PFAS planning

April 2024
May 2024 revision

PFAS Monitoring Plan: Initial findings and next steps

Early results and follow-up actions based on monitoring for PFAS at permitted solid waste, hazardous waste, wastewater, and stormwater facilities, and facilities with air emissions permits. Additional information is provided regarding the development of guidance for remediating sites in the Brownfield or Superfund programs.

MINNESOTA POLLUTION CONTROL AGENCY

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Acronyms

3:3 FTCA	3-Perfluoropropyl propanoic acid, 3:3 Fluorotelomer carboxylic acid
5:3 FTCA	5:3 Fluorotelomer carboxylic acid
7:3 FTCA	3-Perfluoroheptyl propanoic acid, 7:3 Fluorotelomer carboxylic acid
10:2 FTS	1H,1H,2H,2H-perfluorododecane sulfonate (10:2)
6:2 FTS	6:2 Fluorotelomersulfonic acid
AOC	Area of Concern
AFFF	Aqueous film-forming foams
BML	Benchmark Monitoring Location
BMP	Best management practice
C&D	Construction and demolition
EPA	U.S. Environmental Protection Agency
EQuIS	Environmental Quality Information System
FY24	Fiscal year 2024 (Minnesota)
GenX	Brand name of Hexafluoropropylene oxide dimer acid, or HFPO-DA
HBV	Health-Based Value
HFPO-DA	Hexafluoropropylene oxide dimer acid (also known as GenX)
HRL	Health Risk Limit
ISW	Industrial Stormwater
IWW	Industrial Wastewater
LCCMR	Legislative-Citizen Commission on Minnesota Resources
MCL	Maximum contaminant level
MDH	Minnesota Department of Health
MDL	Method detection limit
MERLA	Minnesota Environmental Response and Liability Act
MNELAP	Minnesota Department of Health Environmental Laboratory Accreditation Program
MOU	Memorandum of Understanding
MPCA	Minnesota Pollution Control Agency
MSW	Municipal solid waste
MWW	Municipal Wastewater
NAICS	North American Industry Classification System
NPDES	National Pollutant Discharge Elimination System
PFAS	Per- and polyfluoroalkyl substances

PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonate
PFCA	Perfluorinated carboxylic acid
PFDA	Perfluorodecanoic acid
PFDoDA	Perfluorododecanoic acid
PFDS	Perfluorodecane sulfonic acid
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptane sulfonic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonate
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PFOSA	Perfluorooctane sulfonamide
PFPeA	Perfluoropentanoic acid
PFSA	Perfluorinated sulfonic acid
PFTeDA	Perfluorotetradecanoic acid
PFTrDA	Perfluorotridecanoic acid
PFUnDA	Perfluoroundecanoic acid
PMP	Pollutant Management Plan
PQL	Practical Quantitation Limit
QAPP	Quality Assurance Project Plan
RL	Reporting Limit
SAP	Sampling and Analysis Plan
SDS	State Disposal System
SIC	Standard Industrial Classification
SIU	Significant Industrial User
TOP	Total oxidizable precursor
TRI	Toxics Release Inventory
WQS	Water Quality Standards
WWTF	Wastewater treatment facility

Executive summary

Per- and polyfluoroalkyl substances (PFAS) are a class of human-made chemicals that have been widely used in commerce since the 1950s. PFAS have since been discovered in natural environments across the world, as well as in humans.

PFAS pollution is a complex problem. There are thousands of types of PFAS used in even more kinds of industrial processes and products. Understanding their risk to human health and the environment, and how PFAS pollution moves through the waste stream into the environment, will greatly assist us in effectively addressing the problem – but no easy task.

To get a better picture of the challenges at hand so that solutions can be developed, the MPCA developed a PFAS Monitoring Plan in 2022, after publishing Minnesota's PFAS Blueprint in 2020.

Goals of the PFAS Monitoring Plan were to:

- Gather Minnesota-specific information in order to craft effective policies around PFAS and their incorporation into MPCA programs;
- Identify areas of particular concern (due to PFAS concentrations or routes of exposure) that need quick action; and
- Gather data that galvanizes support for PFAS source reduction and pollution prevention.

Permitting programs at the MPCA worked internally and with regulated facilities to implement program-specific PFAS monitoring projects at facilities belonging to industrial sectors associated with potential PFAS use or release. These program plans were ambitiously tailored to address the goals of the 2022 PFAS Monitoring Plan. This report includes initial findings and preliminary takeaways from those sampling efforts.

To date, sampling has occurred at twelve locations with air permits (where snow was collected); 83 municipal wastewater treatment facilities (WWTFs); twelve facilities with industrial wastewater permits; 77 solid waste landfills; and at or near 18 facilities with industrial stormwater permits (with data from six additional facilities expected). Samples were collected from facilities across the state and were analyzed for up to 40 PFAS compounds. Many facilities participated in voluntary sampling, and MPCA conducted sampling, as well.

Data resulting from these monitoring efforts has demonstrated that PFAS are, in fact, present at these facilities. The number of unique PFAS and concentrations of PFAS varied across samples and sites, but most samples yielded at least one detection of one or more PFAS. Six PFAS for which the Minnesota Department of Health has developed health-based values (HBVs) – PFOS, PFOA, PFHxS, PFHxA, PFBA, and PFBS – were found ubiquitously across sites. Two other compounds for which EPA has proposed Maximum Contaminant Levels (MCLs) – PFNA and HFPO-DA, or GenX – were also found in some samples, though not universally.

Based on these initial results, MPCA permitting programs developed and are implementing a variety of permitting approaches to address PFAS at these facilities, particularly in areas where sampling indicated quick actions may be necessary to protect human health and the environment. Efforts to address PFAS through pollutant management plans, permits, and other work are underway in tandem with other rulemaking and policy efforts addressing PFAS pollution prevention efforts, including prohibitions on PFAS in products. The MPCA anticipates implementing actions broadly in programs starting later in 2024 or early 2025. The MPCA continues to work with community members, regulated facilities, partnering state agencies, and other stakeholders to prevent, mitigate, and remediate PFAS pollution in Minnesota.

Background

Per- and polyfluoroalkyl substances (PFAS) are a class of human-made chemicals that have been widely used in commerce since the 1950s. PFAS are characterized by carbon-fluorine bonds, which are one of the strongest bonds known in organic chemistry, and consequently do not break down in the environment. PFAS are highly mobile and are therefore capable of long-range atmospheric transport and long migration distances in groundwater compared to many conventional pollutants. Due to their persistence, mobility, and numerous applications in industrial processes and consumer products, PFAS are now virtually ubiquitous in the environment. They have been discovered in water, soil, air, fish, wildlife, snow, and ice around the globe, including in remote regions with little or no industrial activity. PFAS are also present in humans.

Many PFAS have been associated with adverse human health effects at relatively low concentrations compared to other types of pollutants. The Minnesota Department of Health (MDH) has conducted risk assessments and developed health-based guidance values (HBVs) for six PFAS compounds in water and air. Observed health impacts include immune suppression, changes in liver function, lower birth weight, and certain cancers.

Minnesota has been addressing PFAS contamination since 2002, when perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) were discovered in groundwater resulting from historical disposal sites of industrial PFAS waste. In the last two decades, further investigation has revealed concerning levels of PFAS in water, soil, air, fish, wildlife, and people across the state. In 2021, the State of Minnesota released Minnesota's PFAS Blueprint, a strategic approach to prevent, manage, and clean up PFAS pollution. Efforts to implement projects and concepts introduced in the PFAS Blueprint are ongoing and included the development of the MPCA's PFAS Monitoring Plan in 2022.

This report addresses overall data quality as it relates to PFAS monitoring in Minnesota and implementation of the PFAS Monitoring Plan by six Minnesota Pollution Control Agency (MPCA) permitting programs. Additionally, for each of the six permitting programs, this report provides summaries of the original Program Plans, describes how the plans were implemented (including strategic changes), presents preliminary findings, and outlines next steps.

PFAS Monitoring Plan

Minnesota has worked to address PFAS since 2002, when detections of PFOS and PFOA were first discovered in groundwater at industrial waste disposal sites in the East Twin Cities Metro. Since then, research studies and site investigations have revealed PFAS contamination in groundwater, surface water, soil, air, fish and wildlife, and people around the state. In 2021, Minnesota published the PFAS Blueprint, detailing strategic short- and long-term approaches that state agencies can undertake to address PFAS.[1] The MPCA released the PFAS Monitoring Plan in 2022 as a coordinated effort to implement several of the short-term monitoring initiatives outlined in the Blueprint.[2] These included:

- Develop a plan for monitoring PFAS at permitted landfills,
- Develop a plan for monitoring PFAS at NPDES-permitted facilities,

[1] MPCA. Minnesota's PFAS Blueprint (p-gen1-22). https://www.pca.state.mn.us/air-water-land-climate/minnesotas-pfas-blueprint. Accessed 3/25/2024.
[2] MPCA. PFAS Monitoring Plan (p-gen1-22b). March 2022. https://www.pca.state.mn.us/sites/default/files/p-gen1-22b.pdf.

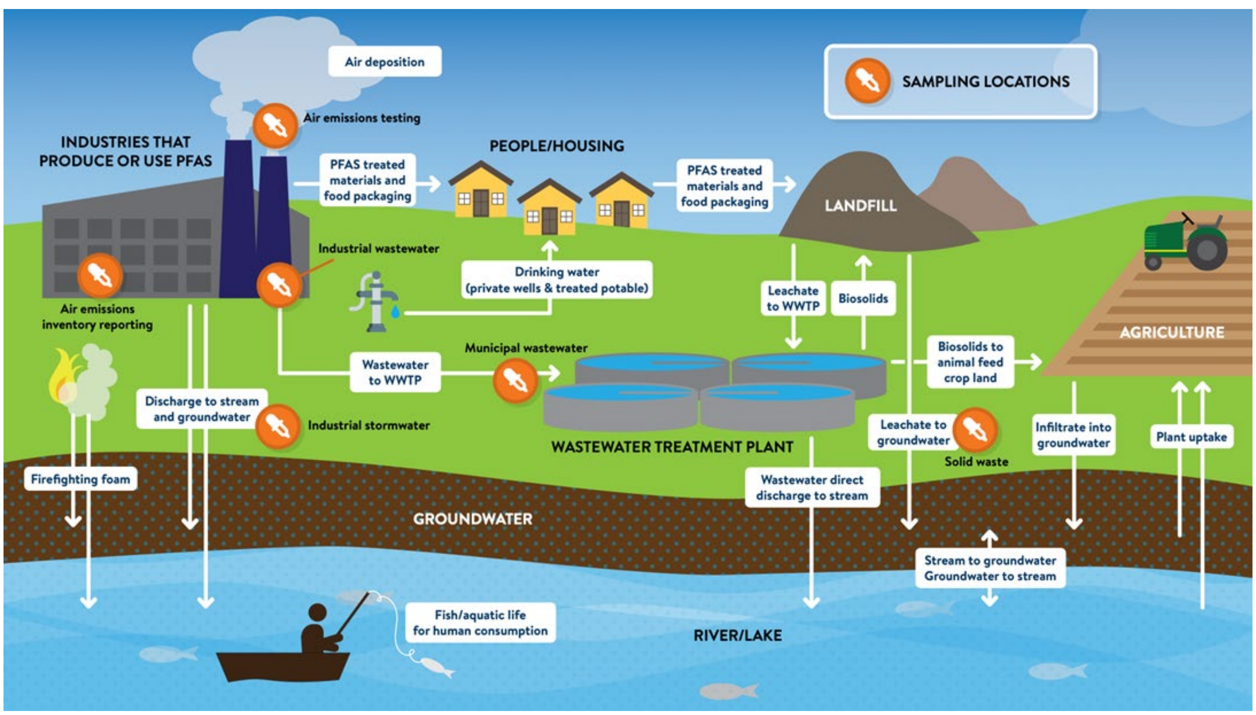
- Add PFAS to Minnesota's Air Emissions Inventory,
- Develop a plan for performance testing for PFAS at permitted air facilities; and
- Update guidance for sampling at clean-up sites to include PFAS.

The primary goal of this agency-wide monitoring effort was to collect statewide, Minnesota-specific data from regulated facilities and contaminated sites that could be used to inform PFAS policy development, particularly the incorporation of PFAS into the MPCA's permitting programs.

Another key goal was to bolster support for PFAS pollution prevention efforts, which the Blueprint identifies as the most important strategy for addressing PFAS due to their difficulty in being removed from the environment and destroyed. By prioritizing monitoring based on likelihood of PFAS release and potential human health risk, MPCA also seeks to identify any areas warranting quick response actions to assess and mitigate potential risks.

Permitting and Remediation programs across MPCA collaborated with stakeholders to target monitoring at facilities and in the media most likely to present pathways for significant release to the environment. Ultimately, six distinct Program Plans emerged to monitor for PFAS at unique subsets of regulated facilities around Minnesota (Figure 1).

Figure 1. Graphic depiction of the PFAS cycle and the parts of the cycle where sampling took place to better understand likely PFAS releases to the environment.



Those six Program Plans cover:

- Air emissions inventory reporting and air emissions testing
- Municipal Wastewater
- Industrial Wastewater
- Solid Waste and Hazardous Waste
- Industrial Stormwater
- Remediation

Facilities and sites at which monitoring eventually occurred were chosen based on their North American Industry Classification System (NAICS) codes, which are intended to classify and categorize businesses into economic sectors based on the products they manufacture or services they provide. Several sectors are associated with potential PFAS use or release; the Program Plans focused on those sectors, thereby focusing efforts on facilities or sites most likely to have release PFAS into the environment.[3]

Monitoring plan updates

This report addresses overall data quality as it relates to PFAS monitoring in Minnesota and implementation of the PFAS Monitoring Plan, to date. Additionally, for each of the six permitting programs, this report provides summaries of the original Program Plans, describes how the plans were implemented (including strategic changes), presents preliminary findings, and outlines next steps.

At the time of this report, each Program Plan is in varying stages of completion, due to differences in sampling timelines, numbers of samples, and other program-specific provisions originally outlined in the PFAS Monitoring Plan. External factors such as laboratory analytical capacity and weather challenges have also played a role in delaying data collection as planned. Crucially, the voluntary nature of participation in this project and subsequent implementation of MPCA program actions necessitated flexibility in MPCA's approach to gathering the requested data. In programs without sufficient voluntary participation to establish a robust dataset, MPCA identified alternative strategies and internal funding sources to gather more information when and where appropriate.

For programs that were able to complete data collection and analysis prior to report release, the data reflected here include which PFAS were found in their sampling efforts and in what concentrations. Of particular interest to the MPCA are six PFAS compounds for which the Minnesota Department of Health (MDH) has developed health-based values (HBVs) and/or Health Risk Levels (HRLs), plus two additional compounds for which the U.S. Environmental Protection Agency (EPA) has established Maximum Contaminant Levels (MCLs) for drinking water. The six PFAS for which MDH has HBVs are PFBA, PFBS, PFOA, PFOS, PFHxA, and PFHxS (Table 1); EPA also has MCLs for HFPO-DA (commonly referred to as GenX) and PFNA (Table 2). Although there is overlap in the PFAS compounds for which MDH and EPA have developed HBVs and MCLs, the methods behind determining the levels differ – for example, EPA has proposed a hazard index for four PFAS compounds, including HFPO-DA and PFNA, making a direct comparison to MDH’s HBVs more difficult. Even so, programs were generally able to compare their PFAS concentration data to the corresponding HBVs (and MCLs, where appropriate) to inform next steps, and to allow for some level of consistency across program efforts as we report these findings.

It should be noted that MDH revised the drinking water HBVs for two PFAS (PFOS and PFOA), and that EPA announced their final MCLs, after the permitting programs analyzed initial data and made decisions

[3] *See* PFAS Monitoring Plan (p-gen1-22b), Appendix F for a list of NAICS codes associated with potential PFAS use or release.

regarding next steps. Since implementation was ongoing at the time of the release of the new HBVs, and since MDH has not yet developed additional context around the consideration for and implementation of the new HBVs, references in this report will be made to “MDH’s 2023 HBVs”. References will also be made to EPA’s proposed MCLs, rather than the final values. Programs will address the new HBVs and finalized MCLs as PFAS monitoring and other requirements are integrated into permitting strategies and subsequent permit issuance.

Table 1. History of changes to MDH health-based guidance values for six PFAS in drinking water, 2002 - March 2024. Values shown are in parts per billion (ppb). Values in bold text are those that were in place while MPCA's permitting programs developed implementation strategies for addressing PFAS under the PFAS Monitoring Plan (MDH's 2023 HBVs).

<table>
<tr><th>Year</th><th>PFOA</th><th>PFOS</th><th>PFHxS</th><th>PFHxA</th><th>PFBA</th><th>PFBS</th></tr>
<tr><td>2002</td><td>7</td><td>7</td><td rowspan="4">n/a</td><td rowspan="8">n/a</td><td>n/a</td><td rowspan="3">n/a</td></tr>
<tr><td>2006</td><td>1</td><td>0.6</td><td>1</td></tr>
<tr><td>2007</td><td>0.5</td><td rowspan="3">0.3</td><td rowspan="8">7</td></tr>
<tr><td>2009</td><td rowspan="2">0.3</td><td rowspan="3">7</td></tr>
<tr><td>2013</td><td>0.3</td></tr>
<tr><td>2016</td><td>0.07</td><td>0.07</td><td>0.07</td></tr>
<tr><td>2017</td><td rowspan="3">0.035</td><td>0.027</td><td>0.027</td><td rowspan="2">2</td></tr>
<tr><td>2019</td><td rowspan="2">0.015</td><td rowspan="3">0.047</td></tr>
<tr><td>2022</td><td rowspan="2">0.2</td><td rowspan="2">0.1</td></tr>
<tr><td>2024</td><td>0.0000079</td><td>0.0023</td></tr>
</table>

Table adapted from the Minnesota Department of Health website, "PFAS and Health".[4]

Table 2. U.S. EPA's proposed and final Maximum Contaminant Level Goals (MCLGs) and Maximum Contaminant Levels (MCLs) for six PFAS (March 2023, April 2024). Where applicable, values have been converted to parts per billion (ppb) for comparison to MDH values. EPA's proposed and final values are listed in parts per trillion (ppt).

<table>
<tr><th></th><th>Proposed MCL Goal (health-based, not enforceable)</th><th>Proposed MCL (enforceable)</th><th>Final MCLG (health-based, not enforceable)</th><th>Final MCL (enforceable)</th></tr>
<tr><td>PFOA</td><td>0 ppb</td><td>0.004 ppb</td><td>0 ppb</td><td>0.004 ppb</td></tr>
<tr><td>PFOS</td><td>0 ppb</td><td>0.004 ppb</td><td>0 ppb</td><td>0.004 ppb</td></tr>
<tr><td>PFNA</td><td rowspan="4">Mixture: 1.0 (unitless) Hazard Index</td><td rowspan="4">Mixture: 1.0 (unitless) Hazard Index</td><td>0.01 ppb</td><td>0.01 ppb</td></tr>
<tr><td>PFHxS</td><td>0.01 ppb</td><td>0.01 ppb</td></tr>
<tr><td>PFBS</td><td>n/a</td><td>n/a</td></tr>
<tr><td>HFPO-DA (GenX)</td><td>0.01 ppb</td><td>0.01 ppb</td></tr>
<tr><td colspan="3">Mixtures containing two or more of PFNA, PFHxS, PFBS, and/or HFPO-DA</td><td>1.0 (unitless) Hazard Index</td><td>1.0 (unitless) Hazard Index</td></tr>
</table>

Table adapted from the EPA website, "Safe Drinking Water Act: Per- and Polyfluoroalkyl Substances (PFAS) Proposed PFAS National Primary Drinking Water Regulation".[5]

[4] MDH. PFAS and Health. https://www.health.state.mn.us/communities/environment/hazardous/topics/pfashealth.html. Accessed 3/25/2024.

[5] EPA. Safe Drinking Water Act: Per- and Polyfluoroalkyl Substances (PFAS) Proposed PFAS National Primary Drinking Water Regulation. https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas. Accessed 3/26/2024, 4/10/2024.

MDH has also developed air guidance values for PFAS in air; since there were no air samples collected for comparison at the time of report issuance, however, the report focuses on the HBVs developed for drinking water as a means of comparison for results across programs. More information about plans to collect air samples via emissions testing is included in the section discussing Air Program updates.

PFAS data quality assurance

Data integrity is a priority at the MPCA. To ensure that PFAS monitoring data collected as part of the PFAS Monitoring Plan implementation met agency standards, the MPCA developed a PFAS-specific Quality Assurance Project Plan (QAPP) that identified data collection and analytical criteria appropriate for monitoring efforts. Sufficient quality control activities were outlined to address the different program goals and use of information collected.

The data quality performance criteria are outlined in the *PFAS Monitoring Plan Quality Assurance Project Plan for Minnesota Based Projects*, March 2023 (PFAS QAPP), included in Appendix A. This overarching PFAS QAPP was used to provide uniform data quality to enable comparisons between sites. Project-specific Work Plans were used by different programs to meet more specific needs; these Work Plans were aligned with the PFAS QAPP.

Data quality performance objectives identified in the PFAS QAPP include:

- **Laboratory Accreditation:** All PFAS data submitted to the MPCA are required to come from a laboratory accredited with the Minnesota Environmental Laboratory Accreditation Program (MNELAP), which ensures that the laboratory utilizes recognized analytical methods and maintains an appropriate laboratory quality system related to capability and data reporting.
- **Reporting Limits (RL):** RL goals were outlined in the MPCA's *Guidance for Per- and Polyfluoroalkyl substances: analytical* (p-eao2-28), incorporated by reference into the PFAS QAPP. The RL goal for 33 PFAS compounds was set at 4 ng/L for aqueous samples, 50 ng/g dry weight for solid samples, and 50 ng/g wet weight for biotic samples. These goals were set for clean matrices with no sediment. As laboratories adopt a solid phase extraction preparation process, RL goals may be more difficult to meet for different matrices.
- **Blanks:** Field and method blanks are used throughout the process to determine if there are PFAS compound sources that are introduced into the sample during the sampling to analysis process. Field blanks accompany the sampling containers into the field and are analyzed with samples to verify that contamination did not occur from sampling, shipping, and storage. Method blanks are used by laboratories to ensure that contamination does not occur during the sample preparation and analysis process. For more information on field quality control sample see the *Guidance for Per- and Polyfluoroalkyl substances: sampling* (p-eao2-27).[6] Blank concentrations were reported with sample results to look for any potential contamination.
- **Analytical Accuracy:** The accuracy of the analysis is measured through the analysis of laboratory control samples. The laboratory prepares and analyzes lab control samples with environmental samples to ensure the analytical accuracy. The MPCA defined the project goals for accuracy in the *Guidance for Per- and Polyfluoroalkyl substances: analytical* (p-eao2-28).[7]

[6] MPCA. Guidance for Per- and polyfluoroalkyl substances (PFAS): Sampling (p-eao2-27). January 2022. https://www.pca.state.mn.us/sites/default/files/p-eao2-27.pdf.
[7] MPCA. Guidance for Per- and polyfluoroalkyl substances (PFAS): Analytical (p-eao2-28). October 2023. https://www.pca.state.mn.us/sites/default/files/p-eao2-28.pdf.

Analytical methods

PFAS samples collected for the implementation of the Monitoring Plan were analyzed using a variety of methods, depending on the media sampled (air, water, and/or soil), and for a variety of PFAS compounds (analytes). Facilities were given flexibility about where to send samples for analysis; since different labs use different techniques and look for different PFAS analytes, data shared by different programs in this progress report may not be directly comparable. Every analytical method is, however, capable of detecting the six PFAS compounds for which MDH has HBVs, as well as PFNA and HFPO-DA.

Methods used to analyze samples collected by the MPCA and facilities include the following:

- **EPA Method 1633:** This is a liquid chromatography/mass spectrometry (LC-MS/MS) method that can be used to detect PFAS in aqueous, solid, biosolid, and tissue samples. The EPA supports the use of this method for up to 40 PFAS target analytes.
  The EPA approved and finalized Method 1633 in January 2024; samples that were analyzed prior to this were analyzed using Draft Method 1633, which was capable of detecting the same analytes and is substantially similar to the finalized method. Though EPA recommends its use under the Clean Water Act, the Method 1633 has not been promulgated through rulemaking as a required test method.[8]
- **OTM-45:** This method is applicable to the collection and analysis of certain semi-volatile and particulate-bound PFAS in air emissions from stationary sources. Up to 50 PFAS target analytes (listed under 51 Chemical Abstracts Service Registry Numbers, or CASRNs) can be detected using this method.[9,10]
- **SW-846 Method 8327:** This LC-MS/MS method is used for PFAS extraction from surface water, groundwater, and wastewater samples. Although the method has been evaluated for up to 24 PFAS target analytes, the method may be applicable to additional PFAS analytes and other matrices depending on laboratory performance.[11]
- **EPA Method 537.1:** This LC-MS/MS method was specifically developed to detect up to 18 PFAS target analytes in drinking water. There is some flexibility in this method to allow for modifications of certain techniques and conditions for sample analysis of non-potable matrices and additional PFAS target analytes, though sample collection and preservation, extraction, and

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[8] U.S. EPA. Method 1633: Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS. January 2024. https://www.epa.gov/system/files/documents/2024-01/method-1633-final-for-web-posting.pdf.

[9] U.S. EPA. Other Test Method (OTM-45) Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources. Revision 0, 1/13/2021.https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf.

[10] EPA treats two compounds listed under the abbreviation 11Cl-PF3OUdS (11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid and 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate) as one for the purposes of describing the target analytes detectable under OTM-45. These two compounds have distinct CASRNs, however, and are therefore treated as two distinct compounds under air emissions inventory reporting in Minnesota. In some places the MPCA has referred to 51 PFAS target analytes detectable by OTM-45; this note is to address that potential discrepancy.

