PFAS ambient background concentrations

Per- and polyfluoroalkyl substances (PFAS), previously called perfluorochemicals (PFCs), are a large family of manmade, persistent chemicals that are found throughout the environment. PFAS are used in a wide variety of industrial processes and commercial products; however, not all uses of PFAS in industrial or commercial settings are known. The ubiquity of PFAS use coupled with their long environmental half-lives contributes to the widespread occurrence of PFAS in the environment and in our bodies. PFAS cannot solely be considered a problem around areas where large quantities have been manufactured, disposed of, or spilled. PFAS are present in nearly all parts of our environment due to long-range atmospheric transport. Many PFAS are also highly mobile in the environment and can travel long distances via groundwater and surface water. PFAS are currently detected globally, even in parts of the world that have never been inhabited by humans. For additional information about PFAS refer to the Minnesota Pollution Control Agency's (MPCA) PFAS Blueprint.¹

The goal of this document is to summarize the best available information related to ambient background levels of PFAS in various environmental media, with preference given to Minnesota (MN) specific datasets.

Ambient background can be defined as the concentration of a contaminant in water, soil or other media that is the sum of the naturally occurring background concentration (if applicable) and the contaminant levels that have been introduced by general anthropogenic activity (not specifically related to a direct release/source). Given that PFAS are manmade, there is no natural background for these contaminants, therefore, they can only be classified to have anthropogenic background.

Where the term "ambient" is used to refer to monitoring activities such as for ambient groundwater or ambient air monitoring, it represents the assessment of pollutant levels by measuring the pollutants in the surrounding environment.

Why is it important to understand PFAS ambient background in Minnesota?

There are several reasons why understanding ambient background concentrations of PFAS is useful to regulators, regulated entities, and the public. Ambient background concentrations inform our understanding of baseline levels of contamination that can be expected even in "pristine" or "non-impacted" regions of the state. This understanding could inform policy development regarding chemical management and disposal. It could also inform site-specific decisions regarding the management of contaminated soil or water and shed light on potential proximal sources of contamination present. Finally, this information could be useful to members of the public who wish to understand baseline levels of PFAS they may encounter in the MN environment.

This document is not intended to provide numeric thresholds for determining if a site exceeds ambient background conditions. Rather, this document provides a narrative summary of existing information and a range of PFAS concentrations that could be generally expected to be found in the ambient environment.

This document describes ambient background conditions for the environmental media outlined in **Table 1**, which also provides a summary of overall conclusions. It is important to note that there are variations in study design and analytical methods that add uncertainty to cross-study comparisons. Therefore, the information presented in this document should be interpreted with this important caveat in mind.

¹ MPCA 2021. Minnesota's PFAS Blueprint. Minnesota Pollution Control Agency. February 2021. <u>https://www.pca.state.mn.us/sites/default/files/p-gen1-22.pdf</u>.

Table 1. Summary of general conclusions for PFAS ambient background concentrations.

| Environmental media / Document section | Location | Ambient background concentrations | Comment |
|---|------------------------------|---|---|
| Groundwater | MN | Generally, below current ¹ laboratory reporting limits | Refer to the "Groundwater" section and Table 2 |
| Air, precipitation, and surface water | MN and other locations | Air: inhalation is not likely to be a significant route of exposure to PFAS with existing inhalation guidance values Precipitation and surface water: generally, close to or below current ¹ laboratory reporting limits | Refer to the "Air, precipitation, and surface water" section. PFAS do not readily break down in the environment, any deposition to aquatic and terrestrial environments leads to PFAS building up over time and could lead or contribute to water quality and ecosystem impairments. |
| Soil | MN and other locations | Except for PFOA, appear to be below 2024 MPCA soil reference values | Refer to the "Soil" section and Table 13 |

1 – current as of the publication of this document. Reporting limits are likely to change and improve over time.

