcontam.html>

No further updates.

Fourth Update June 30, 2020 (July 17, 2020)

No further update.

Fifth Update January 31, 2021

No further update.

Sixth Update June 30, 2021

Monitoring plan update in preparation. Overall sampling objectives are the same. Updated plan will include sites and parameters not included in first round of sampling due to budget concerns. Second phase of sampling will allow more robust characterization of the occurrence and distribution of parameters of concern based on phase one results and the ability to investigate settings that were not prioritized on phase one sampling efforts.

Final Update January 31, 2022

Monitoring plan completed and distributed to partners for feedback. Plan was implemented as will be described in next activity update.

Final Report Summary

This project used existing capacity within MDH's Drinking Water Protection program to identify, assess, and prioritize sources of supply used by public water systems in the state in order to establish a system or group of sampling sites. These sampling sites were categorized based on their vulnerability (i.e., sensitivity to contamination from activities at the land surface) and their potential to be affected by 1) land uses dominated by agricultural land uses, 2) sources of contamination that include wastewater disposal, or general surface water conditions. Sites meeting these separate criteria were grouped into, respectively, an agricultural monitoring system, a wastewater monitoring system, and a surface water monitoring system.

Parameter selection varied depending on the potential for usage or occurrence in the recharge area for the well or the intake. For example, samples collected at agricultural sites were subject to analysis for a comprehensive list of pesticides, including herbicides, insecticides and fungicides. Wastewater sites were analyzed for a wide range of pharmaceuticals. Samples from surface water sites were analyzed for the widest range of parameters, including pharmaceuticals, organic wastewater compounds, PFAS, and pesticides, among other things.

Results of the sample site and parameter selection processes were reviewed with a technical advisory team comprised of experts from other state and federal agencies, as well as public water systems. Monitoring plans documenting this work were published on the MDH web site.

ACTIVITY 2: Execute monitoring plan developed in Activity 1

Description: Collect and analyze water samples from public water system wells/intakes identified as at risk for wastewater disposal and agricultural chemicals. The work for this activity constitutes the primary data collection effort of the project. It will consist of coordinating the sampling needs for this project with other MDH sampling and inspection in support of compliance activities associated with federal Safe Drinking Water Act compliance. Assessments will need to be made each sampling round after evaluation of initial screening information to identify those samples associated with drinking water sources with the highest potential for presence of unregulated contaminants of concern. These assessments will be used to identify samples for laboratory analysis.

ENRTF BUDGET: \$ 836,644

Outcome	Completion Date
1. Collect water samples from drinking water sources identified in monitoring plan completed in activity 1 for ELISA analyses and in-depth quantitative laboratory analyses.	November 2020
2. ELISA and quantitative laboratory analysis of source and finished water samples and data quality assurance	March 2021

3. Collect water samples from drinking water sources identified in supplemental monitoring plan completed in Activity1, Task 4 for in depth laboratory analyses.	December 2021
--	---------------

First Update January 31, 2019

No activity during this working period.

Second Update June 30, 2019

Activity 2 work activities did not formally commence, but preparations were made for initiating the work in July or August of 2019. This work consisted of 1) initiating hiring process for samplers who will travel statewide to collect and ship samples, 2) coordinating logistical support with project partners (USGS) to provide field and lab training for new staff, 3) communication and coordination with Community public water supply staff (MDH) re: roles and responsibilities relative to this new project, 4) outreach to key partners to secure engagement (city of Minneapolis, Water Utility Council, etc), 5) development of communication materials (factsheets, webpage, message blocks, etc) to help assure clear and consistent messaging relative to project goals and outcomes, 6) identification and purchase of field equipment and supplies, and 7) contracting with USGS and other laboratories.

Third Update January 31, 2020

Activity 2 work was initiated in July, 2019. MDH hired two temporary sampling staff in July 2019 to conduct the sampling. Training on field sample collection, handling, and shipping was conducted in conjunction with USGS staff in July and August 2019. Staff prepared scheduling plans to optimize travel and shipping needs. Formal sample collection began in August 2019 by starting on the first round of samples from surface water systems. Subsequently, thirty samples each were collected from each of the groundwater networks – the sites with potential wastewater influence and those with potential agricultural influence. The second round of surface water samples were collected by mid-November, when the sampling was complete. At all sites where it was possible, samples were collected from both the source (i.e., well or intake) and the entry point into the distribution system.

Full laboratory analytical results are not expected until mid 2020.

Fourth Update June 30, 2020 (July 17, 2020)

Analytical results from Fall 2019 sampling have been delivered piecemeal to MDH because the analytical work was distributed among three different laboratories. While results from MDH and AXYS are complete, results from specialized laboratories operated by the USGS are still pending. As results have been received, they are screened against known health-based guidance. Should results exceed threshold values, MDH staff will follow the Drinking Water Protection CEC Framework for guiding system response. Partial results are sorted into data systems for later analysis.

Fifth Update January 31, 2021

Based on remaining financial resources, additional sampling is being planned for the spring of 2021 to further evaluate the sampling locations and parameters omitted in the fall 2019 sampling because of budget concerns. We will be updating the monitoring plan in the spring of 2021 and commence additional sampling prior to next status report. This additional data collection stage will require extending the data analysis completion dates as described in Activity 3 (see fifth update for activity 3, below).

Sixth Update June 30, 2021

Execution of the supplemental monitoring plan will proceed in third quarter of 2021.

Final Update January 31, 2022

Phase 2 monitoring activities commenced and were completed since last update. Approximately 120 samples were collected at public water systems in vulnerable and non-vulnerable environments across the state. Per the monitoring plan and original study design, samples of both source water and finished drinking water were collected at each of these systems.

Final Report Summary

Prior to any actual sampling, much advance work needed to happen to prepare MDH staff and public water systems. Studies and research that examine the water quality conditions at real world operating drinking water systems is understandably sensitive for regulators and public water systems alike because the results might cause confusion and undermine trust in public drinking water systems. Studies of unregulated contaminants in drinking water is relatively new, is rapidly evolving, and necessarily involves areas of uncertainty, especially for

people who lack the background and experience to interpret the results. Because the MDH could not compel participation in the study we had to earn the trust of participants. We did this in three principal ways: 1) we developed risk and project communications materials for participants and assured them that MDH would continue to help them with these needs depending on what the project outcomes were, 2) the drinking water program developed a response framework (e.g. CEC Framework) so that systems would know in advance how MDH would treat detections that might result during the study, and 3) MDH staffers connected personally with participating systems to invite their participation and to answer questions. In the end, only a few systems declined participation. The work products from items 1 and 2 in the list above represent true program innovations that will serve our needs well into the future.

Field sampling was conducted in two phases. Phase 1 occurred in 2019 and phase 2 occurred in 2021. As part of this work more than 230 sampling locations statewide were visited, some of them on multiple occasions, resulting in over 160 site visits. During each visit samplers needed to exercise strict QAQC to avoid inadvertent contamination and to assure safe and secure chain of custody from the sampling site to the laboratory. In the end, samples were collected from over 300 sites and were subject to hundreds of analyses.

ACTIVITY 3: Data analysis and report writing

Description: Upon receipt of quantitative data from the laboratory, data will be quality assured to ensure a robust dataset is available for data analysis. Once the dataset is finalized, different statistical methods will be explored to identify the appropriate method for determining differences between sample types (source and treated), among facilities, and between different types of risk (e.g. agriculture or wastewater). Results will be summarized in a peer-reviewed publication.

ENRTF BUDGET: \$ 104,015

Outcome	Completion Date
1. <i>Statistical analyses and interpretation of quantitative data</i>	May 2021
2. <i>Report preparation</i>	June 2021

First Update January 31, 2019

No activity during this working period.

Second Update June 30, 2019

No activity during this working period.

Third Update January 31, 2020

No activity during this working period.

Fourth Update June 30, 2020

Analytical results received during this update period have been screened against known health based guidance and screening values for drinking water. Data have been compiled and organized for a later, more complete analysis.

Fifth Update January 31, 2021

Plans for full data analysis are underway. Analysis will take several months and will commence in the next reporting period. Analysis activities may extend beyond June 2021 because of phase II sampling planned for the spring of 2021.

Sixth Update June 30, 2021

Draft professional paper developed describing ELISA work.

Final Update January 31, 2022

Final data analysis plan, incorporating data from phase 1 and phase 2 is in development and is under review by project partners. Once all laboratory data are received from contractors, then the plan will be executed.

Final Report Summary

Results for individual systems showed that most contaminants analyzed were not detected in drinking water, but some contaminants were present at low levels. The detections included 84 pesticides, 51 pharmaceuticals, 43 wastewater indicators, 15 PFAS, eight benzotriazoles, and one inorganic compound. Some contaminants

were detected at multiple systems. Results were compared against health-based guidance values for contaminants with available guidance, although most contaminants analyzed lack health-based guidance values. A few results exceeded available guidance values. In those instances, MDH staff coordinated with the public water system to validate results and take action where appropriate.

There were detections of contaminants from most classes analyzed, but pesticides and PFAS were the most commonly detected. The most frequently detected contaminants across the study included lithium, pesticides (metolachlor, atrazine, deethylatrazine), PFAS (PFBA, PFHxS, PFOS, PFOA), and tribromomethane. Differences in occurrence or 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 contaminant concentrations than those collected from non-vulnerable sites.

IV. DISSEMINATION:

Description: A report will be prepared at the conclusion of each project activity, as described above. Each report will contain key data and results generated by the work as well as an evaluation of the information relative to water quality and public health criteria. Reports will be submitted to the LCCMR, published on the MDH web site, and submitted to the Minnesota Water Research Digital Library. As appropriate, project data and results will be summarized and evaluated in peer-reviewed professional publications and presented at local and national conferences.

First Update January 31, 2019

No activity during this working period.

Second Update June 30, 2019

Activity 1 is complete and resulting report (monitoring plan) is complete and available upon request. Will be posted to website upon review and approval relative document accessibility.

Third Update January 31, 2020

No activity during this working period.

Fourth Update June 30, 2020

No activity during this working period.

Fifth Update January 31, 2021

USGS and MDH staff presented a summary of limited data analysis at the University of Minnesota's Water Resources Conference in October.

Sixth Update June 30, 2021

Draft professional paper prepared and distributed for comments.

Final Update January 31, 2022

No activity during this working period.

Final Report Summary

The project and associated materials are described on the MDH website. This project has spurred creation of risk communication resources for public water systems and MDH staff. Also a formal response action framework for unregulated contaminants, entitle the CEC Response Framework, was developed by MDH staff to guide departmental response expectations of public water systems in the event of CEC detections.

A project summary report has been prepared, is in review, and will be available on the MDH website by October 2022.

Preliminary results from the project have been presented at the University of Minnesota's Water Resource Conference (October 2020). A complete analysis of the results is forthcoming and will be prepared for publication.

A professional paper describing the ELISA methodology used in this project is in press for publication. (Krall, A.L., Elliott, S.M., de Lambert, J.R., and Robertson, S.W., in press, Comparison of the results of enzyme-linked

immunosorbent assay (ELISA) to mass-spectrometry based analytical methods for six unregulated contaminants in source water and finished drinking-water samples: U.S. Geological Survey Scientific Investigations Report 2022–5066, 29 p., <https://doi.org/10.3133/sir20225066>.)

V. PROJECT BUDGET SUMMARY:

A. Preliminary ENRTF Budget Overview: See attached budget spreadsheet

Explanation of Capital Expenditures Greater Than \$5,000: NA

Explanation of Use of Classified Staff: Classified staff will not be paid for with ENRTF.

Total Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation:

Enter Total Estimated Personnel Hours: 986	Divide by 2,080 = TOTAL FTE: 0.47
--	-----------------------------------

Total Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation:

Enter Total Estimated Personnel Hours: 1664	Divide by 2,080 = TOTAL FTE: 0.8
---	----------------------------------

B. Other Funds:

SOURCE OF AND USE OF OTHER FUNDS	Amount Proposed	Amount Spent	Status and Timeframe
Other Non-State \$ To Be Applied To Project During Project Period:			
EPA Section 106 Grant	\$ 14,011	\$ 12,402	Expended amounts are final as of June 30,2022
USGS match	\$ 69,084	\$129,150	Expended amounts are final as of June 30,2022
EPA DWRLF Set-aside	\$ 91,700	\$ 115,648	Expended amounts are final as of June 30,2022
Other State \$ To Be Applied To Project During Project Period: NA			
Past and Current ENRTF Appropriation: NA			
Other Funding History: NA			

VI. PROJECT PARTNERS:

A. Partners receiving ENRTF funding

Name	Title	Affiliation	Role
Sarah Elliot, Mark Brigham	Scientists	US Geological Survey	Project partner/collaborator

B. Partners NOT receiving ENRTF funding

Name	Title	Affiliation	Role
Mark Ferrey	Research Scientist	MPCA	Project Advisor
Bill van Rsywyk	Hydrologist 4	MDA	Project Advisor

VII. LONG-TERM- IMPLEMENTATION AND FUNDING:

The outcomes of this work will be used to inform work efforts involving source water protection, development of health-based guidance, drinking water treatment, as well as other means of managing unregulated contaminants in drinking water sources. Additionally, the results of this work will help to facilitate interagency coordination and cooperation to prioritize and target drinking water protection efforts. Our intent is to use the project to leverage other funding partners to support ongoing and permanent drinking water source characterization efforts. Lastly, the laboratory analytical techniques required for the work described in this proposal are, at present, cost-prohibitive to carry out routinely. Accordingly, this study will include the development of strategies (e.g., indicator parameter lists, simplified analytical protocols, use of new technology) that could be used in general practice by MDH, public water systems and other stakeholders to evaluate risks relative to unregulated contaminants.

As of August 2022, many of the expected outcomes of this project work have been achieved. Staff have used results from this project to prioritize and nominate contaminants for the development of health-based guidance. A Drinking Water Protection Section response action framework provides a predictable process for following up on detections above threshold values. Risk communication materials have been developed to assist public water systems and MDH staff in presenting information to others regarding the work. A data summary report will be posted to MDH website in the fall of 2022. MDH has requested ongoing funding for a Drinking Water Ambient Monitoring Program. Preliminary steps towards formal establishment of this program are underway now as the Drinking Water Protection Section is engaged in monitoring activities designed to ascertain the presence or absence of PFAS compounds in drinking water systems statewide. The more general program will be used to screen drinking water sources for CECs, to monitor drinking water sources where prior detections have been observed, and to characterize aquifer resources on a regional scale. This initiative will be housed in the Drinking Water Protection Section of MDH.

VIII. REPORTING REQUIREMENTS:

- **The project is for 4.0 years, will begin on July 1, 2018 and end on June 30, 2022.**
- **Periodic project status update reports will be submitted January 31 and June 30 of each year.**
- **A final report and associated products will be submitted between July 3 and August 15, 2022.**

IX. SEE ADDITIONAL WORK PLAN COMPONENTS:

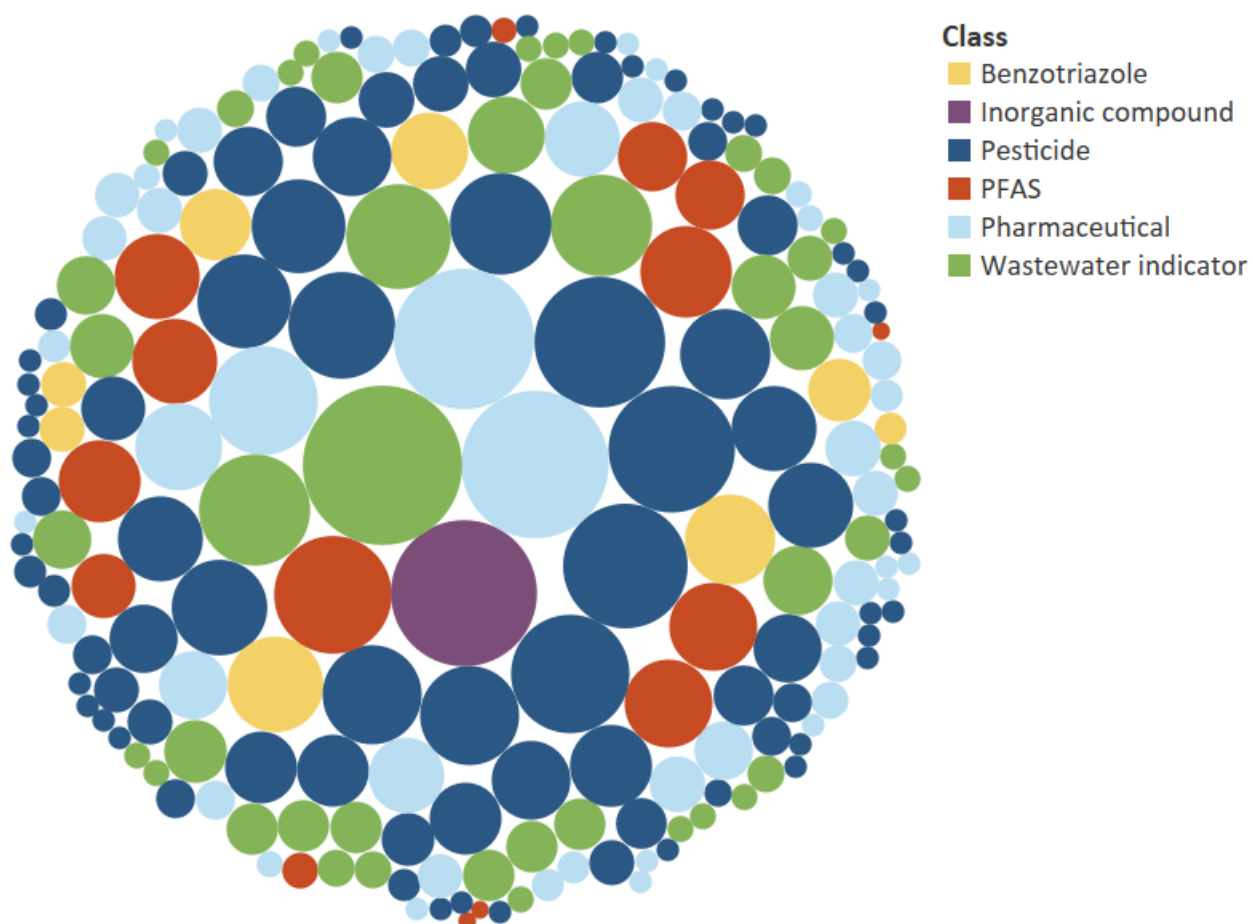
- A. Budget Spreadsheet (attached)**
- B. Visual Component (attached)**

Attachment A:
Environment and Natural Resources Trust Fund
M.L. 2018 Budget Spreadsheet Final



Project Title: Characterize Unregulated Contaminants in Source Water and Drinking Water
Legal Citation: M.L. 2018, Chp. 214, Art. 4, Sec. 02, Subd. 04g
Project Manager: Steve Robertson
Organization: Minnesota Department of Health
College/Department/Division: Environmental Health
M.L. 2018 ENRTF Appropriation: \$1,000,000
Project Length and Completion Date: 4 years; June 30, 2022
Date of Report: 8/11/2022

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	TOTAL (original) BUDGET	Revised Budget October 5, 2021	AMOUNT SPENT	TOTAL BALANCE
BUDGET ITEM				
Personnel (Wages and Benefits)				
Temporary samplers 0.25 FTE for years 1 and 2 and 0.276 in year 3, base cost is \$40,000 per FTE plus 31% fringe, distributed over duration of project (\$52,400)	\$52,400	\$39,438.25	\$39,438	\$0
Professional/Technical/Service Contracts				
Private analytical laboratory (Laboratory analytical services for pharmaceuticals, personal care products, pesticides (exact vendor not yet determined and will depend on monitoring plan developed in Activity 1))	\$679,800	\$731,653.41	\$705,087	\$26,566
U.S. Geological Survey (Professional and technical services related to monitoring plan design, sample collection, laboratory analytical services, data review and analysis, and report preparation) (\$214,915 not including USGS cost share)	\$214,915	\$189,922.00	\$183,006	\$6,917
MDH Public Health Laboratory (Routine water quality analysis in support of water chemistry and vulnerability characterizations) (\$21,235-\$26,400 not including EPA Section 106 cost share)	\$21,235	\$26,400.00	\$26,400	\$0
Equipment/Tools/Supplies				
Sampling equipment, supplies	\$13,500	\$9,559.08	\$9,559	\$0
Travel expenses in Minnesota				
Travel	\$18,150	\$3,027.26	\$3,027	\$0
COLUMN TOTAL	\$1,000,000	\$1,000,000	\$966,517	\$33,483



Attachment B. Visual summary of unregulated contaminants detected at all sites by class and relative frequency of detection. MDH Unregulated Contaminants Monitoring Project 2019-2022.

Size of dot represents frequency based on number of sites sampled for contaminant with detection.

Monitoring Plan

UNREGULATED CONTAMINANTS MONITORING PROJECT

Background and Purpose

The Minnesota Department of Health (MDH) received a grant from the Minnesota Environment and Natural Resources Trust Fund (ENRTF) in July 2018 to conduct monitoring at public drinking water systems. The goals of this project are to: 1) characterize the presence of selected unregulated contaminants in drinking water sources and associated samples of treated drinking water in Minnesota; and 2) identify screening approaches to simplify and target future monitoring efforts.

Broadly speaking, drinking water in Minnesota comes from either groundwater or surface water. The monitoring approaches described in this plan will apply to both types of source water. Prior work in Minnesota and elsewhere has established that different classes of unregulated contaminants (e.g., pharmaceuticals, pesticides, etc.) are derived from different land uses. Key land uses of concern in Minnesota are those subject to agricultural operation and, separately, those affected by wastewater disposal. While there is some overlap, the types of unregulated contaminants that come from agricultural land uses differ from those subject to wastewater disposal. Consequently, we created separate monitoring networks for wastewater and for agricultural land uses. Site selection criteria and parameter selection for these networks are described below (see Table 1, Figure 1).

Monitoring will consist of sample collection from drinking water sources, as well as from other selected sampling points within the drinking water system, and analysis of the samples using several different approaches. Screening techniques and targeted laboratory analytical approaches will be used to characterize water quality. The sampling and analysis approaches described in this plan are limited by the time frame and budget laid out in the original grant.

Site Selection

Site selection criteria were developed separately for each network. A set of prospective sampling sites have been defined for wells that may have been affected by wastewater and by agricultural land uses. We expect that some of these sites will not be sampled for any number of unforeseen circumstances, but we plan to sample approximately 30 wells for each network. An additional 17 surface water sites will be sampled. Each sample from either a groundwater or surface water source will be accompanied by a sample from the distribution system entry point, as defined by the community public water system. Accordingly, a total of approximately 200 samples will be collected and analyzed for this study.

Agricultural network

The following considerations were used to select prospective sample sites:

- Prior water quality conditions
 - Elevated nitrate
 - Detections in 2015 MDH/Minnesota Department of Agriculture (MDA) Pesticide study
 - Groundwater Virus Monitoring study results indicating the presence of bacteria or viruses associated with livestock or manure
- Land use in drinking water supply management area for well
- Measures in wellhead protection plan directed at agricultural land uses
- Geographical diversity

Wastewater network

The following considerations were used to select prospective sample sites:

- Water quality indicative of wastewater influence
 - Cl/Br ratio between 500 and 800, with chloride between 40-100 mg/L
 - Bacteria positive water quality result
 - Groundwater Virus Monitoring study results
 - Prior pharmaceutical or artificial sweetener detection
- Known wastewater sources in drinking water supply management area for well
 - Wastewater treatment plants
 - Subsurface sewage treatment systems/residential septic
 - National Pollutant Discharge Elimination System (NPDES) permits
 - Sewer infrastructure

Surface water network

There are 24 community public water systems in Minnesota. All of these will be sampled except for several of the systems that use Lake Superior, the Red Lake River, and mine pit lakes as a source of supply.

Parameter Selection

General Considerations:

1. Association of compounds with wastewater disposal or agricultural land use activities, tailoring the parameters to the setting being sampled.
2. Results from prior studies. Preference given to characterizing presence of compounds found in previous work in groundwater or surface water in Minnesota, or nationally.
3. Availability of resources.

For example, study design does not lend itself to multiple sample selection events, at a short frequency, as would be required to fully characterize compounds that may exhibit short term or seasonal/climatic dependencies.

4. Technology or laboratory analytical limitations.
5. Availability of prior studies that are specific to drinking water. For example, the MDH Groundwater Virus Monitoring study, the 2015 MDA/MDH Pesticide Study, and ongoing cyanotoxin work by St. Paul Regional Water Services.
6. Compounds that are of current public health interest or concern (i.e. per- and polyfluoroalkyl substances (PFAS), iopamidol).

Agricultural network

Parameters that were chosen for the agricultural network were selected, in addition to the considerations listed above, based on their association with agricultural land use. Detection of these parameters will serve as an indication that chemicals involved in agricultural activities at the land surface are reaching the aquifers below and impacting the public water supply wells. These compounds primarily include pesticides.

Wastewater network

Parameters that were chosen for the wastewater network were selected, in addition to the considerations listed above, based on their association with wastewater disposal. Detection of these parameters will serve as an indication that compounds in human waste and wastewater are reaching the aquifers below and impacting the public water supply wells. These compounds include pharmaceuticals, personal care products, specific wastewater indicators, and PFAS.

Surface water network

The surface water sites contain the most vulnerable water supplies of the three sampling networks included in this study, as such, the parameters selected for the surface water network consist of the parameters selected for both the agricultural and wastewater networks, as well as additional parameter groups. These additional parameters include benzotriazoles, illicit drugs, alkyl phenols and alkyl phenol ethoxylates, hormones, and an expanded array of pharmaceuticals and personal care products that are more broadly detected in surface waters.

Scheduling

Sites included in the agricultural network and wastewater networks will be sampled one time during the summer of 2019. Surface water sites will be sampled twice during the summer of 2019. All site visits will include coupled samples from both the source (raw water) and finished water.

Quality Assurance/Quality Control

Quality control samples will be collected at approximately 10% of all sites within each sampling network. These will include a mixture of field blanks and duplicate samples, as well as trip blanks.