[11] U.S. EPA. Method 8327: Per- and polyfluoroalkyl substances (PFAS) by liquid chromatography/tandem mass spectrometry (LC/MS/MS). Revision 0, July 2021. https://www.epa.gov/system/files/documents/2021-07/8327.pdf.

quality control requirements cannot be modified. No components of the method can be modified for analyzing PFAS in drinking water matrices, per EPA.[12]

- **3M Company Method ETS-8-154.3:** This high-performance (HP) LC-MS/MS method was developed by the 3M Company and can be used to identify up to 15 PFAS target analytes from samples in water matrices.[13]
- **Pace® PFAS ID:** This method, developed by Pace® Analytical Services (now Pace®), is used to analyze PFAS by Isotope Dilution. This method is essentially a modified version of EPA Method 537 useable for samples from all matrices.[14]
- **SGS AXYS Method MLA-110:** This LC-MS/MS method, developed by SGS AXYS, was the basis of EPA Draft Method 1633, and can be used to identify the same target analytes.[15]
- **Total Oxidizable Precursor (TOP) Assay:** Some permitting programs collected samples for analysis using a TOP Assay, which is a method that helps to evaluate approximate concentrations of PFAS precursors in a sample. A TOP Assay oxidizes PFAS precursors, most of which are not found on targeted analyte lists, into terminal PFAS compounds (target analytes), which are able to be quantified by other PFAS analytical methods (like those listed above). Samples are analyzed using other methods pre- and post-oxidation and the relative increase of PFAS between the two results will give an estimated concentration of total PFAS precursors present in a sample.[16] Results from TOP Assay analyses are not included in this report.

A comparison of the PFAS target analytes detectable under each of the first four methods above is included in Appendix B. Other methods not listed above exist for analyzing PFAS, but they were not utilized by programs participating in sampling under the PFAS Monitoring Plan and are therefore not included in this report.

Next steps

Quality assurance staff are assessing whether the data quality assurance and control criteria are sufficient and if any changes are needed as the MPCA continues to implement the PFAS Monitoring Plan. Any updates or changes will be reflected in future progress reports or other documents.

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[12] U.S. EPA. Method 537.1: Determination of selected per- and polyfluorinated alkyl substances in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS). Version 2.0, March 2020. EPA Document No. EPA/600/R-20/006. Version 2.0, March 2020. Download link: https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=539984&Lab=CESER.

[13] Since the publication of 3M Company's Method No. ETS-8-154.3 (2008), newer Method No. ETS-8-154.4 has been finalized and published by 3M (method was adopted 4/28/2000, effective 5/26/2011). One of the labs used by facilities to analyze PFAS data used the previous Method ETS-8-154.3, but a document describing Method No. ETS-8-154.3 does not appear to be available for public download. More information regarding the updated Method is available from 3M. See: Determination of Perfluorinated Compounds In Water By Solid Phase Extraction and High Performance Liquid Chromatography/Mass Spectrometry. Method No. ETS-8-154.4. Effective Date 5/26/2011. https://multimedia.3m.com/mws/media/1828270O/ets-8-154-4-determination-of-perfluorinated-compounds-in-water-pdf.pdf.

[14] Pace®. 2020 PFAS Testing Methodologies. https://www.pacelabs.com/wp-content/uploads/2020/12/2020-05-04-PFAS-testing-methodologies_FINAL.pdf.

15 SGS AXYS. SGS AXYS Now Offers PFAS Analysis by the new EPA 1633 Draft Method. September 14, 2021. https://www.sgsaxys.com/2021/09/14/epa-announces-availability-of-epa-1633-draft-pfas-method-developed-by-sgs-axys-sgs-axys-continues-to-expand-range-of-pfas-testing-methods/. Accessed 3/25/2024.

[16] Interstate Technology Regulatory Council. PFAS – Per- and Polyfluoroalkyl substances: 11. Sampling and Analysis. 11.2.2.2 TOP Assay. September 2023. https://pfas-1.itrcweb.org/11-sampling-and-analytical-methods/#11_2_2_2. Accessed 3/25/2024.

Air Program updates

The PFAS Monitoring Plan included two PFAS monitoring initiatives related to the MPCA's Air Program: collecting PFAS emissions inventory data via facility reporting and collecting PFAS emissions data through emissions testing. Emissions inventory data consist of estimates of emissions reported by facilities, in tons per year. Estimates are based on the best available information a facility has for pollutants from sources like material use and stack testing. Emissions testing, on the other hand, is a direct method of determining the concentration of pollutants in emissions as they leave a facility through a controlled emissions point, like a stack, at the time the time a test is conducted.

This section provides updates on planned and implemented Air Program activities.

Emissions inventory reporting

What did we set out to do?

The MPCA identified 163 facilities with air permits that have activities encompassed by the "known or likely to be contributing" industrial categories identified in the Air Program Plan. The MPCA requested that those identified facilities voluntarily report air emissions of the 50 PFAS target analytes (51 distinct CASRNs) included in EPA's air testing method OTM-45. The MPCA planned to use this information to estimate risks from facilities, work with facilities that have elevated risks with efforts to reduce those emissions, and collaborate with other MPCA programs on potential cross-media impacts from air emissions.

What did we actually do?

The air emissions reporting program is proceeding as originally planned. MPCA requested voluntary PFAS emissions reporting from the 163 facilities that were scoped in based on industry sectors associated with PFAS usage. Facilities were asked to voluntarily add 50 PFAS compounds (51 CASRNs) to their 2023 emissions inventories, which were due to MPCA in April 2024. MPCA held an information session in November 2022 to provide guidance on the expected review process and is working individually with facilities as needed to assist with their reporting efforts.[17] Emissions inventory data will be publicly available following internal review in mid-2024.

What did we find?

No emissions inventory data from reporting year 2023 (January 1st through December 31st) are available for review at the time of report publication. Air emissions inventory data for reporting year 2023 were due April 1, 2024.

What are the next steps?

Facilities that reported their PFAS emissions were asked to include the 50 pollutants (51 CASRNs) analyzed by EPA test method OTM-45. Hundreds of additional PFAS compounds have been made available for facilities to optionally report, including salts and anions of the OTM-45 pollutants and PFAS compounds reported in EPA's Emissions Inventory System (EIS), Toxics Release Inventory (TRI), and/or

[17] A recording of the info session held by the MPCA, titled "PFAS Monitoring Plan – Air Emission Inventory and Reporting", is available on the MPCA's YouTube Channel at https://youtu.be/c0-iEmbb-qo.

MPCA's EQuIS database. Facilities required to report air emissions but not scoped into the Air Program Plan also had the option to voluntarily report. The annual emissions reporting for emissions inventory year 2023 were due April 1, 2024, and program staff anticipate completing review of the PFAS emissions estimates by the end of June 2024. The MPCA will follow up with facilities that did not meet the April 1, 2024, reporting deadline, and/or those that did not complete one or more components of the requested PFAS review.

There were few stack tests and/or emission factors available in time for facilities to report for the 2023 emissions inventory. The resulting data may be of limited use, and the issue will not be resolved until more testing and emissions factors can be developed. Still, Minnesota's PFAS ban should make it easier for facilities and MPCA to identify the amount of PFAS in materials.[18] This will be useful in producing emissions estimates based on mass balances.

The MPCA plans to have more details regarding next steps once the agency has quality assured and reviewed the 2023 emissions data in July 2024. Data will be made available once data assurance and data quality work is complete.

Air toxics emissions reporting rule

The MPCA is in the process of establishing new rules for air toxics emissions reporting requirements as directed by the Minnesota Legislature in 2023.[19] The new rules must apply to permitted facilities (except those with Option B registration permits) located in Anoka, Carver, Dakota, Hennepin, Ramsey, Scott, or Washington counties (the 7-county metro area). The list of PFAS addressed by the air toxics reporting rule may include PFAS listed under the TRI (189 reportable PFAS compounds in 2023) and/or other compounds. These additional data will provide deeper insight into PFAS emissions in the 7-county metro area.

An estimated date for final adoption of the rules has not yet been determined, but the current schedule indicates that MPCA plans to publish the Notice of Intent to Adopt Proposed Rules in State Register by November 2024. Under the current timeframe, the rules will not be final in time to require facilities to record and report their PFAS emitted during reporting years 2024 or 2025 but would be adopted and in effect in time for reporting year 2026. At the earliest, then, the MPCA would require air toxics emissions reporting for the facilities subject to the new rule by April 1, 2027 (due date for emissions inventory for reporting year 2026).

Note that additional emissions-reporting facilities not included in the 7-county metro area will be asked to voluntarily submit the PFAS compounds from the rule for reporting year 2026.

Emissions testing

What did we set out to do?

For a subset of the 163 identified facilities that regularly conduct stack tests as part of their air permit, MPCA planned to request that the facility conduct one test using analytical method OTM-45 at their next scheduled stack testing date. The Air Program planned to use the stack test data in conjunction

[18] MPCA. PFAS in products. https://www.pca.state.mn.us/get-engaged/pfas-in-products. Accessed 3/27/2024.
[19] Minnesota Legislature Office of the Revisor of Statutes. 2023 Session Law, Chapter 60, Sec. 21, https://www.revisor.mn.gov/laws/2023/0/Session+Law/Chapter/60/#laws.3.21.0. See also: Minnesota Legislature Office of the Revisor of Statutes. 2023 Minnesota Statutes 116.943, Products containing PFAS. https://www.revisor.mn.gov/statutes/cite/116.943. Accessed 3/27/2024.

with air emissions inventory reporting to estimate risks from facilities, work with facilities that have elevated risks on emissions reduction efforts, and collaborate with other MPCA programs on potential cross-media impacts from air emissions.

What did we actually do?

The MPCA requested voluntary stack testing from 29 facilities as part of the Air Program Plan. Only two facilities proceeded with stack testing; results from those tests are pending. Given the limited voluntary participation, MPCA instead designed a plan to sample snow from rooftops of facilities in the stack testing program. PFAS compounds are known to be subject to atmospheric deposition, wherein PFAS in the air may reach the ground after being absorbed by rain or snow (wet deposition), or by falling out of the air onto the land surface on dry soil or other particles, or by gravity (dry deposition). In either case, PFAS compounds could be expected to be present in snow that has accumulated on rooftops or around buildings with suspected PFAS emissions. The MPCA successfully used this approach in a previous investigation at a chrome plating facility, where PFAS-based etchant solution was discovered in snow underlying one of the facility's vents, which was confirmed by laboratory analysis of a snow sample.[20]

In general, facilities were selected for snow sampling if they were scoped into the PFAS Monitoring Plan/Air Program Plan, submit an annual report to the air emissions inventory, are required to perform air quality stack tests as part of their permit, and were not asked to sample for PFAS by any of the other permitting programs. Based on the conditions above and the budget available for sampling and data analysis, 20 facilities were selected, including one facility that was not originally scoped into the PFAS Monitoring Plan/Air Program Plan but that belonged to a company responsible for significant PFAS contamination in another state.

The MPCA worked with a contractor to collect samples in March 2023. Snow samples were collected from roofs where possible; if rooftops were inaccessible, unsafe for sampling personnel, or lacked snow, then water samples were collected from ground-level downspouts. Ultimately, samples were collected from 12 of the 20 planned facilities due to hydrologic conditions at the time of sampling. Samples were analyzed using EPA Draft Method 1633, version 3, and total organic precursor (TOP) Assay.

No samples were collected in fiscal year 2024 (winter 2023/2024) due to hydrologic conditions.

[20] MPCA. PFAS Air and Deposition Monitoring Report (tdr-g1-23). April 2022. https://www.pca.state.mn.us/sites/default/files/tdr-g1-23.pdf.

What did we find?

Results

Sampling was performed at 12 out of the planned 20 facilities during winter 2023. Six facilities were in the 7-county metro area, one was in Rochester, and five were in other areas across the state (Table 3).

Table 3. Number of facilities where snow sampling occurred across Minnesota.

Facility Location	Planned number of facilities to test	Facilities tested	Number of samples collected
7-County Metro Area	11	6	13
Rochester	2	1	2
Duluth	0	0	0
Other	7	5	22
Total	20	12	37

Sample recovery availability at each tested site was variable due to the preceding weather conditions at each location. EPA Draft Method 1633 sample recovery availability ranged from one sample to five samples. The recovery of TOP Assay samples varied for similar reasons, with only seven samples collected out of twelve possible.

Of the samples collected, 62% had a laboratory value above zero (Table 4). Many of these values were flagged by the laboratory for various reasons, but the primary reason is a "J" flag, which means the results were below the limits of quantification, or the reporting limit, but above the method detection limit (MDL). Of the 23 samples that had a detection above zero, only three samples, from three different facilities, were not flagged at all.

Table 4. Number of lab-analyzed snow samples with PFAS concentration values greater than zero for each area of the state.

Facility Location	Number of samples collected	Number of samples with any laboratory reading above zero
7-County Metro Area	13	7
Rochester	2	2
Other	22	14
Total	37	23

Across the 23 samples collected with detections above zero, there were 87 detections of the up to 40 target analytes findable by EPA Draft Method 1633. Seven blanks were found to be contaminated by 6:2 FTS, and one blank was contaminated by PFOSA. Since the values of PFAS detected were so small, and because only eight analytes (found in three samples from three facilities) did not have any data flags, additional criteria for evaluating the lab analyses results were applied to the dataset. PFAS compound values were further evaluated if they met, or were greater than, the respective method detection limit; if they are within the bounds of 50%-150% within their spike matrices in that evaluation; and the relative percentage difference is ≤50%.[21] Data for 29 of the 87 analyte detections using EPA Draft Method 1633 did not meet these criteria, leaving 58 for further evaluation. The remaining distribution of detected analytes meeting the consideration criteria fell within the same distribution of the samples taken, with the 7-county metro area and other areas having the most analytes for evaluation. None of the analyzed samples used for the TOP Assay method met the criteria for further evaluation (Table 5).

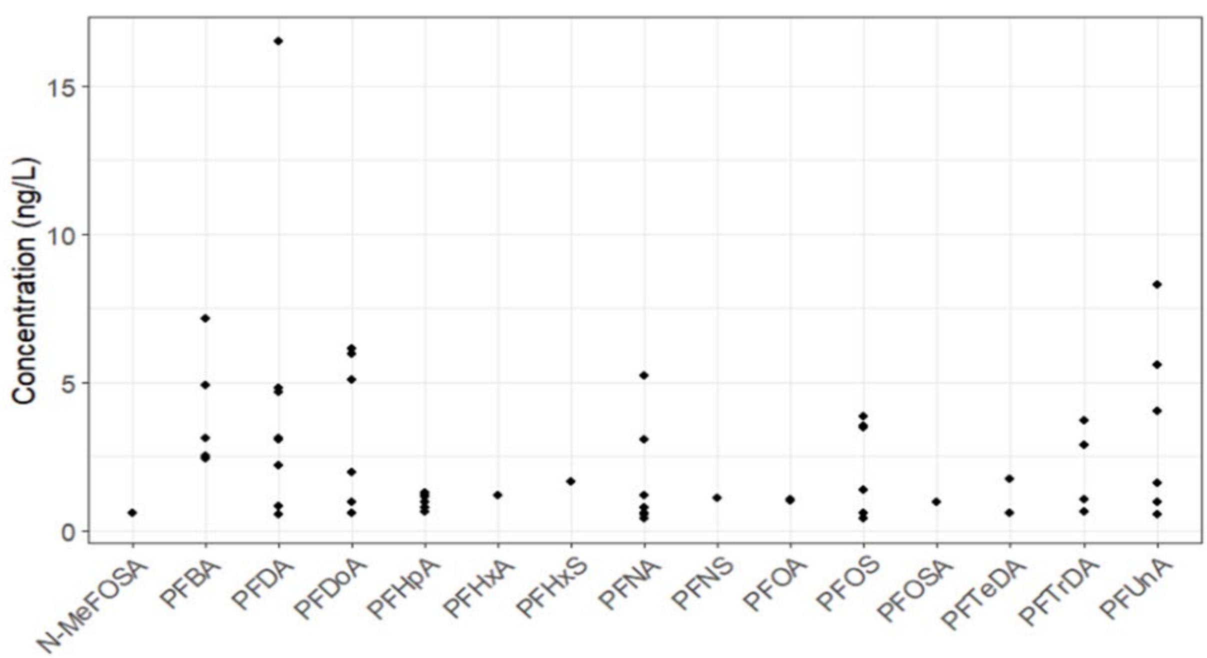
Table 5. Number of PFAS target analytes detected in snow samples in the 7-county metro area, Rochester, and other parts of the state.

Facility Location	EPA Draft Method 1633 analytes	TOP Assay analytes
7-County Metro Area	26	0
Rochester	5	0
Other	27	0
Total	58*	0

*This total reflects the number of detections of the up to 40 target analytes found using EPA Draft Method 1633, version 3, across sampled sites. This total does not reflect the number of unique PFAS detected (see Table 6).

Fifteen unique PFAS target analytes were detected in the 58 samples meeting the criteria for further evaluation (Figure 2). The single highest concentration of PFAS found was of PDFA, at 16.5 ng/L. The remaining concentrations varied from as low as 0.402 ng/L (PFOS) to 8.31 ng/L (PFUnA).

Figure 2. Concentrations of PFAS target analytes found across all snow samples meeting the criteria for further evaluation: PFAS compound values were further evaluated if they met, or were greater than, the respective method detection limit; if they are within the bounds of 50%-150% within their spike matrices in that evaluation; and the relative percentage difference is ≤50% (n=58). No non-detect data are included.



[21] MPCA. Guidance for Per- and polyfluoroalkyl substances (PFAS): Analytical (p-eao2-28). https://www.pca.state.mn.us/sites/default/files/p-eao2-28.pdf.

The concentration and distribution of PFAS compounds throughout the state is not uniform (Table 6). The highest concentration found in the 7-county metro area was the 16.5 ng/L measurement of PFDA. The highest concentration in the Rochester area was 4.89 ng/L of PFBA. The highest sampled value from other areas of the state was 7.15 ng/L of PFBA.

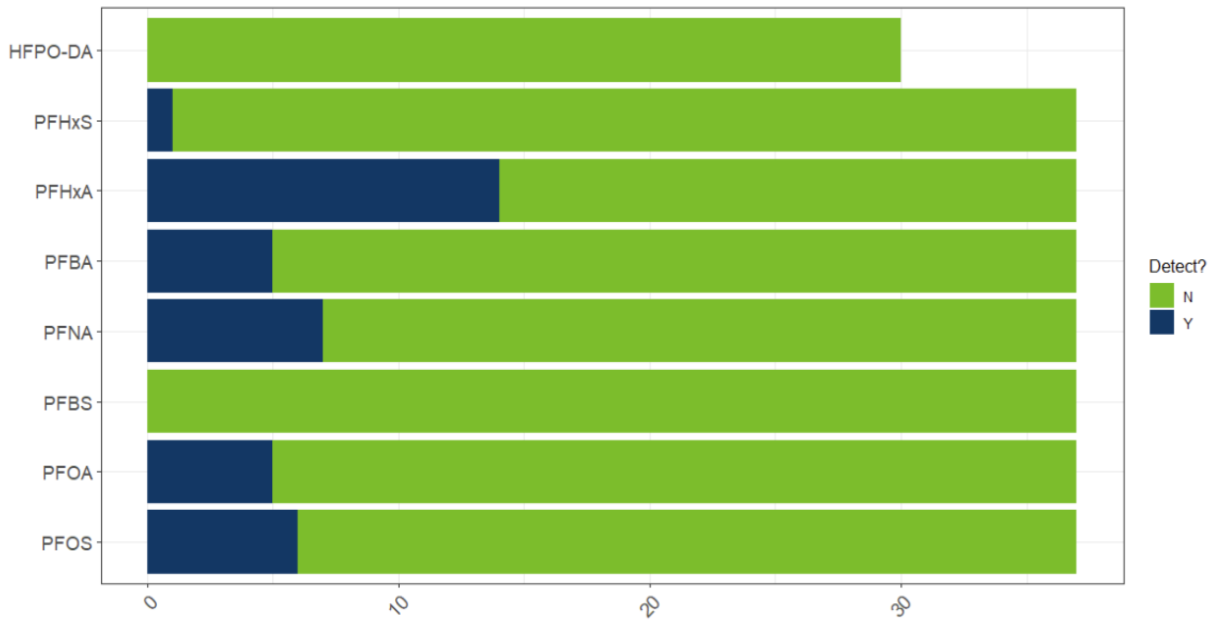
Table 6. PFAS compounds detected from all snow samples taken across Minnesota.

Compounds detected	Compound detected range (ng/L): Seven-County Metro Area (n samples)	Compound detected range (ng/L): Rochester (n samples)	Compound detected range (ng/L): Other (n samples)
N-MeFOSA	0.566 (1)	0	0
PFBA*	0	3.13 – 4.89 (2)	2.4 – 7.15 (3)
PFDA	2.2 – 16.5 (5)	0	0.521 – 3.1 (4)
PFDoA	1.97 – 6.15 (4)	0	0.572 – 0.949 (2)
PFHpA	1.16 (1)	0.938 – 1.28 (2)	0.611 – 1.14 (3)
PFHxA*	0	0	1.2 (1)
PFHxS*†	0	0	1.63 (1)
PFNA†	1.2 – 5.2 (3)	0.788 (1)	0.406 – 0.578 (3)
PFNS	0	0	1.07 (1)
PFOA*†	1.03 (1)	0	0.999 (1)
PFOS*†	1.37– 3.85 (2)	0	0.402-3.54 (4)
PFOSA	0.944 (1)	0	0
PFTeDA	1.73 (1)	0	0.578 (1)
PFTrDA	1.03 – 3.72 (3)	0	0.638 (1)
PFUnA	1.59 – 8.31 (4)	0	0.558 – 0.937 (2)

* PFAS compounds that have an MDH HBV for drinking water.
† PFAS compounds for which EPA has proposed MCLs.

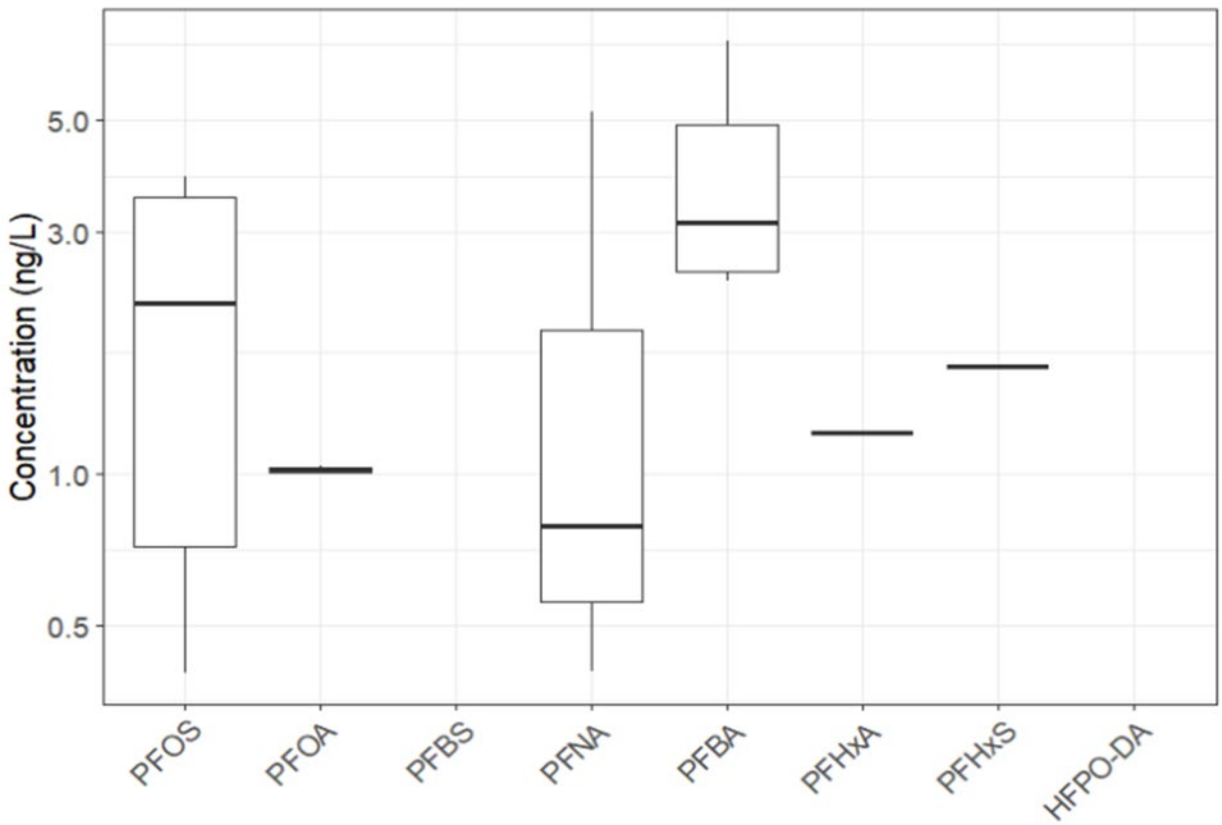
There are six PFAS compounds that currently have HBVs through the Minnesota Department of Health (MDH) for drinking water: PFBA, PFBS, PFOA, PFOS, PFHxA, and PFHxS.[22] Two other PFAS compounds, HFPO-DA (GenX) and PFNA, have MCLs for drinking water. PFOS, PFOA, PFNA, PFBA, PFHxA, and PFHxS were all detected in snow samples (Figure 3). Neither PFBS nor HFPO-DA were detected in any snow samples. None of the PFAS analytes were detected at concentrations above MDH's 2023 HBVs (Figure 4).

Figure 3. Detections and non-detections of eight PFAS target analytes across all analyzed snow samples (n=298).



[22] MDH. PFAS and health. https://www.health.state.mn.us/communities/environment/hazardous/topics/pfashealth.html. Accessed 3/27/2024.

Figure 4. Boxplot comparing concentrations of eight PFAS target analytes found across all snow samples meeting the criteria for further evaluation: PFAS compound values were further evaluated if they met, or were greater than, the respective method detection limit; if they are within the bounds of 50%-150% within their spike matrices in that evaluation; and the relative percentage difference is ≤50% (n=22). No non-detect data are included.



Background deposition in snow samples

To account for background deposition, sample values were compared to two environmental background settings, 0.5 ng/L and 2.0 ng/L, with their spike matrixes between 50-150% recovery.[23] Two of the 58 analytes, PFOS and PFNA, were detected at concentrations less than 0.5 ng/L background setting in other areas of the state. Of the 58 analytes that met the additional criteria for evaluation, 34 were found at concentrations between 0.5 ng/L and 2.0 ng/L background; 22 PFAS compounds were found in concentrations greater than the 2.0 ng/L background concentration (Table 7). The 7-county metro had the most PFAS compounds detected at concentrations greater than 2.0 ng/L, with a total of 16 samples (66.67%). PFDA was the most prevalent PFAS compound found above the 2.0 ng/L background concentration, found in five samples (20.83%) in the 7-county metro area.