PFAS Acronyms

| PFAS | Per- and polyfluoroalkyl substances |
|----------|--|
| PFCA | Perfluorocarboxylate |
| PFSA | Perfluorosulfonate |
| PFOS | Perfluorooctane sulfonate |
| PFOA | Perfluorooctanoate |
| PFBA | Perfluorobutanoate |
| PFBS | Perfluorobutane sulfonate |
| PFHxS | Perfluorohexane sulfonate |
| PFHxA | Perfluorohexanoate |
| PFHpA | Perfluoroheptanoate |
| PFNA | Perfluorononanoate |
| PFDA | Perfluorodecanoate |
| PFUnDA | Perfluoroundecanoate |
| PFDS | Perfluorodecanesulfonate |
| PFPeA | Perfluoropentanoate |
| PFPeS | Perfluoropentane sulfonate |
| PFHpS | Perfluoroheptane sulfonate |
| HFPO-DA | Hexafluoropropylene Oxide Dimer Acid |
| N-MeFOSA | N-Methylperfluorooctanesulfonamide |
| N-MeFOSE | N-Methylperfluoro-1-octanesulfonamidoethanol |
| N-EtFOSA | N-Ethylperfluoroctanesulfonamide |
| PFOSA | Perfluorooctane sulfonamide |
| 6:2 FTS | Fluorotelomer sulfonate (1H, 1H, 2H, 2H-perfluorooctane sulfonic acid) |
| | |

Groundwater

Minnesota monitors for contaminants of concern in the statewide Ambient Groundwater Monitoring Network (AGWN). Since 2006, MPCA has monitored for PFAS in 276 wells within the AGWN. About three-quarters of these wells are shallow monitoring wells (wells that intersect the water table and are generally ≤ 75 feet deep), and the remainder are mostly domestic water-supply wells. Fifty of the AGWN wells were chosen for this analysis because of their location within an "undeveloped" land use – primarily located in state forests and away from urban or agricultural development (**Figure 1**). Specifically, these wells are in areas where 75% of the area within a 500-meter (m) buffer surrounding the well was undeveloped land at the time of well installation; the U.S. Geological Survey National Land Cover Database was used to determine land use. PFAS concentrations for wells in the "undeveloped" land use (areas with no known proximal sources of PFAS) are interpreted to represent ambient background conditions.

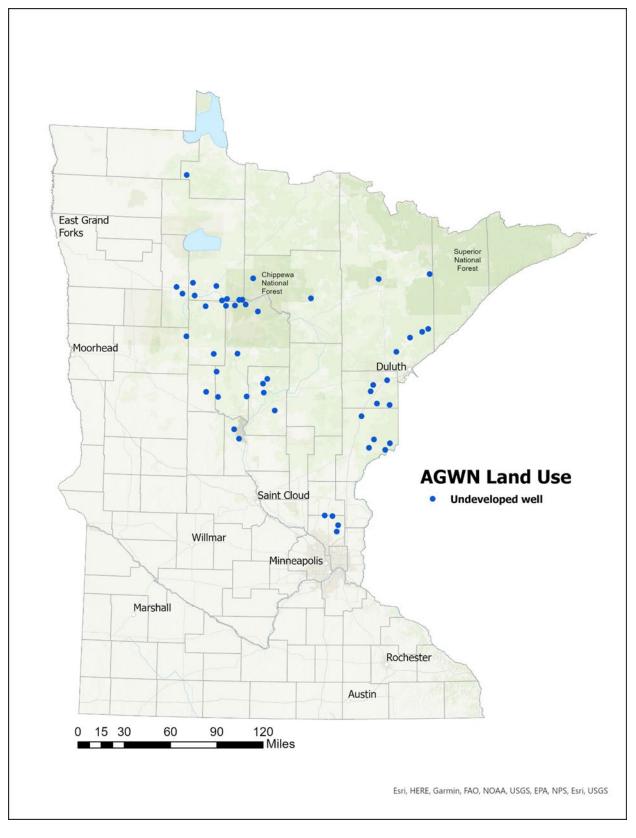
This summary is focused on the most recent PFAS monitoring data for the 50 chosen wells in the well network. In the majority of wells, the most recent samples were collected in 2019. **Table 2** provides summary statistics for the 50 wells included in the analysis. All wells included in the analysis are shallow monitoring wells (\leq 75 feet deep) with the few PFAS detects reported in **Table 2** occurring within the \leq 25-foot depth. One GenX chemical, HPFO-DA, has not been detected in any ambient groundwater well.

