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| Minnesota Pollution Control Agency (MPCA), 520 Lafayette Road North, St. Paul, MN 55155-4194 | MPCA Municipal Wastewater PFAS Monitoring Sampling Template  Wastewater permitting  Municipal Wastewater PFAS Monitoring Plan  Doc Type: Form |

## Instructions:This form will be used by all Wastewater Facilities that will be participating in the Municipal Wastewater *Per- and polyfluoroalkyl substances* (PFAS) Monitoring Plan. Please fill out form and submit to [jaramie.logelin@state.mn.us](mailto:jaramie.logelin@state.mn.us). For questions, please contact Jaramie Logelin at 218-302-6640.

Contact information

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| Facility name: | |  | | | | | | | | | | |
| Permit number: | |  | | | | |  | | | |  | |
| Facility PFAS Monitoring contact: | | | |  | | | | | |  |  | |
| Email: |  | | | | | | | | | Phone: |  | |
| Hours of operation: | | |  | | | Days of the week: | | |  | | |  |
| Preferred sample collection time\*: | | | | |  | | |  | | | | |
| *\*Preferred sample times will try to be honored but may not always able to be accommodated.* | | | | | | | | | | | | |

Project objectives and project description

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| Example summary: |  | |
| *Monitoring Plan objective: Our facility will identify the specific influent monitoring location as part of this plan and will allow the MPCA sample collection and sample analysis contractor to collect and analyze the first two influent sampling events. If the MPCA does not acquire funding for the remaining two influent sampling events, our facility will complete the remaining portions of the municipal wastewater treatment facility PFAS sampling template.*  *\*Please indicate here if your community has separate influents for the domestic and industrial sources that are not combined prior to primary wastewater treatment. The MPCA will is willing to collect two influent samples when deemed appropriate.* | | |
| **Please summarize the project objectives and project description:** | | |
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| **Please describe the specific influent sampling location, all samples will be collected as an individual grab sample independent of the facility’s composite sampler.** | | |
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| Please indicate if your facility will be asking the MPCA contractor to complete a split influent sample: Yes  No | | |
| Note: The MPCA is offering to include TOP Assay in the covered cost of the sampling for the first and second sampling events. The MPCA also intends to offer this analysis for the third and fourth sampling events if additional funding is obtained. The MPCA asks that each facility consider opting in to have this analysis included. The MPCA believes the TOP Assay will assist permittees in obtaining a more complete understanding of PFAS entering their wastewater facility and will help to guide source identification and reduction efforts. If funding is not obtained for the third and fourth sampling events, the sampling plan can be amended to reflect any needed changes. The TOP Assay results are for informational purposes only. The MPCA will not use the post oxidation results for development of the response thresholds as it applies to the PFAS MOU. Response thresholds will be developed by the selected method based on the individual influent samples before any oxidation process may take place as part of the optional TOP Assay analysis. | | |
| Yes  No | | Total Oxidizable Precursors (TOP): PFAS are a large family of over 5,000 individual chemicals that have diverse chemical structures. Only about 25-40 individual chemical structures in the PFAS family are available for analysis from commercial laboratories – the rest are not captured by current PFAS target analyte lists. However, some of these thousands of PFAS can transform into the chemicals that *are* on the regularly measured PFAS analyte list (like PFOA, PFOS, PFHxA….). These compounds are often called “precursors.” Often, the group of PFAS that are all precursors to the same chemical are called “pre-that chemical,” like “pre-PFOA” or “pre-PFHxA.” For example, complicated or obscure PFAS with chemical structures containing an 8-carbon chain of fluorinated carbons will likely break down into perfluoro-*octanoic* acid (PFOA) or perfluoro-*octanoic* sulfonate (PFOS) in the environment. These are called “pre-PFOA” or “pre-PFOS.” Similarly, PFAS with 6-carbon chains of fluorinated carbons will likely break down into perfluoro-*hexanoic* acid (PFHxA) or perfluoro-*hexanoic* sulfonate (PFHxS). The TOP assay, in which the samples are first oxidized and then analyzed for a target list of PFAS, was developed to estimate the number of precursors there are to each of the analytes in the target list. By comparing a traditional chemical analysis with the TOP assay, you can determine how much of the PFAS coming into a facility is in the form of the targeted substance (like PFOA) and how much in entering in the form of a precursor to that chemical (“pre-PFOA”). This information can useful when trying to discover the sources of certain PFAS into the facility and can give a worst-case scenario of the number of targeted analytes that might be released from the facility after transformation occurs |