[23] MPCA. PFAS ambient background concentrations (tdr-g1-25). March 2024. https://www.pca.state.mn.us/sites/default/files/tdr-g1-25.pdf.

Table 7. PFAS compounds with sample concentrations greater than the 2.0 ng/L background.

Compounds detected	Compound detected range (ng/L): Seven-County Metro Area (n samples)	Compound detected range (ng/L): Rochester (n samples)	Compound detected range (ng/L): Other (n samples)
PFBA*	0	3.13 – 4.89 (2)	2.4 – 7.15 (3)
PFDA	2.2 – 16.5 (5)	0	3.1 (1)
PFDoA	5.1 – 6.15 (3)	0	0
PFNA†	3.06 – 5.2 (2)	0	0
PFOS*†	3.85 (1)	0	3.46 – 3.54 (2)
PFTrDA	2.87 – 3.72 (2)	0	0
PFUnA	4.01 – 8.31 (3)	0	0

* PFAS compounds that have an MDH HBV for drinking water
† PFAS compounds for which EPA has proposed MCLs.

Limitations in sampling and data quality

There were several factors that impacted the study that should be considered, and which provide context the results shared above. These factors include unknown fate and transport of PFAS from facility emissions; PFAS accumulation time on rooftop snow; snow/water availability for sampling, due to weather dynamics; movement of ground-level snow; PFAS accumulation time in ground-based samples; and other external factors that may influence detection. Further, the concentrations of the PFAS compounds found were not high enough to determine if any given facility was emitting PFAS, if the sampled concentrations were background related, or if a combination of the two scenarios exist.

Other analytical issues may have impacted some resulting data, as well. Four EPA Draft Method 1633 samples (BE00476, BE00479, LD00763, LD00764) and three TOP Assay samples (BE00385, BE00481, and LD00768) fluctuated outside the recommended temperature control parameters, on intake of the analytical laboratory – the samples were warmer than the method requires, which, over a long period of time, could lead to PFAS transforming within the sample. Samples BE00476, BE00479, LD00763, and LD00764 had an 8.33~% (0.5°C) increased temperature above the EPA Draft Method 1633 guidance sample temperature of 6.0°C. Sample BE00385 had an 2.5% (0.1°C) increase in temperature from TOP Assay's recommended sample temperature maximum of 4°C. Samples BE00481 and LD00768 each had a 62.5% (2.5°C) increase in temperature from TOP Assay's recommended sample temperature maximum of 4°C. These samples were still run in normal accordance with EPA Draft Method 1633 and TOP Assay methodologies, as the amount of time above temperature was not thought to be detrimental to the samples in this case.

There were two facilities that did not have any form of PFAS detection, laboratory flagged or not, from samples analyzed by SGS AXYS. Each of these facilities had only one sample taken. All of the other ten sampled facilities had a laboratory detection, though not all were above the method detection limit or reporting limit.

There were seven lab blanks utilized in the TOP Assay that came with spiked matrices below the 50-150% guidance levels. The only PFAS compound affected by this issue was 6:2 FTS.

Conclusions

The results from the PFAS snow sampling showed the presence of PFAS compounds in small quantities at the facilities tested, though the determination of the source is inconclusive. Snow sampling on rooftops and near facilities may provide information regarding deposition of PFAS from facility emissions, but ultimately it is impossible to distinguish PFAS deposition from a specific facility independently of background concentrations of PFAS that are ubiquitous in the environment. Further follow-up on these facilities is warranted, including stack testing, to determine concentrations coming out of the stacks.

Unrelated depositional background studies of PFAS around Minnesota may also provide more insight into fluctuations and concentrations of wet and dry deposition, including proposed studies examining PFAS levels in coniferous tree leaves (needles) and soil.[24] Findings from those proposed efforts may be comparable to those from the snow sampling done under the Air Program Plan.

The methodology used for this study and subsequent results demonstrate that PFAS is detectable on the roof and ground around the facilities. Isolation of high concentration areas or areas of suspicion are key to potentially having elevated concentrations of PFAS. High concentration areas and areas of suspicion include drainage areas, edges of the downward slope of the roof where the drainage occurs, and visible discoloration of the snow on the rooftop snow or exhaust. Steps should be taken to minimize or prevent contamination from other sources, including cars or other motorized transportation that require fluids.

What are the next steps?

Few of the facilities MPCA requested to stack test as a part of the PFAS Monitoring Plan/Air Program Plan chose to test. Two facilities have performed stack tests independent of our request through efforts to implement the Air Program Plan, and others plan to do the same. Some facilities plan to investigate PFAS emissions through cooperation with an industry coalition; it is unclear at this time whether those data would be publicly available. Overall, stack testing is costly for permittees, and most of the facilities the MPCA contacted declined to voluntarily stack test as part of the Air Program Plan implementation effort. The MPCA currently does not have the regulatory authority under non-permitting actions to compel these facilities to participate, but additional monitoring requirements may be considered on a case-by-case basis as permits are reissued. In some instances, facilities undergoing the Environmental Review process are subject to emissions testing, the results of which may also provide a means of understanding PFAS emissions for a given facility

Snow sampling is an alternative and less-expensive method of identifying the presence of PFAS. MPCA planned to acquire PFAS snow sample data from some facilities in fiscal year 2024 (winter 2023/2024), but weather conditions did not permit the collection of additional samples.

Air toxics regulatory rule

[24] Two separate project proposals have been submitted to the Legislative-Citizen Commission on Minnesota Resources (LCCMR) in hopes of receiving grant funding from the state of Minnesota's Environment and Natural Resource Trust Fund (ENRTF). One project is intended to investigate ambient background PFAS concentrations in soil, including from deposition; the other is to examine PFAS in coniferous tree leaf (needle) growth and the accumulation of PFAS in living leaf tissue from ambient air. The project to determine ambient background PFAS concentration in soil was submitted for the 2024 LCCMR cycle, and was one of the projects recommended to the 2024 Legislature for final consideration. The proposal to examine PFAS in coniferous leaves was submitted under the 2025 cycle, and has not gone through the review process.

In addition to requiring the MPCA to develop an air toxics emissions reporting rule, the Minnesota Legislature directed the MPCA to develop a complementary air toxics regulatory rule.

The MPCA is in the process of establishing new rules for regulating air toxics emissions in the state of Minnesota.[25] The new rules would apply to permitted facilities located in the 7-county metro area. Several components of this rulemaking are yet to be determined, including which air toxics are to be regulated, the types of facilities to be regulated, what kinds of performance testing may be required to measure emissions, and associated monitoring, recordkeeping, and inspection requirements. It is possible that some number of PFAS could be regulated under this rule, but no specific determinations have been made.

An estimated date for final adoption of the rules has not yet been determined, but the current schedule indicates that the MPCA plans to publish the Notice of Intent to Adopt Proposed Rules in the State Register by May 2026.

Wastewater Program updates

Municipal Wastewater Program

What did we set out to do?

The Municipal Wastewater (MWW) Program Plan described a multi-phase approach to determine PFAS levels entering municipal wastewater treatment facilities (WWTFs), prioritize source reduction activities, and evaluate the effectiveness of source reduction actions. Specifically, the MWW Program Plan requested voluntary participation from all municipal WWTFs in Minnesota with significant industrial users (SIUs), as defined in Minn. R. ch. 7049.0120, Subp. 24(A). These facilities would monitor PFAS levels in influent wastewater for two quarters before and after a dedicated source reduction period. The MPCA committed to supporting WWTFs with source reduction actions, and facilities would sign memoranda of understanding (MOUs) to signify their participation in the plan. The MPCA committed to using the data collected through the MWW Program Plan to inform development of a regulatory framework for addressing PFAS in municipal wastewater in Minnesota.

What did we actually do?

The MWW Program identified 91 communities with at least one SIU discharging to their WWTF. The MPCA invited these communities to sample WWTF influent as a basis to support implementation of the MWW Program Plan. An MOU was developed in partnership with the identified communities to further refine the MWW Program Plan and document the desired outcomes from both the MPCA’s and selected communities’ engagement. The two main goals outlined in the MWW Program Plan and resulting MOU were to develop a general characterization of PFAS entering municipal WWTFs across the state and to support source identification and reduction efforts at these facilities.

The action items included in the MOU are summarized below.

[25] Minnesota Legislature Office of the Revisor of Statutes. 2023 Session Law, Chapter 60, Sec. 21, https://www.revisor.mn.gov/laws/2023/0/Session+Law/Chapter/60/#laws.3.21.0. See also: Minnesota Legislature Office of the Revisor of Statutes. 2023 Minnesota Statutes 116.943, Products containing PFAS. https://www.revisor.mn.gov/statutes/cite/116.943. Accessed 3/27/2024.

Community responsibilities

1. Conduct four quarterly influent sampling events for PFAS, with a six month pause between the first two and second two events.
2. Analyze samples for 40 PFAS compounds using EPA Draft Method 1633.
3. Optionally, perform total oxidizable precursor (TOP) Assay on one sample from either the first or second sampling event.
4. Participate in source identification and reduction work based on PFAS results from the first two sampling events.

MPCA responsibilities

1. Provide funding to offset sampling costs for the first two sampling events, for all communities voluntarily participating in the Monitoring Plan through the MOU.
2. Establish priority thresholds for source identification and reduction activities in the participating communities.
3. Provide resources available from the MPCA and partners to assist communities with source identification and reduction activities.
4. Continue to pursue funding to help cover sampling costs for the third and fourth sampling events required under the MOU.

Ultimately, 83 of the 91 communities signed the MOU and agreed to move forward with influent PFAS monitoring. Sampling started in February 2023 and was completed in June 2023 for the first two sampling events. In addition to the EPA Draft Method 1633 analysis, 55 communities opted into TOP Assay analysis of their samples. Laboratory analyses for the first two sampling events were completed in September 2023.

What did we find?

Results

In quarters 2 and 3 of 2023, two influent grab samples – one from each quarter – were collected from each of the 83 participating WWTFs. Results presented in this report include Q2 and Q3 samples analyzed by the end of September 2023. All 83 WWTFs had detectable levels of PFAS in at least one of their influent samples analyzed using EPA Draft Method 1633 (Figure 5). PFOA and PFHxS were present in influent wastewater from all 83 communities.

Overall PFAS concentrations in influent wastewater varied widely in communities across the state. The six PFAS compounds that currently have MDH HBVs for drinking water were the most frequently detected compounds in the influent wastewater samples; PFNA and HFPO-DA were also detected (Figure 6).

Figure 5. Concentrations of PFAS target analytes found in samples collected from municipal wastewater influent, displayed on a logarithmic scale (n=1384). This figure only includes results above the method detection limit and does not include any non-detect data.

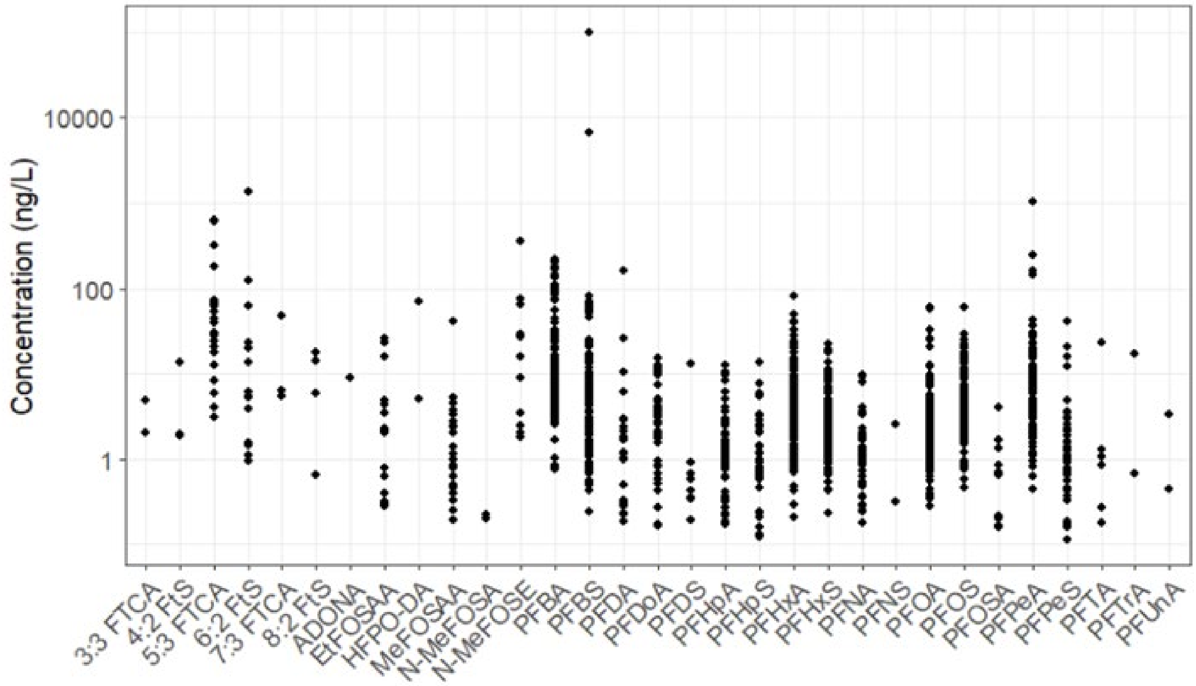
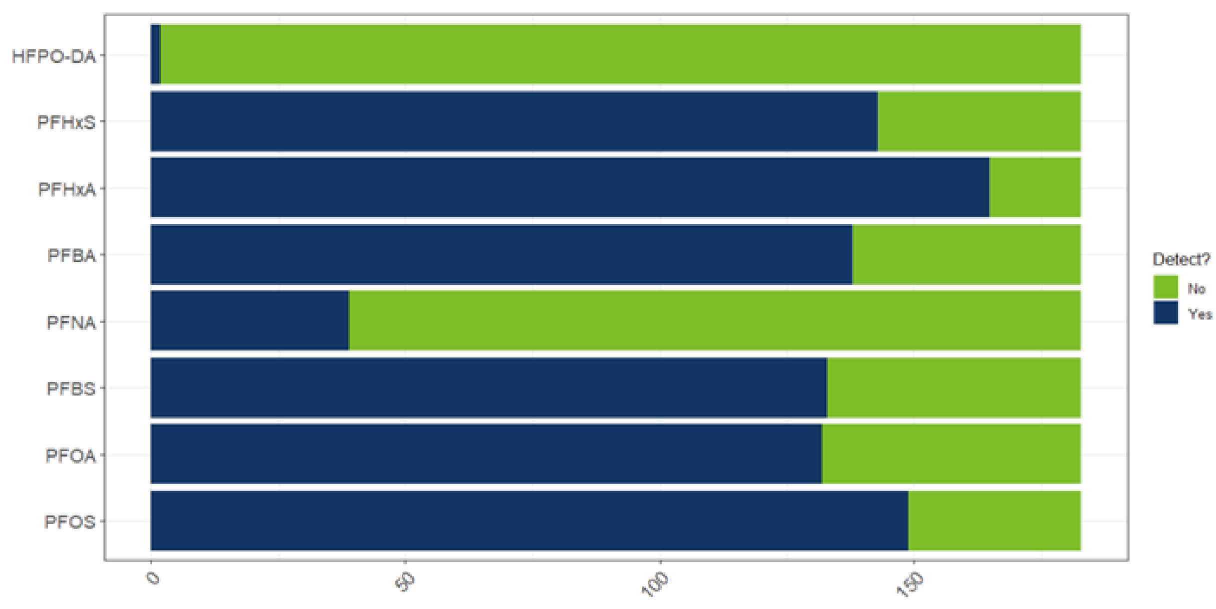
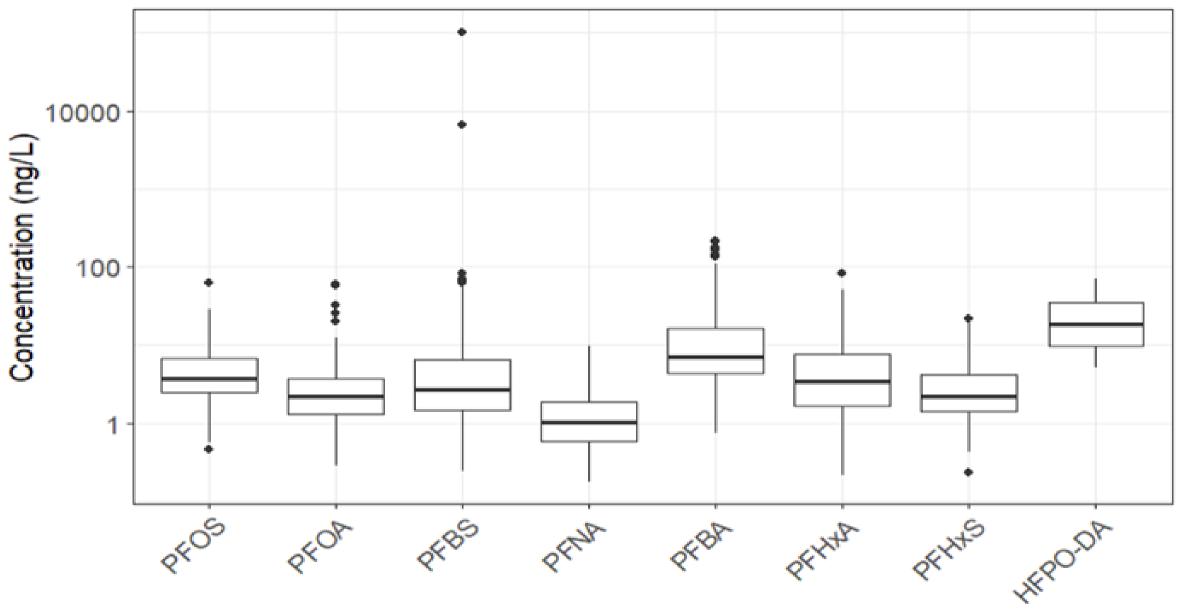


Figure 6. Detects and non-detects of eight PFAS target analytes from all samples of municipal wastewater influent (n=1464).



Three PFAS compounds – PFOS, PFOA, and PFBS – were identified as compounds of special interest for the development of priority thresholds to address source identification and reduction work with each of the communities, due to their prevalence across samples and the concentrations found. Each of these three PFAS compounds had the least amount of variation in practical quantitation limits (PQLs) amongst communities. Across communities, detected PFOS concentrations ranged from 0.3 ng/L to 61.0 ng/L; PFOA concentrations ranged from 0.9 ng/L to 59.0 ng/L; and PFBS concentrations ranged from 1.1 ng/L to 101,000.0 ng/L (Figure 7).

Figure 7. Boxplot comparing concentrations of eight PFAS target analytes from samples of municipal wastewater influent, displayed on a logarithmic scale (n=900). This figure only includes results above the method detection limit and does not include any non-detect data.



Communities were divided into priority categories for source identification and reduction work based on each facility's highest result (out of two samples) for PFOS, PFOA, and PFBS. At WWTFs where sample results were above 15 ng/L for PFOS, 35 ng/L for PFOA, and/or 10 ng/L for PFBS, the facilities were scoped into the "high priority" category. WWTFs with selected PFAS concentrations falling between 2.1 ng/L and the above values were scoped into the "medium priority" category, and WWTFs with results less than 2.0 ng/L for all three target PFAS compounds were scoped into the "low priority" category. Note that only results that were not flagged for data quality assurances were used to place communities in the "high priority" category; estimated values were not considered.

Using this prioritization method, 12 out of the 83 WWTFs and associated communities were designated "high priority" for source identification and reduction work. Preliminary investigations show that most communities in this category have at least one industrial user (not necessarily an SIU) contributing PFAS to the facility effluent. Represented industries include, but are not limited to, paper industries, metal finishing industries, and textile industries, among others, that are known to use or release PFAS. The MPCA is asking communities to develop management plans targeting the six PFAS compounds for which

MDH has HBVs, plus two more PFAS that are subject to upcoming MPCA water quality standards revisions: PFBA, PFBS, PFOA, PFOS, PFHxA, PFHxS, PFNA, and HFPO-DA (GenX).[26]

Limitations in sampling and data quality

Monitoring influent wastewater is challenging due to matrix interference effects resulting from the presence of complex constituents, including organics and total suspended solids. As a result, a wide range of reporting limits (RLs) were observed across the sampling datasets using EPA Draft Method 1633. The nature of sampling as part of this monitoring plan should also be taken into consideration. Due to the possibility of cross-contamination from composite sampling, all influent wastewater samples were grab samples. However, these represent a limited snapshot in time, when in reality the composition of wastewater can vary significantly over the course of a day.

The results from the optional TOP Assay provide insight into the presence of precursor PFAS that could be used to support further source identification and reduction work. The TOP Assay results themselves are inconsistent across facilities and labs, however, and were therefore not used to make decisions regarding action thresholds and are subsequently not presented in this report. In future studies, adsorbable organic fluorine (AOF) analysis could be a valuable tool in understanding total PFAS presence in wastewater.

Overall, the two sampling events proved valuable in developing an initial characterization of the PFAS being discharged to WWTFs across Minnesota.

What are the next steps?

Moving forward, the MWW Program will complete the work committed to in the MOU. This includes assisting communities with source identification and reduction work, implementing PFAS pollutant minimization plans (PFAS PMPs), and gathering two additional influent samples. In addition, the MWW Program is considering when and how to include PFAS-related requirements in MWW permits.

PFAS pollutant minimization plans, source identification, and source reduction

The next steps for WWTFs have been defined by the two PFAS monitoring results collected to date. Each community was assigned a priority category to guide the pace of their implementation and completion of their PFAS PMPs. In general, a PFAS PMP details the source identification and reduction work the community will undertake, including prioritization of sampling and action items.

Low, medium, and high priority source identification and reduction work categories were developed based on the prevalence of PFOS, PFOA, and/or PFBS in sampled influent. Per the PFAS MOU, communities in the medium and high categories must develop and submit a PFAS PMP by July 2024. MPCA recommended, but did not require, that communities in the low category develop a PFAS PMP.

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[26] The MPCA was directed by the Legislature to develop Class 1 water quality standards for six PFAS: PFOA, PFOS, PFNA, HFPO-DA (GenX), PFHxS, and PFBA. These are the same PFAS compounds for which the EPA has proposed MCLs, but are not the same six for which MDH has developed HBVs/HRLs. The two PFAS for which EPA has not developed MCLs, but for which MDH has HBVs, are PFBA and PFHxA. Additional information on this rulemaking can be found on the MPCA website at https://www.pca.state.mn.us/get-engaged/standards-for-sources-of-drinking-water. Accessed 4/1/2024.

The MPCA recommended each municipality not only consider large dischargers, like SIUs, but also smaller users that discharge to the WWTF. As such, the MPCA provided a list of potential industrial PFAS dischargers in each municipality by querying a database of NAICS codes reported by businesses.[27] Each community is expected to provide continuing educational information pertaining to PFAS products to the community and industries within their service area.

Source identification and reduction activities are community-specific, but activities in a PFAS PMP may include the following:

- Chemical and product evaluations at industrial users;
- Monitoring at specific locations throughout the community's collection system and/or at specific SIUs to help determine presence and quantities of PFAS discharged;
- Evaluation of historical uses with potential to contribute influent PFAS concentrations; and
- A review of public drinking waters.

Communities in the high category were asked to implement their PFAS PMP activities within 12 months. Facilities in the high category were also required to meet individually with the MPCA to further discuss the PFAS PMP development. The MPCA also strongly encouraged any facilities producing Class A/Exceptional Quality Biosolids to complete all the action items in the high priority category even if their sample results placed them in the medium or low priority categories. Communities in the medium category were asked to implement their PFAS PMP and source identification and reduction activities within 24 months.

The MPCA will complete two additional quarterly monitoring events in summer and fall 2024 to gather more data. Originally MPCA hoped this round of sampling would show reductions in influent PFAS concentration resulting from source identification and reduction work, but the MPCA acknowledges full implementation of the PFAS PMPs will be an ongoing effort. These additional sampling events may or may not show reductions in PFAS but will provide important data to better understand PFAS contributions to WWTFs throughout the state.

Inclusion of PFAS requirements in NPDES/SDS permits

The MPCA currently considers PFAS effluent limits and monitoring requirements for NPDES/SDS permits that discharge to waters with an applicable PFAS water quality criteria.[28] By 2026, when statewide PFAS water quality standards are promulgated for Class 1 waters (designated for human consumption), we will broaden the inclusion of PFAS effluent limits and monitoring requirements for NPDES/SDS permits that discharge to those waters.[29]

In parallel, the MPCA will more broadly consider and define PFAS requirements for municipal wastewater facilities in a NPDES/SDS permitting strategy. In creating this NPDES/SDS permitting strategy the MWW Program will use what's been learned from monitoring efforts to date, as well consider information and guidance from other Minnesota state agencies, other states, EPA, and the evolving

[27] *See* PFAS Monitoring Plan (p-gen1-22b), Appendix F for a list of NAICS codes associated with potential PFAS use or release.

[28] There are currently PFAS water quality criteria for a small number of surface waters in the state, including Bde Maka Ska, Pool 2 of the Mississippi River, and Lake Elmo. More information about PFAS water quality criteria is on the MPCA website at https://www.pca.state.mn.us/business-with-us/site-specific-water-quality-criteria and https://www.pca.state.mn.us/air-water-land-climate/developing-water-quality-criteria-for-pfas. Accessed 4/1/2024.

[29] U.S. EPA. Status of Risk Assessment Work on Per- and Polyfluoroalkyl Substances (PFAS) Found in Biosolids. https://www.epa.gov/biosolids/risk-assessment-pollutants-biosolids#pfas. Accessed 4/1/2024.

science of PFAS. For example, the MWW Program will consider the EPA memo "Addressing PFAS Discharges in NPDES Permits and Through the Pretreatment Program and Monitoring Programs" (December 2022).[30] The MPCA is also considering biosolids efforts currently being implemented in other states, including Michigan and Wisconsin. The MWW Program is following the work on EPA's PFAS biosolids risk assessment, which has the potential to impact regulations that would affect all WWTFs in Minnesota that land apply their biosolids.