| Compound | Detection frequency | Concentrations range – detects (ng/L) | Reporting limit range (ng/L) |
|----------|------------------------|--|---------------------------------|
| PFOA | 2% (1 of 50) | 1.85 | <1.56 - <3.11 |
| PFOS | 0% | N/A | <1.56 - <3.11 |
| PFBS | 2% (1 of 50) | 2.95 | <1.55 - <3.11 |
| PFBA | 6% (3 of 50) | 8.44 - 166 | <6.23 - <12.4 |
| PFHxS | 0% | N/A | <1.62 - <3.25 |
| PFHxA | 0% | N/A | <1.62 - <10.3 |
| HFPO-DA | 0% | N/A | <6.08 - <12.4 |

Table 2. PFAS occurrence in undeveloped land use wells (n = 50).

Less than (<) values are reported at the limit of quantitation (LOQ)

Concentrations of PFAS in groundwater are understood to vary as a function of water age. As more modern water mixes with ancient water stored in groundwater aquifers, PFAS prevalence in these aquifers will increase. For example, in the MPCA ambient groundwater dataset, decreasing detection frequency of PFOA and PFOS is observed with well depth. For the AGWN wells selected for this analysis, most ambient background concentrations of PFOA, PFOS, PFBS, PFBA, PFHxS, PFHxA, and HFPO-DA were not detected at or above the laboratory reporting limits (**Table 2**).



Air, precipitation, and surface water

PFAS have variable physicochemical properties, which influence their partitioning to the vapor phase, particulates, or precipitation. PFAS may transform to other PFAS, but the carbon-fluorine bonds characteristic of PFAS do not break down in the environment. When PFAS are released to the air, they can sometimes travel long distances in the atmosphere before they are deposited to the earth's surface in rain or through dry particulates. For example, a recent study of PFAS emissions indicates that a single PFAS facility in New Jersey potentially resulted in PFAS soil contamination as far away as New Hampshire (approximately 450 km from the New Jersey facility).² PFAS have been found to accumulate in high concentrations in snow and biota in the Arctic due to patterns of long-range atmospheric transport.³ PFAS can exist in the gas phase or can sorb to particulate material suspended in the air – both particulate and gaseous PFAS can be transported long distances. This high potential for PFAS to move through the atmosphere and contaminate other environmental media via deposition to terrestrial and aquatic environments is the main reason why there is continued focus and concern regarding PFAS emissions to air.

Summary of regional studies

This section summarizes findings from the MPCA PFAS Air and Deposition Monitoring Report⁴ and two journal publications related to PFAS concentrations in precipitation and surface water:

- Pfotenhauer et al. 2022⁵ PFAS concentrations and deposition in precipitation study at National Atmospheric Deposition Program National Trends Sites (NADP-NTN) across Wisconsin, USA.
- Gewurtz et al. 2019⁶ Perfluoroalkyl Acids in Great Lakes Precipitation and Surface Water (2006–2018) Indicate Response to Phase-outs, Regulatory Action, and Variability in Fate and Transport Processes.

MPCA 2020 – 2021 study

In this year-long study, gas and particulate phase samples were collected at four sites across MN, including:

- Grand Portage, MN rural site selected as a reference site (most likely to represent ambient background conditions)
- Duluth, MN urban site
- St. Louis Park, MN urban site
- Eagan, MN urban site

The urban sites are part of MPCA's ambient air monitoring network and were selected near known or potential emission sources. These sites may not necessarily represent ambient background conditions although only one site (St. Louis Park) seems to have been directly impacted by a local point source based on data reported in **Table 3**. Grand Portage (selected as the reference site), Eagan, and Duluth had comparable total PFAS air concentrations. Thirty gas and particulate phase atmospheric samples were collected at each site over the course of one calendar year (July 2020 – June 2021) and analyzed for a suite of 30 PFAS. Of the 30 PFAS analyzed, 17 were detected in ambient air at varying frequencies. Additionally, wet and dry deposition samples were collected at two of the four sites – St. Louis Park and Grand Portage.

² Washington et al. 2020. Non-targeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey soils. Science. 368(6495): 1103-1107. <u>https://doi.org/10.1126/science.aba7127</u>.