MONITORING PLAN

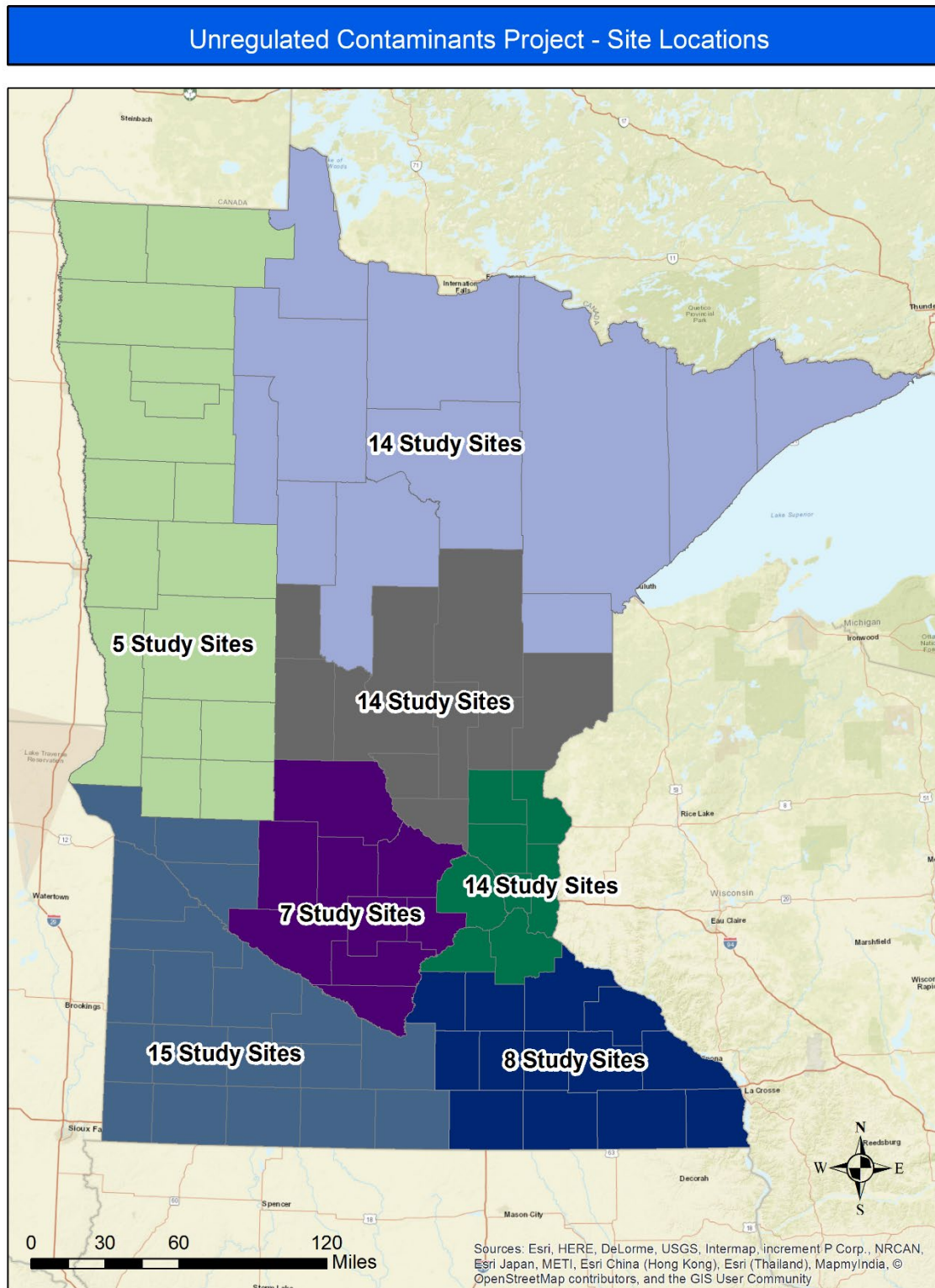
Table 1. Parameter Selection by Network

Parameter Group	Lab	Agricultural Network	Wastewater Network	Surface Water Network
General water chemistry	MDH	X	X	X
ELISA ¹ Pharmaceuticals	USGS ²		X	X
ELISA Pesticides	USGS	X		X
Wastewater indicators	USGS NWQL ³		X	X
Pharmaceuticals	USGS NWQL		X	X
PFAS	AXYS		X	X
Benzotriazoles	MDH			X
Illicit Drugs	MDH			X
Pharmaceuticals and Personal Care Products (Lists 1, 6)	AXYS		X	
Pharmaceuticals and Personal Care Products (Lists 1, 3, 6)	AXYS			X
Alkyl Phenols and Alkyl Phenol Ethoxylates	AXYS			X
Hormones	AXYS			X
Pesticides	USGS NWQL	X		X

¹Enzyme-linked immunosorbent assay; ²U.S. Geological Survey; ³National Water Quality Laboratory

MONITORING PLAN

Figure 1. Study Sites by Region



MONITORING PLAN

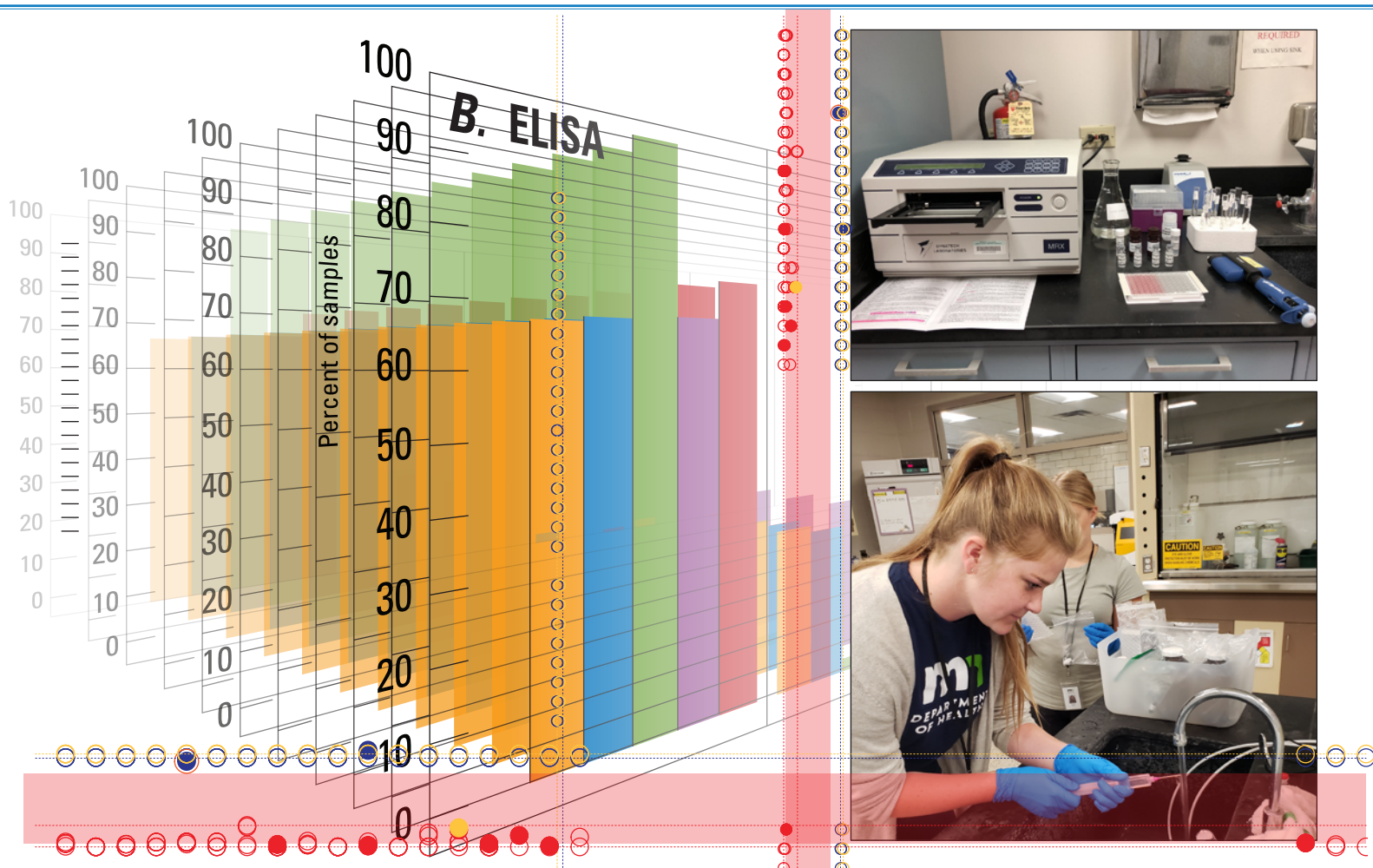
Minnesota Department of Health
PO Box 64975
St. Paul, MN 55164-0975
651-201-4700
health.drinkingwater@state.mn.us
www.health.state.mn.us

7/1/2019

To obtain this information in a different format, call 651-201-4700.

Prepared in cooperation with the Minnesota Department of Health

Comparison of the Results of Enzyme-Linked Immunosorbent Assay (ELISA) to Mass-Spectrometry Based Analytical Methods for Six Unregulated Contaminants in Source Water and Finished Drinking-Water Samples



Scientific Investigations Report 2022–5066

Cover. Arianna Giorgi, Minnesota Department of Health, sampling groundwater from a tap.
Photo by Jane De Lambert, Minnesota Department of Health

Enzyme-linked immunosorbent assay analysis at the U.S. Geological Survey, Upper Midwest Water Science Center in Mounds View, Minnesota. Photo by Aliesha Krall, U.S. Geological Survey

Comparison of the Results of Enzyme-Linked Immunosorbent Assay (ELISA) to Mass-Spectrometry Based Analytical Methods for Six Unregulated Contaminants in Source Water and Finished Drinking-Water Samples

By Aliesha L. Krall, Sarah M. Elliott, Jane R. de Lambert, and Stephen W. Robertson

Prepared in cooperation with the Minnesota Department of Health

Scientific Investigations Report 2022–5066

**U.S. Department of the Interior
U.S. Geological Survey**

U.S. Geological Survey, Reston, Virginia: 2022

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment—visit <https://www.usgs.gov> or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit <https://store.usgs.gov/>.

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this information product, for the most part, is in the public domain, it also may contain copyrighted materials as noted in the text. Permission to reproduce copyrighted items must be secured from the copyright owner.

Suggested citation:

Krall, A.L., Elliott, S.M., de Lambert, J.R., and Robertson, S.W., 2022, Comparison of the results of enzyme-linked immunosorbent assay (ELISA) to mass-spectrometry based analytical methods for six unregulated contaminants in source water and finished drinking-water samples: U.S. Geological Survey Scientific Investigations Report 2022–5066, 29 p., <https://doi.org/10.3133/sir20225066>.

Associated data for this publication:

Krall, A.L., and Elliott, S.M., 2022, Concentrations and laboratory quality-assurance data for six unregulated contaminants measured in source and finished drinking-water samples collected from public water systems throughout Minnesota by using ELISA and MS-based analytical methods: U.S. Geological Survey data release, <https://doi.org/10.5066/P9MLY0GM>.

ISSN 2328-0328 (online)

Acknowledgments

Funding for this study was provided by a grant from the Minnesota Environment and Natural Resources Trust Fund to the Minnesota Department of Health and the U.S. Geological Survey's Cooperative Matching Funds.

Contents

Acknowledgments	iii
Abstract	1
Introduction	1
Purpose and Scope	2
Study Area	3
Study Methods	4
Collection of Water Samples	4
Laboratory Analyses	4
Enzyme-Linked Immunosorbent Assay (ELISA) Methods	4
Direct Aqueous Injection with Liquid Chromatography and Tandem Mass Spectrometry (LC-MS/MS) Pesticide Analysis at the U.S. Geological Survey National Water Quality Laboratory (NWQL)	5
Direct Aqueous Injection with High Performance Liquid Chromatography and Tandem Mass Spectrometry (HPLC/MS/MS) Pharmaceutical Analysis at the U.S. Geological Survey National Water Quality Laboratory (NWQL)	5
Direct Aqueous Injection with Liquid Chromatography and Tandem Mass Spectrometry (LC-MS/MS) Pharmaceutical Analysis at the SGS AXYS Analytical Services Ltd. (AXYS)	8
Field and Laboratory Quality Assurance/Quality Control	8
Data Processing	8
Immunologically Similar Contaminants	8
Pesticides	8
Pharmaceuticals	9
Analytical Method Comparisons	9
Results of Analyses	9
Pesticides and Pharmaceuticals Determined by Enzyme-Linked Immunosorbent Assay (ELISA)	10
Pesticides and Pharmaceuticals Determined by the National Water Quality Laboratory (NWQL)	10
Pharmaceuticals Determined by the SGS AXYS Analytical Services Ltd. (AXYS)	13
Presence-Absence Agreement Among Analytical Methods	13
Implications of Using ELISA as a Screening Tool	18
Summary	18
References Cited	19
Appendix 1. Censoring Analytical Result Data	22
Appendix 2. False Negative and False Positive Analysis	23
Appendix 3. Paired Prentice-Wilcoxon Test	24
Appendix 4. Comparison of Sample Concentration Ranking Among Analytical Methods	29

Figures

1. Map showing general locations of sampled Minnesota public water systems, 2019 3

2. Graphs showing percent of sample detections for six unregulated contaminant groups in source and finished drinking-water samples collected from public water systems throughout Minnesota, 2019	12
3. Graphs showing concentrations of three unregulated pesticide contaminant groups in source and finished drinking-water samples collected from public water systems throughout Minnesota, 2019	15
4. Graphs showing concentrations of three unregulated pharmaceutical contaminant groups in source and finished drinking-water samples collected from public water systems throughout Minnesota, 2019	16
5. Graphs showing percent of samples with zero to five contaminant group detections in a single source or finished drinking-water sample by public water system collected from public water systems throughout Minnesota, 2019, and by public water system source water type	17

Tables

1. Unregulated contaminants analyzed in source water and finished drinking-water samples collected from public water systems throughout Minnesota, 2019, and associated laboratory reporting limits and human health-based advisory levels in nanograms per liter	6
2. Summary of pesticide and pharmaceutical detections analyzed in source and finish drinking-water samples collected from public water systems throughout Minnesota, 2019	10
3. Paired result ties and presence-absence agreement between enzyme-linked immunosorbent assay and more advanced analytical methods by the U.S. Geological Survey National Water Quality Laboratory and SGS AXYS Analytical Services Ltd	14

Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
mile (mi)	1.609	kilometer (km)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F = (1.8 × °C) + 32.

Supplemental Information

Concentrations of chemical constituents in water are given in nanograms per liter (ng/L).

Samples sizes are given in milliliters (mL) or microliters (µL).

Filter sizes are given in micrometers (µm).

Abbreviations

ATZ _{TOT}	atrazine and immunologically similar contaminants
ATZ1	atrazine
ATZ2	ametryn
ATZ3	2-Chloro-4-isopropylamino-6-amino- <i>s</i> -triazine
ATZ4	2-Hydroxy-4-isopropylamino-6-ethylamino- <i>s</i> -triazine
ATZ5	propazine
ATZ6	simazine
AXYS	SGS AXYS Analytical Services Ltd.
CAF _{TOT}	caffeine and immunologically similar contaminants
CAF1	caffeine
CAF2	1,7-Dimethylxanthine
CAF3	theophylline
CBZ _{TOT}	carbamazepine and immunologically similar contaminants
CBZ1	carbamazepine
CBZ2	amitriptyline
CV	coefficient of variation
ELISA	enzyme-linked immunosorbent assay
EPA	U.S. Environmental Protection Agency
GW _{Ag}	groundwater influenced by agriculture
GW _{WW}	groundwater influenced by wastewater
GW _{WW/Ag}	groundwater influence by both wastewater and agriculture
HPLC/MS/MS	direct aqueous injection with high performance liquid chromatography and tandem mass spectrometry
IMD _{TOT}	imidacloprid and immunologically similar contaminants
IMD1	imidacloprid
LC-MS/MS	direct aqueous injection with liquid chromatography and tandem mass spectrometry
MDH	Minnesota Department of Health
NWQL	National Water Quality Laboratory
PPW	Paired Prentice-Wilcoxon test
PYR _{TOT}	pyrethroids and immunologically similar contaminants
PYR1	<i>cis</i> -Permethrin
PYR2	bifenthrin
QC	quality control
R^2	correlation coefficient

RPD	relative percent difference
SMX _{TOT}	sulfamethoxazole and immunologically similar contaminants
SMX1	sulfamethoxazole
SMX2	sulfamethizole
SMX3	sulfadimethoxine
SMX4	sulfamerazine
SMX5	sulfamethazine
SW	surface water
UMID	U.S. Geological Survey, Upper Midwest Water Science Center
USGS	U.S. Geological Survey

Comparison of the Results of Enzyme-Linked Immunosorbent Assay (ELISA) to Mass-Spectrometry Based Analytical Methods for Six Unregulated Contaminants in Source Water and Finished Drinking-Water Samples

By Aliesha L. Krall,¹ Sarah M. Elliott,¹ Jane R. de Lambert,² and Stephen W. Robertson²

Abstract

Regulatory entities, such as the Minnesota Department of Health, monitor public water systems for conformance with Federal and State monitoring requirements and water-quality standards. Although some contaminants have Federal and (or) State regulations and guidance values, many contaminants, such as pesticides and pharmaceuticals, are unregulated in that only non-enforceable health-based guidance values have been assigned to them. Furthermore, because these contaminants are not regulated, commonly only limited resources are available to public water systems or regulatory entities to monitor them in drinking water. Focused screening efforts on contaminants that are frequently detected in the environment can provide information to help monitoring entities prioritize their sampling efforts.

Here we assess the use of enzyme-linked immunosorbent assay (ELISA) method, a rapid, inexpensive screening method, as an alternative to more expensive methods to analyze source and finished drinking-water samples collected from public water systems throughout Minnesota for three commonly detected pesticides (atrazine, imidacloprid, and pyrethroids) and three commonly detected pharmaceuticals (caffeine, carbamazepine, and sulfamethoxazole). The ELISA results were compared to results provided by more advanced mass-spectrometry analytical methods at the U.S. Geological Survey National Water Quality Laboratory (NWQL) and SGS AXYS Analytical Services Ltd. (AXYS).

Overall, these datasets are highly censored (>80 percent) and contain multiple reporting limits within and between laboratories. To discern agreement between paired contaminant group results (target contaminant plus immunologically similar contaminants) by ELISA and the advanced analytical methods at NWQL and AXYS, presence-absence agreement

analysis was coupled with false negative and false positive analysis. Analysis of presence-absence agreement shows that ELISA has generally good agreement (77.9 to 100 percent) with both NWQL and AXYS for all unregulated contaminant groups. Imidacloprid, pyrethroids, and caffeine contaminant groups have relatively low false positivity rates (16, 6, and 5 percent, respectively) when analyzed by ELISA, which indicates the ELISA method, for these contaminant groups, could be experiencing low-level interference attributed to the detection of immunologically similar contaminants. Similarly, sulfamethoxazole has a low false positivity rate (0.8 percent), which indicates ELISA is likely not overestimating results for this contaminant group. Analyses for carbamazepine and sulfamethoxazole by ELISA resulted in low false negativity rates (1.6 and 0.8 percent, respectively), which indicates the ELISA method is likely not underestimating the results for this contaminant group. Conversely, the atrazine contaminant group has a high false negativity rate (84 percent), which indicates the method has a strong negative bias and that ELISA underestimates results for this contaminant. These qualitative results indicate that the ELISA method could potentially serve as a reliable and cost-effective screening method to help drinking water monitoring entities prioritize sampling efforts for analyzing carbamazepine and sulfamethoxazole in source and finished drinking-water samples collected from public water systems. At the same time, although ELISA did not prove to be a good screening method for atrazine, evaluation of ELISA results indicated that its use for screening imidacloprid, pyrethroids, and caffeine could be beneficial for water testing.

Introduction

Given the frequent occurrence of unregulated contaminants (for example, pharmaceuticals, pesticides, personal care products, and so on) in aquatic environments (Noguera-Oviedo and Aga, 2016; Ebele and others, 2017; Glassmeyer

¹U.S. Geological Survey.

²Minnesota Department of Health.

2 Comparison of the Results of ELISA to Mass-Spectrometry Based Analytical Methods for Six Unregulated Contaminants

and others, 2017; Wilkinson and others, 2017), and in groundwater and surface water in Minnesota (Erickson and others, 2014; Elliott and others, 2018; Elliott and others, 2017; Lee and others, 2011), it is plausible that these contaminants pose a threat to the quality of drinking water in the State. Furthermore, because these contaminants are unregulated, resources available for monitoring them in drinking water is commonly limited. Rapid, inexpensive screening methods may offer monitoring entities an alternative for assessing the presence of unregulated contaminants in drinking water to fill this gap in knowledge.

More than 75 percent of Minnesotans get their drinking water from a public water system (Minnesota Department of Health, 2020b). The Minnesota Department of Health (MDH) monitors all public water systems in the State (approximately 7,000) for conformance with Federal monitoring requirements and water-quality standards. Currently, the U.S. Environmental Protection Agency (EPA) has primary drinking-water standards and requirements for 88 compounds or chemicals, including disinfectants, disinfection byproducts, metals, microorganisms, radionuclides, and various organic compounds or chemicals (U.S. Environmental Protection Agency, 2020). In addition to the EPA primary drinking-water requirements, EPA and (or) MDH non-enforceable health-based guidance values have been established for another approximately 150 contaminants (Minnesota Department of Health, 2020a). Existing regulations and guidance values represent only a small fraction of the roughly 86,000 chemicals that are currently in use in the United States (U.S. Environmental Protection Agency, 2021). Although it is not feasible to expect drinking-water facilities or monitoring entities to test for every chemical that may be present, focusing screening efforts on particular chemicals that are more frequently used and (or) detected in the environment can provide information in prioritizing sites for more extensive monitoring.

Enzyme-linked immunosorbent assay (ELISA) methods are a rapid, inexpensive way to screen environmental samples. Briefly, ELISA relies on binding of antigens in the environmental sample to chemical-specific antibodies. The unbound antibodies are removed, and an enzyme substrate added. If antigen-antibody binding occurs, the enzyme substrate produces a color change in proportion to the amount of binding. Although ELISA data are semi-quantitative, they have been used successfully in environmental studies as a screening tool and often produce data comparable to those

obtained by liquid chromatography or high-performance liquid chromatography methods (Trost and others, 2013; Bradley and others., 2014; Krall and others, 2018). ELISA test kits are commercially available for various current-use chemicals such as pesticides and pharmaceuticals.

To evaluate the use of ELISA as a screening method for monitoring contaminant presence in drinking water, the U.S. Geological Survey (USGS), in cooperation with the Minnesota Environmental and Natural Resources Trust Fund and the MDH, collected both source and finished drinking-water samples from 67 public water systems throughout Minnesota (fig. 1). Samples were analyzed at accredited laboratories for a large suite of pesticides and pharmaceuticals. Samples were also analyzed by ELISA for a subset of the contaminants: three pesticides (atrazine, imidacloprid, and pyrethroids) and (or) three pharmaceuticals (caffeine, carbamazepine, and sulfamethoxazole). These contaminants were chosen on the basis of expected sources from surrounding land use (for example, agriculture or urban), current knowledge of their frequent occurrence in the environment, and based on results from previous monitoring studies by MDH, Minnesota Department of Agriculture, Minnesota Pollution Control Agency, and USGS (Minnesota Department of Agriculture, 2016a; Minnesota Department of Agriculture, 2019; Erickson and others, 2014; Elliott and others, 2018).

Purpose and Scope

The purpose of this report is to present results of the analysis to discern agreement between ELISA and other analytical methods at two accredited laboratories on the prevalence of six unregulated contaminants (atrazine, imidacloprid, pyrethroids, caffeine, carbamazepine, and sulfamethoxazole) in source and finished drinking-water samples collected from public water systems throughout Minnesota. The laboratories used were the USGS National Water Quality Laboratory (NWQL) and SGS AXYS Analytical Services, Ltd (AXYS). The analysis objectives were threefold: (1) to document and describe the ELISA, NWQL, and AXYS results, (2) to statistically compare ELISA concentrations to the NWQL and AXYS concentrations, and (3) to describe implications of the results.

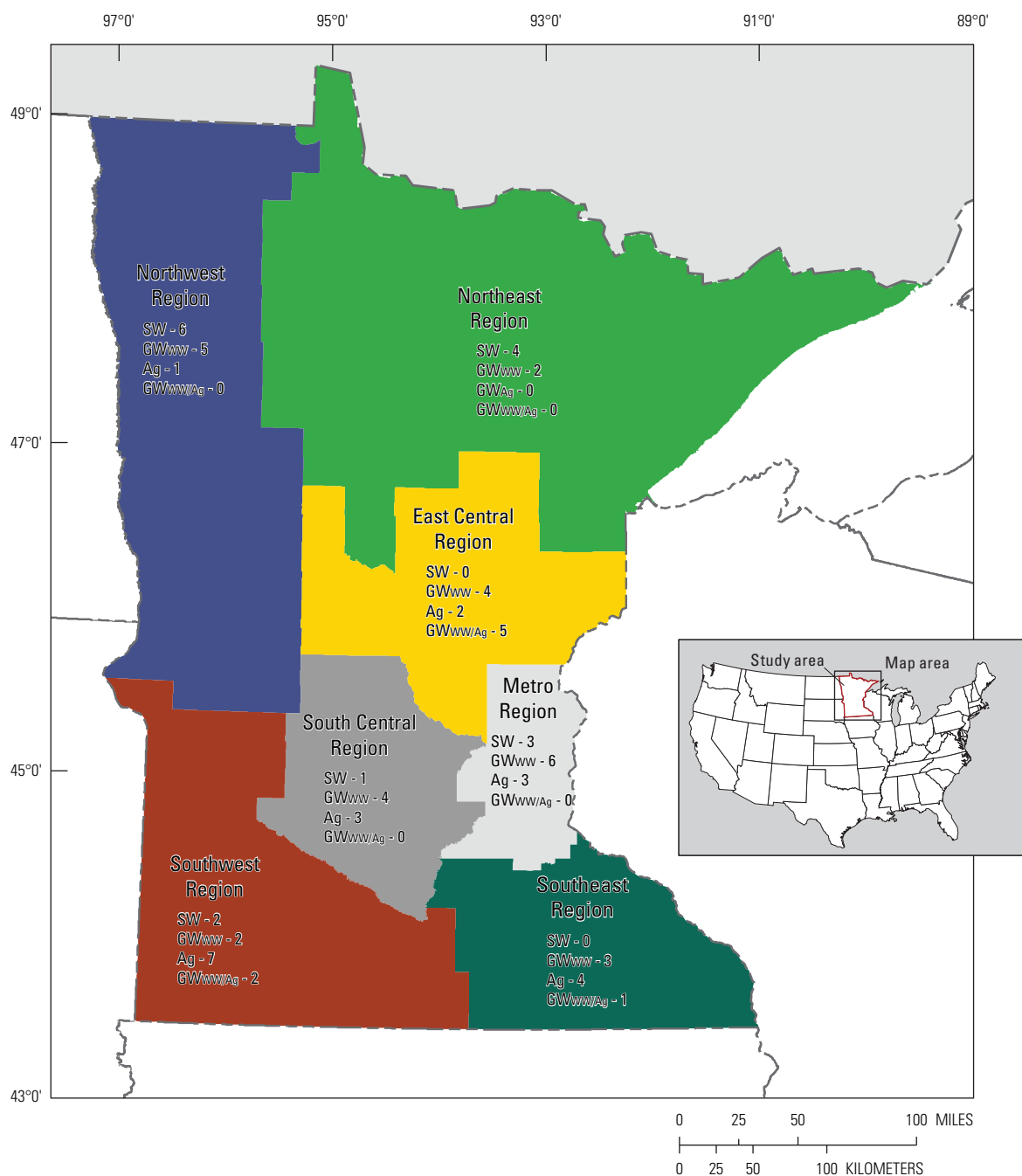


Figure 1. General locations of sampled Minnesota public water systems, 2019. [SW, surface water sourced public water system; GW_{WW}, groundwater sourced public water system influenced by wastewater; GW_{Ag}, groundwater sourced public water system influenced by agricultural activities; GW_{WW/Ag}, groundwater sourced public water system influenced by a mix of wastewater and agricultural activities]

Study Area

The data used in this assessment of analytical methods are the results of analyses of samples collected from 67 public water systems throughout Minnesota. To retain anonymity of the sampled facilities, the number and source water type for the public water systems sampled are shown only within

geographic regions in [figure 1](#). The public water systems were categorized on the basis of the source of their water, whether surface water or groundwater. Groundwater sources were further categorized by expected sources of contamination—whether influenced by wastewater, agricultural activities, or a combination of those influences. The source waters for the 67 public water systems sampled consisted of 16 surface-water

(SW) sources, 22 groundwater sources influenced by wastewater (GW_{WW}), 21 groundwater sources influenced by agricultural activities (GW_{Ag}), and 8 groundwater sources influenced by both wastewater and agricultural activities ($GW_{WW/Ag}$).

Study Methods

Water samples were collected and handled using methods specified in the USGS National Field Manual for the Collection of Water-Quality Data (USGS, 2006), and analyzed both by the ELISA method at the USGS Upper Midwest Water Science Center (UMID) and by advanced liquid mass-spectrometry based methods at the two accredited laboratories. Quality-assurance and quality-control practices were followed at both field and laboratory analytical phases of sample processing.

Collection of Water Samples

Source water and finished drinking-water samples were collected by MDH staff at public water systems between August and November 2019. Samples were collected once from groundwater sourced public water systems (GW_{WW} , GW_{Ag} , and $GW_{WW/Ag}$) and twice from surface-water-sourced facilities (SW). Source water samples were grab samples collected from raw water taps inside water treatment plants or well houses or from surface-water intakes. Finished water samples were grab samples collected from sampling taps inside the water treatment plant or well house. Prior to sample collection, the water lines were flushed for about 15 minutes and physical or field measurable properties (water temperature, dissolved oxygen concentration, pH, and specific conductance) were monitored and recorded with a YSI ProDSS water-quality meter (YSI Inc., Yellow Springs, Ohio) every three minutes until five consecutive sets of field properties indicated stabilization of those properties. Samples for ELISA analyses were collected in two 40 milliliter (mL) amber vials to about the half-full mark, immediately put on ice, and stored at MDH at 4 degrees Celsius until frozen within 5 days at UMID in Mounds View, Minnesota. For pesticide and pharmaceutical analyses at the NWQL, the water was passed through a 0.7 micrometer (μm) syringe-tip filter, from which 10 mL samples were dispensed into an amber glass vial. For pharmaceutical analyses at AXYS, two samples of approximately 450 mL each were collected. Field (blank and sequential replicate) quality-control (QC) samples were collected and analyzed in the same manner as environmental samples. Samples were stored at MDH at 4 degrees Celsius for up to 5 days prior to shipment to the appropriate analyzing laboratories. Samples for analyses at the NWQL were delivered to UMID for preparation and shipment overnight on wet ice. Samples for analyses at AXYS were shipped to the laboratory on wet ice by MDH personnel.

Laboratory Analyses

Concentrations of three target pesticides (atrazine, ATZ; imidacloprid, IMD; and pyrethroids, PYR) plus several immunologically similar contaminants; and three target pharmaceuticals (caffeine, CAF; carbamazepine, CBZ; and sulfamethoxazole, SMX) plus several immunologically similar contaminants were determined. Target contaminants and immunologically similar contaminants (as defined by ELISA specifications) are referenced by the subscript “TOT” following the target contaminant acronym (for example, ATZ_{TOT} , CBZ_{TOT}) and are referred to as contaminant groups. Note that ATZ_{TOT} and all contaminant group “TOT” results may represent a different set of compounds across analysis methods. Target contaminants are referenced by the number 1 following the acronym (for example, ATZ_1 , CBZ_1). Immunologically similar contaminants are referenced by a number greater than 1 following the acronym (for example, ATZ_2 , CBZ_2). This referencing scheme does not apply to pyrethroids because pyrethroids are a family of contaminants, so there is no single target contaminant. A description of each referenced contaminant is provided in [table 1](#). Samples collected from SW (66 samples) and $GW_{WW/Ag}$ (16 samples) public water systems were analyzed for all six contaminants. Samples collected from GW_{Ag} (40 samples) public water systems were analyzed for the three pesticides, and samples collected from GW_{WW} (40 samples) public water systems were analyzed for the three pharmaceuticals. A total of 162 water-quality samples were analyzed by three different laboratory entities. Analytical results are available in a USGS data release (Krall and Elliott, 2022).

Enzyme-Linked Immunosorbent Assay (ELISA) Methods

Concentrations of six target contaminants plus their immunologically similar contaminants (ATZ_{TOT} , IMD_{TOT} , PYR_{TOT} , CAF_{TOT} , CBZ_{TOT} , and SMX_{TOT}) in 162 samples from 67 public water systems were determined at UMID using commercially available ELISA kits (Eurofins-Abraxis Inc., Warminster, Pennsylvania). The contaminants analyzed in each sample differed depending on the source water used at a public water-supply system. A total of 122 source and finished drinking-water samples collected from 45 public water systems (SW, $GW_{WW/Ag}$, and GW_{Ag}) were analyzed for three pesticide contaminant groups (ATZ_{TOT} , IMD_{TOT} , and PYR_{TOT}). A total of 122 source and finished drinking-water samples collected from 48 public water systems (SW, $GW_{WW/Ag}$, and GW_{WW}) were analyzed for three pharmaceutical contaminant groups (CAF_{TOT} , CBZ_{TOT} and SMX_{TOT}).

The ELISA analytical procedure is described in detail elsewhere (Eurofins-Abraxis Inc., 2019a, 2019b, 2019c, 2019d, 2019e, 2019f). Briefly, all environmental and quality-control (QC) samples were analyzed in duplicate and hereafter are referred to as analysis pairs. Several types of QC

samples were provided by the manufacturer, including five to six calibration standards and up to two control samples of a known concentration. Other QC samples included laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified sample matrix samples. First, the environmental and QC samples were dispensed into separate wells on the microplate. Antibody solution was then added to each well, mixed, and allowed to incubate either at ambient temperature or between 2 and 8 °C for between 30 and 90 minutes, depending on the contaminant being analyzed. After incubation, the contents in the wells were discarded and washed with a 1:5 wash buffer solution. Following the wash, the contents in the wells were discarded, a color solution was added to each well, and the microplate was incubated at ambient temperature or between 2 and 8 °C for 20 to 30 minutes, depending on the contaminant being analyzed. Lastly, stop solution was added to each well and within 15 minutes the plate was placed into a Bio Tek Microplate Reader (Bio Tek Instruments Inc., Winooski, Vermont) to read the absorbance of each well's contents at 450 nanometers. The reporting limits for each contaminant range from 50 to 2,000 nanograms per liter (ng/L) for pesticides, and from 25 to 175 ng/L for pharmaceuticals (table 1).