Ultimately, the MWW Program expects that the permitting strategy will detail when and how to include influent, effluent, and biosolids monitoring and other related PFAS requirements in a municipality's NPDES/SDS permit. The strategy will include an implementation plan with a timeline.

There will be opportunities to participate in the development of these strategies through calendar year 2024. We expect the NPDES/SDS permitting and the biosolids strategy to be finalized by the end of 2024 and implemented in 2025.

Industrial Wastewater Program

What did we set out to do?

The Industrial Wastewater (IWW) Program Plan focused on IWW permittees that have individual NPDES/SDS discharge permits and perform activities that fall within the industrial categories included in the NAICS codes that are the most likely industries to use or have previously used PFAS.[31] Samples would be of internal process wastewater discharged either to a municipal WWTF or directly to surface water. Sampling from both types of discharges was intended to help identify where PFAS are present in the waste stream. Facilities participating in the IWW Program Plan would be asked to collect four quarterly PFAS samples – one per quarter – of internal process wastewater. During the first two quarters, the facilities would be asked to inventory potential PFAS sources internal to their processes. Then, after four quarters, facilities would be asked to report back to MPCA on outcomes of source identification and reduction efforts. The MPCA committed to using this data to determine if PFAS use is present at a given facility, evaluate the effectiveness of source reduction activities, and inform regulatory framework development needs to address PFAS in IWW discharges.

What did we actually do?

Of the twelve industrial facilities that were selected for wastewater monitoring, six facilities agreed to sample voluntarily, while the remaining six declined to do so. The MPCA provided funding to offset the sampling and analytical costs of up to four discrete samples at the facilities that volunteered. The MPCA hired a contractor to collect samples in May and June of 2023 at facilities that declined to voluntarily monitor.

The IWW Program met with all twelve facilities to discuss implementation of the IWW Program Plan. The IWW Program also communicated with each facility regarding technical assistance opportunities for PFAS source identification and reduction, and sent the results of internal process wastewater sampling to the corresponding WWTF, as appropriate, to assist with their source identification efforts.

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[30] U.S. EPA. Memorandum: Addressing PFAS Discharges in NPDES Permits and Through the Pretreatment Program and Monitoring Programs. December 5, 2022. https://www.epa.gov/system/files/documents/2022-12/NPDES_PFAS_State%20Memo_December_2022.pdf.

[31] *See* PFAS Monitoring Plan (p-gen1-22b), Appendix F for a list of NAICS codes associated with potential PFAS use or release.

Additionally, for the six facilities that agreed to collect voluntary samples, the MPCA requested that they develop and submit to the MPCA a PFAS source identification and reduction plan. The facilities proceeded with collecting at least four quarterly samples representative of internal process wastewaters where PFAS could be present. Facilities elected to use a variety of analytical methods, providing data on either 33 or 40 PFAS compounds, depending on the selected method.

For the facilities that declined to sample voluntarily, the MPCA contractor proceeded with collecting samples in May and June 2023. Samples were analyzed for 33 PFAS target analytes using SW-846 Method 8327, which was the method provided by the analytical lab that was selected under the state contract at the time sampling occurred.

Data from both facility- and MPCA-led sampling are included in this report, although the results presented in this report from voluntarily participating facilities include only the data submitted to MPCA. All six facilities that voluntarily sampled submitted data; of those, five have completed and submitted results from all four rounds of sampling. One facility has reported two sampling results (see summary of reported data in Table 8). The remaining data are anticipated to be reported to the MPCA in 2024.

Table 8. Summary of facility types and sampling data in the IWW Program Plan. The number of samples refers to the sampling events reported to MPCA.

Industry	Number of facilities	Number of samples
Building materials	2	4
Chemicals	2	6
Leather tanning	1	2
Medical	1	2
Paper	2	8
Semiconductor	2	17
Water purification	2	4
Total	12	43

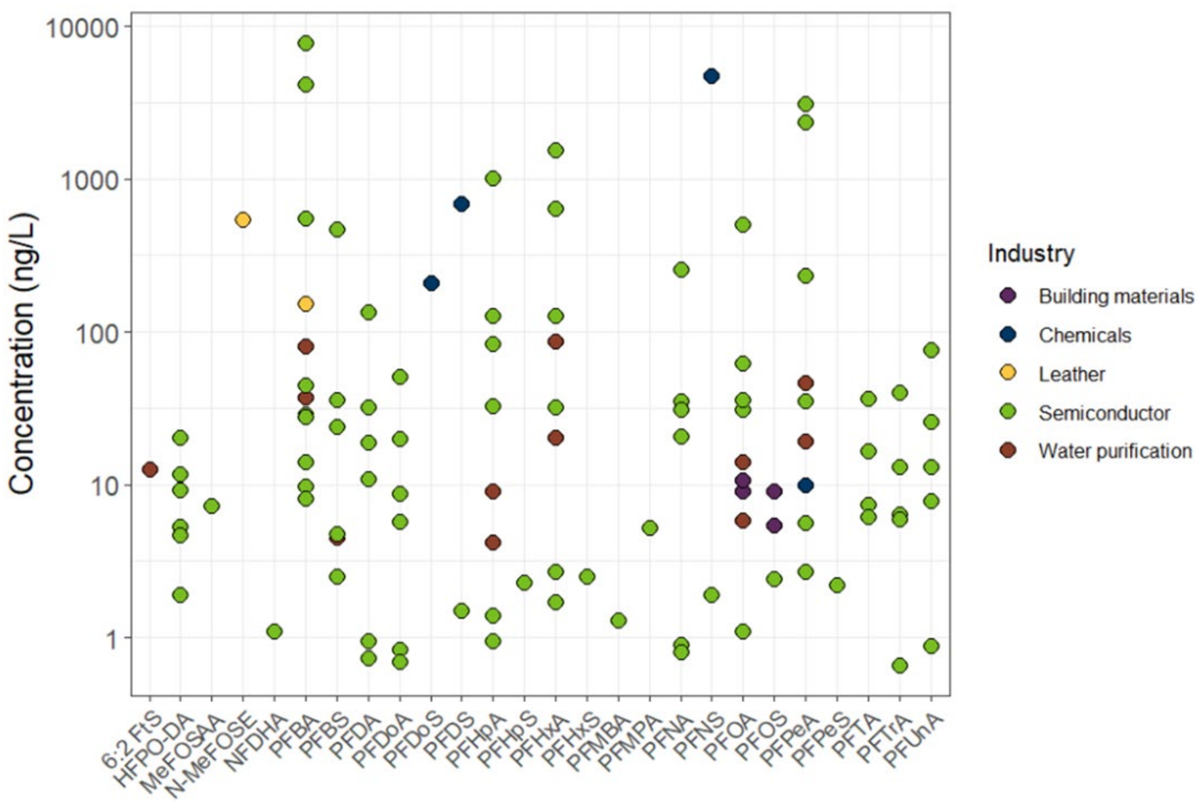
What did we find?

Results

Results of at least two sampling events are available from all twelve facilities at which sampling occurred. Of these twelve facilities, seven reported at least one detection of a PFAS compound in process wastewater. PFAS were detected at facilities representing the building materials, water purification, leather tanning, chemicals, semiconductor, and paper industries. The medical device manufacturer did not report detections of PFAS. Results presented in this report include data submitted to the MPCA by mid-October 2023.

Twenty-six distinct PFAS compounds were detected across the facilities' samples (Figure 8). Fourteen PFAS compounds were not detected at any facility. The most frequently detected compounds, and those found in the greatest concentrations, were PFBA, PFOA, and PFPeA, each of which was found in wastewater at four of the reporting facilities.

Figure 8. PFAS analytes found in process wastewater from all sampled industrial wastewater facilities, by category, displayed on a logarithmic scale (n=112). This figure only includes results above the method detection limit and does not include any non-detect data.



Each of the six PFAS for which MDH has current drinking water HBVs (PFBA, PFBS, PFOA, PFOS, PFHxA, and PFHxS) and two additional PFAS for which the U.S. EPA has MCLs (PFNA and HFPO-DA) were detected in wastewater from at least one facility (Figure 9). Concentrations of each of the eight PFAS varied across samples (Figure 10). Three PFAS compounds – PFOS, PFOA, and PFBS – were used to create response thresholds to address source identification and source reduction work with each of the facilities. These compounds were selected to align with source reduction priorities for municipalities as the sampled process wastewater is discharged to municipalities.

Figure 9. Detects and non-detects of eight PFAS target analytes from all industrial wastewater samples (n=248).

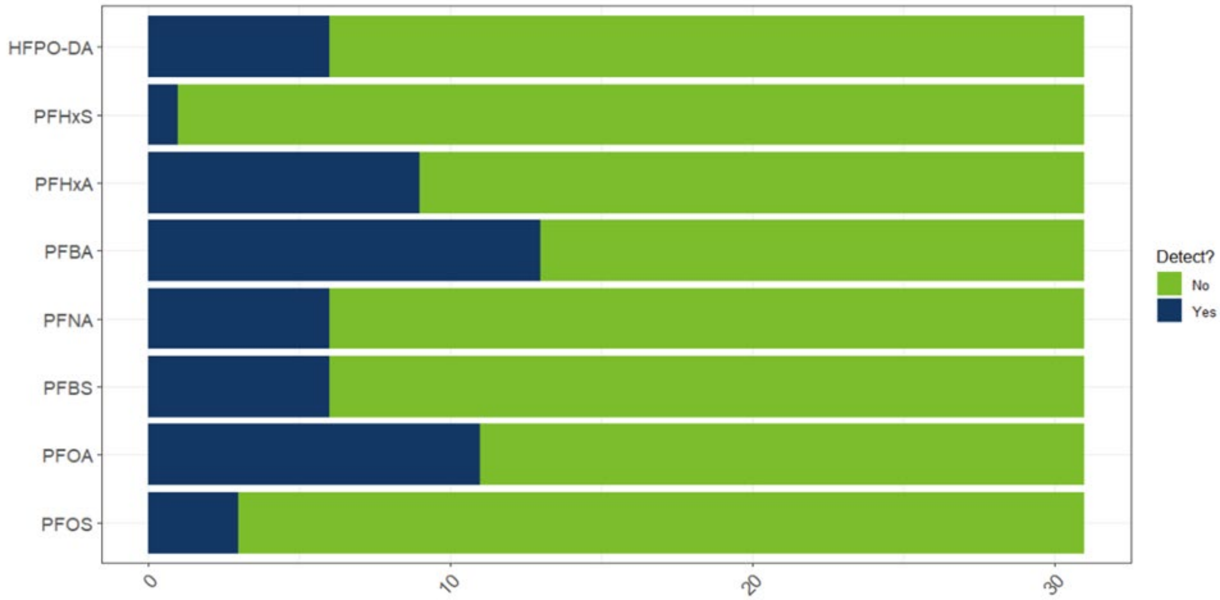
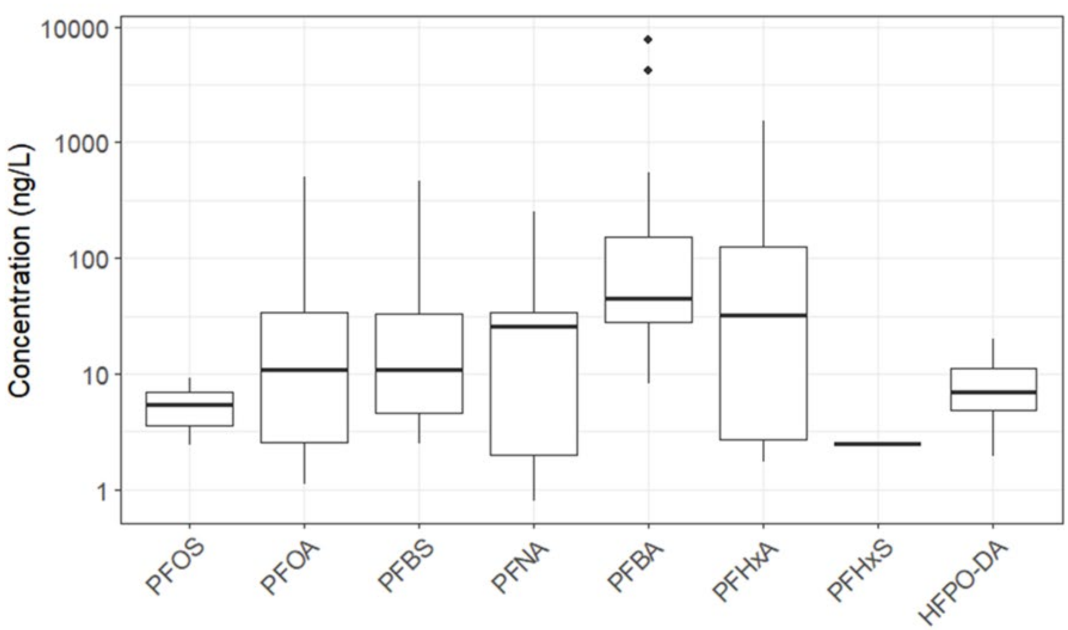


Figure 10. Boxplot comparing concentrations of eight PFAS target analytes from all industrial wastewater samples, displayed on a logarithmic scale (n=331). This figure only includes results above the method detection limit and does not include any non-detect data.



Facilities were divided into response categories for source identification and reduction work based on each facility's highest result (of all samples) for PFOS, PFOA, and PFBS. At facilities where sample results were above 15 ng/L for PFOS, 35 ng/L for PFOA, and/or 10 ng/L for PFBS, the facilities were scoped into the "high" category. Facilities with selected PFAS concentrations falling between 4.1 ng/L and the above values were scoped into the "medium" category, and facilities with results less than 4 ng/L for all three target PFAS compounds were scoped into the "low" category (Table 9).

Table 9. Number of industrial wastewater facilities, by industry type, in each response category (high, medium, or low).

Industry	High	Medium	Low
Building materials		1	1
Chemicals	1		1
Leather tanning	1		
Medical	1		
Paper		2	
Semiconductor	1	1	
Water purification		1	1

In its analytical guidance for PFAS, MPCA established a goal reporting limit of 4 ng/L for all PFAS compounds.[32] The reporting limit was used for non-detect observations. Using this prioritization method, four of the twelve facilities were designated "high" for source identification and reduction work. Scoping was not entirely driven by detects of PFAS. For chemical, medical, and paper industry facilities, elevated RLs increased their priority. RLs decreased between quarter one and quarter four at the chemical facility in the high category. RLs varied between samples at the medical facility. The leather tanning facilities samples were all non-detect, but at an elevated RL. Overall, the PFAS detections in this dataset were most common in samples from wastewater at semiconductor manufacturing facilities. Of the 43 samples collected, 17 (40%) are from semiconductor manufacturers, but these samples represent 89 of the 112 total PFAS detections (79%). PFAS concentrations detected across the facilities range from 0.66 ng/L (PFTrA) to 7,750 ng/L (PFBA).

Importantly, PFAS compounds can be harmful to human health at widely varying concentrations. For example, while MDH's 2023 drinking water HBV was 15 ng/L for PFOS, the HBV for PFBA is 7,000 ng/L. Out of the 112 measured PFAS detections across facilities, eight of these values were greater than an HBV developed by MDH. Concentrations were greater than the 2023 HBVs for PFBA, PFBS, PFOA, and PFHxA, but not for PFOS or PFHxS. Each of the eight samples with a PFAS concentration greater than one of MDH's 2023 HBVs was taken from a semiconductor manufacturing facility.

Limitations in sampling and data quality

Elevated analytical reporting limits for many facilities' samples presented a challenge in interpreting this dataset. Of the 946 total non-detect observations in this dataset, 446 observations (47%) were above the MPCA's 4 ng/L RL goal.

[32] MPCA. Guidance for Per- and polyfluoroalkyl substances (PFAS): Analytical (p-eao2-28). October 2023. https://www.pca.state.mn.us/sites/default/files/p-eao2-28.pdf.

The MPCA has a more limited understanding of the levels of PFAS potentially present in samples with elevated reporting limits. Reporting limits were as high as 300 times the goal limit, making it difficult to assess whether non-detect results indicate the absence of PFAS in wastewater or if PFAS were present at any concentrations below the elevated reporting limits. Elevated reporting limits were likely caused by the presence of organics and other dissolved or suspended solids in the untreated or partially treated industrial wastewater samples making up this dataset. We anticipate improved laboratory methods and proficiency will reduce reporting limits in many wastewater matrices over time.

The transient nature of constituents present in IWW poses an additional limitation to interpreting this dataset. Wastewater grab samples were collected from industrial facilities once per quarter, with sampling duration on the order of seconds. The constituents present in wastewater discharge can, however, vary over relatively short or long periods of time, depending on the processes taking place at the facility at the time of sampling. For example, one facility reported different results before and after a routine shutdown. A sample taken before the shutdown showed no detections of any PFAS analyte. After the shutdown and associated maintenance activities (cleaning and parts replacement), there were several PFAS detections. Grab samples are therefore not representative of the full range of processes at a facility and may provide an incomplete or biased picture.

Conclusions

The IWW PFAS monitoring effort looked at wastewater discharged from a subset of industrial facilities which are the most likely to use or have used PFAS. Although the monitoring effort has been helpful in identifying some sources of PFAS in Minnesota, the IWW Program Plan has not been a robust tool for systematically identifying sources. Data did demonstrate, however, that the semiconductor manufacturing industry is a PFAS source in the state.

The voluntary nature of this sampling work resulted in a variety of analytical methods used, timescales for data collection and reporting, and number and types of sampling locations. In order to comprehensively assess permitted discharges, the IWW Program has concluded that routine, prescriptive, and uniform PFAS monitoring must be implemented within existing NPDES/SDS permit programs. Coupled with progress in laboratory analytical capacity for PFAS, additional monitoring is necessary to both fully understand the universe of industrial PFAS sources in Minnesota and to take data-driven action to reduce PFAS discharges from those sources.

What are the next steps?

Low, medium, and high response categories were developed based on the concentration level of PFOS, PFOA, and PFBS in process wastewater at facilities sampled as part of the IWW Program Plan. MPCA may adjust response thresholds used in the future to prioritize source reduction activities. In addition, the IWW Program is considering when and how to include PFAS-related requirements in IWW permits.

Facilities in the high category are expected to take immediate actions to reduce PFAS in discharges, both those to municipal WWTFs and directly to surface water. All facilities are expected to submit a PFAS source reduction plan. The MPCA will evaluate the source reduction plan to determine the adequacy and completeness of the document. The MPCA will meet with facilities to determine responses that may be needed to further investigate and/or reduce PFAS sources, including providing additional monitoring results to MPCA.

Going forward, the IWW Program will focus on facilities with NPDES/SDS surface discharge permits. In 2024, the IWW Program will work to develop an IWW PFAS permitting strategy and implement the strategy by 2025. Building material, chemical, and water purification facility permits are planned to be reissued with PFAS monitoring and source reduction activities in calendar year 2024. The IWW Program will respond quickly to address facilities that are found to be of concern based on water monitoring results (permit required monitoring) and implementation of applicable water quality criteria and/or water quality standards.

Solid Waste Program and Hazardous Waste Program updates

What did we set out to do?

In the Solid Waste and Hazardous Waste Program Plan, the MPCA acknowledged that landfills have limited options for managing PFAS inputs into their facilities, and PFAS levels will reflect a composite of historic and ongoing levels in disposed materials. For that reason, the Solid Waste and Hazardous Waste Program Plan focused on collecting groundwater data from wells adjacent to landfills to characterize levels and understand potential PFAS impacts on the environment and human health that may be stemming from these facilities, rather than on source reduction efforts. Relevant to this work is the fact that all of the hazardous waste landfills in Minnesota are closed and no longer accept waste.

The SW/HW Program Plan set forth an ambitious plan for facilities to voluntarily collect PFAS groundwater samples during three rounds of sample collection (in the spring, summer, and fall). Due to the large number of permitted solid waste facilities in Minnesota, the Program Plan proposed that this monitoring would be completed in two waves over the course of two years based on risk prioritization. The Program Plan also proposed that groundwater results at levels of concern would result in further conversations between the facility and MPCA to determine the need for next steps, including the potential for additional monitoring.

What did we actually do?

The Solid Waste Program initially performed a basic prioritization of monitored landfills based on risk factors, including recent non-PFAS contamination in monitoring wells, the potential for release from unlined components, and the presence of nearby receptors. Facilities were then divided in two groups, with the first group being asked to sample voluntarily in 2023 and the second group being asked to sample voluntarily in 2024. The 2023 group included approximately 50 facilities that were asked to sample two times within the year at a set of targeted wells. The requests included both upgradient and downgradient monitoring wells in areas most likely to identify any releases. Because there are only five permitted closed hazardous waste landfills in Minnesota, all five were asked to voluntarily sample for PFAS.

The MPCA held an initial stakeholder meeting in June 2022 to explain the process and gather feedback. Based on stakeholder feedback the MPCA drafted a memorandum of understanding (MOU) modeled after the MWW Program and reevaluated the initial proposal to sample leachate for PFAS (where available). A second stakeholder meeting was held in November 2022 to review the updated process and gather additional feedback.

As part of the stakeholder outreach process, MPCA conducted facility-specific meetings to discuss well selection and review the process for sampling, including submittal of an addendum to the existing sampling and analysis plan (SAP) for the facility. The SAP addendum was meant to confirm the final monitoring well selection and any PFAS-specific monitoring procedures. MPCA met with 36 individual facilities who agreed to discuss voluntary PFAS sampling. Ultimately, three facilities submitted a SAP addendum before the spring 2023 sampling event, and one facility signed the MOU.

Due to the lack of voluntary participation from both solid waste facilities and hazardous waste landfills, the MPCA pursued limited funding to perform one round of targeted PFAS sampling at solid waste landfills that are either unlined or have unlined components. To maximize the value of the data collected, the MPCA refined the risk-based prioritization process and selected 82 facilities, including one facility adjacent to a closed hazardous waste landfill. Targeted monitoring well selection was performed to identify wells near the unlined component of each landfill, where a release was estimated to be most likely. Sampling took place in 2023. A total of 322 monitoring locations were selected for sample collection and analysis. Samples were obtained at upgradient, sidegradient, variable, and downgradient monitoring wells. Quality control samples included an equipment blank, field blank, and duplicate sample at most facilities. No drinking water wells or surface water bodies were sampled as part of this effort.

The MPCA used three sampling contractors to collect groundwater samples at the facilities. Samples were analyzed at two different laboratories, Eurofins Lancaster Laboratories Environment Testing and Pace® Minneapolis. They used EPA Draft Method 1633 and modified EPA Method 537.1, respectively.

What did we find?

Ultimately, samples were successfully collected from monitoring wells at 79 of 82 selected facilities. At two facilities, monitoring results showed contaminated field or equipment blanks; these results are not reflected in the data summary below, leaving 77 facilities for which results are reported.

Results

Results described in this report include samples collected in 2023. Each of the 77 landfills sampled had at least one sample with a PFAS concentration greater than the method detection limit (MDL). Of the 77 facilities sampled, 30 facilities (39%) had a PFAS concentration greater than MDH's 2023 HBVs in at least one downgradient monitoring well and reporting limits at or below the associated MDH guidance value.

The Solid Waste Program purposefully sampled PFAS only at solid waste landfills that were either unlined or had unlined components. Of the 30 facilities with a downgradient monitoring well sample value greater than one or more of MDH's 2023 HBVs, six were Municipal Solid Waste (MSW) landfills with a historically unlined portion; 22 were unlined construction and demolition waste landfills; and two were unlined industrial waste landfills. Those landfills accounted for 32% of MSW landfills (six of 19), 41% of construction and demolition waste landfills (22 of 54), and 50% of the industrial waste landfills (two of four) that were sampled (Table 10).

Table 10. Numbers of solid waste facilities, by waste type, with PFAS concentrations greater or less than MDH's 2023 HBVs.

Waste (facility) Type	Number of facilities with no values greater than HBVs	Number of facilities with values greater than HBVs	Total number of facilities sampled
Municipal solid waste (MSW)	13	6	19
Construction and Demolition (C&D)	32	22	54
Industrial solid waste	2	2	4
Total	47	30	77

Thirty unique PFAS compounds were detected above the minimum detection limits across all facilities sampled (Figure 11). The six compounds subject to MDH's 2023 HBVs – PFBA, PFBS, PFOA, PFOS, PFHxA, and PFHxS – were detected across all waste types, as well as PFNA and HFPO-DA. Three other PFAS compounds for which no HBVs currently exist – PFHpA, PFPeA, PFPeS – were found consistently across all facility types, as well, at more than 50 of the groundwater wells sampled (Figure 12).

Figure 11. PFAS analytes found across all groundwater well samples collected from groundwater wells at solid waste facilities, sorted by waste type (n=1760). This figure only includes results above the method detection limit and does not include any non-detect data.