³ Joerss et al. 2020. Transport of legacy perfluoroalkyl substances and the replacement compound HFPO-DA through the Atlantic Gateway to the Arctic Ocean – is the Arctic a sink or source? Environmental Science and Technology. 54(16): 9958-9967. https://doi.org/10.1021/acs.est.0c00228.

⁴ MPCA. 2022. PFAS Air and Deposition Monitoring Report. Minnesota Pollution Control Agency. April 2022. <u>https://www.pca.state.mn.us/sites/default/files/tdr-g1-23.pdf</u>.

⁵ Pfotenhauer et al. 2022. PFAS concentrations and deposition in precipitation study at National Atmospheric Deposition Program – National Trends Sites (NADP-NTN) across Wisconsin, USA. Atmospheric Environment. 291: 119368 https://doi.org/10.1016/j.atmosenv.2022.119368.

⁶ Gewurtz et al. 2019. Perfluoroalkyl Acids in Great Lakes Precipitation and Surface Water (2006–2018) Indicate Response to Phase-outs, Regulatory Action, and Variability in Fate and Transport Processes. Environ. Sci. Technol. 53(15): 8543–8552. https://doi.org/10.1021/acs.est.9b01337.

Summary of ambient air results (particulate and gas) for all sites is as follows:

- PFOS, PFOA, PFBA, and PFBS were detected in 100% of samples
 - PFBA was the most abundant PFAS detected in terms of concentration in each sample
- PFHxS was detected in 99% of samples
- The remaining PFAS were detected in the following order based on detection frequency: N-MeFOSA > PFHxA > PFHpA > PFPeA > PFHpS > 6:2 FTS = N-MeFOSE > PFOSA > PFPeS = PFNA > N-EtFOSA > PFDA
 - N-MeFOSE and 6:2 FTS were detected at high concentrations relative to other PFAS

Surprisingly, the mean total PFAS concentration at Grand Portage, selected as the reference site, was the second highest of the four sites (**Table 3**). PFAS concentrations were not significantly different between the Grand Portage (reference) and Eagan site, and the lowest PFAS concentrations were found at the Duluth site, located in an industrial harbor. The Grand Portage findings may indicate a potential unidentified local source or may reflect long-range atmospheric transport impacts.

Wet and dry deposition sample results are only available for the St. Louis Park site (**Table 4**), which is not representative of ambient background concentrations due to its proximity to a chrome plating facility known to emit PFAS to air but are provided for informational purposes. Specifically, the results for 6:2 FTS and PFHxA, a breakdown product of 6:2 FTS, may be elevated because the chrome plating facility close to this sampling location is a known point source of 6:2 FTS. Deposition sample results from the Grand Portage site were rejected due to data quality concerns.

| Site | Mean | Standard deviation | Max |
|-----------------------------------|------|--------------------|-----|
| St Louis Park | 130 | 71 | 310 |
| Grand Portage – reference site | 100 | 21 | 150 |
| Eagan | 96 | 17 | 160 |
| Duluth | 88 | 15 | 120 |

 Table 3. Summary of total PFAS air concentrations (gas + particulate) in pg/m³ (parts-per quadrillion).

| PFAS | Median (all data) ¹ | Max | % Detects |
|----------------------|--------------------------------|------|-----------|
| 6:2 FTS ² | <0.75 | 6.4 | 48% |
| PFBA | <0.8 | 4.2 | 20% |
| PFHxA ² | <0.2 | 0.93 | 17% |
| PFOA | <0.2 | 0.52 | 10% |
| PFOS | <0.2 | 0.73 | 7% |
| PFNA | <0.2 | 0.46 | 7% |
| PFBS | <0.2 | 1.1 | 3% |

Table 4. Select PFAS in wet plus dry deposition samples at St. Louis Park (ng/L).

1 – Medians are non-detect at the reporting limit

2 - 6:2 FTS and PFHxA (breakdown product of 6:2 FTS) concentrations may be elevated due to a known point source of 6:2 FTS

The Minnesota Department of Health (MDH) developed human health inhalation air guidance values called risk assessment advice (RAA)⁷ for six PFAS compounds – PFBS, PFBS, PFHxA, PFHxS, PFOA, and PFOS. These guidance values represent outdoor air concentrations below which health effects are negligible and above which risk may occur. At 11,000 pg/m³, PFOS has the lowest guidance value. None of the monitoring results were above the PFOS air guidance value. In fact, the sum of the maximum concentration for each PFAS analyte at the St. Louis Park site is two orders of magnitude below the PFOS RAA.