A four-parameter logistic curve was produced for calibration of each batch assay analysis in Gen5 Microplate Software for Windows (Bio Tek Instruments, Winooski, Vermont). The calibration curve was validated by evaluating the percent coefficient of variation (CV) between absorbance values for each calibration standard pair. To accept the assay calibration, the CV must be less than or equal to 10 percent for each calibration standard pair. However, one calibration standard analysis pair can have less than or equal to 15 percent CV, providing the assay curve correlation coefficient (R^2) is greater than or equal to 0.98. If the calibration fails the percent CV limits of absorbance and R^2 less than 0.98, then the assay analysis is invalid. The percent CV for control and environmental analysis pairs is acceptable at less than 20 percent. When the percent CV exceeds this limit, the individual control or environmental sample analysis is invalid. Acceptable relative percent recovery limits for spiked samples range from 70 to 130 percent of the expected concentration. If recoveries are outside of this range, the results may be matrix biased. The relative percent difference (RPD) of laboratory fortified sample matrix samples should be less than 30 percent, and if RPD exceeds this limit then the precision of the plate analysis may be matrix biased.

Direct Aqueous Injection with Liquid Chromatography and Tandem Mass Spectrometry (LC-MS/MS) Pesticide Analysis at the U.S. Geological Survey National Water Quality Laboratory (NWQL)

A total of 122 source and finished drinking-water samples were collected from 45 SW, GW_{Ag}, and GW_{WW/Ag} public water systems and analyzed at the NWQL for 225 pesticides by LC-MS/MS, using methods described in Sandstrom and others (2016). Briefly, a 100-microliter (μL) sample was directly injected into the LC-MS/MS without any sample preparation. Samples were analyzed in electrospray ionization positive and negative mode using two multiple-reaction monitoring conditions. The target contaminant atrazine (ATZ1) and five immunologically similar contaminants (ametryn [ATZ2], 2-chloro-4-isopropylamino-6-amino-*s*-triazine [ATZ3], 2-hydroxy-4-isopropylamino-6-ethylamino-*s*-triazine [ATZ4], propazine [ATZ5], and simazine [ATZ6]), along with the target contaminant imidacloprid (IMD1), and pyrethroids (*cis*-permethrin [PYR1] and bifenthrin [PYR2]), were included in the analysis. Reporting limits for each contaminant ranged from 3.2 to 250 ng/L (table 1).

Direct Aqueous Injection with High Performance Liquid Chromatography and Tandem Mass Spectrometry (HPLC/MS/MS) Pharmaceutical Analysis at the U.S. Geological Survey National Water Quality Laboratory (NWQL)

A total of 122 source and finished drinking-water samples collected from 46 SW, GW_{WW}, and GW_{WW/Ag} public water systems were analyzed at the NWQL for 110 pharmaceuticals by HPLC/MS/MS, using methods described in Furlong and others (2014). Briefly, 100 μL of sample was directly injected into a HPLC/MS/MS. Samples were analyzed using an electrospray ionization source in the positive ion mode. The target contaminant caffeine (CAF1) and two immunologically similar compounds (1,7-dimethylxanthine [CAF2] and theophylline [CAF3]), the target contaminant carbamazepine (CBZ1) and one immunologically similar contaminant (amitriptyline [CBZ2]), and the target contaminant sulfamethoxazole (SMX1) and two immunologically similar contaminants (sulfamethizole [SMX2] and sulfadimethoxine [SMX3]), were included in analysis. Reporting limits for each contaminant ranged from 11 to 200 ng/L (table 1).

6 Comparison of the Results of ELISA to Mass-Spectrometry Based Analytical Methods for Six Unregulated Contaminants

Table 1. Unregulated contaminants analyzed in source water and finished drinking-water samples collected from public water systems throughout Minnesota, 2019, and associated laboratory reporting limits and human health-based advisory levels in nanograms per liter.

[CASRN, Chemical Abstracts Services Registry Number; NWIS, National Water Information System; ELISA, enzyme-linked immunosorbent assay analytical method; Min, minimum; Max, maximum; NWQL, U.S. Geological Survey National Water Quality Laboratory; AXYS, SGS AXYS Services Ltd.; ATZ, atrazine; --, no data available; HRL, Minnesota Department of Health health risk limit; MCL, U.S. Environmental Protection Agency enforceable maximum contaminant level; HBV, Minnesota Department of Health health risk limit; HBSL, U.S. Geological Survey cancer health-based screening level; IMD, imidacloprid; PYR, pyrethroids; HHBP, U.S. Environmental Protection Agency carcinogenic or chronic noncancer human health benchmark for pesticide; CAF, caffeine; CBZ, carbamazepine; SMX, sulfamethoxazole; RAA, Minnesota Department of Health risk assessment advice]

Contaminant	Immunologically similar contaminant	Immunologically similar contaminant definition	CASRN	NWIS parameter code	ELISA		
					Reporting limit	Mini	Max
ATZ	ATZTOT	Atrazine and immunologically similar contaminants analyzed by respective laboratory	--	--	50	<50	163
	ATZ1	Atrazine	1912-24-9	65065			
	ATZ2	Ametryn	834-12-8	68533			
	ATZ3	2-Chloro-4-isopropylamino-6-amino- <i>s</i> -triazine	6190-65-4	68552			
	ATZ4	2-Hydroxy-4-isopropylamino-6-ethylamino- <i>s</i> -triazine	2163-68-0	68660			
	ATZ5	Propazine	139-40-2	68678			
	ATZ6	Simazine	122-34-9	65105			
IMD	IMDTOT	Imidacloprid and immunologically similar contaminants analyzed by respective laboratory	--	--	300	76	<300
	IMD1	Imidacloprid	138261-41-3	68426			
PYR	PYRTOT	Pyrethroids and immunologically similar contaminants analyzed by respective laboratory	--	--	2,000	1,053	2,245
	PYR1	<i>cis</i> -Permethrin	61949-76-6	68769			
	PYR2	Bifenthrin	82657-04-3	65067			
CAF	CAFTOT	Caffeine and immunologically similar contaminants analyzed by respective laboratory	--	--	175	<175	384
	CAF1	Caffeine	58-0-2	67440			
	CAF2	1,7-Dimethylxanthine	611-59-6	67446			
	CAF3	Theophylline	58-55-9	67494			
CBZ	CBZTOT	Carbamazepine and immunologically similar contaminants analyzed by respective laboratory	--	--	25	<25	118
	CBZ1	Carbamazepine	298-46-4	67441			
	CBZ2	Amitriptyline	50-48-6	67522			
SMX	SMXTOT	Sulfamethoxazole and immunologically similar contaminants analyzed by respective laboratory	--	--	25	24	27
	SMX1	Sulfamethoxazole	723-46-6	67454			
	SMX2	Sulfamethizole	144-82-1	67476			
	SMX3	Sulfadimethoxine	122-11-2	67503			
	SMX4	Sulfamerazine	127-79-7	--			
	SMX5	Sulfamethazine	57-68-1	--			

Table 1. Unregulated contaminants analyzed in source water and finished drinking-water samples collected from public water systems throughout Minnesota, 2019, and associated laboratory reporting limits and human health-based advisory levels in nanograms per liter.—Continued

[CASRN, Chemical Abstracts Services Registry Number; NWIS, National Water Information System; ELISA, enzyme-linked immunosorbent assay analytical method; Min, minimum; Max, maximum; NWQL, U.S. Geological Survey National Water Quality Laboratory; AXYS, SGS AXYS Services Ltd.; ATZ, atrazine; --, no data available; HRL, Minnesota Department of Health health risk limit; MCL, U.S. Environmental Protection Agency enforceable maximum contaminant level; HBV, Minnesota Department of Health health risk limit; HBSL, U.S. Geological Survey cancer health-based screening level; IMD, imidacloprid; PYR, pyrethroids; HHBP, U.S. Environmental Protection Agency carcinogenic or chronic noncancer human health benchmark for pesticide; CAF, caffeine; CBZ, carbamazepine; SMX, sulfamethoxazole; RAA, Minnesota Department of Health risk assessment advice]

NWQL			AXYS			Human health-based guidance value	Human health-based guidance value type
Reporting limit	Min	Max	Reporting limit	Min	Max		
6.80–20.0	1.46	453.06	--	--	--	--	--
6.80–20.0	1.46	363	--	--	--	3,000	HRL, MCL
2.60–25.0	<2.60	<25	--	--	--	--	--
11.0–250	5.45	111	--	--	--	3,000	HRL, MCL
8.0–250	5.81	<250	--	--	--	20,000	HBV
3.2–10.0	1.04	<10	--	--	--	40,000	HBSL
7.2–250	4.26	<250	--	--	--	4,000	HRL, MCL
16.0–250	6.08	<250	--	--	--	--	--
16.0–250	6.08	<250	--	--	--	2,000	HBV
4.2–250	<4.2	<250	--	--	--	--	--
4.2–5.0	<4.2	<5.0	--	--	--	3,340	HHBP
19.0–250	<19.0	<250	--	--	--	70,000	HHBP
91	9.03	<91.0	13.8–85.2	<13.8	<85.2	--	--
91	9.03	<91.0	13.8–85.2	<13.8	<85.2	--	--
88.0–200	<88.0	<200	55.0–291	<55.0	<291	--	--
80.0–140	<80.0	<140	--	--	--	--	--
11	1.27	178	1.38–7.28	<1.38	157	--	--
11	1.27	178	1.38–7.28	<1.38	157	40,000	HRL
37.0–140	<37.0	<140	--	--	--	--	--
20.0–26.0	5.81	101	0.573–6.46	<0.573	86.7	--	--
20.0–26.0	5.81	101	0.573–6.46	<0.573	86.7	100,000	RAA
104–200	<104	<200	0.550–4.32	<0.550	<4.32	--	--
30	2.17	<30.0	0.275–7.85	<0.275	<7.85	--	--
--	--	--	0.572–4.27	<0.572	<4.27	--	--
--	--	--	0.575–9.7	<0.575	<29.5	100,000	HRL

Direct Aqueous Injection with Liquid Chromatography and Tandem Mass Spectrometry (LC-MS/MS) Pharmaceutical Analysis at the SGS AXYS Analytical Services Ltd. (AXYS)

A total of 122 source and finished drinking-water samples collected from 46 SW, GW_{WW}, and GW_{WW/Ag} public water systems were analyzed at AXYS in British Columbia, Canada by LC-MS/MS (SGS AXYS Analytical Services Ltd., 2019). Briefly, samples were filtered and cleaned using solid-phase extraction. Extracts were then analyzed using LC-MS/MS run in multiple reaction monitoring mode. The target contaminant CAF1 and one immunologically similar contaminant (CAF2), the target contaminant CBZ1, and the target contaminant SMX1 and four immunologically similar contaminants (SMX2, SMX3, sulfamerazine [SMX4], and sulfamethazine [SMX5]), were included in analysis. Reporting limits for each contaminant ranged from 0.275 to 291 ng/L (table 1).

Field and Laboratory Quality Assurance/Quality Control

Field and laboratory QC samples were used to validate and interpret the environmental sample data. Field QC samples are used to assess the quality of the sampling process, including the collection, processing, preservation, transportation, and handling of the samples. Laboratory QC samples are used to assess the quality of the analytical procedure. Each laboratory analyzed blanks, reagent spikes, matrix spikes, and surrogates along with each batch of environmental samples. A detailed summary of the QC data for each of the three laboratory entities is available in Krall and Elliott (2022).

Eight field blanks and eight sequential replicates were collected. Field blank sample results were below the detection limit, with one exception. IMD_{TOT} was detected by ELISA in one source and one finished water field blank sample. Many sequential field replicate sample results by each of the three laboratories were reported as below the detection limit, so RPD could not be assessed. For those that could be assessed, the RPD ranged from 2 to 30 percent for ATZ1, ATZ3, and ATZ4 (analyzed by NWQL) and was 51 percent for SMX5 (analyzed by AXYS).

Each laboratory analyzed blanks, reagent spikes, matrix spikes, and surrogates with each batch of environmental samples. CAF1 was detected in two laboratory blanks by AXYS, and SMX_{tot} was detected in one laboratory blank by ELISA at UMID. Reagent and laboratory matrix spike sample recoveries ranged from 50 to 274 percent and from 16 to 211 percent, respectively. Reagent and matrix spike percent recoveries outside acceptable limits (greater than or equal to 70 and less than or equal to 130 percent) indicate the recoveries could be matrix biased.

Data Processing

The datasets from each laboratory were processed individually prior to making comparisons among them. Data generated by the three analytical laboratories are left censored, meaning that the true values of the censored values are unknown and lie between zero and the reporting limit. Each laboratory had different reporting limits for each contaminant, and some had multiple reporting limits for each contaminant (table 1). Appendixes 1 and 2 provide further discussion on the methods of both censoring contaminant groups and assessing false negative and false positive ELISA observations.

Immunologically Similar Contaminants

The ELISA method responds to immunologically similar (cross-reactive) contaminants, which provides an advantage of detecting target contaminants and associated degradates or metabolites (Eurofins-Abraxis Inc., 2019a, 2019b, 2019c, 2019d, 2019e, 2019f), and may provide an indication of the presence of contaminant mixtures. Therefore, the ELISA results were expected to be higher compared to the target contaminant results from NWQL and AXYS. The summation of the concentrations of target contaminants and immunologically similar contaminants reported by NWQL and AXYS were compared with ELISA results (table 1), and as previously mentioned, are referred to as contaminant groups. Not all immunologically similar contaminants with the potential to cross-react during the ELISA method analyses were analyzed by the other laboratories. The contaminants that make up each contaminant group are described in detail below.

Pesticides

The NWQL ATZ_{TOT} results are the summation of ATZ1 and five immunologically similar contaminant (ATZ2, ATZ3, ATZ4, ATZ5, and ATZ6; table 1) concentrations. Both ATZ3 and ATZ4 are metabolites and environmental degradation products of ATZ1, whereas ATZ2, ATZ5, and ATZ6 are herbicides belonging to the triazine class. The ELISA analytical method for ATZ_{TOT} also indicates the potential of cross-reactivity with terbuthylazine, an herbicide belonging to the triazine class, but this contaminant was not analyzed by the NWQL. The exclusion of terbuthylazine is considered trivial for this study because of its circumscribed use in industrial recirculating cooling water applications and ornamental fountains within the US (U.S. Environmental Protection Agency, 2010) and because it has a low cross-reactivity rate (0.33 percent) (Eurofins-Abraxis Inc., 2019a).

The NWQL IMD_{TOT} results used in this analysis represent only IMD1 because none of the immunologically similar contaminants indicated by the ELISA method were analyzed. The only immunologically similar contaminant that could be of importance is clothianidin because it has a high potential cross-reactivity rate (121 percent) with ELISA and has been detected in both surface water and groundwater in

Minnesota (Eurofins-Abraxis, 209d; Minnesota Department of Agriculture, 2020). Exclusion of the other immunologically similar contaminants from the comparison methods is expected to be trivial because of low cross-reactivity rates (less than 5 percent) or discontinued use in the State (Eurofins-Abraxis, 2019d, Minnesota Department of Agriculture, 2016b and 2020). The NWQL PYR_{TOT} results are the summation of *cis*-permethrin (PYR1) and bifenthrin (PYR2) concentrations. Both PYR1 and PYR2 are insecticides belonging to the pyrethroid family. The ELISA analysis method for PYR_{TOT} does not indicate the potential for cross-reactivity of any other contaminants outside the pyrethroid family (Eurofins-Abraxis Inc., 2019e), and no other contaminants within the pyrethroid family were analyzed at the NWQL.

Pharmaceuticals

The NWQL CAF_{TOT} results are the summation of CAF1, CAF2, and CAF3 (table 1) concentrations. CAF2 is a metabolite and environmental degradation product of CAF1. CAF3 is a bronchodilator used to treat breathing disorders in human and veterinary medical practices (Jilani and others, 2021). The ELISA analytical method for CAF_{TOT} indicates the potential of three other immunologically similar contaminants to exhibit cross-reactivity during analysis that were not analyzed by NWQL so were not included in the summation of CAF_{TOT} . The exclusion of the latter three potentially cross-reactive contaminants is considered trivial because the cross-reactivity rate for each contaminant is <3 percent (Eurofins Abraxis Inc., 2019b).

The AXYS CAF_{TOT} results are the summation of CAF1 and CAF2 (table 1) concentrations. The exclusion of CAF3 could be notable because it has been detected in Minnesota surface water (Minnesota Pollution Control Agency, 2017). Not including the other three potentially cross-reactive contaminants is considered trivial because the cross-reactivity rate for each contaminant is <3 percent (Eurofins Abraxis Inc., 2019b) and the presence of these contaminants in surface water and groundwater is unknown.

The NWQL CBZ_{TOT} results are the summation of CBZ1 and CBZ2 whereas the AXYS CBZ_{TOT} results represent CBZ1 only. The ELISA method indicates potential cross reactivity of six other immunologically similar contaminants that were not analyzed by NWQL. Only two of the immunologically similar contaminants are of potential importance (10,11-dihydro carbamazepine and 10,11-epoxy carbamazepine) because they have been detected in surface waters in Minnesota and worldwide (Miao and Metcalfe, 2003; Bahlmann and others, 2009; Writer and others, 2013) and have high cross-reactivity rates (97 and 78 percent, respectively).

The NWQL SMX_{TOT} results are the summation of SMX1–SMX3, whereas the AXYS SMX_{TOT} results are the summation of SMX1–SMX4. One sample was unquantifiable, resulting in one fewer sample result for SMX1, SMX2, and SMX4. The ELISA method indicates potential cross reactivity of 12 other immunologically similar contaminants (Eurofins-Abraxis, Inc., 2019f), none of which were analyzed

by NWQL. The exclusion of 4 of the 12 immunologically similar contaminants is potentially important because these contaminants have been detected in Minnesota surface water (Minnesota Pollution Control Agency, 2017). The importance of excluding the other eight immunologically similar contaminants is unknown because their presence in the environment is unknown at the time of this report.

Analytical Method Comparisons

To evaluate the use of ELISA as a screening method for monitoring drinking water, we analyzed paired presence-absence agreement and concentration differences between ELISA and both the mass-spectrometry based analytical methods, as appropriate. The paired results have different reporting limits, and prior to comparison, each result of a pair was re-censored to the highest reporting limit of the two results. More detail is provided in appendix 1. Furthermore, because the data are highly censored (greater than 80 percent), the results of statistical analyses to discern agreement between paired concentrations by the Paired Prentice-Wilcoxon (PPW) test are tenuous. The PPW test and results are described in more detail in appendix 3.

The presence-absence test is a qualitative and presumptive test used to determine the presence of a contaminant in a sample rather than its concentration. The qualitative results (present or absent) for each result in a pair are then compared for agreement. For the presence-absence test, the contaminant was present in a sample if it was detected above the highest reporting limit; contrarily, the contaminant was determined absent in a sample if the contaminant was not detected above the highest reporting limit. If the contaminant was either present or absent in both results, the pair agreed. The result pair did not agree if the contaminant was present in one sample and absent from the other.

Results of Analyses

Sample data plus laboratory and field QC results for the three pesticides and three pharmaceuticals of interest determined by ELISA and NWQL methods, and for the three pharmaceuticals of interest determined by the AXYS method are available in Krall and Elliott (2022). As the results indicate, there were few detections of the contaminants. This made comparisons between detected concentrations seemingly insignificant. Appendix 4 provides detail on concentration differences between contaminant detections.

Table 2. Summary of pesticide and pharmaceutical detections analyzed in source and finish drinking-water samples collected from public water systems throughout Minnesota, 2019.

[See [table 1](#) for definitions of immunologically similar contaminants. ELISA, enzyme-linked immunosorbent assay analytical method; CO, censored observation; UO, uncensored observation; *n*, number of observations; %, percent; NWQL, U.S. Geological Survey National Water Quality Laboratory; AXYS, SGS AXYS Services Ltd.; --, no data]

Immunologically similar contaminant	ELISA														
	Total <i>n</i>	False –	False +	Initial				Recensored (ELISA versus NWQL)				Recensored (ELISA versus AXYS)			
				CO		UO		CO		UO		CO		UO	
				<i>n</i>	%	<i>n</i>	%	<i>n</i>	%	<i>n</i>	%	<i>n</i>	%	<i>n</i>	%
ATZTOT	122	27	0	117	95.9	5	4.1	117	95.9	5	4.1	--	--	--	--
ATZ1	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
ATZ2	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
ATZ3	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
ATZ4	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
ATZ5	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
ATZ6	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
IMDTOT	122	0	20	100	82.0	22	18.0	102	83.6	20	16.4	--	--	--	--
IMD1	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
PYRTOT	122	0	7	115	94.3	7	5.7	115	94.3	7	5.7	--	--	--	--
PYR1	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
PYR2	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
CAFTOT	122	0	6	115	94.3	7	5.7	115	94.3	7	5.7	115	94.3	7	5.7
CAF1	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
CAF2	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
CAF3	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
CBZTOT	122	2	0	121	99.2	1	0.8	121	99.2	1	0.8	121	99.2	1	0.8
CBZ1	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
CBZ2	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
SMXTOT	122	1	1	120	98.4	2	1.6	121	99.2	1	0.8	120	98.4	2	1.6
SMX1	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
SMX2	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
SMX3	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
SMX4	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
SMX5	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

Pesticides and Pharmaceuticals Determined by Enzyme-Linked Immunosorbent Assay (ELISA)

Overall, there were few detections by ELISA for all six unregulated contaminants (0.8 to 18 percent; [table 2](#)). ATZ_{TOT}, IMD_{TOT}, and PYR_{TOT} were detected by ELISA in 4.1 (5 of 122 samples), 18 (22 of 122 samples), and 5.7 percent (7 of 122 samples) of samples, respectively ([table 2](#); [fig. 2.4](#)). CAF_{TOT}, CBZ_{TOT}, and SMX_{TOT} were detected by ELISA in 5.7 (7 of 122 samples), 0.8 (1 of 122 samples), and 1.6 percent (2 of 122 samples) of samples, respectively ([table 2](#); [fig. 2.4](#)).

Pesticides and Pharmaceuticals Determined by the National Water Quality Laboratory (NWQL)

Overall, ATZ_{TOT} was detected in 77 percent (94 of 122 samples) of samples analyzed by the NWQL method ([table 2](#); [fig. 2B](#)). A total of 71.3 percent (87 of 122 samples) of samples had ATZ1 detections, while 65.5 percent (80 of 122 samples) of samples had detections of at least one immunologically similar contaminant. The ATZ1 immunologically similar contaminants most frequently detected by the NWQL method were ATZ3 and ATZ4, with detections at 46.7 (57 of 122) and 33.6 percent (41 of 122 samples), respectively.

Table 2. Summary of pesticide and pharmaceutical detections analyzed in source and finish drinking-water samples collected from public water systems throughout Minnesota, 2019.—Continued

[ELISA, enzyme-linked immunosorbent assay analytical method; NWQL, U.S. Geological Survey National Water Quality Laboratory; AXYS, SGS AXYS Services Ltd.; *n*, number of observations; %, percent; --, no data]

NWQL									AXYS								
Total <i>n</i>	Initial				Recensored				Total <i>n</i>	Initial				Recensored			
	CO		UO		CO		UO			CO		UO		CO		UO	
	<i>n</i>	%	<i>n</i>	%	<i>n</i>	%	<i>n</i>	%		<i>n</i>	%	<i>n</i>	%	<i>n</i>	%	<i>n</i>	%
122	28	23.0	94	77.0	90	73.8	32	26.2	--	--	--	--	--	--	--	--	--
122	35	28.7	87	71.3	--	--	--	--	--	--	--	--	--	--	--	--	--
122	121	99.2	1	0.8	--	--	--	--	--	--	--	--	--	--	--	--	--
122	65	53.3	57	46.7	--	--	--	--	--	--	--	--	--	--	--	--	--
122	81	66.4	41	33.6	--	--	--	--	--	--	--	--	--	--	--	--	--
122	114	93.4	8	6.6	--	--	--	--	--	--	--	--	--	--	--	--	--
122	119	97.5	3	2.5	--	--	--	--	--	--	--	--	--	--	--	--	--
122	120	98.4	2	1.6	122	100.0	0	0.0	--	--	--	--	--	--	--	--	--
122	120	98.4	2	1.6	--	--	--	--	--	--	--	--	--	--	--	--	--
122	122	100.0	0	0.0	122	100.0	0	0.0	--	--	--	--	--	--	--	--	--
122	122	100.0	0	0.0	--	--	--	--	--	--	--	--	--	--	--	--	--
112	112	100.0	0	0.0	--	--	--	--	--	--	--	--	--	--	--	--	--
122	115	94.3	7	5.7	121	99.2	1	0.8	122	120	98.4	2	1.6	122	100.0	0	0.0
122	115	94.3	7	5.7	--	--	--	--	122	120	98.4	2	1.6	--	--	--	--
122	122	100.0	0	0.0	--	--	--	--	122	122	100.0	0	0.0	--	--	--	--
122	122	100.0	0	0.0	--	--	--	--	--	--	--	--	--	--	--	--	--
122	114	93.4	8	6.6	119	97.5	3	2.5	122	111	91.0	11	9.0	121	99.2	1	0.8
122	114	93.4	8	6.6	--	--	--	--	122	111	91.0	11	9.0	--	--	--	--
115	115	100.0	0	0.0	--	--	--	--	--	--	--	--	--	--	--	--	--
122	116	95.1	6	4.9	119	97.5	3	2.5	122	102	83.6	20	16.4	119	97.5	3	2.5
110	106	96.4	4	3.6	--	--	--	--	122	108	88.5	13	10.7	--	--	--	--
122	122	100.0	0	0.0	--	--	--	--	122	119	97.5	3	2.5	--	--	--	--
122	120	98.4	2	1.6	--	--	--	--	122	118	96.7	4	3.3	--	--	--	--
--	--	--	--	--	--	--	--	--	122	120	98.4	2	1.6	--	--	--	--
--	--	--	--	--	--	--	--	--	122	118	96.7	4	3.3	--	--	--	--

ATZ2, ATZ5, and ATZ6 were detected in ≤ 7 percent (≤ 8 of 122 samples) of samples. Generally, ATZ3 and ATZ4 made up a significant portion of the summed ATZ_{TOT} concentrations detected by the NWQL method, and ATZ4 > ATZ3 > ATZ1. IMD_{TOT} was detected in 1.6 percent (2 of 122 samples) of samples by the NWQL method, and PYR_{TOT} was not detected in any of the samples (fig. 2b).

Neither CAF2 nor CAF3 were detected in any of the samples by the NWQL method. CAF1 was detected in 5.7 percent (7 of 122 samples; table 2) of samples, thus CAF_{TOT} reflects CAF1 concentrations (table 2; fig. 2b). CBZ2 was not detected in any of the samples analyzed by the NWQL method. CBZ1 was detected in 6.6 percent (8 of 122 samples) of samples,

thus CBZ_{TOT} reflects CBZ1 concentrations. Overall, 4.9 percent (6 of 122 samples) of samples had SMX_{TOT} detections by the NWQL method (table 2; fig. 2b). The target contaminant, SMX1, was detected in 3.3 percent (4 of 122 samples) of samples, while SMX3 was detected in < 2 percent (2 of 122 samples) (table 2). SMX2 was not detected in any of the samples by the NWQL method (table 2).

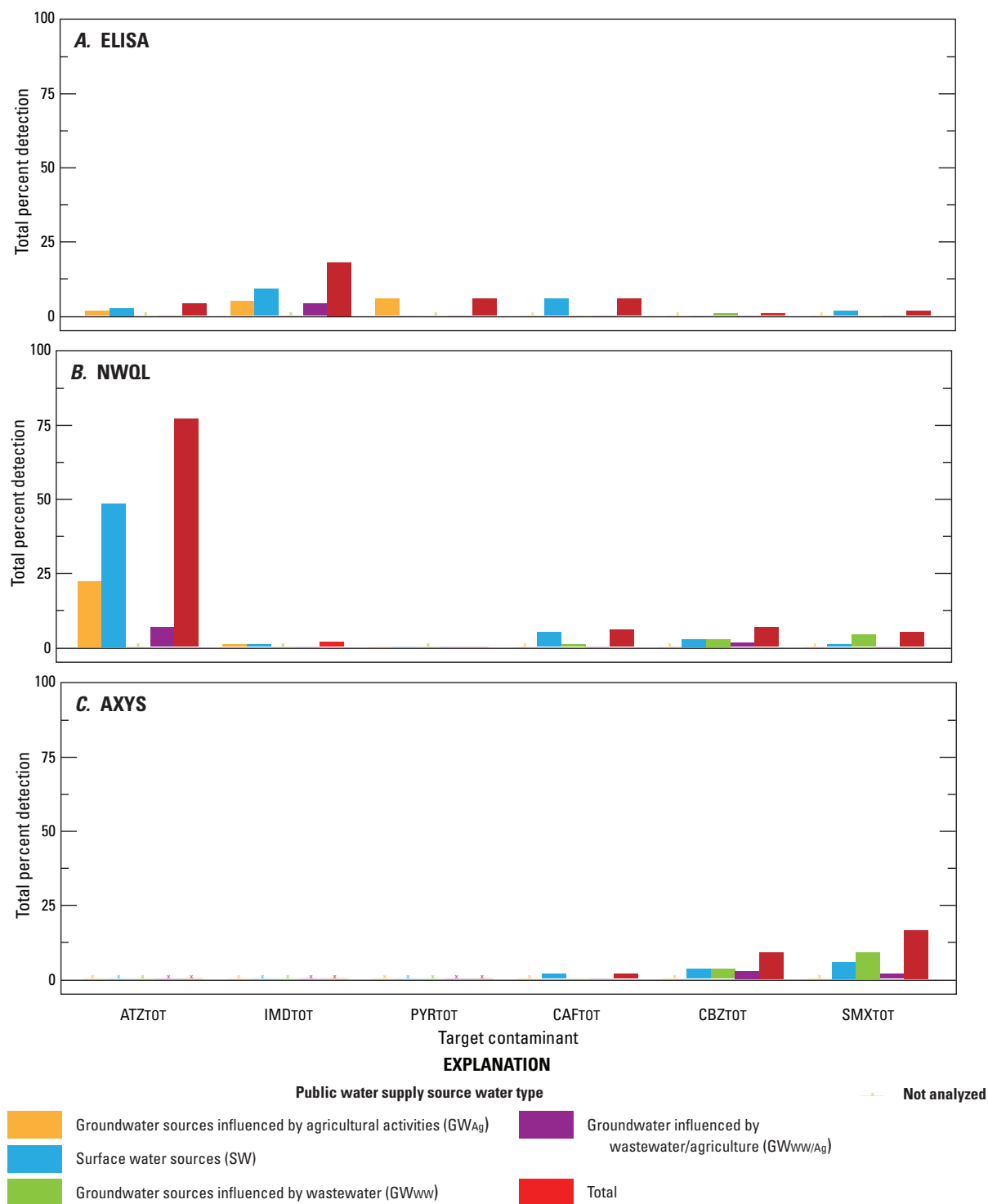


Figure 2. Percent of sample detections for six unregulated contaminant groups (atrazine group [ATZ_{TOT}], imidacloprid group [IMD_{TOT}], pyrethroids group [PYR_{TOT}], caffeine group [CAF_{TOT}], carbamazepine group [CBZ_{TOT}], and sulfamethoxazole group [SMX_{TOT}]) in source and finished drinking-water samples collected from public water systems throughout Minnesota, 2019. Samples were analyzed by A, enzyme-linked immunosorbent assay (ELISA) and by more advanced mass-spectrometry based analytical methods at: B, U.S. Geological Survey National Water Quality Laboratory (NWQL), and C, SGS AXYS Analytical Services Ltd. (AXYS).