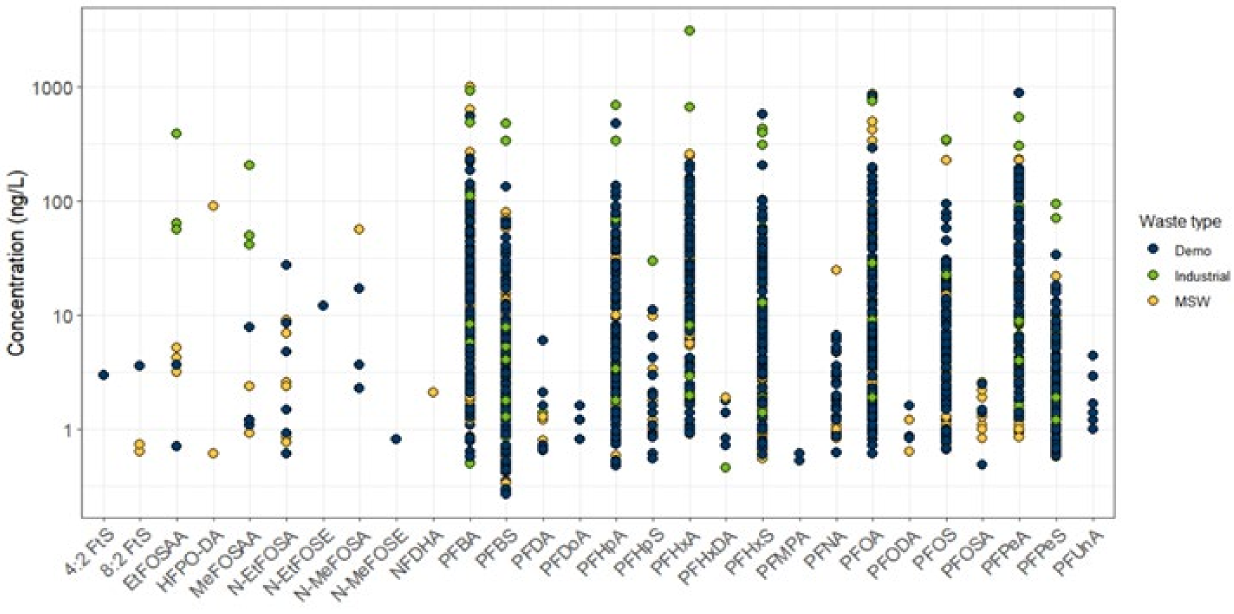
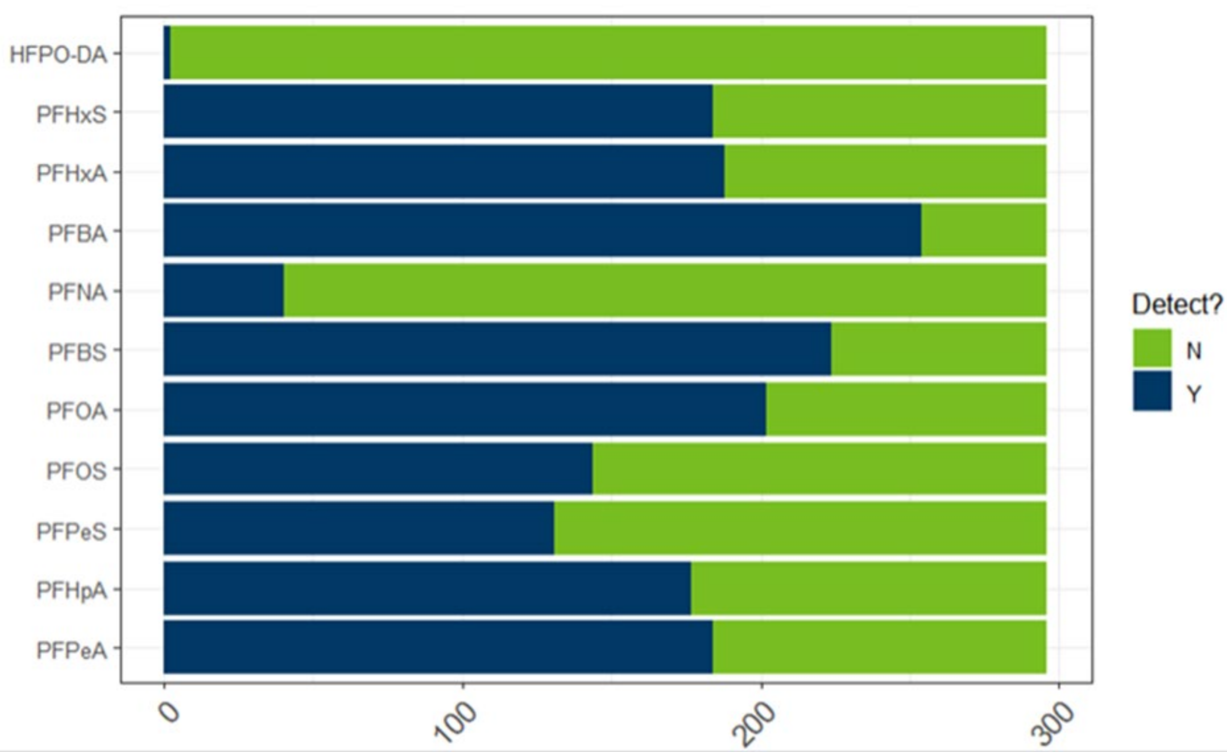
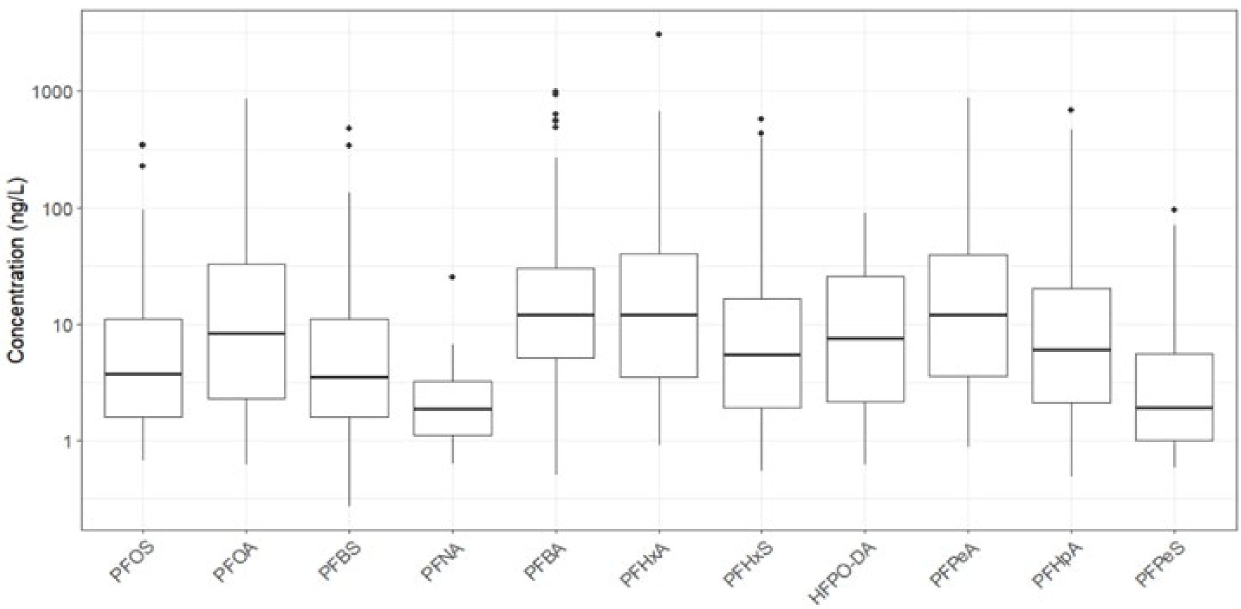


Figure 12. Detects and non-detects of eleven PFAS analytes across all samples collected from groundwater wells at solid waste facilities (n=3256).



Concentrations of the eleven PFAS compounds of interest to the Solid Waste Program (PFOS, PFOA, PFBS, PFNA, PFBA, PFHxA, PFHxS, HFPO-DA, PFPeA, PFHpA, and PFPeS) varied widely across all samples with detections, ranging from less than 1 ng/L to greater than 1000 ng/L (Figure 13). The PFAS analyte with the greatest outlying measurement was PFHxA, though PFBS, PFBA, PFpEA, and PFHpA also had high sample values in relatively similar concentrations.

Figure 13. Boxplot comparing concentrations of eleven PFAS target analytes from samples collected from groundwater wells near solid waste facilities, displayed on a logarithmic scale (n=1643). This figure only includes results above the method detection limit and does not include any non-detect data.

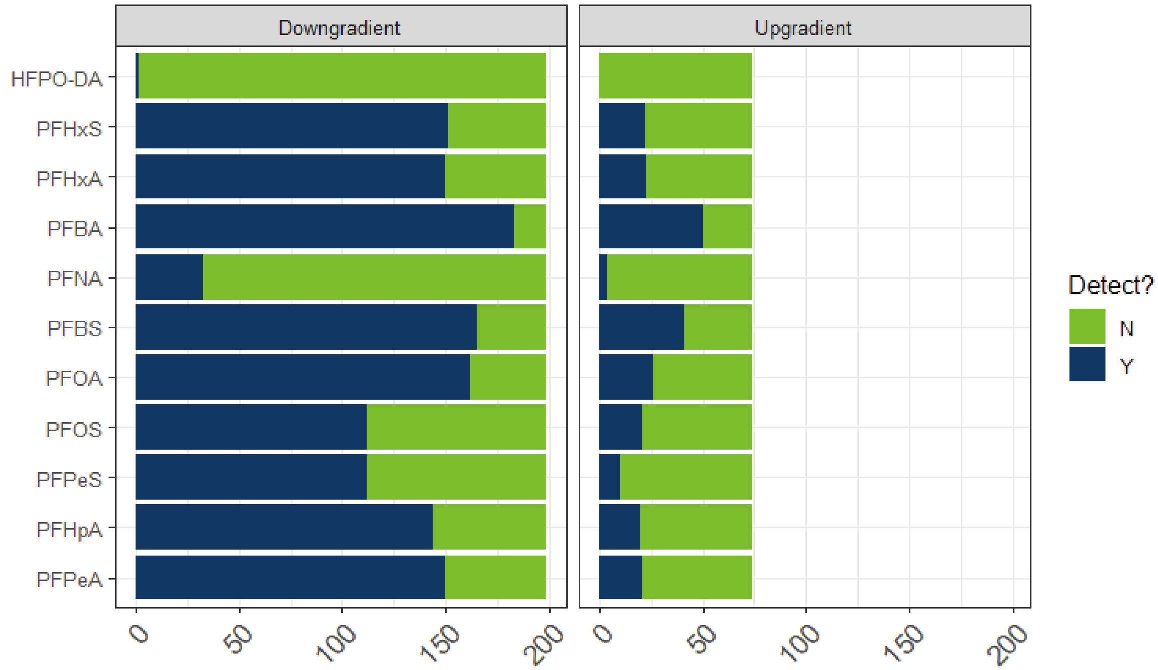


Samples greater than MDH's 2023 HBVs were found for PFOS, PFOA, PFBS, PFHxA, and PFHxS; no samples of PFBA were detected at values greater than the relevant HBV. PFOA and PFOS were most often detected at values greater than MDH's 2023 HBVs, although the HBVs for those PFAS are also the lowest.

The SW Program Plan was unique in that samples were collected both upgradient and downgradient of most selected facilities, which allowed for a comparison of both PFAS detections and concentrations and therefore some idea as to whether solid waste sites are contributing PFAS to downgradient groundwater.

The eleven PFAS compounds of interest to the Solid Waste Program were detected at greater frequency in downgradient wells than in upgradient wells (Figure 14). HFPO-DA was detected only in downgradient samples. A statistical comparison of the concentrations of all PFAS and downgradient and upgradient well locations was conducted, and found that downgradient samples have significantly greater concentrations of PFAS than do upgradient wells (Figure 15). Although there were fewer samples overall from upgradient wells, the statistical analysis performed accounted for this difference.

Figure 14. Detects and non-detects of eleven PFAS analytes, separated into upgradient and downgradient well locations at solid waste facilities (n=2992). This dataset has been filtered to remove side gradient and variable well locations.



Limitations in sampling and data quality

Solid Waste Program staff and the MPCA's Data Quality Unit conducted a quality review of all data submitted by Eurofins and Pace®. Two of the 79 sampled facilities' monitoring results showed contaminated field or equipment blanks, indicating potential cross-contamination that may have impacted monitoring wells. The two contaminated samples were not analyzed (which resulted in the 77 total facilities). Samples from upgradient monitoring wells were unable to be collected at two facilities. Most reporting limits (98% of results) met the MPCA's 4 ng/L RL goal. A qualitative review comparing original and duplicate samples indicated the results were generally comparable across the data set.

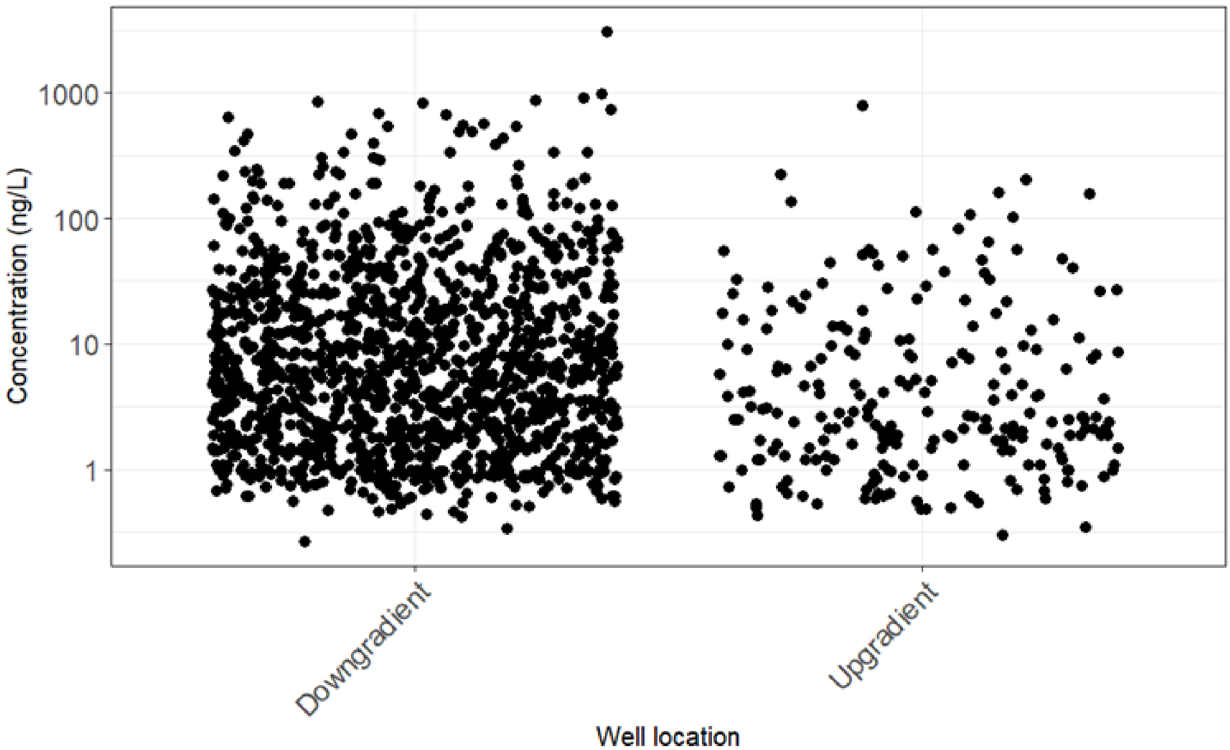
The data from this monitoring event are considered useable as qualified.

For the purposes of this section of the report, all results identified as greater than the method detection limit were considered detections.

Conclusions

Overall, the data quality from the MPCA's sampling efforts were sufficient to support our understanding of the presence of PFAS in groundwater near solid waste landfills. Based on the evaluation of the collected data, including the statistical difference in PFAS concentrations in downgradient and upgradient samples, it appears that some unlined landfills are associated with PFAS impacts to groundwater, including impacts at levels greater that the MDH's 2023 HBVs. There did not appear to be correlations between the types and concentrations of PFAS found at levels above MDH's 2023 HBVs and the type of waste near which samples were collected.

Figure 15. Concentration of PFAS analytes in downgradient versus upgradient wells at solid waste facilities (n=1521). A t-test was performed and a significant difference was found (p-value<0.01). This dataset has been filtered and removed side gradient and variable well locations.



Lastly, given the preponderance of PFHpA, PFPeA, and PFPeS in collected samples, the SW Program will request that MDH include these PFAS compounds for further assessment and evaluation as part of the MDH Contaminants of Emerging Concern Initiative, which is a formal process that allows the MPCA to request MDH review of certain contaminants. If a review is ultimately conducted, MDH would evaluate any human health risks associated with those PFAS compounds as they impact drinking water, and would subsequently decide whether additional drinking water standards or guidance values are needed.

What are the next steps?

Based on review of the groundwater data that MPCA collected at landfills, the SW Program has identified some recommended quick actions, as well as some recommended overall program changes, consistent with the goals outlined in the PFAS Monitoring Plan and the Solid Waste and Hazardous Waste Program Plans. In addition, the Solid Waste Program is considering when and how to include PFAS-related requirements in permits.

Quick action responses

The PFAS Monitoring Plan has three goals, one of which states: Identify areas of particular concern (due to PFAS concentrations or routes of exposure) that need quick action. SW Program staff have identified sites where groundwater sampling results caused concern that more immediate actions are needed to ensure drinking water receptors are protected.

After identifying areas of particularly concerning sample results, the SW Program further examined facilities near private drinking water users. Although 30 facilities had PFAS concentrations greater than one of MDH's 2023 HBVs, only six facilities were identified as needing quick action based on an evaluation of potential drinking water users within 0.5 miles downgradient of the facility showing monitoring well concentrations above MDH's 2023 HBVs. Next steps for these facilities, which depend on the availability of additional downgradient wells for sampling, are as described below.

- **Landfills with additional downgradient monitoring wells:** For the three facilities in this category, the MPCA has asked the facilities to sample downgradient monitoring wells to determine if an off-site plume could impact drinking water users. If the furthest downgradient wells show PFAS concentrations greater than MDH's 2023 HBVs, the facility will be asked to sample private wells.
- **Landfills that do not have monitoring wells further downgradient than the wells MPCA sampled:** For these three facilities, the MPCA identified private drinking water users and will request that these permittees sample private drinking water wells for PFAS.

Four of the six facilities have begun work to implement the additional requested sampling. This will be a stepwise investigation, involving continued sampling of additional downgradient monitoring wells or potential receptors if results show contamination above MDH's 2023 HBVs. In addition, the permits for these six facilities will be modified to add PFAS monitoring or other actions.

Leachate management

Leachate can contaminate groundwater through accidental releases (storage pond leaks, conveyance piping leaks, ineffective stormwater management, etc.) and through percolation of rainwater/leachate through wastes at facilities where liners are not present. Leachate can contaminate surface water when contaminated groundwater travels and discharges to surface waters or when leachate is disposed of at WWTFs and subsequently discharged. Through permitting actions, the MPCA will require the following changes in leachate management:

- Limiting large open areas and requiring smaller working faces;
- Lining all landfills to proactively collect and manage leachate; and
- Timely final cover placement in areas used for leachate recirculation.

In order to prevent leachate from reaching groundwater and surface water, MPCA will continue to require operating MSW and merchant Industrial landfills to be lined. The MPCA has begun a rulemaking process that would require construction and demolition waste landfills to be lined in the future to prevent leaching of contaminants to groundwater.

Land application of leachate

Over the last several years, MPCA has being working with facilities to reduce the level of PFAS in leachate that is land applied. Some facilities are in the process of testing different technologies to pretreat their leachate for PFAS or have discontinued land application. Moving forward, all facilities using leachate land application for disposal and treatment will be required to pretreat leachate for PFAS in order to continue land application where the limits are exceeded in groundwater. Exceedances are defined as concentrations of PFAS greater than ¼ of the relevant HBV and/or HRL. The Solid Waste Program goal is to move forward using Demonstration Research Projects (DRPs) and permit requirements to develop new treatment processes or pilot-test known treatment systems that can be implemented successfully for full-scale treatment at these facilities. The program goal is that within five years, landfills will have a technology option pilot tested, and ready to implement. If no on-site technology is successful, permittees will need to find alternative management methods, such as off-site disposal and treatment. However, landfill facilities using disposal at WWTF will need to work with the local WWTFs to determine if pretreatment is required and when.

Where leachate disposal occurs at WWTFs, the Solid Waste Program will direct solid waste facilities to coordinate with their receiving WWTF on timelines and pretreatment limits that the WWTF and the MWW Program have determined is protective.

Sample remaining landfills and compost facilities

There are approximately 45 solid waste landfill facilities, five closed hazardous waste landfills, and several compost facilities where PFAS sampling was not conducted. MPCA will continue to seek funding to collect PFAS data from these remaining solid waste facilities or include PFAS sampling as a requirement during permit reissuance. A plan to collect PFAS data from these facilities will be implemented based on funding availability and reissuance schedules. MPCA will continue to request that closed hazardous waste landfills sample for PFAS. Recent proposals by EPA to update the definition of hazardous waste applicable to corrective action for releases from solid waste management units and to include nine PFAS to the list of hazardous constituents in Appendix VIII to Part 261 of the Code of Federal Regulations will provide additional regulatory authority for this sampling.[33]

Specifically for compost facilities, the new statute prohibiting intentional addition of PFAS in food packaging (Minn. Stat. 325F.075) went into effect January 1, 2024, and should decrease the amount of PFAS in contact water as old product is used up. Once the EPA Biosolids PFAS Report is completed sometime in 2024, MPCA staff will determine if compost should be sampled and develop a subsequent timeline for sampling. Contact water sampling will begin with permit reissuance and will depend on the contact water management method chosen by the facility.

A review of closed solid waste landfills (outside of the Closed Landfill Program) shows there are more than 100 closed landfills in the Solid Waste Program. Future efforts will include a process to determine facility characteristics and whether further work is needed to examine potential PFAS releases.

Data sharing

The Solid Waste Program sent out facility-specific PFAS results collected to the individual permittees. A number of landfills are in the process of doing their own PFAS monitoring, and the Solid Waste Program has requested the data from these efforts. MPCA staff plan to compare data collected by the permittee to the data collected by MPCA.

Permitting actions

As an overall goal, the Solid Waste Program will continue to request that facilities cooperatively conduct PFAS data collection and/or put PFAS sampling requirements into permits for the initial 82 identified priority landfills within the ten-year permit cycle. During this ten-year timeframe, the additional 45 facilities without PFAS data will be prioritized and PFAS sampling requirements will be added to permits during reissuances.

The Hazardous Waste Program is working with other agency programs to provide letters of support for the two EPA proposals described above which will strengthen the program's authority to include PFAS in permits and permit-related documents. Staff are updating the list of hazardous constituents in the groundwater monitoring programs to include PFAS and will continue to include these analytes as part of investigations of releases from solid and hazardous waste management units.

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[33] *See* "Definition of Hazardous Waste Applicable to Corrective Action for Releases From Solid Waste Management Units", 89 FR 8598, published February 8, 202,4 https://www.govinfo.gov/content/pkg/FR-2024-02-08/pdf/2024-02328.pdf and "Listing of Specific PFAS as Hazardous Constituents", 89 FR 8606, published February 8, 2024, https://www.govinfo.gov/content/pkg/FR-2024-02-08/pdf/2024-02324.pdf.

Industrial Stormwater Program updates

What did we set out to do?

The Industrial Stormwater (ISW) Program Plan focused on facilities that were likely to have ongoing PFAS releases from current uses, historic uses, and/or processing of PFAS-containing materials. As part of the ISW Program Plan, the MPCA identified three categories of facilities believed to have a high likelihood of PFAS releases via stormwater: airports, metal finishers, and automotive shredding facilities. The ISW Program Plan requested that the Minnesota facilities in these categories voluntarily collect two to three quarterly samples of stormwater from locations that include runoff from areas of concern (AOC) for PFAS release and an existing benchmark monitoring location (BML) for stormwater.[34]

AOC locations for PFAS included sampling locations closest to shredder fluff piles, aqueous film-forming foam (AFFF) training areas, or the portions of a facility that vent metal finishing baths. The ISW Program then planned to compare the stormwater results to response thresholds based on PFOS concentrations. If PFOS concentrations in stormwater were greater than the medium- or high-risk response thresholds, MPCA would ask the facility to submit a PFAS source and exposure reduction plan within 180 days or 90 days, respectively, from the last sampling quarter. The ISW Program would also use the data from the three sectors to determine if changes are needed to the broader regulatory landscape for industrial stormwater permittees in industry categories with potential PFAS releases.

What did we actually do?

Seventeen of the 22 metal finishing facilities and all seven of the Part 139 airports that didn't have existing PFAS results from stormwater samples agreed to voluntarily participate. Samples have been or will be collected from two locations at each facility: the AOC and a BML. Facilities are at various stages of sampling plan completion at the time of this report. To date, 18 out of 24 participating facilities from the metal finishing and airport sectors have completed all requested sampling events. The final dataset is anticipated by mid-2024.

In spring 2023, MPCA made funding available to offset the sampling and analytical costs of one sampling event for each of the facilities that agreed to voluntarily monitor. To expand the dataset for this program, MPCA identified funding to perform one sampling event each at five of the automotive shredding facilities identified in the ISW Program Plan that did not opt to voluntarily participate. Samples were collected from the facilities' BMLs between May - August 2023 and analyzed for 36 PFAS compounds using a modified EPA Method 537.1, which was the method available for sample analysis under state contract at the time of sample collection. Only the BMLs were sampled, as the automotive shredding facilities did not agree to MPCA sampling at the AOCs. MPCA sampled BMLs determined most likely to represent runoff from shredding operations.

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[34] BMLs are existing stormwater monitoring locations required by the Minnesota Industrial Stormwater General Permit MNR050000, https://www.pca.state.mn.us/sites/default/files/wq-strm3-67i.pdf. BMLs were primarily designated for stormwater assessment and are located where stormwater discharges from a facility's property, with the goals of evaluating the effectiveness of traditional stormwater best management practices and assessing the contribution of pollutants in stormwater runoff as required by a facility permit. AOC are defined in the ISW Program Plan as an area of a facility where the industrial activity uses or processes PFAS or PFAS-containing materials. AOC may or may not have stormwater runoff captured by an existing BML.

What did we find?