⁷ MDH. 2022. Air Guidance Values. Minnesota Department of Health. <u>https://www.health.state.mn.us/communities/environment/risk/guidance/air/table.html</u>

Pfotenhauer et al. 2022

In spring to fall 2020, 91 precipitation samples (wet deposition) were collected from eight National Trends Network sites across Wisconsin through the National Atmospheric Deposition Program. Precipitation samples were analyzed for a suite of 34 PFAS.

Median precipitation concentrations for select PFAS are provided in **Table 5**. Other notable results are summarized below:

- Individual PFAS compound concentrations were typically below 0.5 ng/L.
 - A few individual samples approached a concentration of 2 ng/L.
- For frequently detected compounds, the highest median concentrations were measured for PFBA (0.32 ng/L), PFHxA (0.26 ng/L), and PFPeA (0.19 ng/L).
- Perfluorocarboxylates (PFCAs) are the most abundant class of PFAS found in the samples.
 - Short-chain PFCAs (<8 carbon) were the most abundant sub-class, with PFBA and PFHxA exhibiting the highest concentrations across all compounds.
- Median concentrations for PFOA and PFOS were 0.16 ng/L and 0.07 ng/L, respectively.
- Concentrations of other perfluorosulfonates (PFSAs), excluding PFOS, were very low.

| PFAS | UW Arboretum | Brule River | Potawatomi | Baraboo | Perkinstown | Trout Lake | Spooner | Marinette |
|---------|-----------------|----------------|------------|---------|-------------|---------------|---------|-----------|
| PFBA | 0.22 | 0.54 | 0.33 | 0.20 | 0.31 | 0.30 | 0.38 | 0.34 |
| PFPeA | 0.17 | 0.26 | 0.16 | 0.21 | 0.20 | 0.13 | 0.22 | 0.20 |
| PFHxA | 0.27 | 0.28 | 0.26 | 0.22 | 0.27 | 0.28 | 0.26 | 0.26 |
| PFOA | 0.13 | 0.22 | 0.13 | 0.33 | 0.16 | 0.14 | 0.14 | 0.20 |
| PFNA | 0.09 | 0.17 | 0.12 | 0.12 | 0.10 | 0.12 | 0.11 | 0.13 |
| PFBS | - | - | - | - | - | - | - | - |
| PFHxS | - | - | - | 0.04 | 0.21 | - | 0.08 | 0.04 |
| PFOS | 0.09 | 0.06 | 0.09 | 0.06 | 0.26 | 0.04 | 0.08 | 0.12 |
| 6:2 FTS | 0.03 | 0.03 | 0.03 | 0.04 | 0.04 | 0.03 | 0.03 | 0.51 |
| HFPO-DA | 0.23 | 0.19 | - | 0.41 | 0.61 | 0.21 | 0.35 | 0.35 |

Table 5. Summary of median precipitation concentrations for select PFAS by site in ng/L.

Gewurtz et al. 2019

Concentrations of PFAS in precipitation and surface water were determined from several Great Lakes locations between 2006 and 2018. Precipitation samples were collected from three sites including:

- Point Petre eastern Lake Ontario, a highly populated rural region.
- Burnt Island/Evansville southwestern end of Manitoulin Island in northern Lake Huron, a remote site. Site was relocated to Evansville in 2013 (22 km east of Manitoulin Island).
- Sibley northwest corner of Lake Superior, a remote location near Thunder Bay, Ontario.

Surface water samples were collected from several stations located on Lakes Superior, Huron, Erie, and Ontario. Precipitation and surface water results are briefly summarized below. The last three bullets are specific to locations on Lake Superior, which are most comparable to remote locations in MN:

- Concentrations in precipitation were comparable to other locations in previous studies, particularly in remote and rural locations.
- Concentrations of PFBA and other short-chain PFCAs were comparable in precipitation samples throughout the Great Lakes; this supports conclusions noted by others that PFBA is evenly distributed in the global atmosphere.
- Most detected precipitation concentrations for PFBA, PFHxA, PFOA, PFBS, PFHxS, and PFOS for the Sibley site are in the range of approximately 0.5 3 ng/L.