Pharmaceuticals Determined by the SGS AXYS Analytical Services Ltd. (AXYS)

CAF2 was not detected in any of the samples by the AXYS method. However, CAF1 was detected in 1.6 percent (2 of 122 samples) of samples, thus CAF_{TOT} reflects CAF1 concentrations (table 2; fig. 2C). Overall, 9 percent (11 of 122 samples) of samples analyzed by the AXYS method had CBZ_{TOT} detections, whereas 16.4 percent (20 of 122 samples) had SMX_{TOT} detections (table 2; fig. 2C). SMX1 was detected in 10.7 percent (13 of 122) of samples. A total of 9 percent (11 of 122 samples) of samples had SMX1 was detected in ions but no immunologically similar contaminant detections.

Presence-Absence Agreement Among Analytical Methods

Figures 3 and 4 illustrate the differences in reporting limits for ELISA and the two comparison methods of analysis, where generally, reporting limits were ELISA > NWQL > AXYS. The higher reporting limits of the ELISA method between paired results (table 1), caused a decrease in the number of contaminant detections by NWQL and AXYS after re-censoring of the data (table 2).

The presence-absence agreement test between ELISA and the two comparison methods (NWQL and AXYS) ranged from 77.9 to 100 percent for all six contaminants (table 3). This indicates a generally good agreement between results of ELISA and those of the other two methods for detecting the

presence of IMD_{TOT}, PYR_{TOT}, CAF_{TOT}, CBZ_{TOT}, and SMX_{TOT} but not for detecting the presence of ATZ_{TOT}, which will be discussed later in this report.

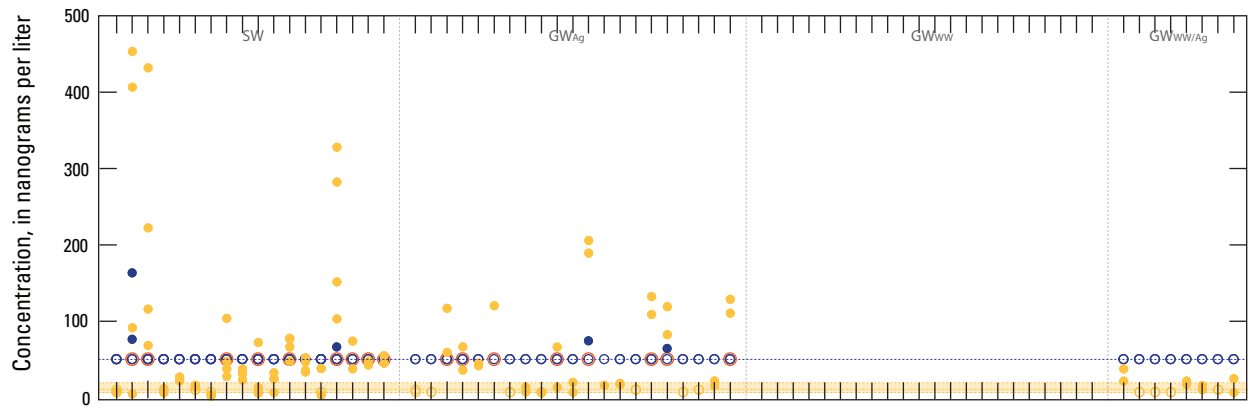
Of the 162 total samples collected from the 67 public water systems, up to five contaminant groups were detected in a single sample across all three methods (Krall and Elliott, 2022; fig. 5). Generally, the greatest number of contaminant group detections across all three methods were in the source water samples. However, differences between detections in source water and finished drinking-water samples were statistically insignificant because of the few detections within each dataset. No contaminant groups were detected in 29 percent (47 of 162) of all samples, across all methods (fig. 5A). Samples collected from GW_{WW} public water systems had the highest percentage (72.5 or 29 of 40) of samples with no contaminant group detections (fig. 5A). In contrast, samples collected from SW, GW_{Ag}, and GW_{WW/Ag} public water systems had 7.6 (5 of 66), 22.5 (9 of 40), and 25 percent (4 of 16) of samples with no contaminant group detections. Two contaminant groups were detected in 21.6 (35 of 162) percent of all samples, across all methods. Samples with two contaminant groups detected were most commonly collected from GW_{WW/Ag} public water systems (37.5 percent or 6 of 16 samples; fig. 5A). Less than 4 percent (1 to 6 of 162) of samples had more than two contaminant groups detected across all methods. Samples in which more than two contaminant groups were detected were most commonly collected from SW public water systems (fig. 5A).

Table 3. Paired result ties and presence-absence agreement between enzyme-linked immunosorbent assay (ELISA) and more advanced analytical methods by the U.S. Geological Survey National Water Quality Laboratory (NWQL) and SGS AXYS Analytical Services Ltd. (AXYS).

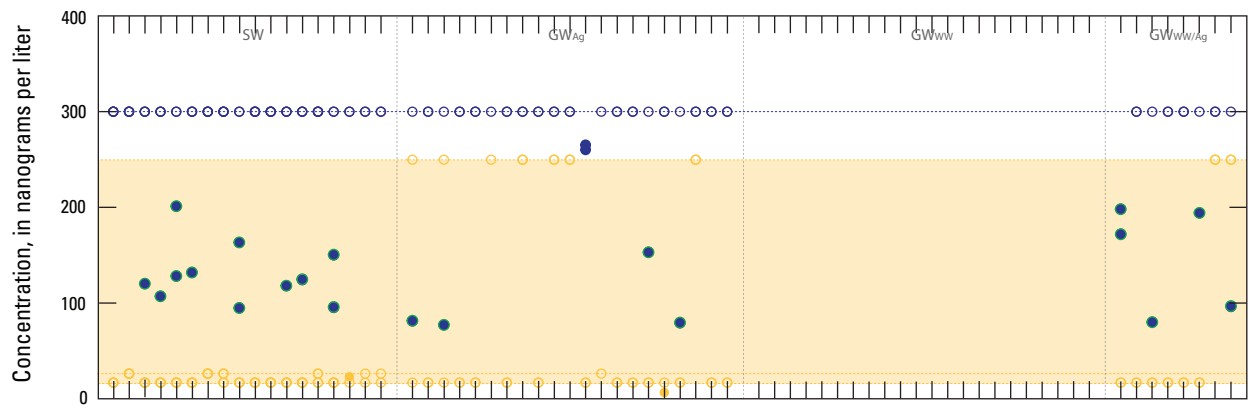
[ELISA, enzyme-linked immunosorbent assay analytical method; NWQL, National Water Quality Laboratory; AXYS, SGS AXYS Services Ltd.; ATZTOT, atrazine plus immunologically similar contaminants; IMDTOT, imidacloprid plus immunologically similar contaminants; PYRTOT, pyrethroids plus immunologically similar contaminants; CAFTOT, caffeine plus immunologically similar contaminants; CBZTOT, carbamazepine plus immunologically similar contaminants; SMXTOT, sulfamethoxazole plus immunologically similar contaminants]

Comparisons	Target contaminant	Number of samples	Number of observation pairs (re-censored data)			Percent of observation pairs (re-censored data)			Percent presence/ absence agreement (re-censored)
			Tied		Untied	Tied		Untied	
			Nondetections in both samples of a matched pair (censored data)	Detections in both samples of a matched pair (uncensored data)	Detection in one sample and nondetection on one samples of a matched pair (censored and uncensored data)	Nondetections in both samples of a matched pair (censored data)	Detections in both samples of a matched pair (uncensored data)	Detection in one sample and nondetection on one samples of a matched pair (censored and uncensored data)	
ELISA versus NWQL	ATZTOT	122	90	5	27	74	4	22	77.9
	IMDTOT	122	102	0	20	84	0	16	83.6
	PYRTOT	122	115	0	7	94	0	6	94.3
	CAFTOT	122	115	1	6	94	1	5	95.1
	CBZTOT	122	119	1	2	98	1	2	98.4
	SMXTOT	122	118	0	4	97	0	3	96.7
ELISA versus AXYS	CAFTOT	122	115	0	7	94	0	6	94.3
	CBZTOT	122	121	1	0	99	1	0	100.0
	SMXTOT	122	118	1	3	97	1	2	97.5

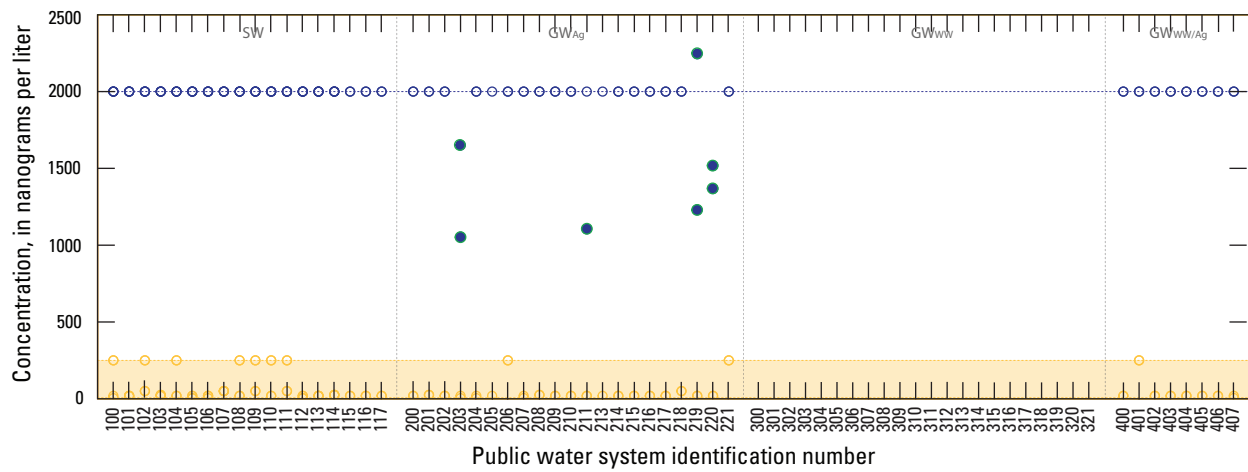
A. ATZTOT



B. IMDTOT



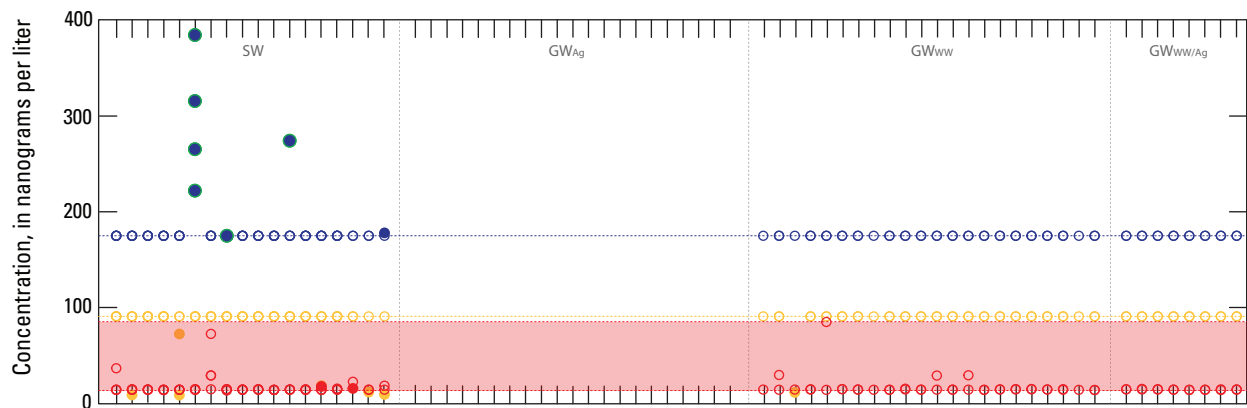
C. PYRTOT



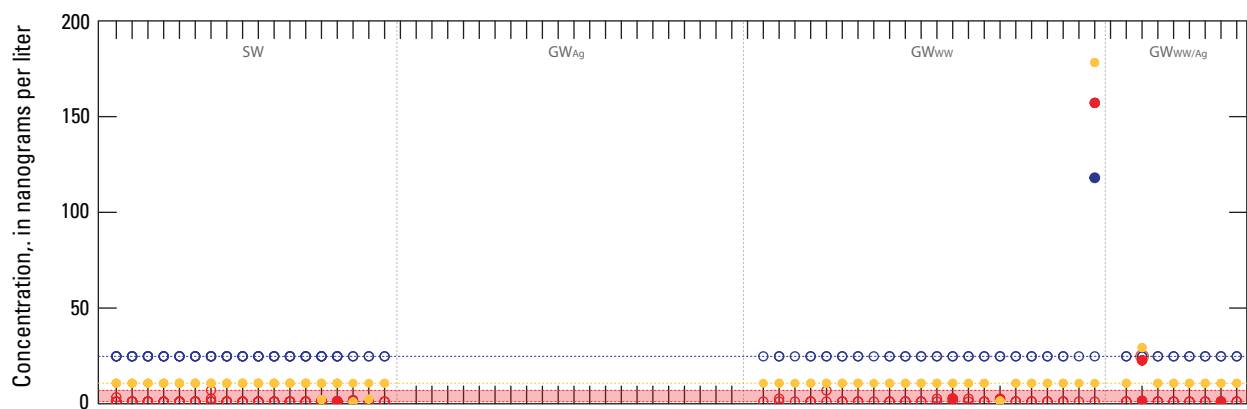
- EXPLANATION
- Nondetection (censored)
 - Detection (uncensored)
 - False negative
 - False positive
 - ELISA
 - NWQL
 - Reporting limit
 - Reporting limit range

Figure 3. Concentrations of three unregulated pesticide contaminant groups: A, atrazine group (ATZ_{TOT}), B, imidacloprid group (IMD_{TOT}), and C, pyrethroids group (PYR_{TOT}) in source and finished drinking-water samples collected from public water systems throughout Minnesota, 2019. Samples were analyzed by enzyme-linked immunosorbent assay (ELISA) and by more advanced mass-spectrometry based analytical methods at the U.S. Geological Survey National Water Quality Laboratory (NWQL).

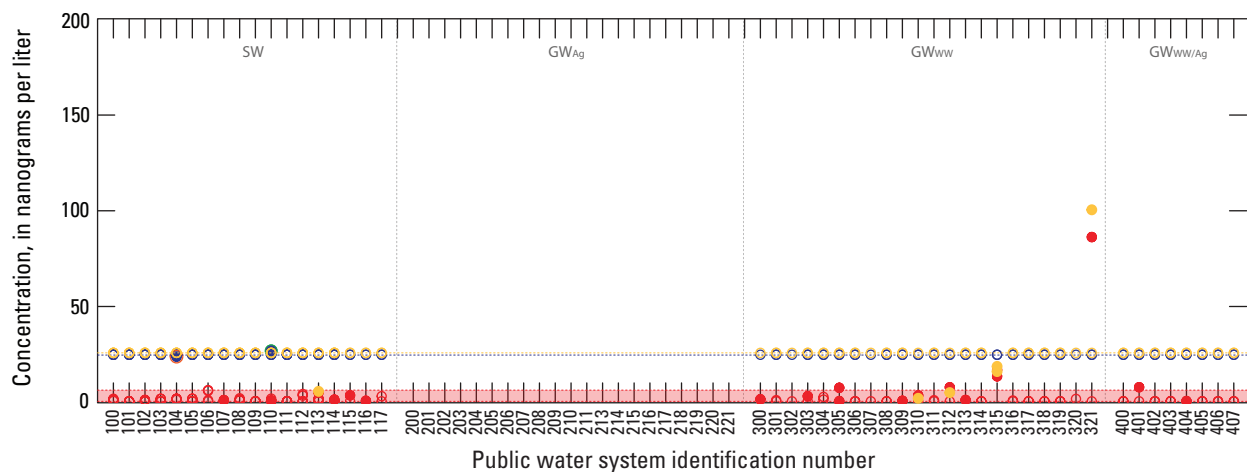
A. CAFTOT



B. CBZTOT



C. SMXTOT



EXPLANATION

○ Nondetection (censored)	○ False negative	● ELISA	Reporting limit range
● Detection (uncensored)	● False positive	● NWQL	Reporting limit
		● AXYS	

Figure 4. Concentrations of three unregulated pharmaceutical contaminant groups: A, caffeine group (CAF_{TOT}), B, carbamazepine group (CBZ_{TOT}), and C, sulfamethoxazole group (SMX_{TOT}) in source and finished drinking-water samples collected from public water systems throughout Minnesota, 2019. Samples were analyzed by enzyme-linked immunosorbent assay (ELISA) and more advanced mass-spectrometry based analytical methods at the U.S. Geological Survey National Water Quality Laboratory (NWQL) and SGS AXYS Analytical Services Ltd. (AXYS).

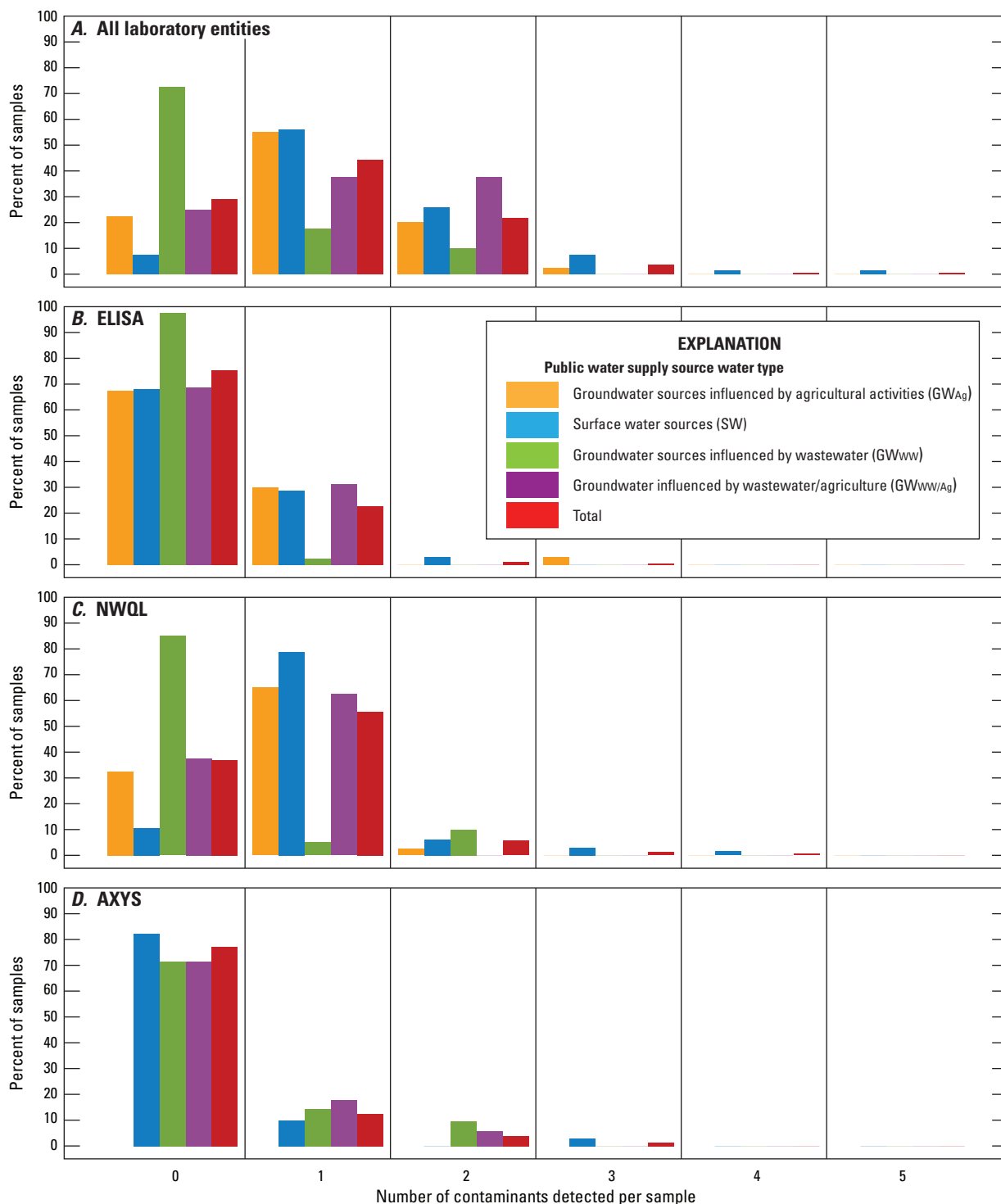


Figure 5. Percent of samples with zero to five contaminant group (atrazine group [ATZ_{TOT}], imidacloprid group [IMD_{TOT}], pyrethroids group [PYR_{TOT}], caffeine group [CAF_{TOT}], carbamazepine group [CBZ_{TOT}], and sulfamethoxazole group [SMX_{TOT}]) detections in a single source or finished drinking-water sample by public water system collected from public water systems throughout Minnesota, 2019, and by public water system source water type (surface water sourced [SW], groundwater sourced influenced by agricultural activities [GW_{Ag}], groundwater sourced influenced by wastewater [GW_{Ww}], groundwater sourced influenced by both wastewater and agricultural activities [GW_{Ww/Ag}]). Percent of samples with contaminant group detections are presented by *A*, all laboratory entities, *B*, enzyme-linked immunosorbent assay (ELISA), *C*, the U.S. Geological Survey National Water Quality Laboratory (NWQL), and *D*, SGS AXYS Analytical Services Ltd. (AXYS).

Implications of Using ELISA as a Screening Tool

Our ELISA ATZ_{TOT} analyses resulted in a high false negativity rate, which has also been documented in other studies (Graziano and others, 2006; Adams and others, 2004; Lydy and others, 1996). Generally, ELISA negatively biased results are assumed to be caused by matrix interference or mis-handling of the test. Although some matrix samples had low recovery rates (<70 percent), most were within an ideal range (70 to 130 percent), indicating that matrix interference did not explain the high false negativity rate. One hypothesis for the negative bias is greater observed bias at higher concentrations. The consistent negative bias (underestimate) of ATZ_{TOT} results poses a monitoring risk if ELISA is used as a screening tool for drinking-water samples.

The false positivity rates of ELISA for analyses of IMD_{TOT} , PYR_{TOT} , and CAF_{TOT} (16, 6, and 5 percent, respectively) can be attributed to the sensitivity of ELISA to cross-react with immunologically similar contaminants. This is of importance because although not all target contaminants are detected in Minnesota surface water and groundwater, immunologically similar contaminants (that is, degradates) have been detected (Minnesota Department of Agriculture, 2020). Some data on the occurrence of immunologically similar contaminants are available, but not all laboratories may include those contaminants in analyses. Thus, the ELISA results may not be false positives, but simply reflect the presence of immunologically similar contaminants. Overall, these results indicate that using ELISA for detecting the presence of IMD_{TOT} , PYR_{TOT} , and CAF_{TOT} would be more overprotective than underprotective, which is considered beneficial for protecting human health.

Our analysis shows that results from ELISA generally are in good agreement (77.9 to 100 percent) with the results of advanced analytical methods for six unregulated contaminant groups: ATZ_{TOT} , IMD_{TOT} , PYR_{TOT} , CAF_{TOT} , CBZ_{TOT} , and SMX_{TOT} . Specifically, the false positivity and false negativity rates for ELISA CBZ_{TOT} and SMX_{TOT} are low, indicating that ELISA is not substantially underestimating or overestimating the presence of these two contaminant groups. The presence-absence agreement analysis, combined with analysis of false positive and false negative rates, indicates ELISA could provide a suitable screening method for analyzing CBZ_{TOT} and SMX_{TOT} in source and finished drinking-water samples collected from public water systems. However, the results also indicate that the use of ELISA as a screening tool for ATZ_{TOT} may not be a suitable method, and the use of ELISA for IMD_{TOT} , PYR_{TOT} , and CAF_{TOT} should be further evaluated.

Summary

We assessed the use of the enzyme-linked immunosorbent assay (ELISA), a rapid, inexpensive screening method for contaminants in water, as an alternative to more expensive and advanced mass-spectrometry analytical methods conducted at two laboratories, the U.S. Geological Survey National Water Quality Laboratory (NWQL) and SGS AXYS Analytical Services Ltd. (AXYS). Samples of source water and finished drinking-water collected from 67 public water systems throughout Minnesota were analyzed for three commonly detected pesticides (atrazine, imidacloprid, and pyrethroids) and three commonly detected pharmaceuticals (caffeine, carbamazepine, and sulfamethoxazole).

The ELISA method detects the target contaminant and immunologically similar contaminants, thereby providing an indication of contaminant mixtures. Other studies have reported positive bias in the results of ELISA compared to results of other analytical methods because of the potential for ELISA to respond to immunologically similar contaminants. Therefore, this study referred to the summation of the target contaminant and immunologically similar contaminants as contaminant groups. The potential cross-reactivity between the ELISA target contaminant and immunologically similar contaminants could not be fully assessed for all contaminants during this analysis because the number of immunologically similar contaminants varied by comparison method.

Overall, these datasets are highly censored (>80 percent) and contain multiple reporting limits within and between laboratories. The highly censored data caused tenuous statistical results when comparing paired concentrations between ELISA and the comparison methods (used at NWQL and AXYS). Thus, qualitative analysis of the data was deemed more appropriate. Generally, ELISA had higher reporting limits than the methods used by both the NWQL and AXYS, except for the analysis for SMX_{TOT} at NWQL. To discern agreement between paired results between ELISA and the comparison methods, the results of the presence-absence agreement analysis was coupled with false negative and false positive result analysis.

Both CBZ_{TOT} and SMX_{TOT} ELISA have very low false negative rates (1.6 and 0.8 percent, respectively) for samples with detections below the reporting limit (25 and 26 ng/L, respectively). These very low false negative results indicate that CBZ_{TOT} and SMX_{TOT} ELISA methods are not underestimating results. Conversely, SMX_{TOT} has a very low false positivity rate (0.8 percent) which indicates the SMX_{TOT} ELISA method is not overestimating results.

Although there is 78 percent agreement between ATZ_{TOT} ELISA and NWQL paired results, the false negativity rate of 84 percent indicates strong negative bias. This strong negative bias indicates that the ELISA method is underestimating ATZ_{TOT} , which is not an ideal result for monitoring drinking water.

The false positivity rates for IMD_{TOT} , PYR_{TOT} , and CAF_{TOT} (16, 6, and 5 percent) are higher than CBZ_{TOT} and SMX_{TOT} but are still relatively low. These results indicate the ELISA method could be overestimating the results in this

contaminant group. This positive bias could be attributed to the detection of other immunologically similar contaminants that have the potential to cross-react during ELISA analysis and are known to be present in Minnesota surface water and groundwater but were not analyzed by the comparison laboratories.

These qualitative results indicate the ELISA method could potentially provide an alternative screening method for the presence of CBZ_{TOT} and SMX_{TOT} in source and finished drinking-water samples collected from public water systems but did not prove to be a good alternative for ATZ_{TOT}. Efforts could be expanded to continue to study the use of ELISA as a reliable and cost-effective screening method to help drinking water monitoring entities prioritize sampling efforts for screening source and finished drinking-water samples for IMD_{TOT}, PYR_{TOT}, and CAF_{TOT}.