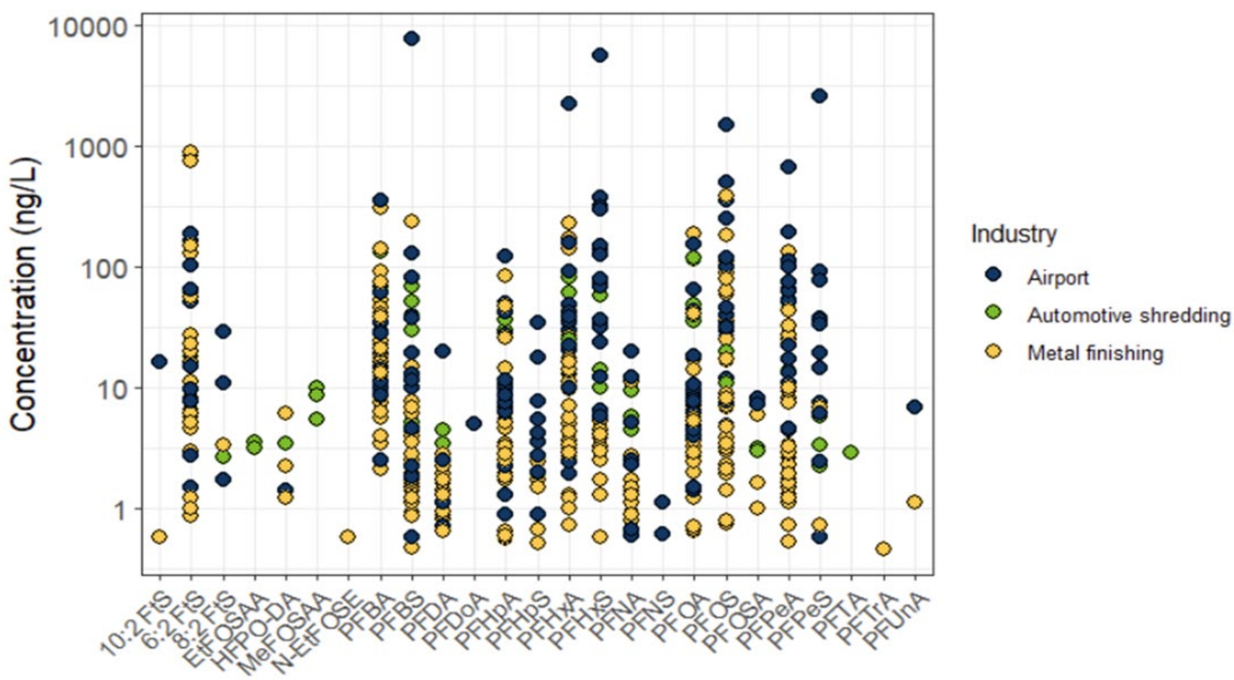
This report presents the sampling results available in MPCA's EQuIS database as of January 2024, collected by all seven of the participating airports and thirteen of seventeen participating metal finishers. Facilities in this group have completed the two to three quarterly sampling events described above.

Results

Twenty-five unique PFAS analytes were detected across all three industrial categories where sampling took place (Figure 16). PFOS was detected in stormwater from at least one sample collected at each of the 25 facilities with submitted data, though there were several sample results from several facilities without detectable concentrations of PFOS. PFBS was another frequently detected compound at facilities in all three industry categories, and was found in stormwater at every airport, every automotive shredding facility sampled by the MPCA, and at 85% of the metal finishing facilities reporting data.

There were several PFAS compounds found at all seven airport facilities, likely indicating common sources: 6:2 FTS, PFBA, PFHpA, PFHxA, PFOA, and PFPeA.

Figure 16. PFAS analytes found across all industrial stormwater samples, sorted by industry type, displayed on a logarithmic scale (n=559). This figure only includes results above the method detection limit and does not include any non-detect data.



Automotive shredding facilities and metal finishing facilities had similar profiles to airports, in terms of which PFAS were most common. A notable exception is the presence of MeFOSAA at three out of five automotive shredding facilities and EtFOSAA at two out of five automotive shredding facilities. In addition to uniformity in chemical profiles, concentrations of commonly detected PFAS at the five automotive shredding facilities are relatively consistent.

Some facilities that did very little metal finishing, and/or had areas where chrome flashing activities ended several years prior to the PFAS sampling, had notable concentrations of PFOS both at the AOC and BML locations.

The six compounds subject to MDH's 2023 HBVs – PFBA, PFBS, PFOA, PFOS, PFHxA, and PFHxS – were detected across all waste types, as well as PFNA and HFPO-DA (Figure 17). Concentrations of these PFAS range broadly; PFBS accounts for both the lowest and highest concentration found, while PFNA and HFPO-DA were both found in concentrations less than 50 ng/L (Figure 18).

Figure 17. Detects and non-detects of eight PFAS analytes from all industrial stormwater samples collected (n=542).

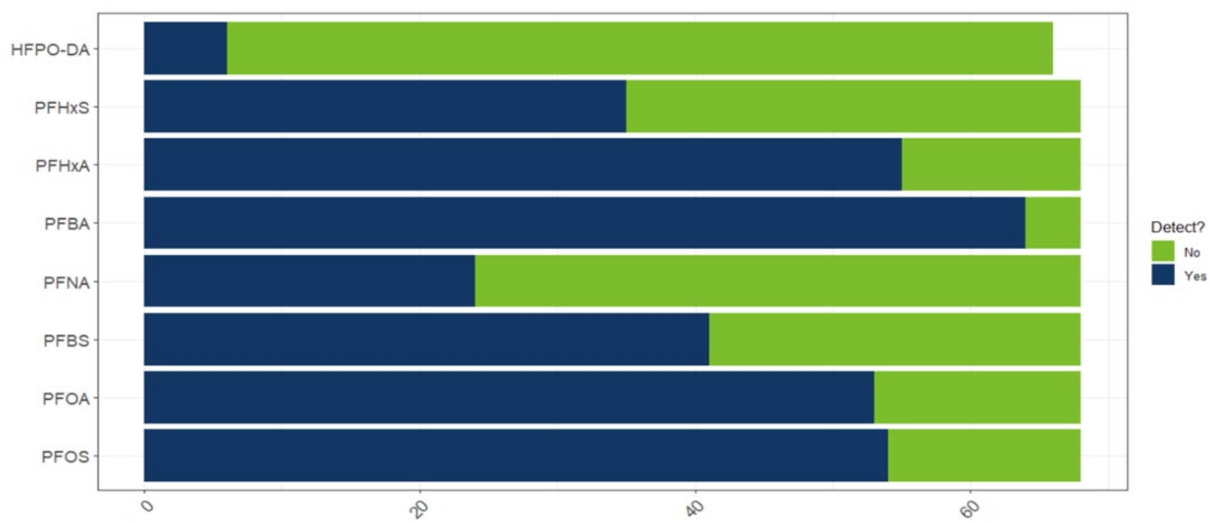
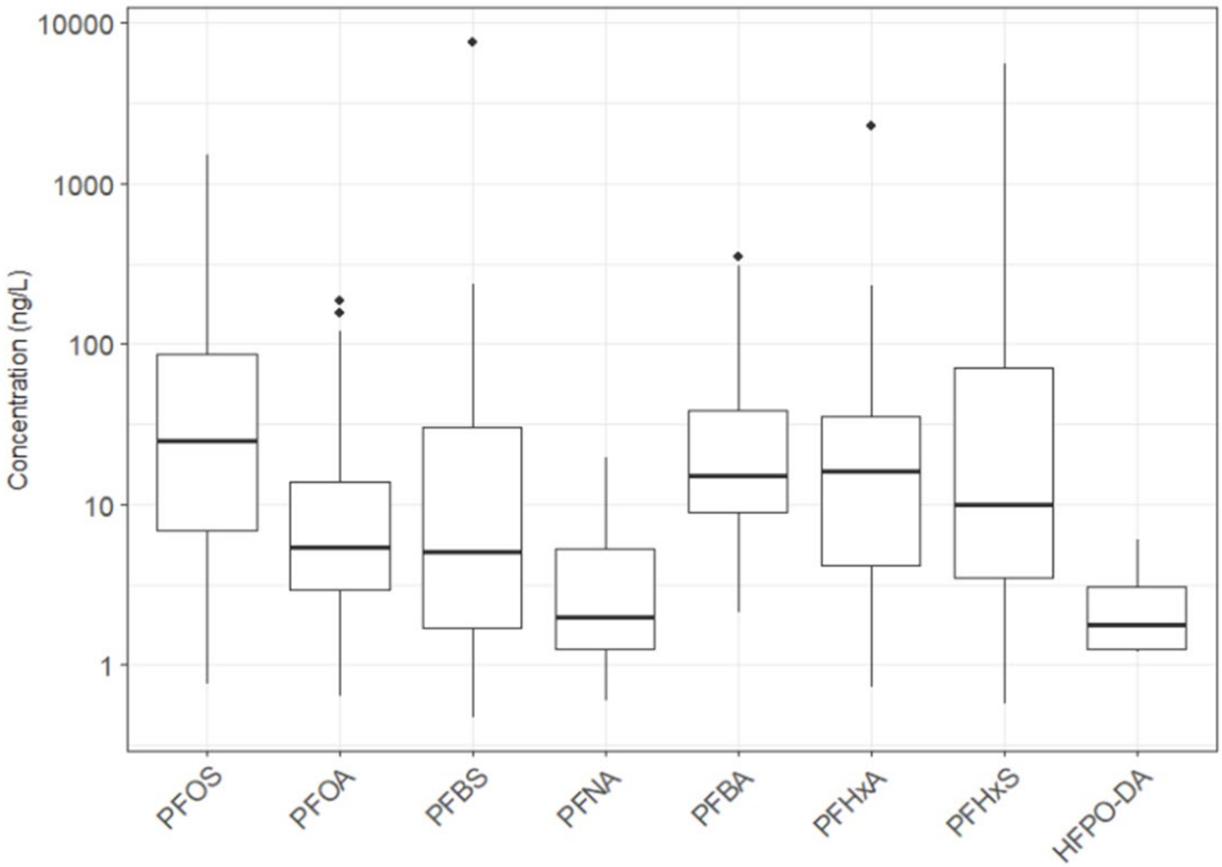


Figure 18. Boxplot comparing concentrations of eight PFAS target analytes from all industrial stormwater samples, displayed on a logarithmic scale (n=331). This figure only includes results above the method detection limit and does not include any non-detect data.



Limitations in sampling and data quality

Although analyzed samples showed consistent analyte detections and concentrations at some sampling sites across the three industrial categories sampled, other PFAS were found in broad ranges of concentrations.

Variation in reported values may be explained by some or all of the following:

- The length of time since PFOS-containing plating fume suppressants were last used (if used at all);
- Roof or gutter replacement since PFOS-containing fume suppressants were last used;
- The duration and spatial extent/footprint of PFOS-containing plating fume suppressant usage at facility;
- Precipitation intensity and sample timing relative to beginning of discharge event; and/or
- Proximity to neighboring facilities that may have had historical and/or current PFAS potential.

Conclusions

The findings of various PFAS in stormwater samples from the three industrial categories are consistent with findings from other studies and sampling efforts.

PFOS response thresholds

Since PFOS was found at all ISW sites sampled, the ISW Program Plan established mean PFOS concentration as the primary driver for follow-up response actions, including source reduction activities. Non-detects were treated as zero when calculating the mean. Based on the data available at the time of report publication, there are five airports, five auto shredders, and six metal finishers that meet the identified minimum response threshold of 10 ng/L, triggering a source reduction plan within 180 days of sampling completion. None of the facilities had a mean PFOS concentration greater than the response threshold for a 90-day source reduction plan (1,000 ng/L). Four airports, four auto shredders, and five metal finishers reported mean PFOS concentrations that were greater than the associated HBV.

The prevalence of PFOS at all sampled sites reflects how ubiquitous PFOS is in the environment but may also reflect local and regional deposition patterns. A December 2022 precipitation study looking at deposition sites in Wisconsin found concentrations of PFAS in rainwater ranging from 0.7 to 6.1 ng/L with PFOS concentrations ranging from <0.05 to 1.41 ng/L. Findings from the study indicated that nearby sources of PFAS have the potential to influence the composition of precipitation across a spatial scale.[35] An August 2019 published precipitation and surface water study on the Great Lakes also found evidence of local PFAS sources potentially causing greater concentrations of PFOS in precipitation in urbanized and/or industrial areas of the Great Lakes compared to more remote locations of the Great Lakes.[36]

Additional findings

At the sampled airports, consistent findings of 6:2 FTS likely indicate an AFFF release source, as it was widely used as the replacement chemical for PFOS in AFFF following the phaseout of PFOS in the early 2000s.[37]Minnesota is currently phasing out the use of Class B firefighting foams containing PFAS and replacing those with fluorine-free foams (F3) when and where possible – some uses of AFFF are required by federal law. On-site discharge of PFAS-containing foams for training has also been prohibited, except as required by federal law; discharges for testing are allowed if the discharge is appropriately collected.[38]

In addition to uniformity in chemical profiles, concentrations of commonly detected PFAS at the five automotive shredding facilities are relatively consistent. PFAS has historically, and/or in present use, been applied to some automotive parts, such as head gaskets, valve stem seals, air conditioner piston rings, steering assist pump piston rings, and brake pad wear indicators, as well as textiles and leather.[39]

[35] Pfotenhauer et al. 2022. PFAS concentrations and deposition in precipitation: An intensive 5-month study at National Atmospheric Deposition Program – National trends sites (NADP-NTN) across Wisconsin, USA. Atmospheric Environment, Vol 291, 119368, ISSN 1352-2310. https://doi.org/10.1016/j.atmosenv.2022.119368.

[36] Gewurtz et al. 2019. Perfluoroalkyl Acids in Great Lakes Precipitation and Surface Water (2006-2018) Indicated Response to Phase-outs, Regulatory Action, and Variability in Fate and Transport Processes. Environ. Sci. Technol. Vol. 53(15), 8543-8552. https://pubs.acs.org/doi/full/10.1021/acs.est.9b01337.

[37] National Academies of Sciences, Engineering, and Medicine. 2023. PFAS Source Differentiation Guide for Airports. Washington, DC: The National Academies Press. https://doi.org/10.17226/27164.

[38] MPCA. Firefighting foam use, replacement and disposal (w-hw4-17). March 2024. https://www.pca.state.mn.us/sites/default/files/w-hw4-17.pdf.

[39] Erin E. Bulson, Christina K. Remucal, and Andrea L. Hicks. End-of-life circulation of PFAS in metal recycling streams: A sustainability-focused review. Resources, Conservation and Recycling, Volume 194, 2023, 106978, ISSN 0921-3449, https://doi.org/10.1016/j.resconrec.2023.106978.

The relatively small range of PFOS and PFOA concentrations at the automotive shredders is somewhat surprising, given the variability in intensity and timing of storm events during sampling, as well as distance of samples from likely source areas. All but one of the facilities sampled have been in operation for several years.

The prevalence of MeFOSAA at three out of five automotive shredding facilities and EtFOSAA at two out of five automotive shredding facilities is a unique finding among the three industrial categories sampled. Since these compounds have been used to manufacture textiles and leather, their occurrence could potentially result from the processing of car interior materials. An estimated 4 – 45% (by weight in percent) composition of automotive shredder fluff is textiles/fibers.[40]

What are the next steps?

Moving forward, the ISW Program will continue PFAS monitoring, identify overall program changes, and other actions consistent with the goals outlined in the PFAS Monitoring Plan. In addition, the ISW Program is considering when and how to include PFAS-related requirements in the next ISW General Permit.

The ISW Program identified three categories of response thresholds effectively categorizing the industrial facilities (airports, chrome plating facilities, and automotive shredding facilities) into three groups; low, medium, and high. The ISW Program currently regulates facilities based upon their Standard Industrial Classification (SIC) code; however, future PFAS work will include facilities that potentially discharge PFAS based on their NAICS code as converted to a regulated SIC code. The facilities identified through this work will be incorporated into development of a PFAS response plan.

The facilities that were identified in the low category will be expected to maintain PFAS inventory and reduction activities at the site along with any PFAS best management practices (BMPs) that are proving effective to prevent release of PFAS or generation of PFAS. MPCA may adjust response thresholds used in the future to prioritize source reduction activities.

The facilities that were identified in the medium category will be expected to submit a PFAS source and exposure reduction plan within 180 days of completing the PFAS monitoring. The MPCA will evaluate the source and exposure reduction plan to determine the adequacy and completeness of the document. The MPCA will meet with these facilities to further determine a proper response and or action that may need to be taken to further reduce PFAS sources and exposure through appropriate regulatory or remediation responses.

The facilities that were identified in the high category will be expected to submit a PFAS source and exposure reduction plan within 90 days of completing the PFAS monitoring. The MPCA will prioritize the evaluation of the source and exposure reduction plan to determine the adequacy and completeness of the document. The MPCA will meet with these facilities to require implementation of immediate actions to reduce PFAS sources and exposure through appropriate regulatory or remediation responses. As of January 2024, no facilities had mean PFOS values that required action under the high category.

In addition to the above detailed response to the current PFAS monitoring, the ISW Program will develop and implement the next Industrial Stormwater General NPDES/SDS permit for issuance in 2025.

[40] Erin E. Bulson, Christina K. Remucal, and Andrea L. Hicks. End-of-life circulation of PFAS in metal recycling streams: A sustainability-focused review. Resources, Conservation and Recycling, Volume 194, 2023, 106978, ISSN 0921-3449, https://doi.org/10.1016/j.resconrec.2023.106978.

The issuance of the next ISW General NPDES/SDS permit will consider components to address and prioritize PFAS, which will be discussed at stakeholder meetings and outreach efforts in the near future.

The ISW Program will continue to contribute to MPCA's broader effort of developing and implementing statewide water-quality standards for PFAS, and to use existing MPCA authority to investigate and respond to past and/or ongoing industrial stormwater discharges that are of particular concern.

Remediation Program updates

What did we set out to do?

The Remediation Program Plan laid out Minnesota's policy regarding PFAS and the Minnesota Environmental Response and Liability Act (MERLA) and described the next steps for formally including PFAS into the Superfund, Site Assessment, and Brownfields investigation and clean-up processes. First, the Remediation Program Plan restated the MPCA's policy that all PFAS are considered "hazardous substances" under MERLA. The Remediation Program Plan also described two future initiatives: a strategy to develop PFAS Remediation Guidance through a stakeholder development process, and a strategy to incorporate PFAS monitoring into existing sites with "known or likely" PFAS releases. The plan described the basic prioritization of sites using a risk-based approach aligned with approaches for how other contaminants of concern are evaluated in these programs. Criteria for PFAS sampling at sites include considerations of site usage, proximity to known PFAS detections or releases, and proximity to dumps or landfills.

What did we actually do?

The Remediation Program has been successful in meaningfully advancing both initiatives described in the PFAS Monitoring Plan.

PFAS Remediation Guidance development

In 2021, MPCA's Remediation Division convened a stakeholder group to develop the PFAS Remediation Guidance (Guidance). The group consisted of representatives from sectors including, but not limited to, environmental consulting, law, academia, environmental laboratories, and local governments. Stakeholder group members were identified from previous participation in other guidance development and expressions of interest. The purpose of the stakeholder group was to ensure that all sectors engaged in addressing PFAS were represented and granted the opportunity to provide feedback on the Guidance during its development. Emphasis was placed on ensuring representation from all sectors that would be affected by the Guidance. The group's goal was to develop clear, concise, predictable, and prescriptive guidance for addressing PFAS at Remediation sites.

The MPCA conducted quarterly stakeholder meetings between December 2021 and March 2023 to discuss progress on the development of the Guidance. The stakeholder group and the MPCA identified five steps, or "life cycle stages", within the general clean-up process to address in the Guidance.

The life cycle stages are:

- **Initial site review:** Criteria to determine if PFAS sampling is necessary at a site
- **Site investigation:** Investigation of all potentially impacted media
- **Risk assessment:** Consideration of health-based values, fate and transport, migration pathways, and additivity

- **Remediation:** Process to address threats to human health and the environment, as well as site-specific cleanup measures
- **Site closure:** Long-term monitoring and land use restrictions

Furthermore, several cross-cutting areas were identified that require consideration throughout each of the life cycle stages. These are:

- **Risk assessment:** Both a life cycle stage and a cross-cutting area, as it is important to consider throughout the entire process
- **PFAS Disposal:** Proper waste characterization and management
- **Brownfield assurances:** Redevelopment by non-responsible parties that remains protective of human health and the environment
- **Communications:** Engagement with relevant stakeholders during all life cycle stages
- **Environmental justice:** Considerations for areas with communities most susceptible to environmental impacts

Smaller subgroups consisting of MPCA team leads and stakeholder group members were formed to develop these focused sections of the Guidance. The larger stakeholder group provided input on each of the sections during quarterly meetings. Feedback was incorporated and content expanded upon within each of the subgroups.

The draft PFAS Remediation Guidance was finalized and released for public comment in August 2023. The final guidance is anticipated to be released in early 2024.

Data collection from active sites

Work is ongoing to collect PFAS data from active cleanup sites. As of March 2024, PFAS sampling has taken place at 62 Remediation sites. These include fund-financed and responsible party (RP) led sites. Fund-financed Remediation sites are where there is no viable responsible party identified to carry out the work, so the MPCA addresses the site. PFAS monitoring is in the FY24 budget for seven fund-financed sites. Incorporation of PFAS sampling at these sites is guided by risk-based prioritization, acknowledging the limitations in staffing and budget in implementing PFAS work at lower risk sites. This year, measures were implemented to track PFAS analytical costs at fund-financed sites so that PFAS activities can be accounted for explicitly at these sites. The number of sites for which PFAS sampling is conducted is projected to increase in the coming years as the understanding of industrial and commercial uses of PFAS grows.

Sites are identified for PFAS sampling following the basic criteria outlined in the PFAS Monitoring Plan and described in detail in the draft PFAS Remediation Guidance. These criteria include historical and current site use, proximity to known or potential PFAS sources and/or releases, and potential risk to receptors. PFAS monitoring at Remediation Program-led sites is ongoing and will continue to be incorporated as regular activity under MERLA, guided by the framework put forth in the PFAS Remediation Guidance.

What did we find?

PFAS Remediation Guidance

The implementation of the Remediation Program Plan requires consistent and predictable instructions to address contamination. Lessons learned during the development of the Guidance are the need for external stakeholder input and the evolving nature of the Guidance document itself.

The cleanup of contamination at MERLA sites are coordinated by regulatory agencies and external stakeholders. The stakeholder group that was established in late 2021 was modeled on the group developed for the MPCA Vapor Intrusion Guidance. The inclusion of external stakeholders provides an opportunity for those engaged in the cleanup process to contribute to the Guidance document. This ensures that implementation of the PFAS Guidance is feasible for use by external parties. The stakeholder group will remain active as the Guidance is the updated.

The PFAS knowledge base is continuously evolving, and it is important that the document reflects the most up to date science. For instance, in 2016, a risk-based methodology to support the identification of sites, "PFAS Protocol", was developed. Prior to the launch of the PFAS Remediation Guidance, the PFAS Protocol governed when PFAS sampling was to be conducted. The primary input for the methodology was NAICS codes. These codes were linked to industries and facilities associated with the use, storage, or disposal of PFAS. The current understanding has shifted to the more-inclusive industrial classifications. This allows facilities to be assessed for potential PFAS association without the limitations of a specific code. In addition, the MPCA launched sector summaries in 2023, which evaluate how PFAS are used in specific industries. The launch of these sector summaries improves our understanding of the role of PFAS at these facilities. The shift from NAICS codes to industrial classifications is captured in the PFAS Remediation Guidance document.

Data collection from active sites

Sampling efforts have been ongoing for several decades at Remediation sites across the state, including at closed landfills, Superfund sites, and Site Assessment sites. A variety of PFAS compounds have been found in numerous media, including surface water, groundwater, drinking water, soil, sediment, tissue, and leachate at these sites. Since sampling was not conducted under the umbrella of the PFAS Monitoring Plan or the Remediation Program Plan, details regarding those data are not shared in this document but are accessible on the MPCA website.[41] The PFAS data on the website are included in three different data tools:

- MPCA Surface Water data explorer, which provides water quality information about specific lakes, rivers, and streams;[42]
- MPCA Groundwater data explorer, which includes an interactive map on which to view data from specific groundwater monitoring stations;[43] and
- MPCA Groundwater Contamination Atlas, which includes information about contamination on specific properties around the state where pollutants have affected groundwater.[44]

Site-specific analytical and field data collected from Remediation sites are stored via EQuIS. As of November 2023, electronic data deliverables (EDDs) are required to be submitted for sampling events at all Remediation sites. Moving forward, this submission format will allow the data to be accessible through MPCA's EQuIS database and will help MPCA to inventory PFAS activities and sampling results at Remediation Program-led sites.

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[41] MPCA. Science and data. https://www.pca.state.mn.us/about-mpca/science-and-data. Accessed 4/2/2024.
[42] MPCA. Surface water data. https://webapp.pca.state.mn.us/wqd/surface-water. Accessed 4/2/2024.
[43] MPCA. EDA: Groundwater search. https://webapp.pca.state.mn.us/edaGwater/stations. Accessed 4/2/2024.
[44] MPCA. Minnesota Groundwater Contamination Atlas. https://www.pca.state.mn.us/about-mpca/minnesota-groundwater-contamination-atlas. Accessed 4/2/2024.

What are the next steps?

The PFAS Remediation Guidance will continue to be updated as the scientific knowledge around PFAS expands. The external stakeholder group that was established for the development of the Guidance will remain active and support the implementation of the Guidance through regular content updates.

The Remediation Program will continue to coordinate with other programs to identify facilities that require further investigation and assess the applicability of enforcement authority.

Themes and conclusions

Five MPCA permitting programs and/or their regulated parties assisted in the sampling of PFAS across the state. Sampling was conducted at or near facilities associated with PFAS use or release based on their reported NAICS code(s). Data from cross-media sampling efforts, when analyzed, confirmed that one or more PFAS compounds were detectable at or near almost all facilities from which samples were collected. This means that PFAS sources in the state are numerous and ubiquitous, and include facilities that directly manufacture or use PFAS; have PFAS-laden equipment; process products including PFAS; or receive PFAS-laden waste streams. These findings were expected, but further strengthen the need for better understanding of primary sources of PFAS and the need to prevent PFAS from entering waste streams in the first place.

Results

PFAS compounds were detected in every sample taken from municipal wastewater influent, solid waste groundwater wells, and industrial stormwater runoff. Snow sampling results at facilities with air permits found detectable levels of at least one PFAS compound in 23 of 37 samples. Seven of twelve industrial facilities with NPDES/SDS wastewater permits had at least one detectable PFAS compound in their internal process wastewater.

Overall, the facilities with the most detections of unique PFAS analytes were municipal WWTFs, with 32 unique PFAS identified across all sampled facilities. This could be an artifact of the robust sampling effort done by municipal WWTFs, and/or the contribution of PFAS from many diffuse sources to the influent waste stream. This could also be due to the detection method used, EPA Draft Method 1633, which has the greatest number of detectable PFAS target analytes of the methods applied (no air sample data were available from OTM-45 at the time of report publication). There were 30 unique PFAS analytes detected at Solid Waste landfill well sites.