- PFBS, PFHxS, and PFOS surface water results for Lake Superior are all non-detect, with reporting limits ranging from approximately 1 2 ng/L.
- PFBA, PFHxA, and PFOA surface water results for Lake Superior are generally non-detect, with reporting limits ranging from approximately 0.5 – 1 ng/L, with most detected results below or close to approximately 1 ng/L.

Conclusion

Direct human exposure through outdoor air inhalation is not likely to be a significant route of exposure to PFAS based on current MDH inhalation guidance values. PFAS in air are problematic due to their long-range transport potential and any subsequent wet and dry deposition to aquatic and terrestrial environments where PFAS can continue to build up and migrate through environmental compartments. While PFAS concentrations in ambient air are generally low, the deposition of these compounds via wet and dry deposition can have major impacts on watersheds. For example, nearly all the median PFOS precipitation concentrations identified by Pfotenhauer et al. 2022 (**Table 5**) exceed MPCA's site-specific water quality criterion for PFOS of 0.05 ng/L.⁸ It is important to note that PFAS concentrations in precipitation are not equivalent to concentrations in a surface water body due to dilution; however, because PFAS do not readily break down in the environment, any deposition to aquatic and terrestrial environments would lead to levels building up over time and could lead or contribute to water quality and ecosystem impairments.

⁸ MPCA. 2020. Water Quality Standards Technical Support Document: Human Health Protective Water Quality Criteria for Perfluorooctane Sulfonate (PFOS). Minnesota Pollution Control Agency. December 2020. <u>https://www.pca.state.mn.us/sites/default/files/wq-s6-61a.pdf</u>.

Soil

This section summarizes findings from a review of publications and studies that have investigated ambient background concentrations of PFAS in soils. The MPCA uses its authority under the Minnesota Environmental Response and Liability Act (MERLA) to respond to PFAS contamination during site cleanups. The information provided in this section can be used to guide remediation work at PFAS-contaminated sites where an ambient background PFAS soil concentration may need to be considered. However, it is *not* recommended that the values provided here be used for establishing site cleanup goals. Rather, they should serve as a preliminary guide of the possible range of ambient background concentrations that may exist. Where possible and needed, site-specific ambient background should be derived when making site cleanup decisions. There are variations in study design and analytical methods that add uncertainty to a cross-study comparison. Therefore, the information presented here should be interpreted with caution.

Literature review

The most notable and relevant studies reporting ambient background PFAS concentrations in soil include:

- Zhu et al. 2019⁹ PFAS background in Vermont shallow soils
- Maine Department of Environmental Protection (DEP) shallow soils study¹⁰
- Santangelo et al. 2022 Statewide survey of shallow soil concentrations of per- and polyfluoroalkyl substances (PFAS) and related chemical and physical data across New Hampshire¹¹
- Strynar et al. 2012¹² Pilot scale application of a method for the analysis of perfluorinated compounds in surface soils
- Rankin et al. 2016¹³ A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence
- Scher et al. 2018¹⁴ Occurrence of perfluoroalkyl substances (PFAS) in garden produce at homes with a history of PFAS-contaminated drinking water

Below is a brief synopsis of each study with relevant data extracted. Priority was given to studies that report PFAS data for locations representing ambient background conditions (i.e., located away from point/emission sources). A large table is provided at the end of this document, which compares various PFAS ambient background soil concentrations, as reported in the studies reviewed, to the 2024 MPCA Residential/Recreational soil reference values (SRVs).¹⁵ SRVs are health-based values used to evaluate potential human health risks from exposure to contaminated soil. SRVs may be lower than background concentrations for certain contaminants. This is true for several metals and some organic contaminants such as certain polycyclic aromatic hydrocarbons and dioxins/furans. Except for the PFOA SRV, which may be below ambient background in some locations, the rest of the 2024 PFAS SRVs are not expected to be below ambient background concentrations. They may drop below ambient background in the future as more information about PFAS toxicity becomes available. Therefore, understanding ambient background PFAS soil concentrations can help inform cleanup decisions and other remedial actions. Where possible, data from published studies are reported for the seven PFAS that MPCA has 2024 SRVs for, including PFBA, PFBS, PFOA, PFOS, PFHxS, PFHxA, and HFPO-DA.