Other Method Considerations

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| Additional PFAS analytical method considerations. Each community may also be interested in knowing about other potential analytical methods that could be employed to further assist in source identification. These additional methods would be above and beyond the scope the MPCA PFAS MOU and would need to complete at the expense of each community if desired.  These types of methods aim to quantify large groups of PFAS in environmental samples   1. Draft Method 1621 for Adsorbable Organic Fluorine (AOF): In the case of PFAS, analytical standards are not available for every compound. A screening level method for AOF can help provide context for what targeted analyses might miss, especially if used on a sample where PFAS contamination is suspected 2. Total Organic Fluorine (TOF): TOF should capture all PFAS, not just the absorbable fraction (e.g., AOF). TOF may be more useful than AOF; however, does not produce results for any specific PFAS compound(s). 3. Non-Targeted Analysis: Uses high resolution mass spectrometry (HRMS) capable of identifying all known and unknown analytes in a sample. In order to identify unknown compounds, liquid chromatography/tandem mass spectrometry (LC/MS/MS) analyses are applied and followed by quantification if an adequate standard exists. Otherwise, semi-quantitation may be possible based on known, structurally similar analytes. These methods can screen for lists of known suspects and can discover new or unknown analytes. HRMS data can be stored and analyzed later for newly identified analytes. |

Lab Considerations

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| If samples three and four are not covered by the MPCA funding or if the facility would like to complete extra analytical work at an accredited lab other than the MPCA selected lab please review and complete as necessary | |
| As of December 2022, there were 14 labs certified with MNELAP for some sort of PFAS work. Not all laboratories will have a full scope of PFAS analytes. To look for labs with MN accreditation (MNELAP), please follow the below steps: | |
| * + - * 1. Visit website: <https://eldo.web.health.state.mn.us/public/accreditedlabs/labsearch.seam> | |
| * + - * 1. Select “Customized Search.” | |
| * + - * 1. Select “Perfluorohexanoic acid (PFHxA)”, a common PFAS analyte, in the analyte field | |
| * + - * 1. Select “search” and see the results populate below. | |
| * + - * 1. You may click on the lab to view the full suite of analytes they are accredited for. Lab capacity will depend on sample types (matrices), sample volume expected and the specific analytes that are going to be requested. Each lab will have different capabilities and timelines. | |
| 1. What is the laboratory’s MN Lab Certification No./State code? |  |
| 1. What is the laboratory’s reporting limits (RLs) for each PFAS compound (obtain list from lab)? At a minimum the RLs should be under 4 ng/l for the following PFAS compounds: PFOA, PFOS, PFHxA, PFBS, and PFHxS. And at least 6 ng/l for PFBA. The remaining PFAS compounds listed in Appendix, may have higher RLs, but as close to the target RLs as possible. | |
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| 1. What method does your laboratory intend on utilizing (check all that apply): | |
| Draft Method 1633 for 40 compounds  EPA Method 8327 for  compounds  Modified EPA Method 537 for  compounds\*\*  \*\*Note: See Appendix A for a list containing the goal for minimum # of desired compounds. Complete the right column for each compound. | |
| 1. Chain of Custody Forms (contact lab), ensure you acquire the facility specific identifier from the MPCA for your location. This unique ID will be used to submit the monitoring data in the EQuIS system. | |

Sampling Considerations

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| 1. Quality Control. Note: The MPCA’s 2022 PFAS Sampling Guidance (see pg. 5 of 7) discusses considerations for quality control samples. |
| 1. Due to the ubiquitous nature of PFAS, sampling crews must review all materials and sampling protocols to avoid contamination and possible adsorption issues. Materials that may come into contact with samples and therefore could potentially introduce bias include, but are not limited to:  * Teflon, polytetrafluoroethylene (PTFE) * Waterproof coatings containing PFAS * Pipe thread compounds and tape * Personal hygiene and personal care products * Food packaging * …and much more (see MPCA’s Guidance for Per- and Polyfluoroalkyl substances (PFAS): Sampling document)   It is recommended to have a detailed discussion with the laboratory chosen for sample analysis to determine recommended sampling procedures. |
| 1. Gloves: Powderless [nitrile gloves](https://youtu.be/9jOArnpBZpU?t=333). |
| 1. [The samples, ice, and chain of custody (COC)](https://youtu.be/zrwhwSI-R9M?t=131) should always be bagged in polyethylene (i.e., Ziploc®) bags. |
| 1. [Chain of Custody](https://youtu.be/zrwhwSI-R9M?t=608) and other forms should be single bagged in polyethylene resealable storage bags and taped to the inside of the cooler lid. |
| 1. The cooler should be taped closed with a custody seal and shipped by overnight courier. Samples should be shipped as soon as possible (e.g. overnight) to ensure the samples arrive within the analytical holding time specified by the lab. |