Among all programs and samples with detected PFAS, the six PFAS compounds for which MDH has developed HBVs – PFBA, PFBS, PFOA, PFOS, PFHxA, PFHxS – were found consistently, and at higher concentrations compared to other PFAS analytes. PFNA and HFPO-DA, two additional PFAS compounds for which the EPA has drinking water MCLs, were also found across almost all types of facilities sampled – these PFAS were notably absent from all snow samples. PFBS was the analyte with the respective highest concentration value among samples taken at ISW sites and municipal WWTFs, but was not detected at all in snow samples, either. At solid waste sites, the distribution of concentration values of PFOA, PFBS, PFBA, PFHxA, and PFPeA were comparable; the single greatest concentration of any PFAS at Solid Waste landfill sites was of PFHxA. PFBA was the analyte for which the single greatest concentration was measured across IWW facilities.

PFNA and HFPO-DA were the least common PFAS analytes detected among all collected samples. Notably, HFPO-DA, which is not manufactured in Minnesota, was not detected in snow samples at facilities with air permits or upgradient solid waste landfill groundwater wells, but was detected in:

- Samples from downgradient solid waste landfill wells;
- Process water at semiconductor facilities;
- Municipal wastewater; and
- Stormwater samples from airports, automotive shredders, and metal finishing facilities.

These findings suggest that HFPO-DA may be entering the environment through other pathways than direct releases attributable to manufacturing, though in low concentrations.

Several other PFAS compounds were found in common across sampled facilities. Those compounds include:

- PFHpA, PFPeA, and PFPeS, though prevalent in Solid Waste landfill well samples, were also detected in samples from municipal wastewater, industrial stormwater (all three industry categories), and in one or more industrial wastewater samples from semiconductor, chemical, and water purification facilities.
- EtFOSAA and MeFOSAA were prevalent at automotive shredders, but were also detected in municipal wastewater and in Solid Waste landfill wells (representing all three waste types). MeFOSAA was detected in one sample from industrial wastewater collected from a semiconductor facility.

There were also a small number of PFAS that were found uniquely in samples from specific types of facilities; this was particularly true of the fluorotelomer sulfonates (FTS) and fluorotelomer carboxylic acids (FTCAs). For example, 10:2 FTS was only found in samples from industrial process wastewater from airports and metal finishers. 3:3 FTCA, 5:3 FTCA, and 7:3 FTCA were only found in municipal wastewater influent.

The detection of these PFAS analytes may again be more of an artifact of which analytical methods were employed and were therefore able to detect these types of compounds (EPA Draft Method 1633 is the only method for water media capable of detecting FTSs and FTCAs), rather than being able to say with certainty they were not detectable in other samples.

Data quality considerations

The figures in this report present PFAS sample concentrations greater than MDLs, but do not account for RLs determined by the analytical labs that performed sample analysis. More information on RLs and specific data concerns are included in relevant program updates. Two programs that conducted sampling – snow sampling at or near air permitted facilities and IWW sampling – had especially poor RLs and fully-unqualified data. In the case of snow samples, PFAS concentrations were very low, and the sample size was very small, leading to many detections but few above RLs. For IWW, many samples were collected, but less than half of the samples had detections that met the MPCA's 4ng/L RL goal, likely due to dissolved particles in the samples making PFAS detection and quantification difficult.

For most programs that collected samples, the resulting data are informative but are not to be considered fully representative data; for example, although 83 WWTFs sampled their influent, only four samples have been collected at each facility (two per quarter). Only twelve facilities were sampled for PFAS in IWW, yielding only 43 samples reported to the MPCA. Similarly, snow sampling was conducted at only twelve facilities, yielding 37 total samples. The MPCA expects to receive additional sample data from municipal WWTFs and IWW sites, as well, later in 2024.

Aggregating the analyzed data provides a means to inform near- and mid-term approaches to permitting PFAS, but facility-specific data, in most cases, is/are not robust enough to make individual permitting decisions and should not be taken as such.

Permitting approaches and Remediation Program actions

Based on the results of these sampling efforts, each permit program, as well as the Remediation Program, has committed to future actions that will help further understand specific sources of these PFAS compounds.

At the time of this report, no Air Program data are available from emissions inventory reporting or emissions testing, though recent actions related to the Environmental Review process have compelled some facilities to do future emissions testing. Snow sampling has provided information, suggesting that further sampling is warranted, but the MPCA currently does not have the regulatory authority under non-permitting actions to compel emissions testing. Environmental Review, when conducted, and ongoing rulemaking efforts for both air toxic reporting and regulatory requirements will include consideration of PFAS emissions.

The MWW, IWW, Solid Waste, and ISW permitting programs used PFAS data shared in this report to create action thresholds and identify facilities at which a rapid response to PFAS is warranted. Of those, one program – the Solid Waste Program – identified PFAS concentrations that were concerning enough to warrant immediate action at six identified sites. The Solid Waste Program is working to ensure follow-up sampling is conducted at those sites as soon as possible; four of the six facilities have already conducted follow-up sampling. The Solid Waste Program will continue exploring and developing permitting and other solutions to address those and other facilities.

The MWW and IWW Programs identified several facilities as high priority for follow-up work. For municipal WWTFs, facilities in the high priority category will be required to submit PFAS PMPs to the MPCA for review by July 2024, with source identification and reduction activities to be completed within 12 months of PFAS PMP submittal. IWW permittees identified as high priority will be expected to take immediate action to reduce PFAS in their surface discharge, and to submit source reduction plans and additional sample results to the MPCA. Both the MWW and IWW Programs are considering how to address PFAS in NPDES/SDS permits. The MPCA is working to develop a permitting strategy for wastewater NPDES/SDS permits during calendar year 2024 and expects to begin putting PFAS-related requirements into permits in calendar year 2025.

Although no permittees were identified as high priority for action by the ISW Program, 16 facilities were identified as being of medium priority. Those permittees will have 180 days after sampling is completed to develop source reduction plans and submit them to the MPCA for review. Like the MWW and IWW Programs, the ISW Program will develop and implement the next Industrial Stormwater General NPDES/SDS permit for issuance in 2025 while considering components that address and prioritize PFAS in stormwater.

The MPCA’s Remediation Program expects to finalize their updated PFAS Remediation Guidance by the end of fiscal year 2024.

Overall, a variety of MPCA programs are identifying, developing, and implementing policies, regulatory tools, technological treatments, and other nonregulatory opportunities to prevent PFAS from entering the environment, and to mitigate and remediate PFAS already there. Underpinning this work is the need to prevent PFAS from entering waste streams in the first place. The MPCA continues to work with community members, regulated facilities, partnering state agencies, and other stakeholders to reduce or eliminate PFAS use and subsequent wastes, mitigate the impacts of PFAS currently in the waste stream and the environment, and remediate PFAS in the environment.

Appendix A. PFAS Monitoring Plan Quality Assurance Project Plan for Minnesota Based Projects, March 2023 (PFAS QAPP)

PFAS Monitoring Plan
Quality Assurance Project Plan for Minnesota Based Projects

March 2023

This quality assurance project plan (QAPP) was prepared according to guidance provided in guidance for Quality Assurance Project Plans (EPA QA/G5), EPA/240/R-02/009, December 2002) and EPA requirements for Quality Assurance Plans (EPA QA/R-5, EPA/240/B-01/003, U.S. Environmental Protection Agency, Office of Environmental Information, Washington, D.C., March 2001), to ensure that environmental and related data collected, compiled, and/or generated for this project are complete, accurate, and of the type, quantity, and quality required for their intended use.

QAPP Approvals

____ Date:____________________
Suzanne Baumann, Municipal Wastewater Section Manager

____ Date:____________________
Sarah Kilgriff, Solid Waste Section Manager

____ Date:____________________
Kari Palmer, Air Assessment Section Manager

____ Date:____________________
Katie Rinker, Environmental Data Quality Supervisor

____ Date:____________________
Jeff Udd, Water and Mining Section Manager

QAPP Distribution List

Table 1. The listed individuals, along with consultants and laboratories listed on associated work plans, will receive copies of the approved QAPP and Subsequent revisions

QAPP Recipients	Title	Organization	Telephone Number	e-mail Address
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List of Acronyms

AFFF	Aqueous Film Forming Foam
COC	Chain of Custody
CW	Clean Water Program
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
EQuIS	Environmental Quality Information System
FB	Field Blank
GPS	Geographic Positioning System
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
MB	Method Blank
MDH	Minnesota Department of Health
MDL	Method Detection Limit
MPCA	Minnesota Pollution Control Agency
MS	Matrix Spike
MSD	Matrix Spike Duplicate
PHL	Public Health Lab
PM	Project Manager
QA	Quality Assurance
QAC	Quality Assurance Coordinator
QAM	Quality Assurance Manual
QAPP	Quality Assurance Project Plan
QC	Quality Control
QMP	Quality Management Plan
RCRA	Resource Conservation and Recovery Act
RL	Reporting Limit
RPD	Relative Percent Difference
SDW	Safe Drinking Water Program
SOP	Standard Operating Procedure
TB	Trip Blank
USEPA/EPA	United States Environmental Protection Agency
WP	Work Plan

Section A: Project Management

A 1: Purpose of the PFAS Monitoring Plan Quality Assurance Project Plan (QAPP)

The purpose for this QAPP is to:

1. Provide guidance on data quality requirements for all private and public contractors undertaking work on behalf of the Minnesota Pollution Control Agency (MPCA) as part of the the PFAS Monitoring Plan (PFAS Monitoring Plan (state.mn.us))
2. Ensure all Per- and Polyfluoroalkyl Substances (PFAS) Monitoring Plan sampling and analytical data meet the MPCA's minimum data quality standards.
3. Provide uniform data quality and consistent labeling for all data in the PFAS Monitoring Plan to enable temporal comparisons within and between sites.

All MPCA-led projects that are designed to address one or more of the sites within the MPCA PFAS Monitoring Plan must have a project specific Work Plan that maintains the agency DQO against the MPCA's Quality Management Plan and Quality Assurance Project Plan Guidance.

This QAPP documents the minimum framework for data quality requirements necessary to aid program staff, partners, and contractors when planning project proposals and Work Plans (WP) and evaluating completed project tasks.

In addition, any MPCA PFAS Monitoring Plan projects that generate data for the use of and/or intended to be stored in the MPCA EQuIS Data System should follow this QAPP.

A 2: Project Organization and Responsibility

In the State of Minnesota, the Minnesota Pollution Control Agency (MPCA) has the primary responsibility and authority for managing and addressing PFAS amongst our programs. In doing so, the MPCA has developed a cross-program PFAS Monitoring Plan as part of ongoing work to investigate PFAS discharges, which the Blueprint (Minnesota's PFAS Blueprint | Minnesota Pollution Control Agency (state.mn.us)) further described as working to understand "the wide range of places where PFAS have been or are currently used and how these uses result in PFAS releases to the environment." The PFAS Monitoring Plan provides the initial understanding of PFAS presence (a necessary step to supporting pollution prevention) and identifies scenarios where immediate measures to protect human health and the environment are necessary.

A 2.1: Program Responsibilities

Air Program: The goal of the PFAS Monitoring Plan for air is to understand release of PFAS emissions and mitigate risks posed from inhalation of PFAS in the air and from exposure in other media that resulted from air emissions. Production and release of PFAS to the air has resulted in a large reservoir of atmospheric PFAS that is deposited back to the surface through rain and dust settling. Single industrial facilities have the potential to cause widespread environmental impacts when PFAS is released through air emissions and is deposited in soil or groundwater offsite or is carried offsite by water runoff. Our understanding of PFAS releases to air and subsequent impacts to other media is less advanced than our understanding of direct PFAS discharges to water; however, MPCA has traced air emissions releases of PFAS constituents to water quality impairments in the state. Incidents of cross-media PFAS impacts are being discovered nationwide. Characterizing which air facilities use PFAS products and may be releasing it to the air is the first step in reducing PFAS impacts to surrounding surface water, soil, and groundwater.

Wastewater Program: This PFAS Monitoring Plan takes a stepwise approach that allows for flexibility to assess and react to incoming data. The goal of the first phase of monitoring is to identify PFAS sources coming into municipal wastewater plants and PFAS used at industrial facilities with wastewater permits. This phase will develop a baseline understanding of influent concentrations at municipal plants and concentrations associated with process waste streams at industrial wastewater facilities – these data will inform source identification and reduction activities.

Future phases of monitoring will be informed based on the sources identified and source reductions realized in the first phase. The MPCA anticipates that it will be necessary to collect effluent and biosolids samples in future phases to further inform PFAS reduction efforts for wastewater discharges and to assess risk. The development of water quality criteria or standards and completion of state or federal risk assessments for biosolids may lead to effluent and biosolids monitoring, effluent limitations, or land application thresholds for some facilities in the future.

Solid Waste and Hazardous Waste Program: The goals of the PFAS Monitoring Plan for solid waste facilities and hazardous waste landfills are primarily focused on understanding and reducing potential PFAS impacts on the environment that may be stemming from these facilities.

Industrial Stormwater Program: There are two main goals for monitoring PFAS in industrial stormwater. The first is to protect human health and the environment by identifying and responding to the most significant PFAS releases through stormwater. Pollutants in industrial stormwater may contaminate waters of the state and impair the use of groundwater or surface water. These waters provide important resources to Minnesota as sources of drinking water, sources of irrigation water, and fisheries. The second goal is to support PFAS source identification and reduction at these facilities.

The first phase of this plan will focus on a subset of industrial stormwater facilities that are likely to have ongoing PFAS releases. Future phases of this plan may consider monitoring at additional facilities and changes to the industrial stormwater general permit.

MPCA Environmental Data Quality Unit: Provides QA oversight and coordination and a dedicated QA Coordinator provides leadership for QA related issues within the MPCA. Staff in the unit are responsible for drafting and updating this QAPP, reviewing and approving all MPCA generated QAPPs, reviewing and commenting on quality documentation, and managing ambient data storage.

A 3: The PFAS Monitoring Plan Background

The PFAS Monitoring Plan will provide the initial understanding of PFAS presence (a necessary step to supporting pollution prevention) and identify scenarios where immediate measures to protect human health and the environment are necessary. The MPCA has received funding for various other initiatives related to PFAS. This includes:

- Funding for a source evaluation and reduction initiative to develop tools that improve the understanding of PFAS sources in two waste streams: municipal wastewater and solid waste.
- Funding to support the development of a protocol that uses available data to identify potential sources of PFAS to support multiple MPCA programs in making data-based interventions at the highest-impact sites.
- Funding under the Infrastructure Investment and Jobs Act, though additional information is pending on the allowable uses of these funds for various PFAS-related activities.

All funding for implementation of the PFAS Monitoring Plan is aimed pollution prevention, investigation of discharges, ambient monitoring, research into toxicity, and regulatory development. The action items, processes, and timelines for each of these goals is outlined in project specific QAPPs and/or WPs.

A 4: Project Descriptions

MPCA has demonstrated the need for gathering PFAS information from facilities and sites across our programs. The PFAS Monitoring Plan outlines an approach to phasing-in monitoring based on potential risks and provides information about implementation schedules that will allow facilities and other responsible parties to understand the path forward. The timeline for implementation of the plans will vary by program and for facilities within each program. Most plans have a phased implementation approach, with some period of initial monitoring followed by future decisions based on how the results compare to response thresholds. In some cases, these phases and processes are laid out in the current PFAS Monitoring Plan. In other cases, the future phases will be designed entirely based on the results of the initial baseline monitoring.

Acquiring PFAS monitoring data is critical to support the MPCA's overall goal to prevent, manage, and mitigate PFAS pollution and by extension, fulfill MPCA's mission to protect human health and the environment. The implementation of MPCA's PFAS Monitoring Plan will coincide with the implementation of EPA's PFAS Roadmap(PFAS Strategic Roadmap: EPA's Commitments to Action 2021-2024 | US EPA). As EPA implements their roadmap from 2021-2024, they will be laying the foundation for nation-wide regulation of PFAS across multiple federal programs. Collecting data on PFAS in Minnesota at this time will facilitate a smoother transition as PFAS shift from contaminants of emerging concern to widely regulated chemicals under state and federal law.

A 4.1: Quality Assurance Process

For consideration in PFAS Monitoring Plan decision-making, all MPCA-led projects that generate data are required to be covered under this QAPP and a project specific Work Plan (WP) that is approved by a MPCA QA Coordinator and a qualified laboratory representative (Project Manager, Sales Manager, Quality Assurance Manager). All MPCA PFAS Monitoring QAPP work plans must reference the current MPCA PFAS Guidance documents (analytical and sampling) and reference this QAPP. Below is a figure of the quality assurance process from sample collection to data review, outlining the specific roles and the impact at each step of the process.

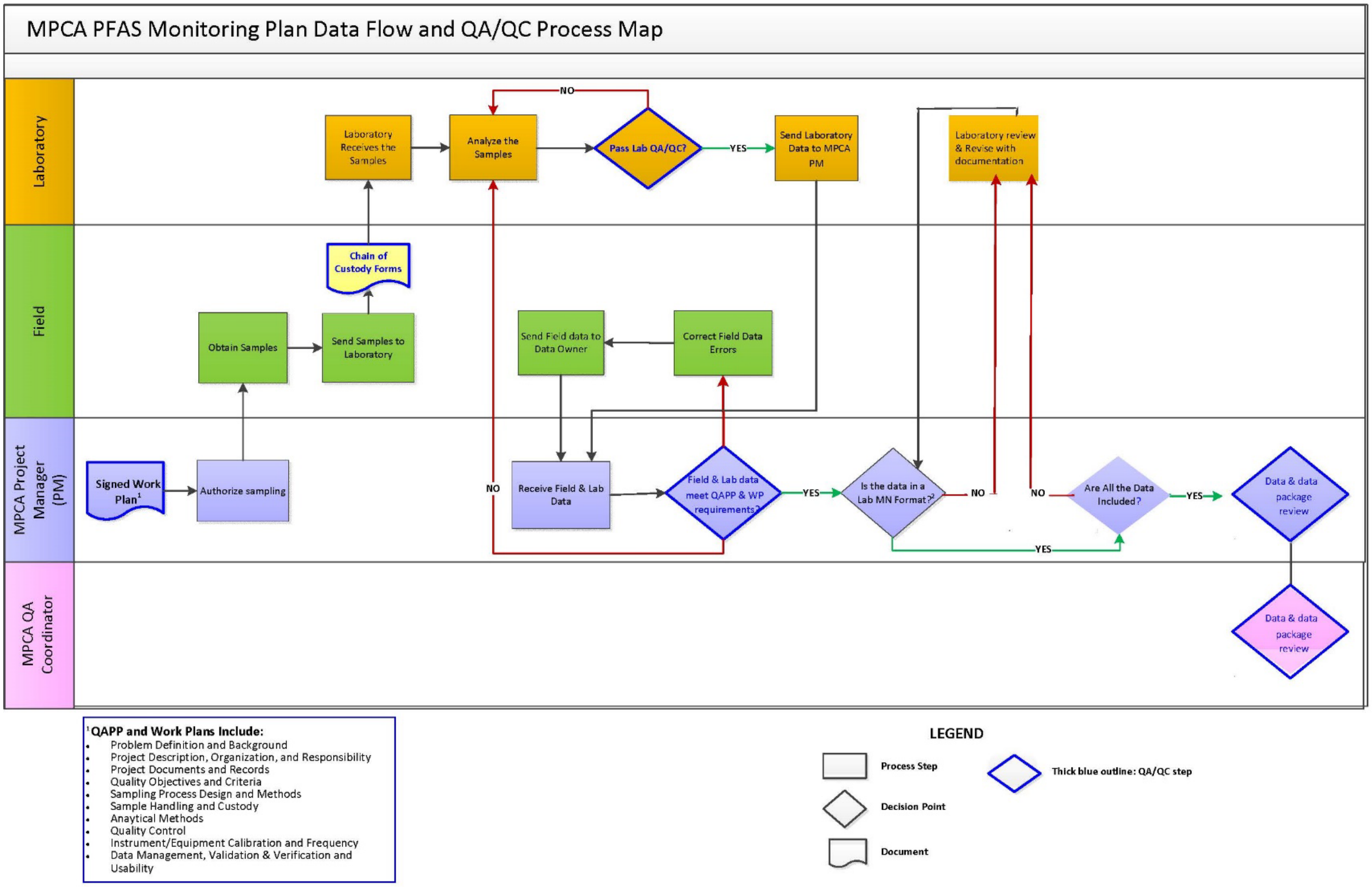

Figure 1. MPCA PFAS Monitoring Plan Data Flow and QA/QC Process Map.
Life Cycle of how data is theorized and developed, sampled, analyzed and the data flow. The rows represent different roles and their part in the sampling and data collection, analyzing, reporting and review. Time is from left to right in order of events. If a process isn't completed correctly the figure demonstrates what step it may go back to continue with the desired data quality standards.

A 4.2: Highly Contaminated Projects

An integral aspect to the first phase of the PFAS monitoring plans for all programs under the MPCA PFAS Monitoring QAPP is to establish locations that contain high levels of PFAS. Any projects that have highly contaminated sites detected through monitoring should be flagged for additional monitoring through funding through other programs, or additional QAPPs. If high levels of PFAS are detected, after the initial laboratory analysis, project staff must contact the laboratories performing the analysis prior to analysis for proper sample dilution

A 4.3: Metadata

For all matrices, the following metadata must be obtained:

1. Geographical coordinates measured by GPS to within 5 meter accuracy (see standard reporting format below)
2. Date of sampling/measurement
3. Sampling Agency/Contractor name
4. Standard Operating Procedure for method utilized

5. Main point of contact for data submittal (MPCA Project Manager/Program point of contact to resolve issues)
6. Use of unaccredited methods

A 4.4: Data Quality Requirements

A 4.4.1: Chemical Parameters

Any laboratory that performs analysis of samples for the PFAS Monitoring Plan should be certified by Minnesota Department of Health or an accreditation body acceptable to the State. Sampling and analysis Standard Operating Procedures (SOPs) for work performed under this QAPP must be submitted to the MPCA due to method modifications and to establish reproducible consistent data. Data submitted will be held to the MPCA 2022 Guidance for Per- and Polyfluoroalkyl Substances: Analytical standard. If data is outside of the set acceptance criteria it must be properly qualified.

The reporting limit (RL) for chemical entities must meet the most current and lowest of the MN standard or guidance for that matrix. When a result is between RL and Method Detection Limit (MDL), the value of that result must be reported with appropriate qualifiers. If a given RL cannot be met due to matrix interferences and high dilution rates or other unanticipated circumstances, the issue should be discussed among the project team and decided on a path forward.

A 5: Intended Data Usage

The monitoring data will be used to support the three main goals:

1. Gather Minnesota-specific information in order to craft effective policies around PFAS and their incorporation into MPCA programs;
2. Identify areas of particular concern (due to PFAS concentrations or routes of exposure) that need quick action; and
3. Gather data that galvanizes support for PFAS source reduction and pollution prevention.

All data gathered will help support future creation of effective policies around PFAS prevention, management, and clean up. Different programs have the ability to gather information that more clearly supports the other two goals – gathering data that PFAS supports source reduction and identifying areas of concern for PFAS exposure that warrant rapid follow-up actions.
At industrial facilities, PFAS monitoring will be used to identify scenarios where PFAS use, and release can be eliminated or minimized. At conduits of PFAS releases to the environment, wastewater treatment plants, waste-to-energy facilities, and auto shredders, the monitoring data will be used to identify upstream PFAS sources so those sources can be targeted for reduction. The data may be used to further motivate bans on nonessential uses of PFAS in commercial and industrial products, especially those that appear to be disproportionately contributing to PFAS pollution in waste streams. Data gathered on environmental conditions will support actions, where needed, to address or prevent impacts to the health of humans, aquatic life, or wildlife.

The project proposal and the WP or other quality documentation must state how the work proposed can achieve the intended data usage.

A 6: Project/ Task Description

Each site covered by the MPCA's PFAS Monitoring plan will have project specific WPs. All WPs developed for this QAPP, or other quality documentation should include a description of each task and which objective(s) the task will accomplish. This section of the WP can also be used to state:

1. Project Summary
2. Project Detail

- Objectives, Tasks, Sub-tasks
- Example Sub-task: Referencing and following the MPCA Guidance for Per- and Polyfluoroalkyl Substances: Analytical

3. Standards to be used
4. Any required technical audits

Project proposals, WPs, or other quality documentation must include a project schedule or timeline. If there are significant deviations from the proposed schedule, a revised schedule must be provided to the project manager, as well as other entities who are involved in the project.

A 7: Data Quality Objectives and Criteria

Data Quality Objective (DQO) process is used in scientific investigations to ensure that the type, quality, and quantity of environmental data used in decision-making are appropriate for the intended application. The DQO process used by Minnesota has seven steps:

1. State the problem that the study is designed to address.
2. Identify the decisions to be made with the data obtained.
3. Identify the types of data inputs needed to make the decision.
4. Define the boundaries (in space and time) of the study.
5. Define the decision rule that will be used to make decisions.
6. Define the acceptable limits on decision errors.
7. Optimize the design for obtaining data in an iterative fashion using information and DQOs identified in Steps 1-6.

Following these seven steps helps ensure that the project plan is carefully thought out and that the data collected will provide sufficient information to support the key decisions that must be made.

A 7.1: Chemical Parameters

A 7.1.1: Overview

The DQOs, as defined in EPA QA/G-4 (USEPA, 2006) for the PFAS Monitoring Plan projects are determined by individual program requirements. The program is responsible for defining the goals to support source reduction and identifying areas of concern for PFAS exposure that impact the program. Based on these decisions, the team will develop objectives, an action plan, and a timeline for each project.

For most PFAS analysis, a modified EPA method has been established for sampling, extraction and analysis protocols for sediment, soil, non-potable water, leachates, etc. When available, EPA protocols/methods must be used for sampling and chemical analysis, unless there is a project specific reason for using a different or modified EPA method. In such situations, the rationale for not using an established method/protocols must be detailed in the project specific WP.

The following contaminants could be found in the PFAS Monitoring Plan program location, and therefore should be considered for analysis when appropriate. The PFAS list includes the 33 analytes, listed in MPCA 2022 Guidance for Per- and Polyfluoroalkyl Substances: Analytical. The analyte list will be address and altered as needed depending on program needs.

Quality assurance objectives and processes should be developed for field sampling, chain of custody (COC), and laboratory analysis and reporting. The sampling entity (e.g., federal, state or local agency, responsible party, contractor, etc.) is responsible for field sampling and COC forms until the laboratory accepts the samples for analysis.