⁹ Zhu et al. 2019. PFAS Background in Vermont Shallow Soils. University of Vermont. February 2019.

https://anrweb.vt.gov/PubDocs/DEC/PFOA/Soil-Background/PFAS-Background-Vermont-Shallow-Soils-03-24-19.pdf. ¹⁰ Maine DEP. 2022. Background Levels of PFAS and PAHs in Maine Shallow Soils Study Report. File No. 5060.00. April 2022. https://www.maine.gov/dep/spills/topics/pfas/Maine_Background_PFAS_Study_Report.pdf.

¹¹ Santangelo et al. 2022. Statewide survey of shallow soil concentrations of per- and polyfluoroalkyl substances (PFAS) and related chemical and physical data across New Hampshire, 2021: U.S. Geological Survey data release, <u>https://doi.org/10.5066/P9KG38B5</u>.

¹² Strynar et al. 2012. Pilot scale application of a method for the analysis of perfluorinated compounds in surface soils. Chemosphere 86(3): 252-257. <u>https://doi.org/10.1016/j.chemosphere.2011.09.036</u>.

¹³ Rankin et al. 2016. A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence. Chemosphere 161: 333-341. <u>https://doi.org/10.1016/j.chemosphere.2016.06.109</u>.

¹⁴ Scher et al. 2018. Occurrence of perfluoroalkyl substances (PFAS) in garden produce at homes with a history of PFAS-contaminated drinking water. Chemosphere 196: 548-555. <u>https://doi.org/10.1016/j.chemosphere.2017.12.179</u>.

¹⁵ MPCA. 2024. Soil reference values spreadsheet. <u>https://www.pca.state.mn.us/sites/default/files/c-r1-06.xlsx</u>

Zhu et al. 2019

This soil survey was conducted by the University of Vermont and Sanborn, Head & Associates with partial funding provided by the Vermont Department of Environmental Conservation. Sixty-six discrete samples were obtained and analyzed for 17 PFAS. PFOS was detected at the highest frequency and found in all soil samples. Background threshold values (BTVs) were established using ProUCL 5.1 software¹⁶ for analytes with detection frequency of more than 10%. The BTVs, which are based on upper tolerance limits (UTL), are summarized in **Table 6.** All PFAS for which a UTL was derived are included.

| Analyte | UTL Type | Proposed UTL (ng/g or ppb) |
|---------|---|-------------------------------|
| PFHxA | 95% Approx. Gamma UTL with 95% Coverage (WH)-KM | 0.87 |
| PFHpA | 95% BCA UTL95% Coverage (Lognormal) | 0.84 |
| PFOA | 95% BCA UTL95% Coverage (Lognormal) | 1.6 |
| PFNA | 95% Approx. Gamma UTL with 95% Coverage (WH)-KM | 0.44 |
| PFDA | 95% percentile | 0.39 |
| PFUnDA | 95% percentile | 0.18 |
| PFBS | 95% KM UTL (Lognormal) 95% Coverage | 0.59 |
| PFHxS | 95% percentile | 0.38 |
| PFOS | 95% UTL95% Coverage (Lognormal) | 3.4 |
| PFDS | 95% Approx. Gamma UTL with 95% Coverage (WH)-KM | 0.15 |

Table 6. Vermont's proposed UTLs.

Maine DEP shallow soils study

This study investigated the presence of PFAS and polycyclic aromatic hydrocarbons (PAHs) in Maine shallow soils. Sixty-four discrete soil samples were collected to a depth of six inches and analyzed for 28 PFAS and 19 PAHs. Of the 28 PFAS analyzed, PFOS, PFBA, and PFOA were detected at the highest frequencies. BTVs were established using ProUCL 5.1 software¹⁶ for nine PFAS as summarized in **Table 7**. Urban and non-urban BTVs were established for PFOS and PFDA. Based on a comparison of urban and non-urban data using a two-sample hypothesis approach, only results for PFOS and PFDA were found to be different at a significance level of 0.05. In addition to BTVs established based on UTLs, upper bound measures of central tendency were also calculated using a 95% upper confidence limit (UCL) of the mean (**Table 7**).