References Cited

- Adams, C., Jiang, H., McGuire, M., Graziano, N., Roberson, A., and Frey, M., 2004, Accuracy and interference for Enzyme-linked Immunoassay tests for atrazine: American Water Works Association, v. 96, n. 12, p. 126–136. [Also available at <https://www.jstor.org/stable/41311948>.]
- Bahlmann, A., Weller, M.G., Panne, U., and Schneider, R.J., 2009, Monitoring carbamazepine in surface and wastewaters by an immunoassay based on a monoclonal antibody: Analytical and Bioanalytical Chemistry, v. 395, no. 6, p. 1809–1820. [Also available at <https://doi.org/10.1007/s00216-009-2958-7>.]
- Bio Tek Instruments, 2018, Gen5 Microplate Software for Windows, Version 3.05.11: VT, Winooski.
- Bradley, P.M., Barber, L.B., Duris, J.W., Foreman, W.T., Furlong, E.T., Hubbard, L.E., Hutchinson, K.J., Keefe, S.H., and Koplin, D.W., 2014, Riverbank filtration potential of pharmaceuticals in a wastewater-impacted stream: Environmental Pollution, v. 193, p. 173–180. [Also available at <https://doi.org/10.1016/j.envpol.2014.06.028>.]
- Ebele, A.J., Abou-Elwafa Abdallah, M., and Harrad, S., 2017, Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment: Emerging Contaminants, v. 3, no. 1, p. 1–16. [Also available at <https://doi.org/10.1016/j.emcon.2016.12.004>.]
- Elliott, S.M., Brigham, M.E., Lee, K., Banda, J.A., Choy, S.J., Gefell, D.J., Minarik, T.A., Moore, J.N., and Jorgenson, Z.G., 2017, Contaminants of emerging concern in tributaries to the Laurentian Great Lakes—I. Patterns of occurrence: PLoS One, v. 23, no. 9, p. 1–21. [Also available at <https://doi.org/10.1371/journal.pone.0182868>.]
- Elliott, S.M., Erickson, M.L., Krall, A.L., and Adams, B.A., 2018, Concentrations of pharmaceuticals and other micropollutants in groundwater downgradient from large on-site wastewater discharge: PLoS One, v. 13, no. 11, p. e0206004. [Also available at <https://doi.org/10.1371/journal.pone.0206004>.]
- Erickson, M.L., Langer, S.K., Roth, J.L., and Kroening, S.E., 2014, Contaminants of emerging concern in ambient groundwater in urbanized areas of Minnesota, 2009–12 (ver. 1.2, September 2014): U.S. Geological Survey Scientific Investigations Report 2014–5096, 38 p., with appendix. [Also available at <https://doi.org/10.3133/sir20145096>.]
- Eurofins-Abraxis, Inc., 2019a, Atrazine ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/pesticides-herbicides/pesticide-elisa-plate-kits/atrazine-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019b, Imidacloprid ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/pesticides-herbicides/pesticide-elisa-plate-kits/imidaclopridclothianidin-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019c, Caffeine ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/markers-for-bioactivity/markers-for-bioactivity-elisa-plate-kits/caffeine-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019d, Carbamazepine ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/markers-for-bioactivity/markers-for-bioactivity-elisa-plate-kits/carbamazepine-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019e, Pyrethroids ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/pesticides-herbicides/pesticide-elisa-plate-kits/pyrethroids-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019f, Sulfamethoxazole ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/veterinary-residues-additives/veterinary-residues-additives-elisa-kits/sulfamethoxazole-smx-elisa-96-test/>.]
- Furlong, E.T., Noriega, M.C., Kanagy, C.J., Kanagy, L.K., Coffey, L.J., and Burkhardt, M.R., 2014, Determination of human-use pharmaceuticals in filtered water by direct aqueous injection–high-performance liquid chromatography/tandem mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B10, 49 p. [Also available at <https://doi.org/10.3133/tm5B10>.]

- Glassmeyer, S.T., Furlong, E.T., Koplin, D.W., Batt, A.L., Benson, R., Boone, J.S., Conerly, O., Donohue, M.J., King, D.N., Kostich, M.S., Mash, H.E., Pfaller, S.L., Schenck, K.M., Simmons, J.E., Varughese, E.A., Vesper, S.J., Villegas, E.N., and Wilson, V.S., 2017, Nationwide reconnaissance of contaminants of emerging concern in source and treated drinking water of the United States: Science of the Total Environment, v. 581–582, p. 909–922. [Also available at <https://doi.org/10.1016/j.scitotenv.2016.12.004>.]
- Graziano, N., McGuire, M., Adams, C., Roberson, A., Jiang, H., and Blute, N., 2006, Using the ELISA method to track atrazine occurrence in a national monitoring program: American Water Works Association, v. 98, n. 10, p. 111–123 [Also available at <https://www.jstor.org/stable/41312283>.]
- Jilani, T.N., Preuss, C.V., and Sharma, S., 2021, StatsPearls: Treasure Island, Fla., StatPearls Publishing. [Also available at <https://www.ncbi.nlm.nih.gov/books/NBK519024/>.]
- Krall, A.L., Elliott, S.M., Erickson, M.E., and Adams, B.A., 2018, Detecting sulfamethoxazole and carbamazepine in groundwater—Is ELISA a reliable screening tool?: Environmental Pollution, v. 234, p. 420–428. [Also available at <https://doi.org/10.1016/j.envpol.2017.11.065>.]
- Krall, A.L., and Elliott, S.M., 2022, Concentrations and laboratory quality-assurance data for six unregulated contaminants measured in source and finished drinking-water samples collected from public water systems throughout Minnesota by using ELISA and MS-based analytical methods: U.S. Geological Survey data release, <https://doi.org/10.5066/P9MLY0GM>.
- Lee, K.E., Langer, S.K., Barber, L.B., Writer, J.H., Ferrey, M.L., Schoenfuss, H.L., Furlong, E.T., and William, T., Foreman, Gray, J.L., ReVello, R.C., Martinovic, D., Woodruff, O.P., Keefe, S.H., Brown, G.K., Taylor, H.E., Ferrer, I., and Thurman, E.M., 2011, Endocrine active chemicals, pharmaceuticals, and other chemicals of concern in surface water, wastewater-treatment plant effluent, and bed sediment, and biological characteristics in selected streams, Minnesota—design, methods, and data, 2009: U.S. Geological Survey Data Series 575, 54 p., with appendixes [Also available at <https://pubs.usgs.gov/ds/575/>.]
- Lydy, M.J., Carter, D.S., and Crawford, C.G., 1996, Comparison of gas chromatography/mass spectrometry and immunoassay techniques on concentrations of atrazine in storm runoff: Archives of Environmental Contamination and Toxicology, v. 31, no. 3, p. 378–385. [Also available at <https://doi.org/10.1007/BF00212676>.]
- Miao, X., and Metcalfe, C.D., 2003, Determination of carbamazepine and its metabolites in aqueous samples using liquid chromatography—Electrospray tandem mass spectrometry: Analytical Chemistry, v. 75, no. 15, p. 3731–3738. [Also available at <https://doi.org/10.1021/ac030082k>.]
- Minnesota Department of Agriculture, 2016a, 2015 reconnaissance study of pesticide compound in community public water supply wells: Minnesota Department of Agriculture, accessed December 15, 2020, at https://www.mda.state.mn.us/sites/default/files/inline-files/2015PesticideReconReport_0.pdf.
- Minnesota Department of Agriculture, 2016b, Review of neonicotinoid use, registration, and insect pollinator impacts in Minnesota: Minnesota Department of Agriculture, accessed August 3, 2021, at <https://www.mda.state.mn.us/sites/default/files/inline-files/neonicreviewrpt2016.pdf>.
- Minnesota Department of Agriculture, 2019, 2019 Water quality monitoring report: Minnesota Department of Agriculture, accessed December 15, 2020, at <https://wrl.mnpals.net/islandora/object/WRLrepository%3A3656/datastream/PDF/view>.
- Minnesota Department of Agriculture, 2020, 2020 Water quality monitoring report: Minnesota Department of Agriculture, accessed December 15, 2020, at <https://wrl.mnpals.net/islandora/object/WRLrepository%3A3746/datastream/PDF/view>.
- Minnesota Department of Health, 2020a, Comparison of State water guidance and Federal drinking water standards: Minnesota Department of Agriculture, accessed August 12, 2020, at <https://www.health.state.mn.us/communities/environment/risk/guidance/waterguidance.html>.
- Minnesota Department of Health, 2020b, Public drinking water program: Minnesota Department of Health, accessed August 12, 2020, at <https://www.health.state.mn.us/communities/environment/water/factsheet/dwprog.html>.
- Minnesota Pollution Control Agency, 2017, Pharmaceuticals and chemicals of concern in rivers—Occurrence and biological effects: Minnesota Department of Agriculture, accessed July 20, 2021, at <https://www.pca.state.mn.us/sites/default/files/tdr-g1-20.pdf>.
- Noguera-Oviedo, K., and Aga, D.S., 2016, Lessons learned from more than two decades of research on emerging contaminants in the environment: Journal of Hazardous Materials, v. 316, p. 242–251. [Also available at <https://doi.org/10.1016/j.jhazmat.2016.04.058>.]
- Sandstrom, M.W., Kanagy, L.K., Anderson, C.A., and Kanagy, C.J., 2016, Determination of pesticides and pesticide degradates in filtered water by direct aqueous-injection liquid chromatography-tandem mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B11, 54 p. [Also available at <https://doi.org/10.3133/tm5B11>.]

- SGS AXYS Analytical Services Ltd., 2019, SGS AXYS METHOD MLA-075—Analysis of pharmaceutical and personal care products and hormones in solid, aqueous, tissue and POCIS samples by LC-MS/MS: SGS AXYS Analytical Services Ltd.
- Trost, J.J., Kiesling, R.L., Erickson, M.L., Rose, P.J., and Elliott, S.M., 2013, Land-cover effects on the fate and transport of surface-applied antibiotics and 17-beta-estradiol on a sandy outwash plain, Anoka County, Minnesota, 2008–09: U.S. Geological Survey Scientific Investigations Report 2013–5202, 51 p. [Also available at <https://doi.org/10.3133/sir20135202>.]
- U.S. Environmental Protection Agency, 2010, Terbutylazine summary document—Registration review: U.S. Environmental Protection Agency, accessed August 3, 2021, at <https://www.regulations.gov/document/EPA-HQ-OPP-2010-0453-0002>.
- U.S. Environmental Protection Agency, 2020, National primary drinking water regulations: U.S. Environmental Protection Agency, accessed August 12, 2020, at <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations>.
- U.S. Environmental Protection Agency, 2021, Toxic Substance Control Act (TSCA) chemical substance Inventory: U.S. Environmental Protection Agency, accessed May 26, 2021, at <https://www.epa.gov/tsca-inventory>.
- Wilkinson, J., Hooda, P.S., Barker, J., Barton, S., and Swinden, J., 2017, Occurrence, fate and transformation of emerging contaminants in water—An overarching review of the field: Environmental Pollution, v. 231, p. 954–970. [Also available at <https://doi.org/10.1016/j.envpol.2017.08.032>.]
- Writer, J.H., Ferrer, I., Barberm, L.B., and Thurman, E.M., 2013, Widespread occurrence of neuro-active pharmaceuticals and metabolites in 24 Minnesota rivers and wastewaters: Science of the Total Environment, v. 461–462, p. 519–527. [Also available at <https://doi.org/10.1016/j.scitotenv.2013.04.099>.]

Appendix 1. Censoring Analytical Result Data

The data in this study are left-censored, meaning the true values of the censored results are unknown and lie between zero and the reporting limit. The datasets in this study had different reporting limits for each laboratory and contaminant, and some had multiple reporting limits for each contaminant (table 1).

result was re-censored to the censored result where the result pair then becomes a tie. No re-censoring occurred if: (1) both results in a result pair were uncensored (and therefore, untied) or (2) the censored result was less than the uncensored result (mixed and untied). Results of re-censoring are provided in table 3.

Contaminant Group Result Censoring

The ELISA method has the potential to detect the target contaminant and immunologically similar (cross-reactive) contaminants (Eurofins-Abraxis Inc., 2019a, 2019b, 2019c, 2019d, 2019e, 2019f). For this reason, the data in this study represent contaminant groups, or contaminant mixtures (the sum of the target contaminant and immunologically similar contaminants indicated by ELISA (Eurofins-Abraxis Inc., 2019a, 2019b, 2019c, 2019d, 2019e, 2019f) if analyzed and detected by the respective laboratory). In the case where a result was both a sum of the target contaminant and immunologically similar contaminants, and censored, the final result value used in analysis is the reporting limit of the target contaminant, except for PYR_{TOT} . PYR_{TOT} was censored to the higher reporting limit between PYR1 and PYR2, which most often was the reporting limit of PYR2 (table 1). A summary of censored and uncensored results for each contaminant group, target contaminant, and immunologically similar contaminants is provided in table 2.

Paired Result Re-censoring

Contaminant group results by ELISA were paired with results by the two comparison methods (NWQL and AXYS). These result pairs have different reporting limits, and for comparison, each result of a paired result was re-censored to the highest reporting limit of the two results. Generally, reporting limits were $\text{ELISA} > \text{NWQL} > \text{AXYS}$ (table 1). The data were re-censored prior to analytical method comparisons under two scenarios: 1) if both results in a result pair were censored at different reporting limits, then the lower censored value was re-censored to the higher censored value where the result pair remains a tie; or 2) if one result in a result pair was censored at a higher limit than its uncensored result, then the uncensored

References Cited

- Eurofins-Abraxis, Inc., 2019a, Atrazine ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/pesticides-herbicides/pesticide-elisa-plate-kits/atrazine-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019b, Imidacloprid ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/pesticides-herbicides/pesticide-elisa-plate-kits/imidaclopridclothianidin-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019c, Caffeine ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/markers-for-bioactivity/markers-for-bioactivity-elisa-plate-kits/caffeine-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019d, Carbamazepine ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/markers-for-bioactivity/markers-for-bioactivity-elisa-plate-kits/carbamazepine-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019e, Pyrethroids ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/pesticides-herbicides/pesticide-elisa-plate-kits/pyrethroids-elisa-96-test/>.]
- Eurofins-Abraxis, Inc., 2019f, Sulfamethoxazole ELISA user guide: Eurofins-Abraxis, Inc. [Also available at <https://abraxis.eurofins-technologies.com/home/products/rapid-test-kits/veterinary-residues-additives/veterinary-residues-additives-elisa-kits/sulfamethoxazole-smx-elisa-96-test/>.]

Appendix 2. False Negative and False Positive Analysis

Determination of False Negative and False Positive Results

In the analysis of false negative and false positive ELISA results, the contaminant group results provided by the NWQL were considered accurate and, therefore, the ELISA results were compared to the NWQL group contaminant results. False negative results indicate the absence of a contaminant when it is present, whereas false positive results indicate the presence of a contaminant when it is either absent or present at a concentration below the detection limit. If the contaminant was not detected by ELISA but was detected by NWQL and above the higher reporting limit between ELISA and NWQL, then the ELISA result was determined to be a false negative. If the contaminant was detected by ELISA and above the NWQL reporting limit but was not detected by NWQL, then the ELISA result was determined to be a false positive.

Occurrence of False Negatives and False Positives

The ELISA analytical method produced 2 (of 122) and 1 (of 122) false negative results for CBZ_{TOT} and SMX_{TOT}, respectively (table 2 and fig. 4). No false negatives were

produced for IMD_{TOT}, PYR_{TOT}, and CAF_{TOT} (table 2 and figs. 3 and 4). A total of 27 (of 122) false negatives were produced for ELISA ATZ_{TOT} (table 2; fig. 3A). CBZ_{TOT} and SMZ_{TOT} false negative results could be explained by the summation of the target contaminant and immunologically similar contaminants from NWQL causing a positive bias in the contaminant group concentrations when actual cross-reactivity is relatively low, whereas ATZ_{TOT} false negative results could be explained by an undetected interference during ELISA analysis, or by systematic bias at higher ATZ_{TOT} concentrations.

A total of 7 (of 122), 6 (of 122), and 1 (of 122) false positive results were produced for PYR_{TOT}, CAF_{TOT}, and SMX_{TOT}, respectively, with ELISA methods (table 2; figs. 3 and 4). No false positive results were produced for ATZ_{TOT} and CBZ_{TOT} (table 2; figs. 3A and 4B). A total of 20 (of 122) false positive results were produced for IMD_{TOT} (table 2; fig. 3B), which were detections below the reporting limit (300 ng/L) but above the detection limit (75 ng/L). False positive results could be explained by the potential of ELISA to detect immunologically similar contaminants that are not included in the NWQL contaminant group concentration (figs. 3 and 4).

Appendix 3. Paired Prentice-Wilcoxon Test

Paired Prentice-Wilcoxon Test Methods

ELISA ATZ_{TOT}, IMD_{TOT}, and PYR_{TOT} were compared to NWQL results, while ELISA CAF_{TOT}, CBZ_{TOT}, and SMX_{TOT} were compared to both NWQL and AXYS results. Paired results were compared using the Paired Prentice-Wilcoxon (PPW) test (O’Brien and Fleming, 1987), a nonparametric score test that compares paired results between two groups. The PPW test is well-suited for analysis of multiply censored data and is built to handle ties (both results in a paired result being censored) between results pairs (Helsel, 2012). Helsel indicates PPW test results can be tenuous when datasets are greater than 80 percent censored and have less than or equal to 2 uncensored result pairs. The PPW tests were computed in RStudio version 4.0.2 (R Studio Team, 2020) using the ppw.test function in the smwrQW package version 0.7.14 (Lorenz, 2017). Scores are computed for each result as a measure of position of the result in the datasets. The numeric differences between scores for the ELISA results and scores for the other laboratory results were computed to determine whether the sum of the differences for the entire dataset was significantly different from zero at the 95-percent confidence level. The computed PPW test provides a Z-score to describe the distribution of the data. The scores for ELISA results were less than scores for the other two laboratory results, if Z less and zero 0, equal if Z equals 0, and greater if Z greater than 0. Because the PPW test is not built to handle different reporting limits between results in a paired result (Helsel, 2012), result

pairs are re-censored to the highest reporting limit of the two results (as described in app. 1) prior to computing the PPW test, as recommended by O’Brien and Fleming (1987) and Helsel (2012).

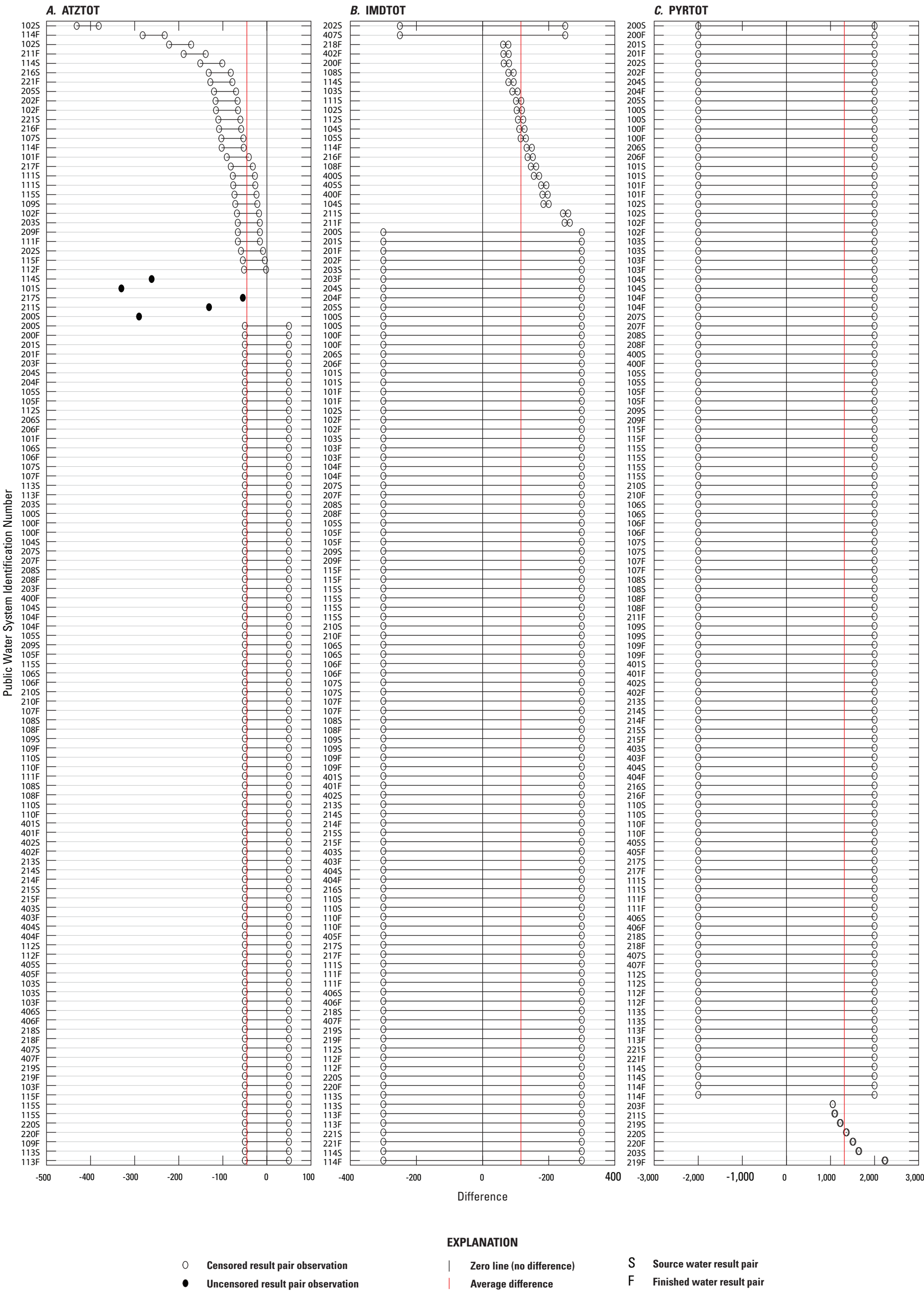
Paired Prentice-Wilcoxon Test Results

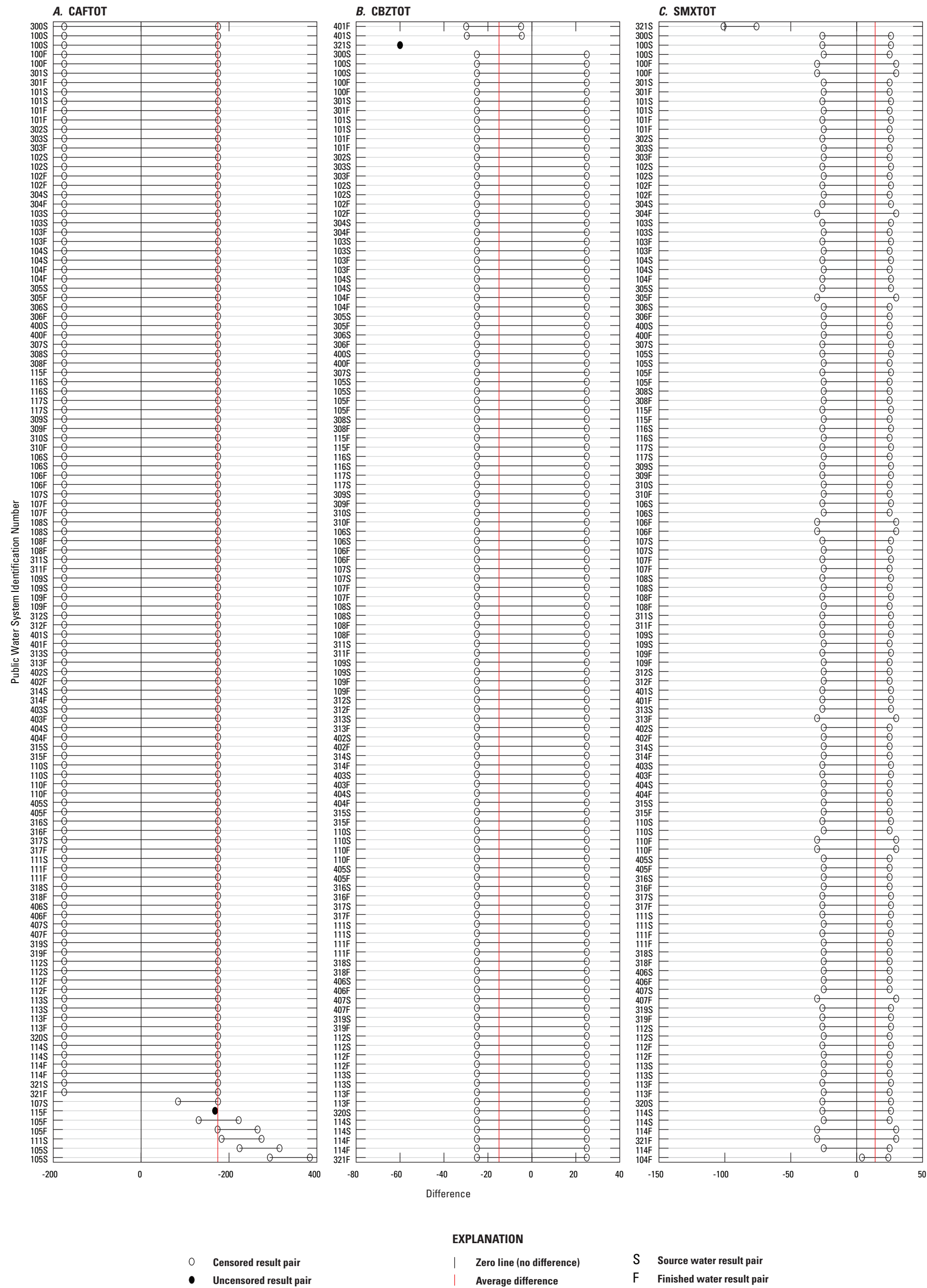
Differences between result pairs were evaluated to discern agreement between concentrations determined by the different methods. Result pairs for IMD_{TOT} could not be compared between ELISA and NWQL methods because of the lack of variance between the two datasets, as a result of re-censoring (described in app. 1), which changed all NWQL results to censored results. Paired results were significantly different for all possible comparisons (*p* less than 0.05), except for CBZ_{TOT} and SMX_{TOT} between ELISA and both comparison methods (table 3.1). Although ELISA CBZ_{TOT} and SMX_{TOT} concentrations deviated slightly from the comparison methods, the differences were not significantly different (*p* greater than 0.05, table 3.1). Plots of numeric differences between ELISA and NWQL and ELISA and AXYS paired results are depicted in figures 3.1 through 3.3. These plots suggest many of the method comparisons have outliers, but this could be explained by the high percent of censored results and little spread in the data.

Table 3.1. Paired Prentice-Wilcoxon test results for paired results for enzyme-linked immunosorbent assay (ELISA) and more advanced analytical methods for both the U.S. Geological Survey National Water Quality Laboratory (NWQL) and SGS AXYS Analytical Services Ltd. (AXYS).

[Z, z-score statistic; ELISA, enzyme-linked immunosorbent assay analytical method; NWQL, National Water Quality Laboratory; ATZTOT, atrazine plus immunologically similar contaminants; IMDTOT, imidacloprid plus immunologically similar contaminants; NA, not available; PYRTOT, pyrethroids plus immunologically similar contaminants; AXYS, SGS AXYS Services Ltd.; CAFTOT, caffeine plus immunologically similar contaminants; CBZTOT, carbamazepine plus immunologically similar contaminants; SMXTOT, sulfamethoxazole plus immunologically similar contaminants]

Comparisons	Target contaminant	<i>p</i> value	Z
ELISA versus NWQL	ATZTOT	1.05×10 ⁻⁷	-5.32
	IMDTOT	NA	NA
	PYRTOT	0.011	2.544
	CAFTOT	0.008	2.65
	CBZTOT	0.156	-1.42
	SMXTOT	0.782	-0.277
ELISA versus AXYS	CAFTOT	0.008	2.65
	CBZTOT	0.317	-1
	SMXTOT	0.576	0.56





References Cited

- Helsel, D.R., 2012, Statistics for censored environmental data using minitab and R (2d ed.): Hoboken, N.J., John Wiley & Sons, Inc.
- Lorenz, D.L., 2017, smwrQW—Tools for censored data analysis (ver. 0.7.14): GitHub, accessed September 1, 2020, at <https://rdr.io/github/USGSR/smwrQW/f/inst/doc/ComparingPairedData.pdf>.
- O'Brien, P.C., and Fleming, T.R., 1987, A paired prentice-Wilcoxon test for censored paired data: *Biometrics*, v. 43, no. 1, p. 169–180. [Also available at <https://doi.org/10.2307/2531957>.]
- RStudio Team, 2020, RStudio: Integrated Development Environment for R (ver. 4.0.2): Boston, Mass., RStudio Team, accessed December 2020 at <http://www.rstudio.com/>.

Appendix 4. Comparison of Sample Concentration Ranking Among Analytical Methods

The contaminant data reflected multiple reporting limits within and between laboratories for each of the contaminant groups. Generally, reporting limits were ELISA>NWQL>AXYS (table 1; figs. 3 and 4). ATZ_{TOT} concentrations were highest at public water system 101 (SW) by both ELISA and NWQL methods (fig. 3A). Most commonly, higher concentrations of ATZ_{TOT} were analyzed in samples collected from SW-sourced public water systems. Public water system 321 (GW_{WW}) had the greatest CBZ_{TOT} concentrations, as determined by all methods, and the greatest SMX_{TOT} concentrations, as determined by NWQL and AXYS

methods (fig. 4B and C). CBZ_{TOT} and SMX_{TOT} concentrations by NWQL and AXYS methods were below or just above the ELISA reporting limit, except at public water system 321 (fig. 4B and C). Generally, the greatest CBZ_{TOT} concentrations by NWQL and AXYS methods were in samples collected from public water system 321, with progressively lower concentrations at public water systems 401, 315, and 117, while the greatest SMX_{TOT} concentrations determined by NWQL and AXYS methods were in samples collected from public water system 321, with progressively lower concentrations at public water systems 315, 401, and 310 (fig. 4B and C).

Director, USGS Upper Midwest Water Science Center
2280 Woodale Drive
Mounds View, MN 55112
763-783-3100

For additional information, visit: <https://www.usgs.gov/centers/umid-water>

Data Summary Report: Unregulated Contaminants Monitoring Project

FINAL REPORT (FEBRUARY 2023)

FINAL REPORT

Unregulated Contaminants Monitoring Project

Minnesota Department of Health
PO Box 64975
St. Paul, MN 55164-0975
651-201-4700
health.drinkingwater@state.mn.us
www.health.state.mn.us

To obtain this information in a different format, call: 651-201-4700.

Authors

Jane de Lambert, Minnesota Department of Health

Alycia Overbo, Minnesota Department of Health

Steve Robertson, Minnesota Department of Health

Sarah M. Elliott, U.S. Geological Survey, Upper Midwest Water Science Center

Technical Advisory Team Members

Mark Ferrey, Minnesota Pollution Control Agency

CheFei Chen, St. Paul Regional Water Services

Bill VanRyswyk, Minnesota Department of Agriculture

Deanna Scher, Minnesota Department of Health

Todd Johnson, Minnesota Department of Health

Lucas Martin, Minnesota Department of Health

James Backstrom, Minnesota Department of Health

Acknowledgements

Funding for this project was provided by the Minnesota Environment and Natural Resources Trust Fund as recommended by the Legislative-Citizen Commission on Minnesota Resources (LCCMR). The Trust Fund is a permanent fund constitutionally established by the citizens of Minnesota to assist in the protection, conservation, preservation, and enhancement of the state's air, water, land, fish, wildlife, and other natural resources.