Specific procedures to be used for sampling, quality control, audits, preventive maintenance, and corrective actions should follow the directions of EPA Requirements for QAPPs (USEPA 2001(a)). The purpose of this section is to define quality assurance goals for precision, accuracy, and completeness. See MPCA 2022 Guidance for Per- and Polyfluoroalkyl Substances: Analytical (http://www.pca.state.mn.us/index.php/view-document.html?gid=16288) for further information.
Establishing these goals will allow the MPCA programs to judge the adequacy of the results and whether corrective actions are necessary. Data quality indicators (precision, bias, accuracy, representativeness, comparability, completeness, and sensitivity) are specific to each program and should be clearly defined in the project specific WP or other quality documentation.

Laboratory reports for chemical analysis must include:

Lab Reports must conform with the national functional guidelines. The laboratories must include level II data reports for all samples and level IV reports when requested by MPCA at a frequency of no less than once a month.

- Date of sampling;
- Date of analysis;
- Signed and completed COC form;
- Narrative of the analysis which notes items outside the laboratory QC limits, if any,
- Analytical results for the collected samples; and,
- QC sample results (e.g., blanks, duplicates, spikes).

In addition to the analytical results, the chemical analysis reports must include the percent recoveries (% R) of surrogates and internal standards and the percent recoveries (% R) and relative percent differences (RPD) of laboratory control sample/laboratory control sample duplicates and matrix spike/matrix spike duplicates. Data will be reviewed by MPCA Environmental data quality QA staff and MPCA project managers. When reviewed, the QA staff will report to the project manager any data found not meeting the requirements as defined by the MPCA 2022 Guidance for Per- and Polyfluoroalkyl Substances: Analytical documentation. Decisions on data usability are made by the project team for questionable (or qualified) data.

A 7.1.2 Quality Control & Quality Assurance

Quality Control Samples

Field quality control (QC) samples are a means of assessing quality from the point of collection. PFAS data are collected for a variety of purposes and reporting limit goals (down to parts per trillion). Appropriate field quality control processes should be taken to ensure that the sensitivity of the results desired is not compromised by potential cross contamination. Collection and analysis of field QC samples are important to ensure accuracy and representativeness of the results to the samples media, and to assess potential cross-contamination. A table of recommended field QC and frequency is attached (MPCA 2022 Guidance for Per- and Polyfluoroalkyl Substances: Sampling) and is based on the most stringent data quality objectives to account for potential contamination.

Laboratory Activities

The quality assurance objectives for accuracy, precision, completeness, representativeness, reporting limits, and comparability are described in a laboratory's Quality Assurance Manual (QAM). The QAM or similar document must include the following

a. The RL for each analyte in accordance with the project specific QAPP/WP. The project manager or principal investigator is responsible for ensuring the laboratory RL meets the DQOs of the project and to communicate any discrepancies with the MPCA QA Coordinator. The levels must be less than or equal to the limits included in the MPCA 2022 Guidance for Per- and Polyfluoroalkyl Substances: Analytical

b. Quality control limits used by the laboratory and the limits used for data validation should be referenced. Note: the control limits must be as good as or better than the data quality indicators.

c. The equations for percent recovery and relative percent difference, and a statement on how this information is used. MPCA recommends a minimum of 90 percent completeness. Note that rejected data or sampling points that do not yield a usable sample count against percent completeness. Completeness is critical to measuring how well the project was managed and completed.

If accuracy cannot be determined using random samples, complete voucher collection identifications will be an appropriate substitute. Voucher collection accuracy should be completed regardless of individual sample QA protocols. The percent accuracy is determined by comparing the agreement rate in nomenclature. The formula for determining percent recovery is as follows:

$$\%\ Accuracy = \frac{(Sample\ Taxa\ not\ in\ agreement)*100}{(Total\ Sample\ Taxa)}$$

If there is no established QA limit specific to the project, the acceptable error rate should fall below 5%.

Definitions of Precision, Accuracy, Representativeness, Comparability, and Completeness

Precision

Laboratory precision is measured through the analysis of duplicate samples. The result for the duplicate sample is compared to the result of the known sample. The relative percent difference (RPD) between the known sample result and the duplicate sample result is calculated according to the following formula:

$$RPD = \frac{|C1 - C2|}{\frac{(C1 + C2)}{2}} * 100$$

Where:
C1 = sample concentration
C2 = duplicate concentration

Precision can also be determined between the results of a laboratory control sample (LCS)/laboratory control sample duplicate (LCSD) or matrix spike (MS)/matrix spike duplicate (MSD) pair.

Accuracy

The accuracy of the measurement is gauged through the analyses of laboratory control samples (LCS)/laboratory control sample duplicates (LCSD) and internal standards. Internal standard compounds are spiked into every sample prior to extraction and analysis. The percent recovery is determined by comparing the spiked sample concentration to the environmental (un-spiked) sample concentration.

The formula for determining percent recovery is as follows:

$$\%R = \frac{(Spiked\ Sample\ Conc. - Environmental\ Sample\ Conc.)*100}{(Spiked\ Concentration\ Added)}$$

Representativeness

Representativeness of the data set is the measure that expresses the degree to which the data accurately represents the population as a whole. The methods for sample collection in the field, sample preservation, transportation to the laboratory, sample preparation, and sample analysis are reviewed to determine if appropriate procedures were followed. If the procedures as described in this QAPP were followed, sample results are considered representative of the site.

Comparability

Comparability is the degree of confidence that one data set can be compared to another data set and whether the data sets can be combined and used for decision-making purposes. The level of comparability between data sets is determined by reviewing sample collection and handling procedures, sample preparation and analytical procedures, holding times, and quality assurance protocols. When a large difference in one of the methods or procedures exists, the comparability of the data is considered low. If all the procedures were followed, data from the same site is considered comparable.

Completeness

Completeness is measured by determining the ratio of valid sample results compared to the total number of samples for a specific matrix. During data verification, the data completeness is determined by the following equation:

$$\%\ Complete = \frac{\#\ of\ valid\ results}{\#\ of\ samples\ tested} * 100$$

A completeness of 90% or better must be obtained in order for a laboratory report to be considered acceptable. Laboratory reports which are not at least 90% complete are rejected. If the laboratory is at fault, they will be responsible for securing the re-collection and re-analysis of samples.

A 8: Special Training/Certification

All field and laboratory technicians should be trained and competent to perform the work assigned to them or work directly under an experienced professional. In addition, all employees must have received Occupation Safety & Health Administration (OSHA) required safety training, such as Hazardous Waste Operations and Emergency Response Standard (HazWOpER), if working in contaminated media. Laboratory technicians must be trained in analytical techniques and remain competent to perform the assigned duties. All laboratory training must be documented via a demonstration of capability (initial and continuing) Field technicians must be trained in water safety, sampling, sample handling, and sample storage protocols and any other training required in order to perform the assigned work. Training documentation must be provided to MPCA upon request.

A 9: Documents and Records

All PFAS Monitoring Plan projects will have procedures in place to secure project records by the laboratory, the consultant, and others responsible for generating and/or storing project data. The project specific WP or other quality documentation will specify where the records are stored and document the retention schedule for the records. Electronic forms of data storage must be recoverable upon request by MPCA. All records and reports are to be maintained for five years.

Section B: Data Generation and Acquisition

B 1: Sampling Design

Sampling design should be able to:

1. Meet the objectives of the project;
2. Be scientifically defensible; and
3. Support PFAS Monitoring Plan goals and the programs stage accomplishments.

The DQOs for each task of the project must guide the sampling designs documented in the WP or other quality documentation and be approved by the appropriate parties involved in the project prior to the commencement of work. The program team for a given site will determine the DQOs which will guide sample density, and the sampling plan(s). The sampling design will normally follow a statistical model and ensuring representativeness and completeness will be considered within the design. The project specific WP or other quality documentation should provide details of statistical methods used to derive the sampling plan.

B 2: Sampling Procedures

All sampling procedures must ensure the data generated is defensible and comparable spatially and temporarily. When available, USEPA sanctioned/approved sampling and analytical methods should be used. All sampling methods, equipment, and quality assurance procedures must be detailed in a project specific WP or other quality documentation. Sampling standard operating procedures should be submitted with all quality documentation for MPCA approval and reference. Sampling procedures will include a description of the sampling method, sample bottle or container, preservatives if required, holding times, and quality assurance samples (e.g., duplicates, splits, blanks).

Field notebooks should clearly identify the sample locations, unique sample identifiers, and sample depths (depth of upper and lower limits in centimeters). Surface samples are generally considered to be 0-15 cm.

For sampling, follow MPCA 2022 Guidance for Per- and Polyfluoroalkyl Substances: Sampling. For samples suspected to be or have the possibility of being highly contaminated use the decontamination steps included in the MPCA PFAS sampling guidance and be sure to notify the laboratory of any samples suspicious of high levels upon receipt.

Any sites with history of AFFF use, extreme care must be taken when sampling to prevent spreading of PFAS into the surrounding environment or samples. Any laboratories performing the analysis must be alerted prior to sample analysis as stated in the MPCA 2022 Guidance for Per- and Polyfluoroalkyl Substances: Sampling.

B 3: Sample Custody

Only trained field personnel should collect samples. The field personnel should keep the samples in their possession, in their view, or in a secured area only accessible to them until such time as they turn custody over to another individual who has signed the COC form.

B 3.1: Chain of Custody (COC) Forms

All samples must be accompanied by a COC form or other documentation that verify the integrity of the samples when the custody changes from one entity to another. The COC will be signed by the sampler with custody maintained by the sampler through securing the samples or keeping visual contact with the samples until they are signed for by the laboratory (or shipped with the COC included in a resealable plastic bag within the cooler).

B 3.2: Handling, Storage and Transportation of Samples

Samples should be transported in a rugged container to maintain sample integrity and secure the samples from tampering. If necessary, the container should be insulated to maintain temperature control. All samples must be properly labeled in accordance with the COC. Samples must be maintained according to the analytical method.

The project specific WP or other quality documentation must detail all such requirements including who will be responsible for meeting and maintaining those requirements. Where appropriate, the COC form should note sample handling requirements.

B 4: Analytical Methods

B 4.1: Chemical Analysis

All chemical analysis methods must be identified in the project specific WP, if using established USEPA methods. If a given USEPA method is being modified, the nature of the modification and the need for the modification must be clearly stated in the WP. The WP should identify who is responsible for corrective actions at the laboratory and discuss the documentation and levels of review by management of corrective actions. The WP should also specify the turn-around time for the samples needed for the project. Any nonstandard methods being used should be discussed in detail (in an appendix, if the methods are lengthy), and how these nonstandard methods would be validated or reviewed by the laboratory and project manager/principal investigator.

B 5: Quality Control

Common field and laboratory QC checks for chemical analysis are identified in PFAS Sampling Guidance. The frequency of analysis and the control limits are also listed in PFAS Analytical Guidance. If the results don't meet the QC acceptance criteria identified, the data must be qualified appropriately, the project manager notified, and any corrective actions taken to remedy the situation should be discussed in reporting.

B 6: Instrument/Equipment Testing, Inspection, Calibration and Maintenance

B 6.1: Field Equipment

Preventive maintenance of field equipment should be performed before each sampling or field measurement event. More extensive maintenance should be performed based on hours of use and manufacturer's recommendations. Maintenance and calibration records must be available to the project team upon request.

B 6.2: Laboratory Equipment

The protocols for testing, inspection, maintenance of laboratory equipment, and preventive maintenance will be addressed in the laboratory's QAM or Standard Operating Procedures (SOP). Routine equipment calibration should be detailed in laboratory SOPs attached to this QAPP and should be available to the MPCA. If there are special calibration requirements of the analytical method (i.e., chemical analysis) used, they must be documented in the project specific WP. All equipment should be routinely serviced and maintained per the manufacturer's instructions. Records of maintenance should be available to the project team upon request. Corrective Actions taken by the laboratory will be documented and noted on laboratory reports when data is affected for the project.

B 7: Inspection/Acceptance of Supplies and Consumables

All sampling supplies and equipment must be inspected to ensure they are in proper working order and are free of contamination. Before setting off for sampling, the field crew must ensure there are adequate supply of labels, sample containers, writing utensil, decontamination supplies, extra batteries for GPS and other electronic equipment, bug spray and sunscreen (if used and will not interfere with sampling or analysis), U.S. Coast Guard approved personal flotation devices, fuel for boats, etc. All items needed by the sampling crew should be listed in the project WP or other quality documentation.

The laboratory performing sample analysis must ensure that supplies and consumables are inspected for usability and quality upon receipt. The laboratory must identify a contact that will ensure the supply and quality of all consumables are tracked and replenished as needed.

B 8: Non-direct Measurements and Secondary Data

Historical data may be used to compare temporal differences. However, the methods and equipment used in the historical data must be similar. If methods and equipment used in the two data sets are different from each other, the project manager must explain why it is appropriate to compare the data sets.

Use USEPA's *Guidance on Quality Assurance Project Plans for Secondary Research Data* (USEPA 1999) for using data from other sources as guidance. The quality of the secondary data must meet the DQOs of the project and the data source and date must be clearly stated.

B 9: Data Management

The environmental consultant or field services contractor will document field data in dedicated notebooks and on field forms.

The contract laboratories will provide data as final analytical reports using a pdf format. The report shall include the report elements required as part of the laboratory's accreditation. These reports will have been reviewed and approved by the laboratory's technical QA/QC and project management staff. Results are also provided electronically in the MPCA-developed EQuIS EDD format Lab_MN (Minnesota Pollution Control Agency Lab_MN Format for EDP - EarthSoft, Inc. Environmental Data Management Software)

Upon laboratory report delivery, the environmental consultant's or MPCA personnel will verify the analytical data for compliance with this QAPP and the WP by completing a data review including elements from the MPCA *Laboratory Data Review Checklist* which follows the general format of the USEPA *National Functional Guidelines*. The usability of results that do not meet QAPP/WP requirements will be discussed in the final report.

The environmental consultant or State contract laboratory may take the laboratories' EQuIS submittal and add any assigned data qualifiers as well as sampling information prior to submittal of the EQuIS deliverable to the MPCA management staff in accordance with MPCA EQuIS data practices.

Data is loaded and maintained in EQuIS following MPCA data practices.

B 10: Data Rejection

Any data which does not meet the established QA/QC criteria defined in the project specific WP or other quality documentation will be qualified as estimated or rejected depending on the use of the data. All field data must be evaluated by the technical staff to ensure they are compliant with this QAPP and the project WP or other quality documentation. Data collected judged to be out of compliance are qualified as estimated or rejected, and maybe re-collected if deemed necessary by the project team

Section C: Assessment and Oversight

C 1: Assessment and Response Actions

The project manager of a given project is responsible for immediately notifying the MPCA project manager of any data that may be questionable or does not meet the QA/QC criteria established for the project. The MPCA staff will determine the best course of action. Assessments to include laboratory or field audits may be performed based upon the identified needs of by the project team.

C 2: Reports to the PFAS Monitoring Plan Program Leaders

The entity conducting the project must provide progress reports to the MPCA PFAS Monitoring Plan program lead on a routine basis. The project specific WP or other quality documentation should state who would be submitting the report and to whom and when they will be submitted.

For reports containing chemical analysis the following must be submitted:

- Tabulated sample results
- COC forms
- Batch QC
- Case Narrative
- Data Qualifiers
- Associated field forms and field notes

All reports must be reviewed and approved by the project manager and laboratory's QA/QC officer, and project management staff. Corrective actions performed by the field or laboratory staff that affect the data will be documented in reports to the project team on a regular basis. Follow up data audits or on-site audits may be performed based upon these reports and/or corrective actions performed.

Section D: Data Validation and Usability

D 1: Data Review, Verification, Validation and Methods

The project manager or designated experienced technician must verify data is correct as reported. 100% of the raw data must be verified against the report and ensure transposition errors were not made.

The laboratory QA/QC officer must review all reports to verify the data meets all QAPP/WP requirements. A third-party data validation may be required for projects conducted under regulatory oversight and the third party will be specified in a project specific QAPP or WP. The MPCA project manager(s) will determine the level of data quality required for a given project, based on program requirements. Raw data must be available to the funding source granter, if requested.

D 1.1: Treatment of non-detect data:

To use statistical methods, for example the Kaplan-Meier method, it is important that the method of reporting non-detect values is clearly specified in the laboratory data report, and that both the MDL and RL are included. Concentrations below the Reporting Limit should be reported as follows:

- Values between the MDL and RL: report the actual value, flagged as estimated.
- Values below the MDL: report as less than (<) MDL.

It is important to notify the analytical laboratory of the above requirement before contracting with them. If the laboratory cannot provide the required information or the project team believes this is not necessary for the project, the reasons must be detailed in the project specific WP or other quality documentation.

The MPCA PFAS Monitoring Plan data quality coordinator will review the submitted data to verify all QC requirements are met and the required information is provided in the laboratory report in accordance with project requirements. If corrective actions are needed the program team and the data quality coordinator will meet to discuss discrepancies and make decisions with PFAS Monitoring Plan partners if necessary, on how to deal with data not meeting requirements or sampling not meeting the completeness requirements.

D 2: PFAS Monitoring Plan Data Submittal Requirements

All PFAS Monitoring Plan data must be submitted in electronic format using the Lab_MN EDD, which is the required EQuIS-ready format. Submit the EDD, COC and Level II data package to wqdata.mpca@state.mn.us. Contact the wqdata email for a list of the current MPCA required qualifiers.

The current Data System manager is the MPCA and file format information is obtained from the Environmental Quality Information System webpage (www.pca.state.mn.us/about-mpca/environmental-quality-information-system-equis). Data inclusion into the MPCA EQuIS Data System will require the data submitters adherence to a hierarchical labeling scheme provided as templates by the MPCA. Facility Code, Project Task Code, Project Manager, MN Location Identifier (SYS_LOC_CODE) and sample details are required to be included on the EDD.

Section E: References

Minnesota Pollution Control Agency, 2022. *PFAS Monitoring Plan*. https://www.pca.state.mn.us/sites/default/files/p-gen1-22b.pdf

Minnesota Pollution Control Agency, 2022. *Guidance for Per- and Polyfluoroalkyl Substances: Analytical.* https://www.pca.state.mn.us/sites/default/files/p-eao2-28.pdf

Minnesota Pollution Control Agency, 2022. *Guidance for Per- and Polyfluoroalkyl substances (PFAS): Sampling*. https://www.pca.state.mn.us/sites/default/files/p-eao2-27.pdf

U.S. Environmental Protection Agency, July 1999. *QAPP Requirements for Secondary Data Research Projects*. http://www.epa.gov/QUALITY/qs-docs/found-data-qapp-rqts.pdf

U.S. Environmental Protection Agency, 2000(b). CIO 2105.0 *Policy and Program Requirements for the Mandatory Agency-wide Quality System*. http://www.epa.gov/irmpoli8/policies/21050.pdf

U.S. Environmental Protection Agency, 2001(a) (Reissued May 2006). USEPA *Requirements for Quality Assurance Project Plans (QA/R-5)*, USEPA/240/B-01/003, Office of Environmental Information. http://www.epa.gov/QUALITY/qs-docs/r5-final.pdf

U.S. Environmental Protection Agency, February 2006. *Guidance on Systematic Planning Using the Data Quality Objectives Process*, (QA/G-4), USEPA/240/B-06/001, Office of Environmental Information. http://www.epa.gov/quality/qs-docs/g4-final.pdf

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Appendix 1

Appendix B. Comparison of PFAS target analytes detectable by analytical methods

Target analyte name	Abbr.	CASRN	EPA Method 1633	OTM-45	SW-846 Method 8327	EPA Method 537.1*
Perfluoroalkyl carboxylic acids (PFCAs)						
Perfluorobutanoic acid	PFBA	375-22-4	x	x	x	
Perfluoropentanoic acid	PFPeA	2706-90-3	x	x	x	
Perfluorohexanoic acid	PFHxA	307-24-4	x	x	x	x
Perfluoroheptanoic acid	PFHpA	375-85-9	x	x	x	x
Perfluorooctanoic acid	PFOA	335-67-1	x	x	x	x
Perfluorononanoic acid	PFNA	375-95-1	x	x	x	x
Perfluorodecanoic acid	PFDA	335-76-2	x	x	x	x
Perfluoroundecanoic acid	PFUnA, PFUnDA	2058-94-8	x	x	x	x
Perfluorododecanoic acid	PFDoA, PFDoDA	307-55-1	x	x	x	x
Perfluorotridecanoic acid	PFTrDA, PFTrA	72629-94-8	x	x	x	x
Perfluorotetradecanoic acid	PFTeDA, PFTA	376-06-7	x	x	x	x
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5		x		
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6		x		
Perfluoroalkyl sulfonic acids (PFSAs) (Acid Form)						
Perfluorobutanesulfonic acid or Perfluoro-1-butanesulfonic acid	PFBS	375-73-5	x	x	x	x
Perfluoropentanesulfonic acid or Perfluoro-1-pentanesulfonic acid	PFPeS	2706-91-4	x	x	x	
Perfluorohexanesulfonic acid or Perfluoro-1 -hexanesulfonic acid	PFHxS	355-46-4	x	x	x	x
Perfluoroheptanesulfonic acid or Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8	x	x	x	
Perfluorooctanesulfonic acid or Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1	x	x	x	x
Perfluorononanesulfonic acid or Perfluoro-1-nonanesulfonic acid	PFNS	68259-12-1	x	x	x	
Perfluorodecanesulfonic acid or Perfluoro-1-decanesulfonic acid	PFDS	335-77-3	x	x	x	

Target analyte name	Abbr.	CASRN	EPA Method 1633	OTM-45	SW-846 Method 8327	EPA Method 537.1*
Perfluorododecanesulfonic acid or Perfluorododecane sulfonate	PFDoS	79780-39-5	x	x		
Sodium perfluoro-1-dodecanesulfonate	PFDoS	1260224-54-1		x		
Fluorotelomer sulfonic acids or Fluorotelomer sulfonates (FTS)						
1*H*,1*H*, 2*H*, 2*H*-Perfluorohexane sulfonic acid	4:2 FTS	757124-72-4	x	x	x	
1*H*,1*H*, 2*H*, 2*H*-Perfluorooctane sulfonic acid	6:2 FTS	27619-97-2	x	x	x	
1*H*,1*H*, 2*H*, 2*H*-Perfluorodecane sulfonic acid	8:2 FTS	39108-34-4	x	x	x	
1H,1H,2H,2H-perfluorododecane sulfonate (10:2)	10:2 FTS	120226-60-0		x		
Perfluorooctane sulfonamides or Perfluorinated sulfonamides (FOSAs)						
Perfluorooctanesulfonamide or Perfluoro-1-octanesulfonamide	PFOSA, FOSA	754-91-6	x	x	x	
N-methyl perfluorooctanesulfonamide	NMeFOSA, MeFOSA	31506-32-8	x	x		
N-ethyl perfluorooctanesulfonamide	NEtFOSA, EtFOSA	4151-50-2	x	x		
Perfluorooctane sulfonamidoacetic acids or Perfluorinated sulfonamidoacetic acids (FOSAAs)						
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA, MeFOSAA	2355-31-9	x	x	x	x
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA, EtFOSAA	2991-50-6	x	x	x	x
Perfluorooctane sulfonamide ethanols or Perfluorinated sulfonamide ethanols (FOSEs)						
N-methyl perfluorooctanesulfonamidoethanol or 2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	NMeFOSE, N-MeFOSE	24448-09-7	x	x		
N-ethyl perfluorooctanesulfonamidoethanol or 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	NEtFOSE, N-EtFOSE	1691-99-2	x	x		
Per- and Polyfluoroether carboxylic acids						
Hexafluoropropylene oxide dimer acid	HFPO-DA (GenX)	13252-13-6	x	x		x
4,8-Dioxa-3*H*-perfluorononanoic acid†	ADONA	919005-14-4	x	x		x
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	x	x		
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	x	x		
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	x	x		

Target analyte name	Abbr.	CASRN	EPA Method 1633	OTM-45	SW-846 Method 8327	EPA Method 537.1*
Ether sulfonic acids						
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS (F-53B Major)	756426-58-1	x	x		x
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate or 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid**	11Cl-PF3OUdS (F-53B Minor)	763051-92-9, 83329-89-9	x	x		x
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	x	x		
Fluorotelomer carboxylic acids						
3-Perfluoropropyl propanoic acid, 3:3 Fluorotelomer carboxylic acid	3:3 FTCA	356-02-5	x	x		
2*H*,2*H*,3*H*,3*H*-Perfluorooctanoic acid, 5:3 Fluorotelomer carboxylic acid	5:3 FTCA	914637-49-3	x	x		
3-Perfluoroheptyl propanoic acid, 7:3 Fluorotelomer carboxylic acid	7:3 FTCA, FHpPA	812-70-4	x	x		
Other compounds						
Decafluoro-4-(pentafluoroethyl)cyclohexanesulfonate	PFecHS	67584-42-3		x		
2H-perfluoro-2-decenoic acid	8:2 FTUCA, FOUEA	70887-84-2		x		
2-perfluorodecyl ethanoic acid	10:2 FDEA	53826-13-4		x		
2-perfluorooctyl ethanoic acid	8:2 FTA, FOEA	27854-31-5		x		
2H-perfluoro-2-octenoic acid	6:2 FHUEA	70887-88-6		x		
2-perfluorohexyl ethanoic acid	6:2 FTCA, 6:2 FHEA	53826-12-3		x		

*This method was modified as allowed by Pace® for the data analysis as presented in this report. Additional PFAS target analytes detected by the modified method are not noted here.

**OTM-45 includes the analyte 11Cl-PF3OUdS under both CASRN 763051-92-9 and CASRN 83329-89-9, and treats the two compounds as one. For the purposes of the MPCA's air emissions inventory, however, the two are treated separately, meaning MPCA expects detections of 51 analytes to be reported, rather than the 50 reflected by EPA's description of OTM-45.

†ADONA, as with many PFAS, is available as both a sodium salt (no CASRN) and an ammonium salt, Ammonium 4,8-dioxa-3H-perfluorononanoate (CASRN 958445-44-8).

Other methods used by facilities reporting data under the PFAS Monitoring Plan include 3M Company method ETS-8-154.3; Pace® PFAS ID; and SGS AXYS Method MLA-110 (similar to EPA Draft Method 1633).