Appendix A

| Compound (Acronym) (Source of Compound list and Reporting Limit (RL) goals\* [found here](https://www.pca.state.mn.us/sites/default/files/p-eao2-06.pdf)) \*Subject to change upon guidance revision | Aqueous Reporting Limit (RL) Goals (ng/L) | CAS Number | Will Lab Analyze? |
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| **Perfluorobutanate (PFBA)** | under 6 | 375-22-4 | Yes  No |
| Perfluoropentanoate (PFPeA) |  | 2706-90-3 | Yes  No |
| **Perfluorohexanoate (PFHxA)** | under 4 | 307-24-4 | Yes  No |
| Perfluoroheptanoate (PFHpA) |  | 375-85-9 | Yes  No |
| **Perfluorooctanoate (PFOA)** | under 4 | 335-67-1 | Yes  No |
| Perfluorononanoate (PFNA) |  | 375-95-1 | Yes  No |
| Perfluorodecanoate (PFDA) |  | 335-76-2 | Yes  No |
| Perfluoroundecanoate (PFUnA) |  | 2058-94-8 | Yes  No |
| Perfluorododecanoate (PFDoA) |  | 307-55-1 | Yes  No |
| Perfluorotridecanoic Acid (PFTrDA) |  | 72629-94-8 | Yes  No |
| Perfluorotetradecanoic acid (PFTeDA) |  | 376-06-7 | Yes  No |
| **Perfluorobutanesulfonate (PFBS)** | under 4 | 375-73-5 | Yes  No |
| Perfluoropentanesulfonate (PFPeS) |  | 2706-91-4 | Yes  No |
| **Perfluorohexanesulfonate (PFHxS)** | under 4 | 355-46-4 | Yes  No |
| Perfluoroheptanesulfonate (PFHpS) |  | 375-92-8 | Yes  No |
| **Perfluorooctanesulfonate (PFOS)** | under 4 | 1763-23-1 | Yes  No |
| Perfluorononanesulfonate (PFNS) |  | 474511-07-4 | Yes  No |
| Perfluorodecanesulfonate (PFDS) |  | 335-77-3 | Yes  No |
| Perfluorododecanesulfonate (PFDoS) |  | 79780-39-5 | Yes  No |
| 4:2 Fluorotelomer sulfonic acid (4:2 FTS) |  | 757124-72-4 | Yes  No |
| 6:2 Fluorotelomer sulfonic acid (6:2 FTS) |  | 27619-97-2 | Yes  No |
| 8:2 Fluorotelomer sulfonic acid (8:2 FTS) |  | 39108-34-4 | Yes  No |
| N-Methylperfluorooctanesulfonamidoacetic acid (N-MeFOSAA) |  | 2355-31-9 | Yes  No |
| N-Methylperfluorooctanesulfonamidoacetic acid (N-EtFOSAA) |  | 2991-50-6 | Yes  No |
| Perfluorooctane Sulfonamide (PFOSA) |  | 754-91-6 | Yes  No |
| N-Methyl perfluorooctane sulfonamide (N-MeFOSA) |  | 31506-32-8 | Yes  No |
| N-Ethyl perfluorooctane sulfonamide (N-EtFOSA) |  | 4151-50-2 | Yes  No |
| N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE) |  | 24448-09-7 | Yes  No |
| N-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) |  | 1691-99-2 | Yes  No |
| Hexafluoropropylene oxide dimer acid (HFPO-DA) |  | 13252-13-6 | Yes  No |
| 3H-Perfluoro-3-[(3-methoxy-propoxy) propanoic acid] (ADONA) |  | 919005-14-4 | Yes  No |
| 9-Chlorohexadecafluoro-3-oxane-1-sulfonic acid (9Cl-PF3ONS) |  | 756426-58-1 | Yes  No |
| 11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11CL-PF3OUdS) |  | 763051-92-9 | Yes  No |