We also thank our project partners at the United States Geological Survey (USGS) and project collaborators at the Minnesota Department of Agriculture (MDA), Minnesota Pollution Control Agency (MPCA), and participating public water systems.

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Table of Contents

Executive Summary.....	9
Introduction	12
CECs and drinking water in Minnesota	13
Problem statement	13
Methodology.....	14
Site selection	14
Selection of CECs for analysis	20
Sample collection	23
Results.....	24
All sites	25
Groundwater sites (agriculture and wastewater networks)	28
Agriculture network sites.....	29
Wastewater sites	38
Agriculture/wastewater sites	44
Surface water sites.....	49
Conclusions	62
References	65
Appendix A: Complete list of parameters.....	70
Inorganic compound	70
Field Parameters (samples were collected and analyzed but results are not assessed in this document).....	70
USGS Pesticides and Pesticide Degradates Analyzed at the National Water Quality Laboratory.....	70
Eurofins Atrazine and Cyanazine Degradates.....	76
AXYS PFAS	76
AXYS Pharmaceuticals and Personal Care Products	77
USGS Pharmaceuticals Analyzed at the National Water Quality Laboratory	79
USGS Wastewater Indicators Analyzed at the National Water Quality Laboratory.....	82
AXYS Alkylphenols.....	84
MDH Benzotriazoles & Benzothiazoles.....	84

AXYS Hormones	85
MDH Illicit Drugs	85

Table of figures

Figure 1. Number of surface water network sites by Hydrologic Unit Code 4 watershed (MNDNR, 2019).	15
Figure 2. Number of agriculture network sites by groundwater province (MNDNR, 2021).	17
Figure 3. Number of wastewater network sites by groundwater province (MNDNR, 2021).	19
Figure 4. Summary of CECs detected at all sites (N = 107) by class and relative frequency of detection.	25
Figure 5. Summary of CECs detected at groundwater sites (N = 90) by class and relative frequency of detection.	28
Figure 6. Ten most frequently detected CECs at vulnerable agriculture sites (N = 30).	30
Figure 7. Boxplot summary of total PFAS sample concentrations in samples collected from agriculture sites.	35
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.	37
Figure 9. Ten most frequently detected CECs at vulnerable wastewater sites (N=30).	39
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).	43
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).	48
Figure 12. Summary of CECs detected at surface water sites (N = 17) by class and relative frequency of detection.	50
Figure 13. Most frequently detected CECs at surface water sites (N=34).	51
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.	54

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.	57
Figure 16. Number of pesticides and pesticide degradates detected in groundwater (source water) and finished water samples collected from agriculture sites.	58
Figure 17. Number of PFAS detected in groundwater (source water) and finished water samples in the wastewater network.....	59
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.....	60
Figure 19. Number of pharmaceuticals detected in groundwater (source water) and finished water samples in the wastewater network.	61

Table of tables

Table 1. CECs sampled by network in Phase 1 of the project during 2019.	22
Table 2. CECs sampled by network in Phase 2 of the project during 2021.	23
Table 3. Overall summary of results.	26
Table 4. Pesticides and pesticide degradates detected in >20% of source and finished water samples collected from vulnerable agriculture sites.....	31
Table 5. PFAS detected in >20% of source and finished water samples collected from vulnerable agriculture sites.....	33
Table 6. Wastewater indicators detected in >10% of source and/or finished water samples collected from vulnerable wastewater sites.	40
Table 7. PFAS detected in ≥15% of source and finished water samples collected from vulnerable wastewater sites.	41
Table 8. Pesticides and pesticide degradates detected in ≥25% of source and/or finished water samples collected from vulnerable agriculture/wastewater sites.	45
Table 9. PFAS detected in >10% of source and finished water samples collected from vulnerable agriculture/wastewater sites.....	46
Table 10. Pesticides and pesticide degradates detected in >40% of source and/or finished water samples collected from surface water sites.	52
Table 11. PFAS detected in >15% of source and finished water samples collected from surface water sites.....	53

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

FINAL REPORT

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.

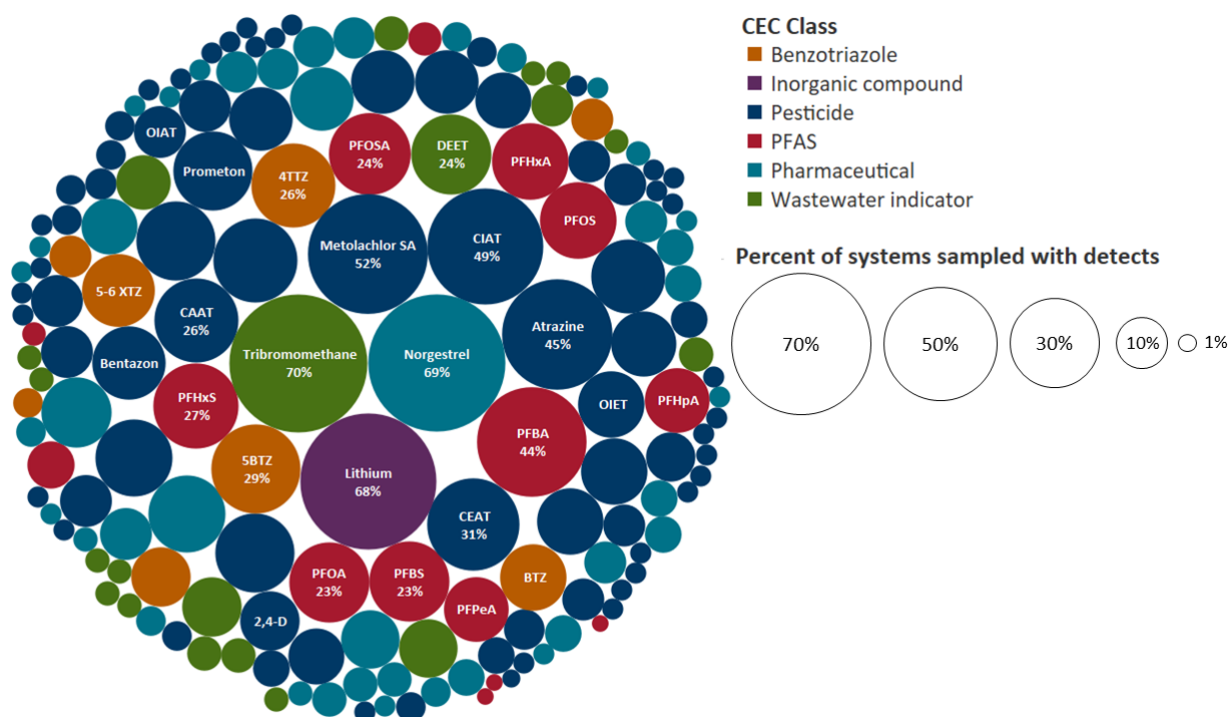
Sampling site and parameter selection were designed with several goals, as follows:

- 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);
 - 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;

FINAL REPORT

- 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 health-based 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 concern¹ (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.

¹ 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 Minnesota².

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.

² We know this from national Gallup polls that show drinking water contamination is the top public environmental health concern (see [A Seven-Year Stretch of Elevated Environmental Concern](#)). 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-treatment³), 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.

³ 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).

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

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

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

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),
 - pesticides, and
 - 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

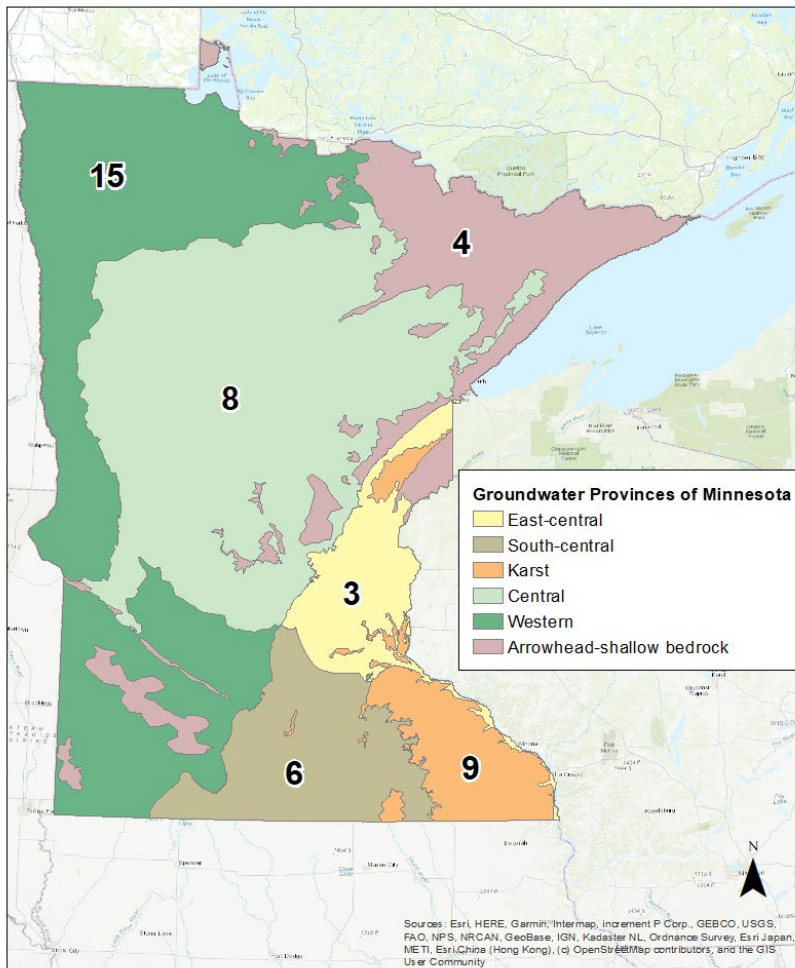


Figure 2. Number of agriculture network sites by groundwater province (MNDNR, 2021).

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

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

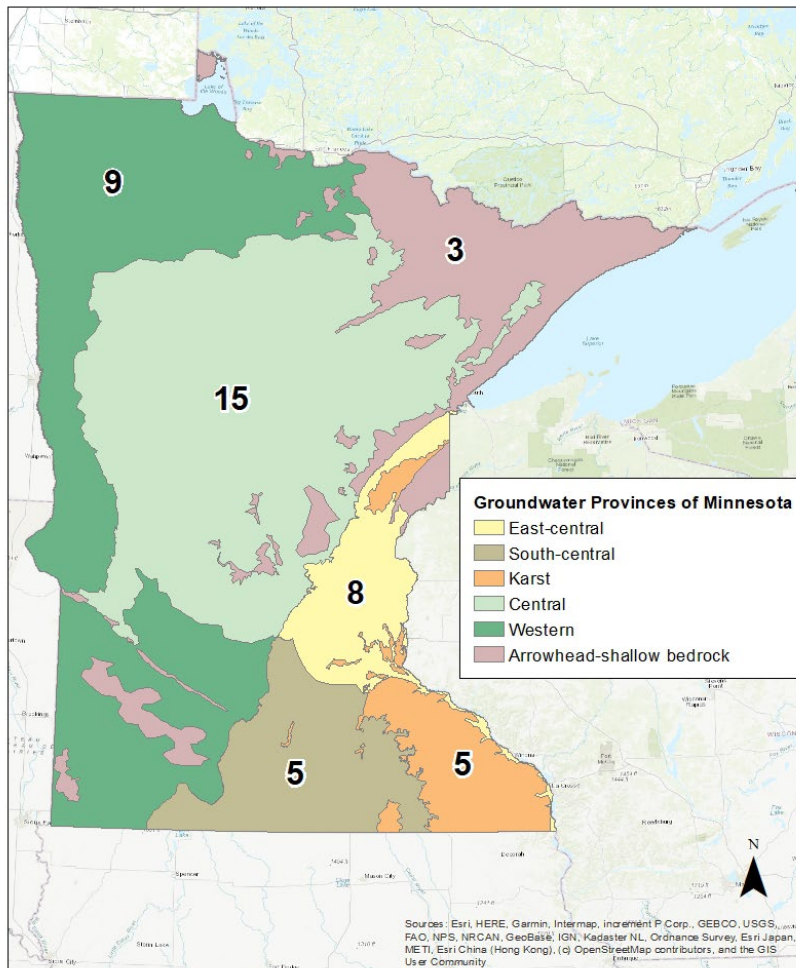


Figure 3. Number of wastewater network sites by groundwater province (MNDNR, 2021).

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

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 degrade 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).
2. 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 interest⁴.

⁴ 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 waters⁵.

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.

⁵ 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	X	X	X
Wastewater indicators	USGS NWQL		X	X
Pharmaceuticals	USGS NWQL		X	X
PFAS	AXYS		X	X
Benzotriazoles/benzothiazoles	MDH			X
Illicit Drugs	MDH			X
Pharmaceuticals and Personal Care Products (limited list, lists 1 & 6 defined in appendix)	AXYS		X	
Pharmaceuticals and Personal Care Products (extensive list, lists 1, 3 & 6 defined in appendix)	AXYS			X
Alkylphenols and Alkylphenol Ethoxylates	AXYS			X
Hormones	AXYS			X
Pesticides/pesticide degradates	USGS NWQL	X		X

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	X	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	X	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 detected⁶. 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).

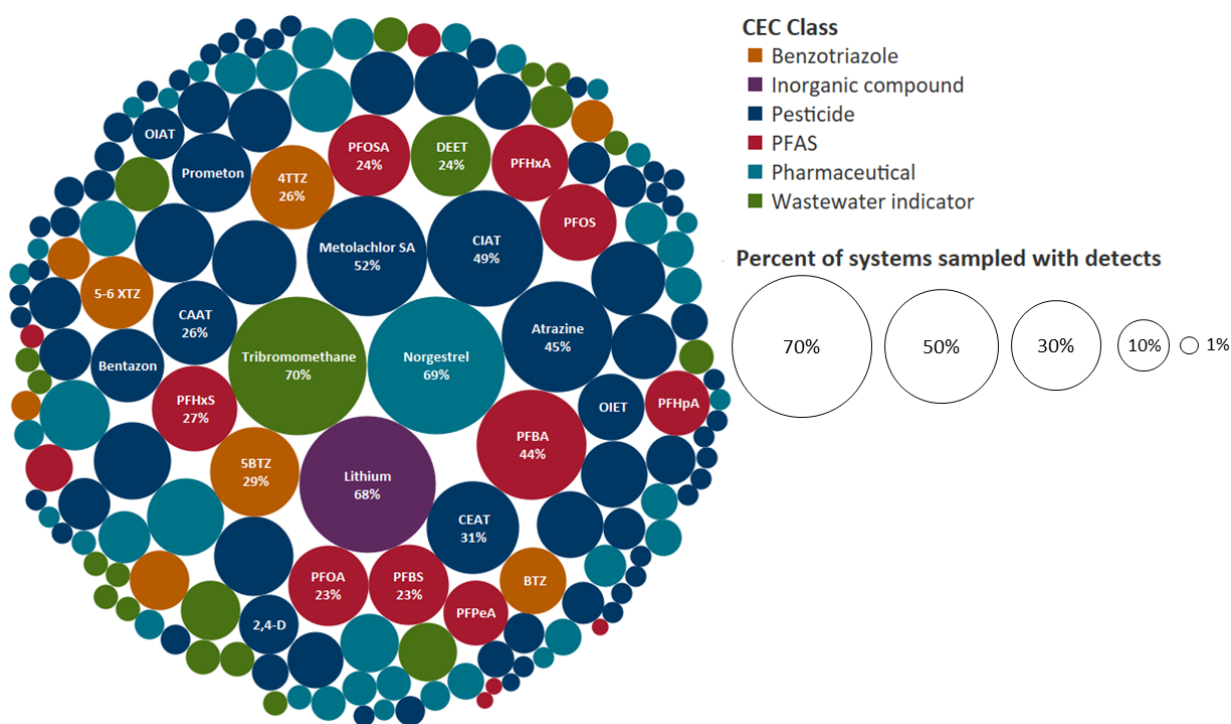


Figure 4. Summary of CECs detected at all sites (N = 107) by class and relative frequency of detection.

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%).

⁶ 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
<i>Vulnerable agriculture sites (n=30)</i>				
Pesticides	48	95	10	Metolachlor SA
PFAS	11	73	11	PFBA
<i>Non-vulnerable agriculture sites (n=15)</i>				
Pesticides	16	47	6	Deethylcyanazine acid
PFAS	9	67	7	PFOSA
<i>Vulnerable wastewater sites (n=30)</i>				
Wastewater indicators	20	95	10	Bromoform
Pharmaceuticals	17	68	6	Sulfamethoxazole
PFAS	11	64	9	PFBA
<i>Non-vulnerable wastewater sites (n=15)</i>				
Pharmaceuticals	1	7	1	Diphenhydramine
PFAS	3	40	2	PFOSA
<i>Vulnerable agriculture/wastewater sites (n=8)</i>				
Pesticides	17	75	9	Metolachlor SA
PFAS	11	63	10	PFBA
Pharmaceuticals	13	50	9	Sulfamethizole Carbamazepine
Wastewater indicators	5	88	4	Bromoform

FINAL REPORT

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
<i>Surface water sites (n=17)</i>				
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).

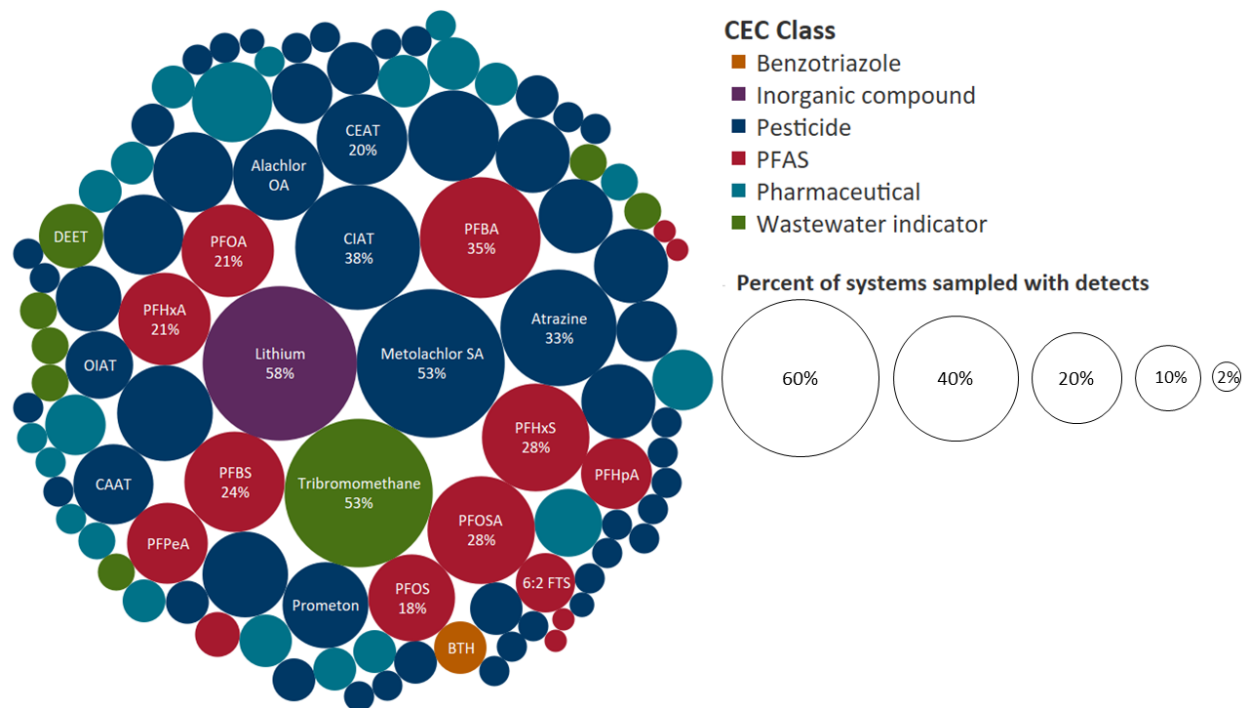


Figure 5. Summary of CECs detected at groundwater sites (N = 90) by class and relative frequency of detection.

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 non-vulnerable 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.

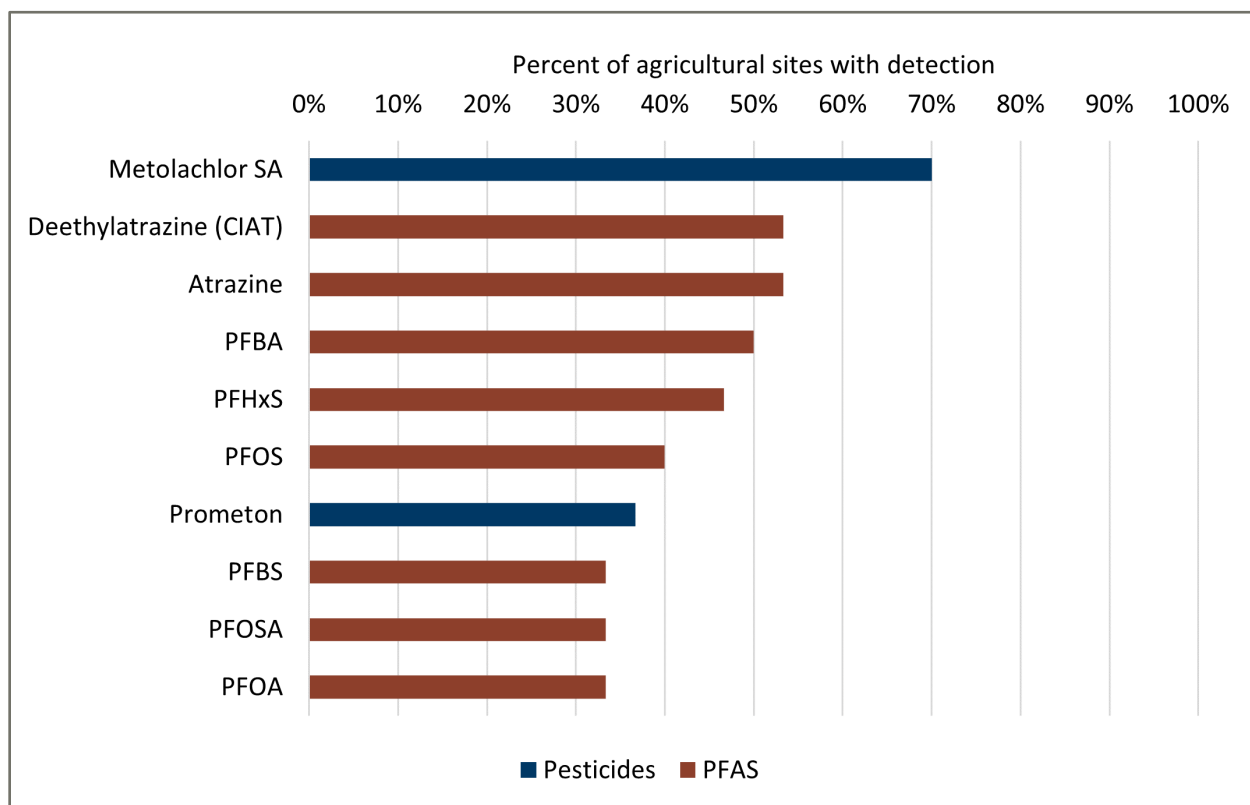


Figure 6. Ten most frequently detected CECs at vulnerable agriculture sites (N = 30).

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 and finished 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 ^a (ng/L)
Metolachlor SA	57	4,910	71	2,470	800,000 ^b
Atrazine	50	94.3	46	80.9	3,000 ^b
Deethylatrazine (CIAT)	43	111	36	108	3,000 ^b
N,N-diethyl-meta-toluamide (DEET)	38	17.3	38	120	200,000 ^b
Metolachlor oxanilic acid (OA)	33	1,130	25	1,200	800,000 ^c
Prometon	33	31.9	36	11.3	100,000 ^c
Alachlor oxanilic acid (OA)	30	98.5	36	106	50,000 ^d
Deethylcyanazine acid	27	160	30	160	1,000 ^d
Hydroxydeethyl atrazine (OIAT)	27	29.1	18	18.4	--
2-hydroxyatrazine (OIET)	23	120	29	44.3	--
Cyanazine acid	21	65	12	63	1,000 ^b

^a Minnesota Department of Health [Human Health-Based Water Guidance Table](#)

^b Health risk limit

^c Health based value

^d 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 cyanazine⁷ (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.

⁷ 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.*Dash (--) indicates no available guidance value.*

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 ^a (ng/L)
PFBA	42	436	46	368	7,000 ^b
PFHxS	39	5.74	38	6.81	47 ^c
PFOS	35	8.58	31	8.27	15 ^c
PFOA	32	19.9	27	18	35 ^b
PFBS	32	4.76	31	5.02	100 ^c
PFHxA	29	14.7	31	14.7	200 ^c
PFPeA	26	24.1	27	20.5	--
PFHpA	23	3.79	23	3.93	--

^a Minnesota Department of Health [Human Health-Based Water Guidance Table](#)^b Health risk limit^c 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.

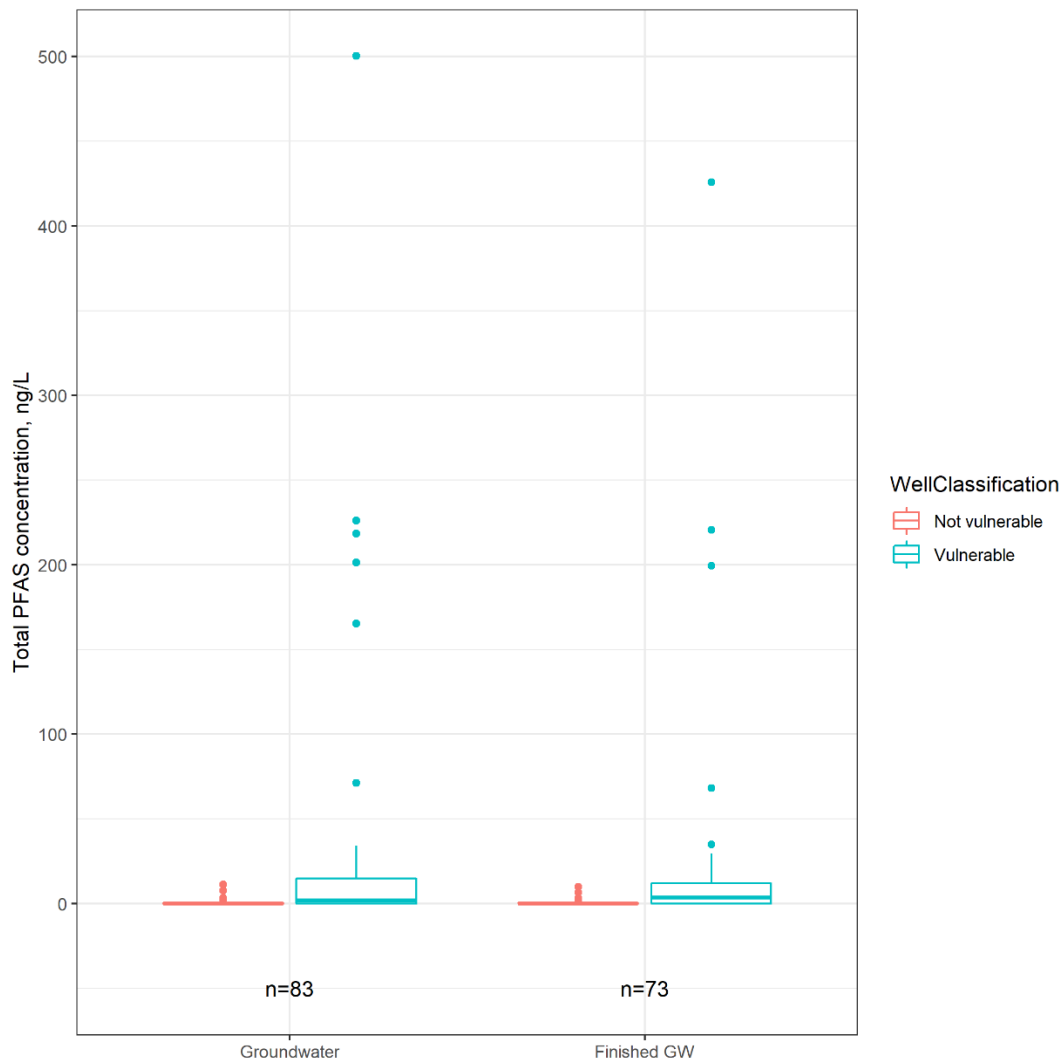


Figure 7. Boxplot summary of total PFAS sample concentrations in samples collected from agriculture sites.

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.

FINAL REPORT

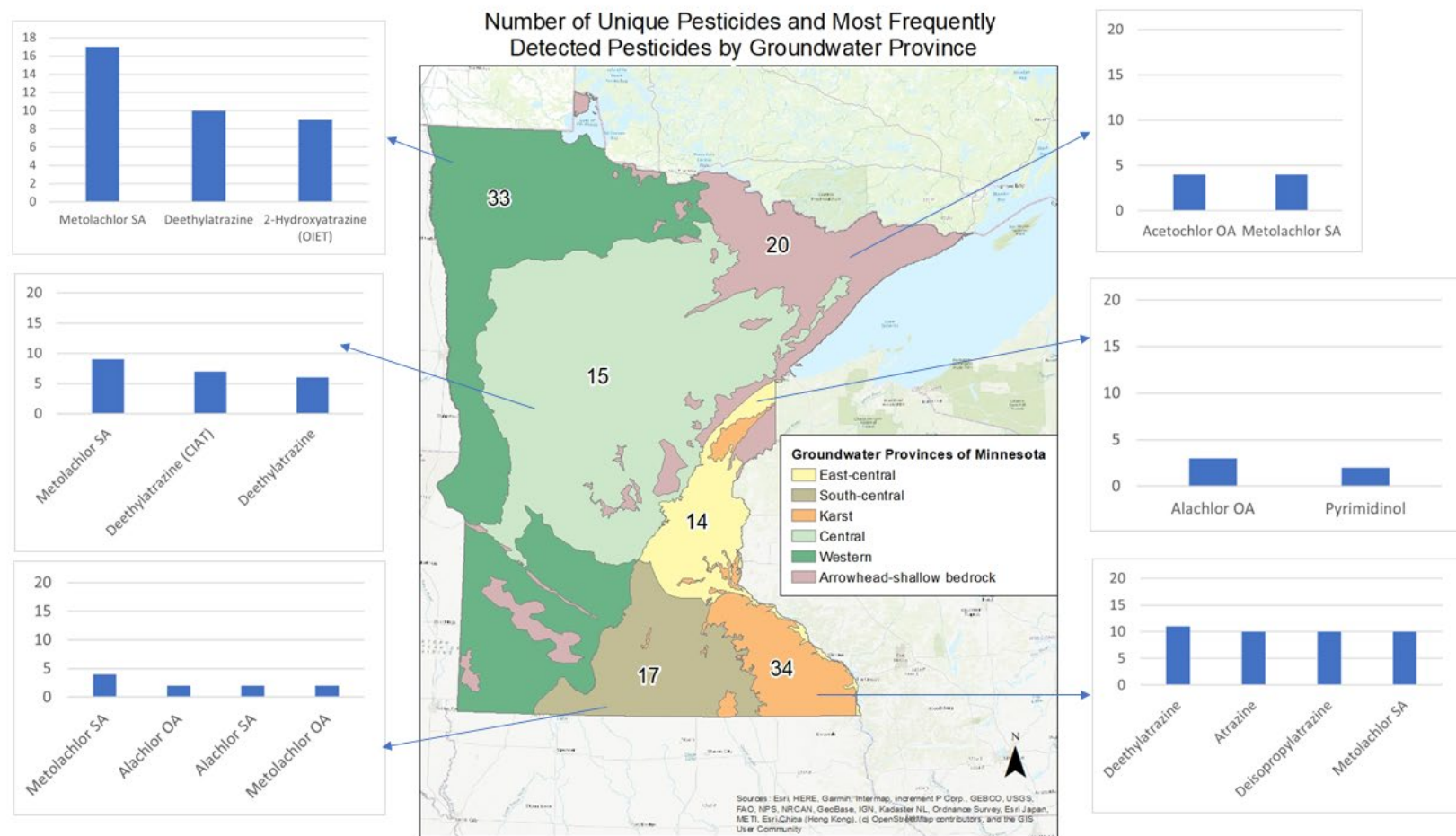


Figure 8. Number of pesticides and pesticide degradates detected in all samples (source and finished) collected from agriculture sites (vulnerable and non-vulnerable) by groundwater province (map; MNDNR, 2021), and the most frequently detected pesticides and pesticide degradates by groundwater province.

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 lithium⁸, 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.

⁸ 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).

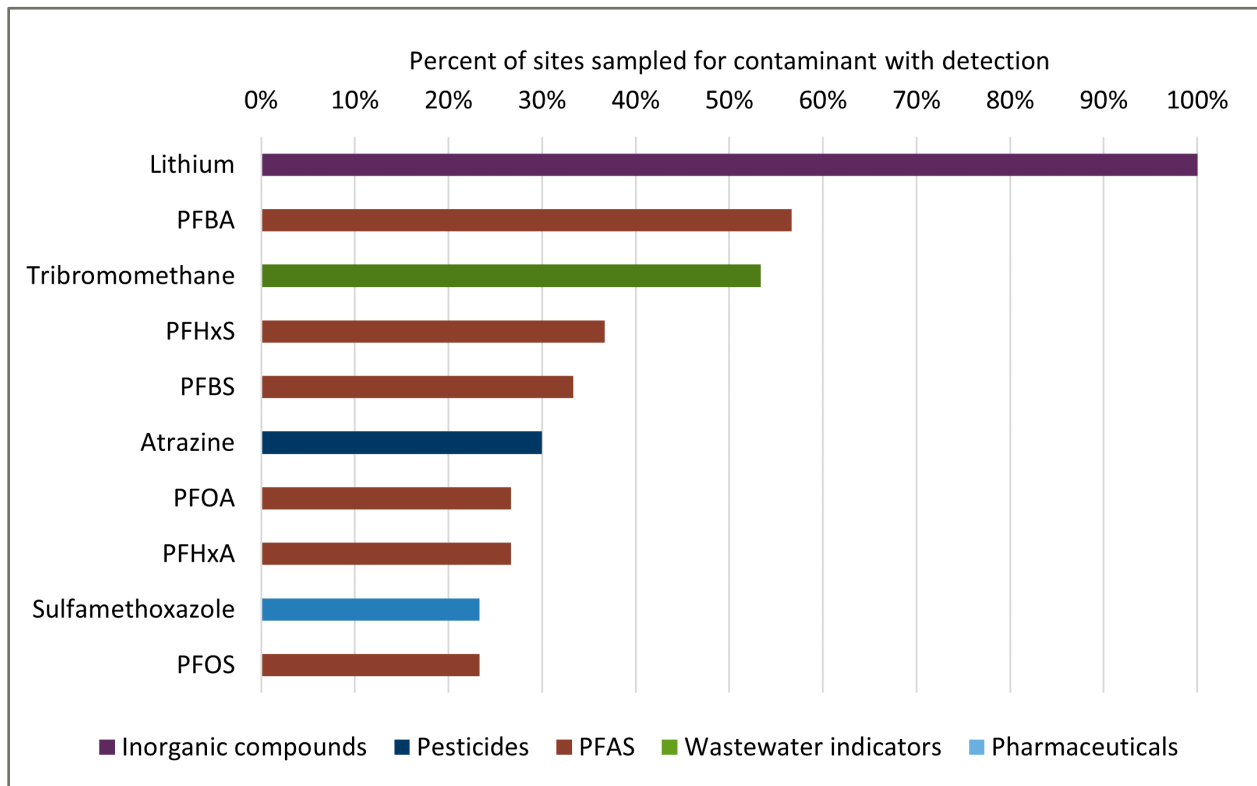


Figure 9. Ten most frequently detected CECs at vulnerable wastewater sites (N=30).

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 finished water samples collected from vulnerable wastewater sites.*Dash (--) indicates no available guidance value.*

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 ^a (ng/L)
Atrazine	32	37.4	22	38.3	3,000 ^b
Prometon	14	20	17	10	100,000 ^c
Bromoform	13	6,300	77	40,900	40,000 ^b
Nicotine	13	39	0	--	--
DEET	9	30	11	30	200,000 ^b
Bromacil	5	10	11	20	70,000 ^d

^a Minnesota Department of Health [Human Health-Based Water Guidance Table](#)^b Health risk limit^c Health based value^d 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 ^a (ng/L)
PFBA	45	190	54	175	7,000 ^b
PFHxS	32	5.74	31	5.34	47 ^c
PFBS	26	3.72	35	3.04	100 ^c
PFHxA	23	14.7	23	14.7	200 ^c
PFOA	19	19.9	23	18	35 ^b
PFPeA	19	11.2	15	8.12	--

^a Minnesota Department of Health [Human Health-Based Water Guidance Table](#)

^b Health risk limit

^c 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 non-vulnerable 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 [PFAS Testing in Public Water Systems](#)).

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.

FINAL REPORT

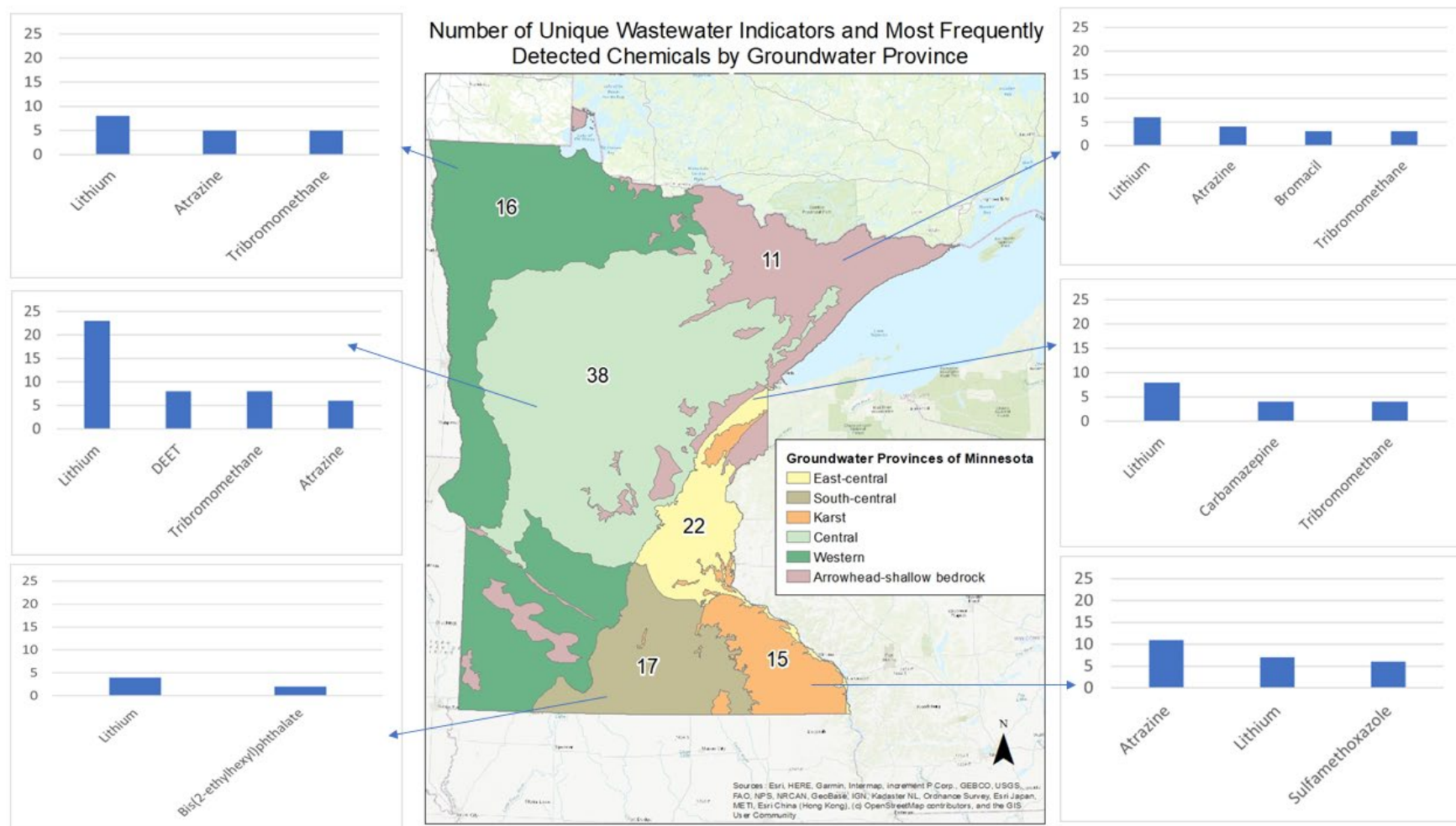


Figure 10. Number of unique wastewater indicators detected in all samples (source and finished) collected from wastewater sites (vulnerable and non-vulnerable) by groundwater province (map; MNDNR, 2021) and the most frequently detected wastewater indicators by groundwater province (bar charts; y-axis 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 $\geq 25\%$ 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.*Dash (--) indicates no available guidance value.*

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 ^a (ng/L)
Deethylatrazine	38	16.2	0	--	3,000 ^b
Metolachlor SA	38	486	50	515	800,000 ^c
DEET	38	100	38	120	200,000 ^c
Alachlor OA	38	37.1	38	31.1	50,000 ^b
Hydroxyatrazine	38	21.9	38	14.4	--
Prometon	38	21.7	38	10.7	100,000 ^d
Atrazine	38	8.26	25	6.85	3,000 ^c
Metolachlor OA	25	111	25	72	800,000 ^d
Metolachlor	25	41.4	29	21.7	300,000 ^c
Dechlorometolachlor	25	12.4	13	12.4	--

^a Minnesota Department of Health [Human Health-Based Water Guidance Table](#)^b Risk assessment advice^c Health risk limit^d 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.

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 ^a (ng/L)
PFOS	33	8.58	38	8.27	15 ^b
PFHxS	33	5.74	25	5.34	47 ^c
PFOA	22	19.9	13	18	35 ^b
PFHxA	22	14.7	25	14.7	200 ^c
PFBA	22	9.71	50	9.44	7,000 ^b
PFPeA	22	6.22	25	5.78	--
PFBS	22	1.55	25	1.24	100 ^c
PFHpA	11	3.79	13	3.93	--
PFNA	11	1.21	13	.891	--

^a Minnesota Department of Health [Human Health-Based Water Guidance Table](#)

^b Health risk limit

^c 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 $\geq 15\%$ 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).

FINAL REPORT

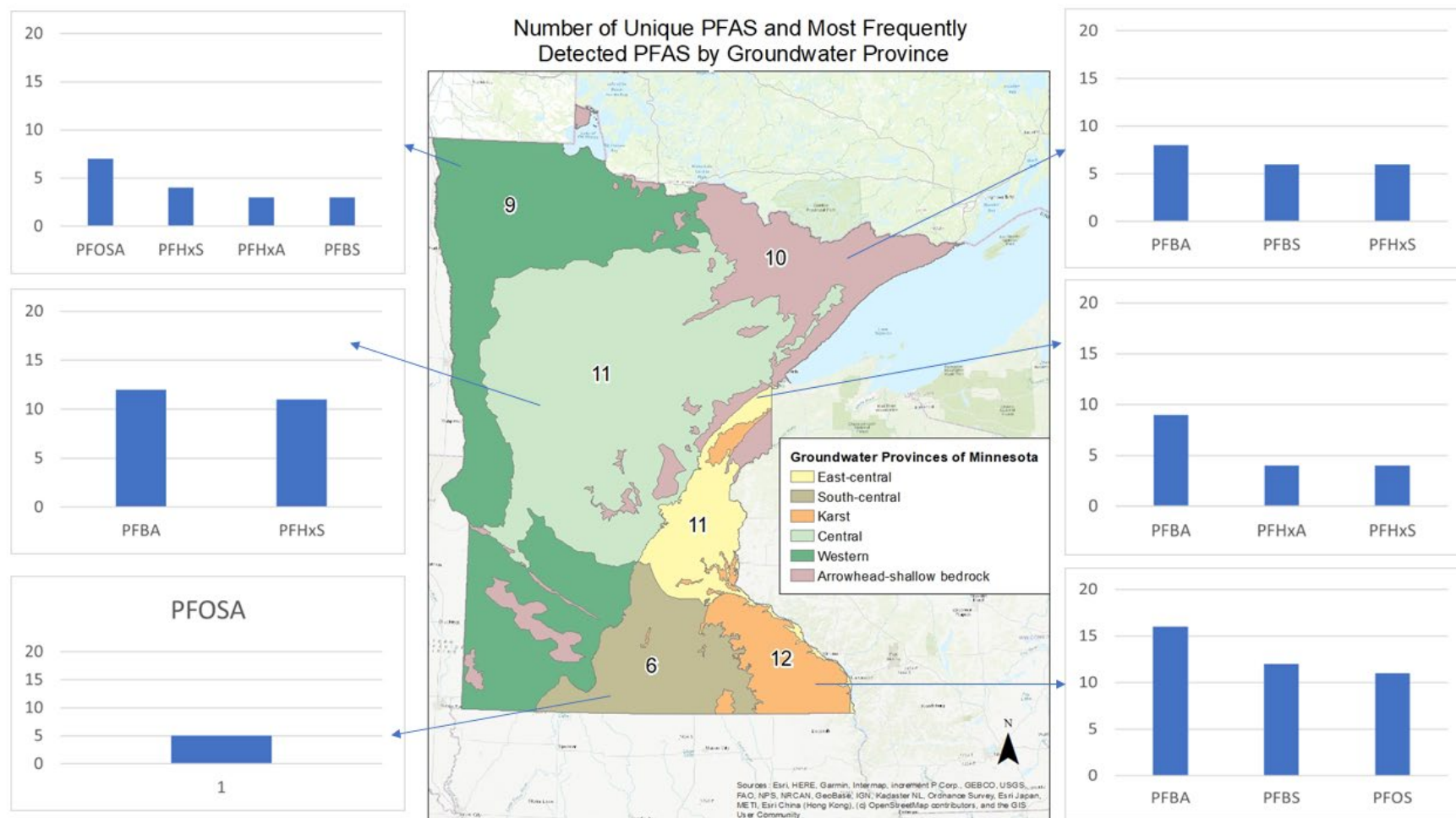


Figure 11. Number of unique PFAS detected in all samples (source and finished) collected from vulnerable groundwater sites by groundwater province (map; MNDNR, 2021) and the most frequently detected PFAS by groundwater province (bar charts; y-axis is detection frequency, in percent).

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 exceeded 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).

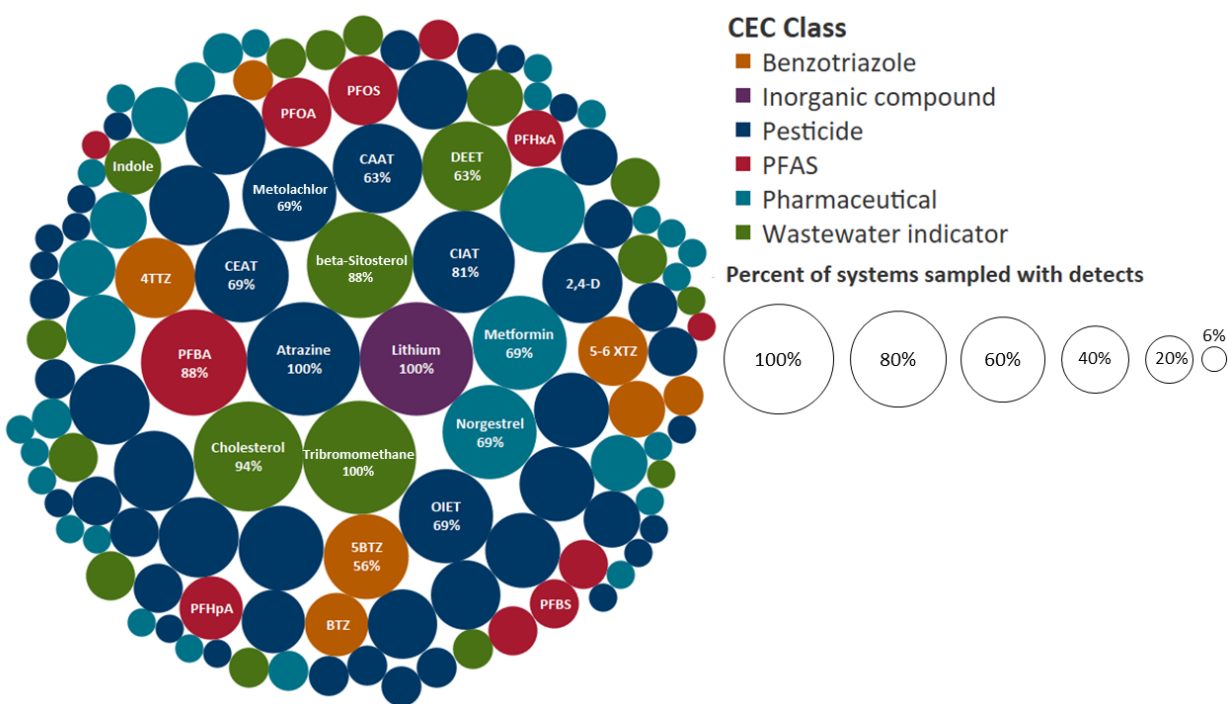


Figure 12. Summary of CECs detected at surface water sites (N = 17) by class and relative frequency of detection.

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%).

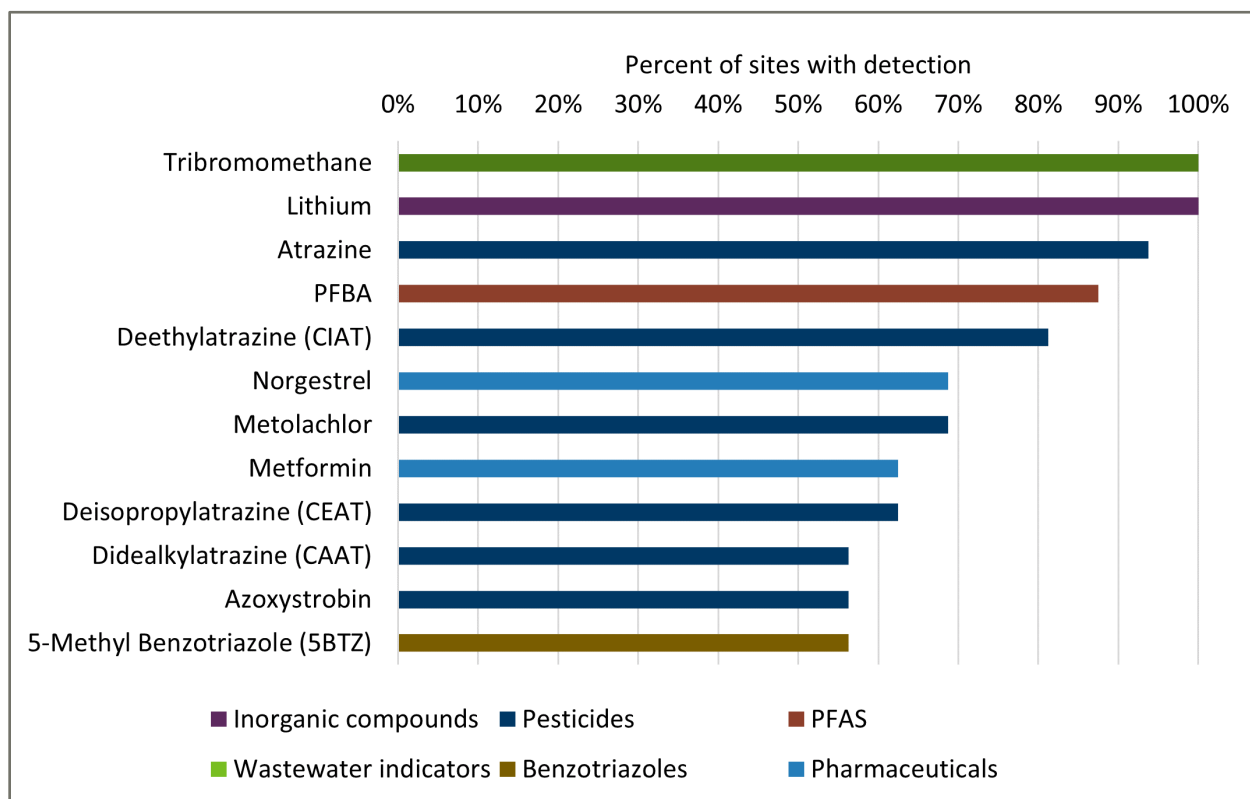


Figure 13. Most frequently detected CECs at surface water sites (N=34).

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

^a Minnesota Department of Health [Human Health-Based Water Guidance Table](#)

^b Health risk limit

^c 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.

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 ^a (ng/L)
PFBA	62	32.9	72	33.2	7,000 ^b
PFOA	26	1.95	22	2.04	35 ^b
PFOS	24	2.96	16	1.15	15 ^c
PFHxA	24	3.26	19	2.79	200 ^c
PFHpA	21	1.22	16	1.25	--

^a Minnesota Department of Health [Human Health-Based Water Guidance Table](#)

^b Health risk limit

^c 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.

FINAL REPORT

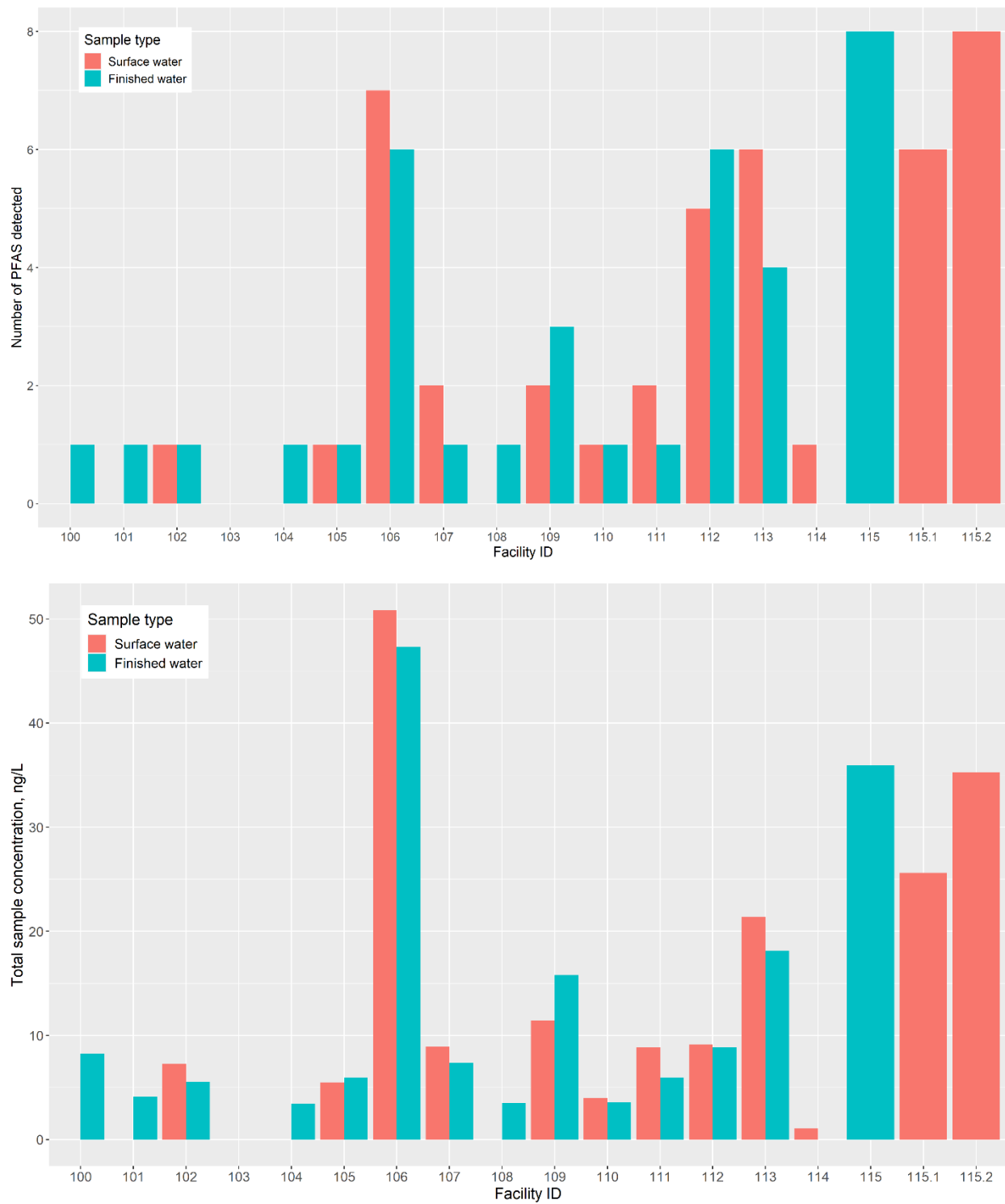


Figure 14. Number of PFAS detected (top graph) and total PFAS sample concentrations (sum of all detected PFAS within a sample; bottom graph) in source and finished water samples collected from surface water sourced sites.

FINAL REPORT

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-Methylenedioxyamphetamine, 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.

FINAL REPORT

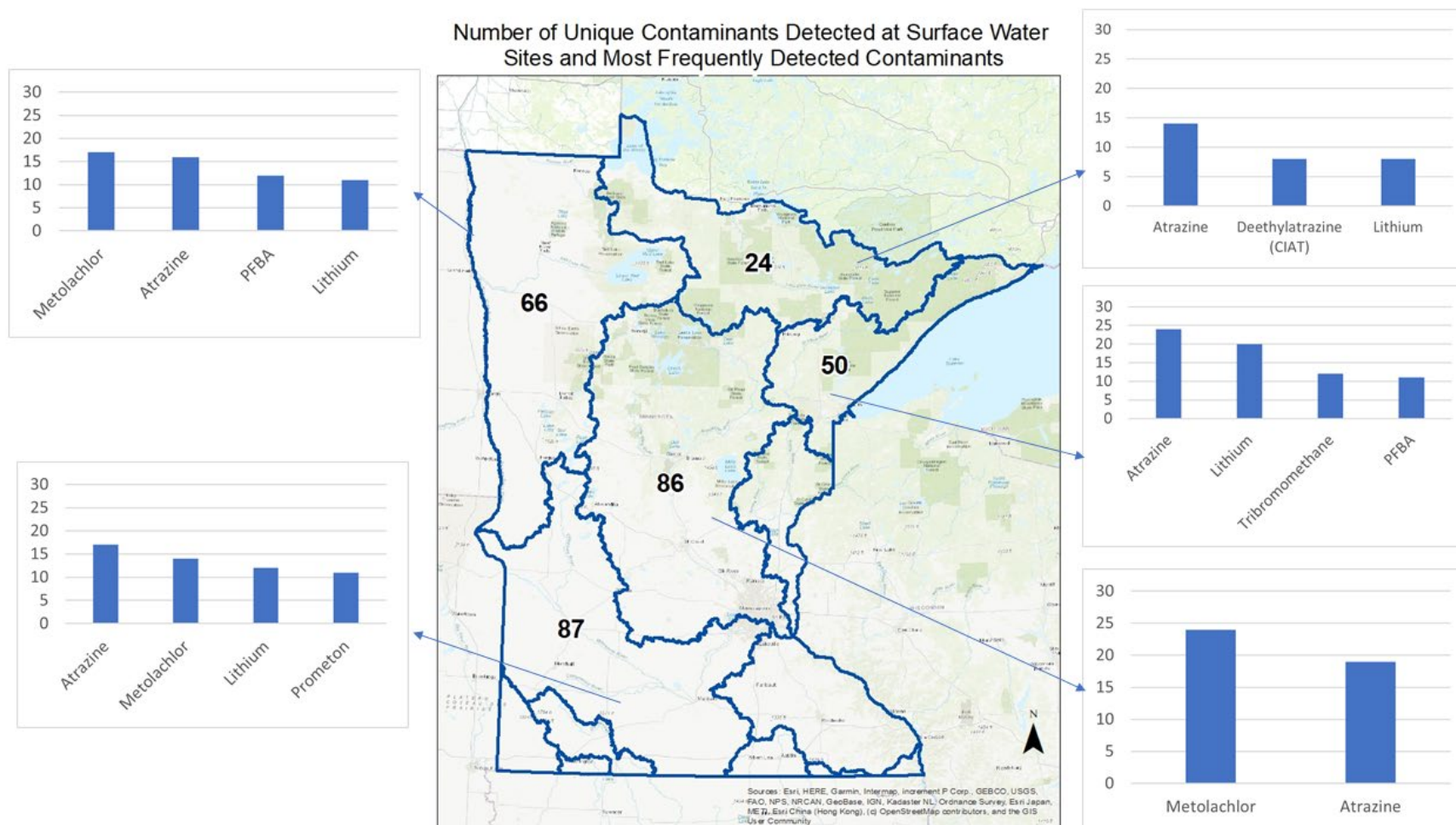


Figure 15. Numbers of unique CECs detected in all samples (source and finished) collected from surface water sites by Hydrologic Unit Code-4 (map; MNDNR, 2019) and the most frequently detected CECs by watershed.

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).

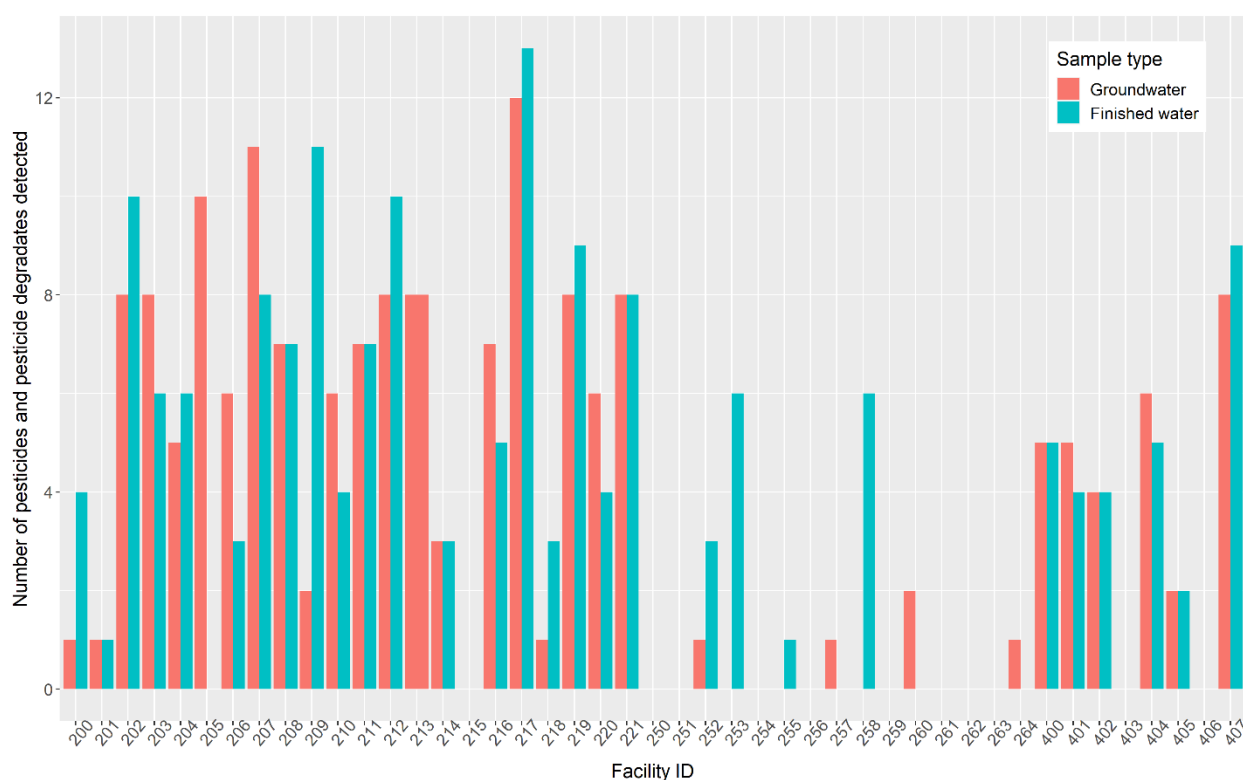


Figure 16. Number of pesticides and pesticide degradates detected in groundwater (source water) and finished water samples collected from agriculture sites.

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

FINAL REPORT

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).

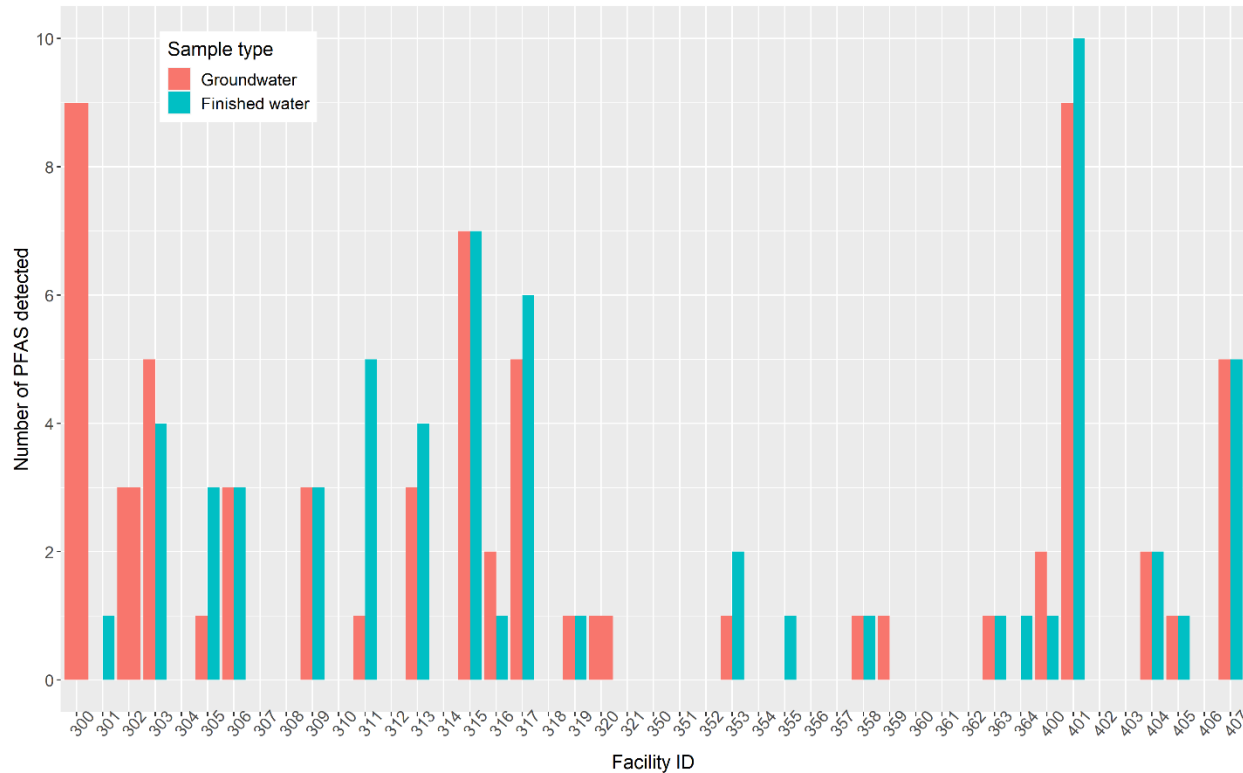


Figure 17. Number of PFAS detected in groundwater (source water) and finished water samples in the wastewater network.

Missing bars indicate that no PFAS were detected.

FINAL REPORT

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.

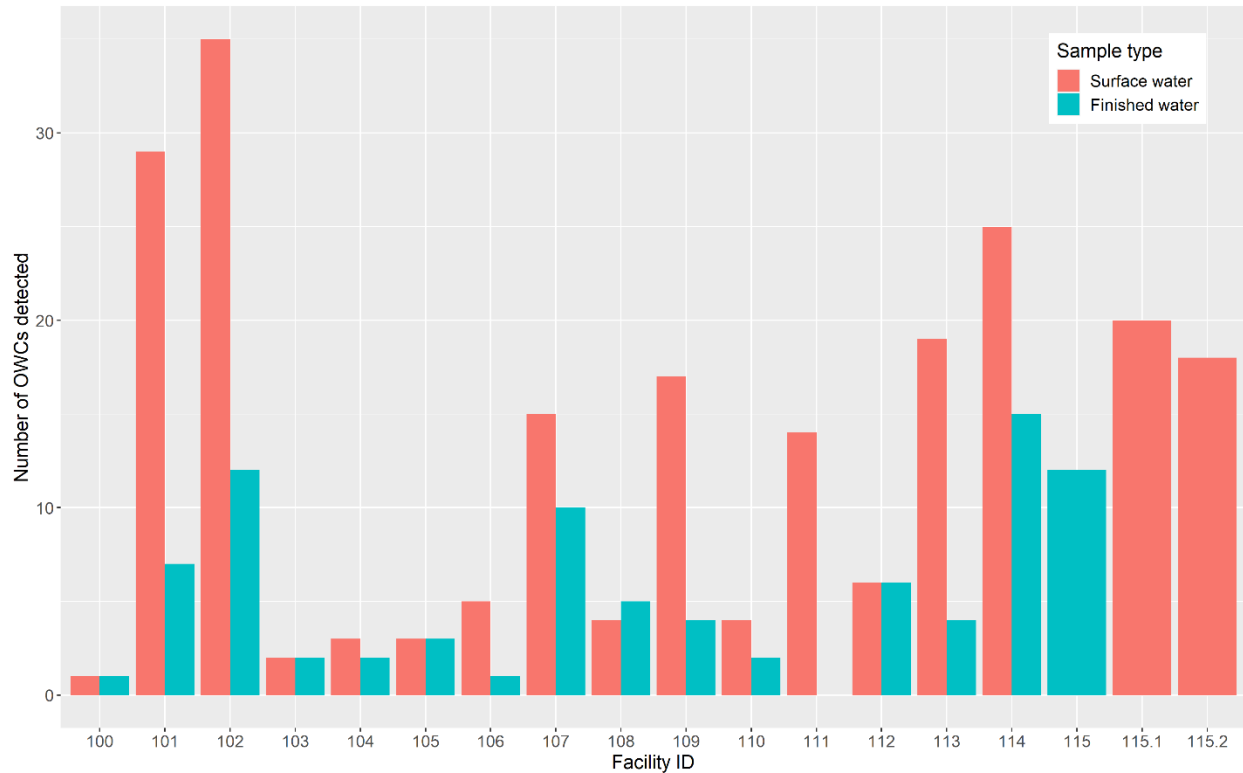


Figure 18. Number of OWCs detected in surface water (source water) and finished water samples collected from surface water sites during the first sample event.

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.

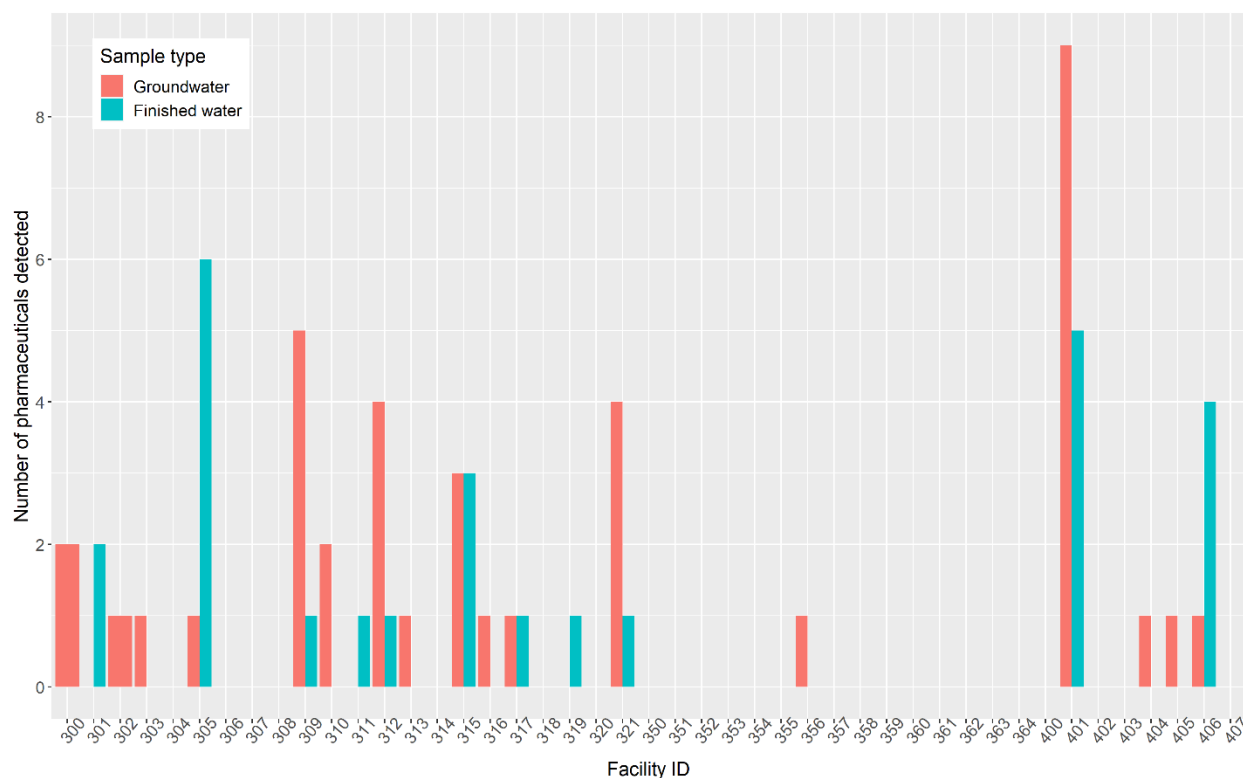


Figure 19. Number of pharmaceuticals detected in groundwater (source water) and finished water samples in the wastewater network.

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 µg/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 µg/L for tribromomethane, or bromoform, which is a disinfection byproduct (DBP)⁹. 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

⁹ Disinfection is necessary to reduce the risk of pathogen exposure in finished drinking water. The benefits of disinfection outweigh the risks of DBPs 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.

References

- ACWA and ASDWA, 2019, Recommendations Report: Contaminants of Emerging Concern Workgroup, 22p., available on internet: <https://www.asdwa.org/wp-content/uploads/2019/05/ASDWA-ACWA-Report-on-Contaminants-of-Emerging-Concern-2019.pdf>
- Banzhaf, S., Filipovic, M., Lewis, J., Sparrenbom, C. J., & Barthel, R. 2017. A review of contamination of surface-, ground-, and drinking water in Sweden by perfluoroalkyl and polyfluoroalkyl substances (PFASs). *Ambio*, 46(3), 335-346.
- Bexfield, L.M., Toccalino, P.L., Belitz, K., Foreman, W.T., and Furlong, E.T. 2019. Hormones and pharmaceuticals in groundwater used as a source of drinking water across the United States. *Environmental Science & Technology*. 53, 6: 2950–2960. <https://doi.org/10.1021/acs.est.8b05592>
- Boone, J. S., Vigo, C., Boone, T., Byrne, C., Ferrario, J., Benson, J., Donohue, J., Simmons, J.E., Kolpin, D.W., Furlong, E.T., and Glassmeyer, S.T. 2019. Per- and polyfluoroalkyl substances in source and treated drinking waters of the United States. *Science of the Total Environment*. 653: 359–369. <https://doi.org/10.1016/j.scitotenv.2018.10.245>
- Karin Broberg, Gabriela Concha, Karin Engström, Magnus Lindvall, Margareta Grandér, and Marie Vahter, 2011, Lithium in Drinking Water and Thyroid Function, *Environmental Health Perspectives* 119:6 CID: <https://doi.org/10.1289/ehp.1002678>
- Centers for Disease Control and Prevention, 2022, “Household Water Treatment”. *Global Water Sanitation and Hygiene (WASH)*. October 22, 2022. <https://www.cdc.gov/safewater/chlorination-byproducts.html>.
- Crone, B. C., Speth, T. F., Wahman, D. G., Smith, S. J., Abulikemu, G., Kleiner, E. J., & Pressman, J. G. 2019. Occurrence of per-and polyfluoroalkyl substances (PFAS) in source water and their treatment in drinking water. *Critical reviews in environmental science and technology*, 49(24), 2359-2396.
- de Lambert, J.R., Walsh, J.F., Scher, D.P., Firnstahl, A.D., and Borchardt, M.A. 2021. Microbial pathogens and contaminants of emerging concern in groundwater at an urban subsurface stormwater infiltration site. *Science of the Total Environment*. 775: 145738. <https://doi.org/10.1016/j.scitotenv.2021.145738>
- Elliott, 2023, Contaminant data from a survey of Minnesota source and finished drinking waters, 2019 – 2022: U.S. Geological Survey, <https://doi.org/10.5066/P9SVEX57>.
- Elliott, S. M., Erickson, M. L., Krall, A. L., & Adams, B. A. (2018). Wastewater indicators, hormones, sterols, antibiotics, and pharmaceuticals in soil at an agricultural field irrigated with domestic septage, central Minnesota, September 2014 (No. 2018-5100). US Geological Survey.
- Glassmeyer, S. T., Furlong, E.T., Kolpin, D.W., Batt, A.L., Bensond, R., Boone, J.S., Conerly, O., Donohue, M.J., King, D.N., Kostich, M.S., Mash, H.E., Pfaller, S.L., Schenck, K.M., Simmons, J.E., Varughese, E.A., Vesper, S.J., Villegas, E.N., Wilson, V.S. 2017. Nationwide

- reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States. *Science of the Total Environment*. 581-582: 909–922. <https://doi.org/10.1016/j.scitotenv.2016.12.004>
- Ferrey, M. 2013. Pharmaceuticals and endocrine active chemicals in Minnesota lakes, Minnesota Pollution Control Agency. 52 pp. <https://www.pca.state.mn.us/sites/default/files/tdr-g1-16.pdf>
- Ferrey, M. 2015. Pharmaceuticals, personal care products, and endocrine active chemical monitoring in lakes and rivers: 2013. Minnesota Pollution Control Agency. 61 pp. <http://dx.doi.org/10.13140/RG.2.1.4349.7127>
- Ferrey, M., Streets, S., and Lueck, A. 2013. Pharmaceuticals and personal care products in Minnesota's rivers and streams: 2010. Minnesota Pollution Control Agency. 39 pp. <https://www.pca.state.mn.us/sites/default/files/tdr-g1-17.pdf>
- Ferrey, M., Martinovic, D., Backe, W., and Andrews, A. 2017. Pharmaceuticals and chemicals of concern in rivers: Occurrence and biological effects. Minnesota Pollution Control Agency. 73 pp. <https://www.pca.state.mn.us/sites/default/files/tdr-g1-20.pdf>
- Furlong, E. T., Batt, A.L., Glassmeyer, S.T., Noriega, M.C., Kolpin, D.W., Mash, H., and Schenck, K.M. 2017. Nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States: Pharmaceuticals. *Science of the Total Environment*. 579: 1629–1642. <https://doi.org/10.1016/j.scitotenv.2016.03.128>
- Hem, J.D., 2005, *Study and Interpretation of the Chemical Characteristics of Natural Water*, University Press of the Pacific, 363p.
- Hruby, C. E., Libra, R. D., Fields, C. L., Kolpin, D. W., Hubbard, L. E., & Borchardt, M. R. (2013). Survey of Iowa groundwater and evaluation of public well vulnerability classifications for contaminants of emerging concern. *Iowa Geol Water Surv Tech Inf Ser*. 2015; 57.
- Johnson, H., Schaefer, B., Timm, D., Rindal, D., and Schliep, A., 2016. 2015 Reconnaissance study of pesticide compounds in community public water supply wells. Minnesota Department of Agriculture and Minnesota Department of Health. 60p. https://www.mda.state.mn.us/sites/default/files/inline-files/2015PesticideReconReport_0.pdf
- Kroening, S. 2012. Endocrine active chemicals and other contaminants of emerging concern in Minnesota's groundwater, 2009-2010. Minnesota Pollution Control Agency. 26 p. <https://www.pca.state.mn.us/sites/default/files/wq-cm4-03.pdf>
- Kroening, S. and Vaughan, S. 2019. The condition of Minnesota's groundwater quality, 2013-2017. Minnesota Pollution Control Agency. 87 pp. <https://www.pca.state.mn.us/sites/default/files/wq-am1-10.pdf>
- Lasee, S, McDermett, K, Kumar, N, Guelfo, J, Payton, P, Yang, Z, Anderson, TA, 2022, Targetted analysis and Total Oxidizable Precursor assay of several insecticides for PFAS: *J. of Hazardous Materials Letters*, v 3, pp 1-7.

- Lee, K.E., Langer, S.K., Barber, L.B., Writer, J.H., Ferrey, M.L., Schoenfuss, H.L., Furlong, E.T., William T. Foreman, Gray, J.L., ReVello, R.C., Martinovic, D., Woodruff, O.P., Keefe, S.H., Brown, G.K., Taylor, H.E., Ferrer, I., and Thurman, E.M. 2011. Endocrine active chemicals, pharmaceuticals, and other chemicals of concern in surface water, wastewater-treatment plant effluent, and bed sediment, and biological characteristics in selected streams, Minnesota—design, methods, and data, 2009: U.S. Geological Survey Data Series 575, 54 p., with appendixes. <https://doi.org/10.3133/ds575>
- Lenka, S.P., Kah, M., and Padhye, L.P. 2021. A review of the occurrence, transformation, and removal of poly- and perfluoroalkyl substances (PFAS) in wastewater treatment plants. *Water Research*. 199: 117187. <https://doi.org/10.1016/j.watres.2021.117187>
- Lindsay, BD, Belitz, K, Cravotta, CA, Toccalino, PL, and Dubrovsky, NM, 2021, Lithium in groundwater used for drinking-water supply in the United States: Science of the Total Environment, v 767, pp
- McMahon, P. B., Tokranov, A. K., Bexfield, L. M., Lindsey, B. D., Johnson, T. D., Lombard, M. A., & Watson, E. (2022). Perfluoroalkyl and Polyfluoroalkyl Substances in Groundwater Used as a Source of Drinking Water in the Eastern United States. *Environmental science & technology*, 56(4), 2279-2288.
- Metropolitan Council. 2020. Sewersheds (Metersheds, WWTP Service Areas). Available at https://resources.gisdata.mn.gov/pub/gdrs/data/pub/us_mn_state_metc/util_sanitary_sewerheds/metadata/metadata.html
- Minnesota Department of Agriculture and Minnesota Department of Health. 2016. 2015 Reconnaissance Study of Pesticide Compounds in Community Public Water Supply Wells, available on internet at: https://www.mda.state.mn.us/sites/default/files/inline-files/2015PesticideReconReport_0.pdf
- Minnesota Department of Agriculture (MDA). 2022. 2021 Water quality monitoring report. 292 p. Available at: <https://wrl.mnpals.net/islandora/object/WRLrepository%3A3880/datastream/PDF/view>
- Minnesota Department of Agriculture, 2021. 2020 Water Quality Monitoring Report, January through December 2020. Available at: <https://wrl.mnpals.net/islandora/object/WRLrepository%3A3746/datastream/PDF/view>
- Minnesota Department of Agriculture, 2022. 2021 Water Quality Monitoring Report, January through December 2020. Available at: https://wrl.mnpals.net/islandora/object/WRLrepository%3A3880/datastream/PDF/download/WRLrepository_3880.pdf
- Minnesota Department of Agriculture (MDA). 2022. 2021 Water quality monitoring report. 292 p. Available at: <https://wrl.mnpals.net/islandora/object/WRLrepository%3A3880/datastream/PDF/view>
- Minnesota Department of Health. 1997, Assessing Well and Aquifer Vulnerability for Wellhead Protection. Available by request from: HEALTH.drinkingwater@state.mn.us.

- Minnesota Department of Health (MDH). 2018. Wellhead Protection Vulnerability Fact Sheet, Available at: <https://www.health.state.mn.us/communities/environment/water/docs/swp/vulnerability.pdf>
- Minnesota Department of Health (MDH). 2019. Drinking water supply management area vulnerability. Available at https://resources.gisdata.mn.gov/pub/gdrs/data/pub/us_mn_state_health/water_drinking_water_supply/metadata/drinking_water_supply_management_area_vulnerability.html.
- Minnesota Department of Natural Resources (MNDNR), 2016, Methods to Estimate Near-surface Pollution Sensitivity. Available at: https://files.dnr.state.mn.us/waters/groundwater_section/mapping/gw/gw03_ps-ns.pdf
- Minnesota Department of Natural Resources (MNDNR). 2019. DNR watersheds – DNR level 02 – HUC 04. Available at <https://gisdata.mn.gov/dataset/geos-dnr-watersheds>.
- Minnesota Department of Natural Resources (MNDNR). 2021. Groundwater provinces of Minnesota 2021. Available at <https://gisdata.mn.gov/dataset/geos-groundwater-provinces-mn>.
- Minnesota Pollution Control Agency (MPCA). 2018. Wastewater sites in Minnesota. Available at https://resources.gisdata.mn.gov/pub/gdrs/data/pub/us_mn_state_pca/util_wastewater_sites/metadata/metadata.html
- Minnesota Pollution Control Agency, What's in my neighborhood, accessed February 2019. Available at: <https://www.pca.state.mn.us/about-mpca/whats-in-my-neighborhood>
- Nicolopoulou-Stamati, P., Maipas, S., Kotampasi, C., Stamatis, P., and Hens, L., 2016, Chemical pesticides and human health: The urgent need for a new concept in agriculture. *Frontiers in Public Health*. 4. <https://doi.org/10.3389/fpubh.2016.00148>.
- Roberson, J. A., & Eaton, A. (2014). Retrospective analysis of mandated national occurrence monitoring and regulatory decisions. *Journal-American Water Works Association*, 106(3), E116-E128.
- Sharma, Naushita, Westerhoff, Paul, and Zeng, Chao, 2022, Lithium occurrence in drinking water sources of the United States: *Chemosphere*, v 305 (October 2022),
- Stokdyk, J.P., Spencer, S.K., Walsh, J.F., de Lambert, J.R., Firnstahl, A.D., Anderson, A.C., Rezania, L.W., and Borchardt, M.A. 2019. Cryptosporidium incidence and surface water influence of groundwater supplying public water systems in Minnesota, USA. *Environmental Science & Technology*. 53(7): 3391-3398. <https://doi.org/10.1021/acs.est.8b05446>
- Stokdyk, J.P., Firnstahl, A.D., Walsh, J.F., Spencer, S.K., de Lambert, J.R., Anderson, A.C., Rezania, L.W., Kieke Jr., B.A., and Borchardt, M.A. 2020. Viral, bacterial, and protozoan pathogens and fecal markers in wells supplying groundwater to public water systems in

- Minnesota, USA. Water Research.178: 115814.
<https://doi.org/10.1016/j.watres.2020.115814>
- U.S. EPA, 2004, Understanding the Safe Drinking Water Act. Available at
<https://www.epa.gov/sites/default/files/2015-04/documents/epa816f04030.pdf>.
Accessed December 6, 2022
- U.S. EPA, 2021, Revisions to the Unregulated Contaminant Monitoring Rule: 40 CFR Part 141,
<https://www.govinfo.gov/content/pkg/FR-2021-12-27/pdf/2021-27858.pdf> .
- U.S. EPA, 2023, About the TSCA Chemical Substance Inventory. Accessed February 14, 2023, at:
www.epa.gov/tsca-inventory/about-tsca-chemical-substance-inventory.
- Van Stempvoort, DR, Roy, JW, Brown, SJ, Bickerton, G, 2011, Artificial sweeteners as potential tracers in urban environments: J. Hydrology, v. 401, pp 126-133.
- Vengosh, A and Pankratov, I, 2005, Chloride/Bromide and Chloride/Fluoride Ratios of Domestic Sewage Effluents and Associated Contaminated Ground Water, Groundwater, V.36, Issue 5, Pages 815-824.
- Vidal-Dorsch, DE, Bay, S, Maruya, K, Snyder, SA,, Trenholm, RA, and Vanderford, BJ , 2012, Contaminants of emerging concern in municipal wastewater effluents and marine receiving water: Environmental Toxicology and Chemistry, v 31, Issue 12, Pages 2674-2682.
- Wolf, L, Zweiner, C, Zemmann, M, 2012, Tracking artificial sweeteners and pharmaceuticals introduced into urban groundwater by leaking sewer networks: Science of the Total Environment, 430, p 8-19.

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

pH

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

FINAL REPORT

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

FINAL REPORT

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
DesaminoMetribuzin	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
Diketoneitrile-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

FINAL REPORT

USGS pesticides and pesticide degradates	Chemical abstracts service registry number (CASRN)	Minimum reporting level (ng/L)
Fipronil sulfide	120067-83-6	4.2
Fipronil sulfonate	209248-72-6	44
Fipronil sulfone	120068-36-2	5.6
Flubendiamide	272451-65-7	4.4
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
MCPA	94-74-6	95
Metaxyl	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

FINAL REPORT

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

FINAL REPORT

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-Aceto chlor 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

FINAL REPORT

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)
11CI-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

FINAL REPORT

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
PFDaA	171978-95-3	0.368
PFDaS	343629-43-6	0.368
PFDS	126105-34-8	0.368
PFEESA	220689-13-4	0.368
PFHpA	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
PFTTrDA	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

FINAL REPORT

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

FINAL REPORT

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

FINAL REPORT

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

FINAL REPORT

USGS pharmaceutical parameters	CASRN	Minimum reporting level (ng/L)
Glipizide	29094-61-9	0.766
Glyburide	10238-21-8	0.766
Guanyllurea	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
Norsertaline	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

FINAL REPORT

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

FINAL REPORT

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

FINAL REPORT

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 Benzothiazole (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
Benzoyllecgonine (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