Table 7. Maine's Interim BTVs and 95% UCLs.

| Analyte | UTL Type | Interim UTL (ng/g or ppb) | UCL Type | Interim UCL95 (ng/g or ppb) |
|------------------|---------------------------|------------------------------|----------------------|--------------------------------|
| PFBA | UTL 95-95 (Lognormal KM) | 0.431 | KM H-UCL (Lognormal) | 0.137 |
| PFPeA | UTL 95-95 (Nonparametric) | 1.02 | KM (Chebyshev) | 0.098 |
| PFHxA | UTL 95-95 (Nonparametric) | 1.49 | KM (Chebyshev) | 0.219 |
| PFHpA | UTL 95-95 (Nonparametric) | 0.246 | Normal (t) KM | 0.085 |
| PFOA | UTL 95-95 (Nonparametric) | 2.18 | KM (Chebyshev) | 0.394 |
| PFNA | UTL 95-95 (Nonparametric) | 1.93 | KM H-UCL (Lognormal) | 0.145 |
| PFDA (urban) | UTL 95-95 (Nonparametric) | 3.24 | KM H-UCL (Lognormal) | 0.094 |
| PFDA (non-urban) | UTL 95-95 (Normal KM) | 0.112 | Normal (t) KM | 0.078 |
| PFUnDA | UTL 95-95 (Nonparametric) | 0.944 | KM Approximate Gamma | 0.073 |
| PFOS (urban) | UTL 95-95 (Gamma KM) | 3.036 | KM Adjusted Gamma | 1.17 |
| PFOS (non-urban) | UTL 90-95 (Nonparametric) | 0.551 | Normal (t) KM | 0.275 |

¹⁶ USEPA. 2022. ProUCL Software. Environmental Protection Agency. <u>https://www.epa.gov/land-research/proucl-software</u>

Santangelo et al. 2022

The U.S. Geological Survey (USGS) conducted a shallow soil survey of PFAS in New Hampshire in 2021. The data were published on the USGS website in 2022. USGS sampled 100 locations within the State of New Hampshire selected through an equal-area grid approach targeting predominantly undisturbed areas. Additionally, they placed a 500-meter buffer around parcels associated with known or potential PFAS sources. Samples were collected from 0 to 6 inches in depth at all locations. Deeper soil samples were also collected at a subset of sites. Samples were analyzed for 36 PFAS compounds. The USGS data release was used to generate the summary statistics in **Table 8**. All samples from the 0 to 6-inch depth increment were used including duplicate and triplicate samples (n = 112).

| | | Min | 95 th PCTL | Max |
|---------|----------|---------------|-----------------------|---------------|
| Analyte | % Detect | (ng/g or ppb) | (ng/g or ppb) | (ng/g or ppb) |
| PFBA | 66 | <0.26 | 1.1 | 1.9 |
| PFHxA | 65 | <0.11 | 0.60 | 1.1 |
| PFOA | 96 | <0.051 | 2.2 | 4.1 |
| PFBS | 83 | <0.025 | 0.16 | 0.82 |
| PFHxS | 56 | <0.022 | 0.13 | 0.22 |
| PFOS | 100 | 0.14 | 2.6 | 5.4 |
| HFPO-DA | 25 | <0.023 | 0.10 | 0.30 |
| | | | | |

Table 8. New Hampshire soil survey summary statistics for select PFAS.

Less than (<) values are reported at the method detection limit (MDL)

Strynar et al. 2012

In this study, 60 soils, consisting of three samples from each of the six nations that were part of the study (U.S., China, Japan, Norway, Greece, and Mexico) were randomly selected from a total pool of 337 samples (includes freshly collected and archived soils) and analyzed for 13 PFAS. Fresh samples were collected as a composite sample from multiple locations in a 1 m² area at a depth of 0-15 centimeters (cm). The most commonly detected PFAS were PFOS and PFOA. Strynar et al.'s supplemental information includes a table with summary statistics for all samples. **Table 9** is a summary of individual PFAS results for U.S. soil samples only. PFBS results for all locations were non-detect and are therefore not provided in the table. The higher PFOA and PFHxA concentrations at the North Carolina RTP sites suggest that there may be a potential local PFAS source.

| Sample ID | Location Description | PFOA (ng/g or ppb) | PFHxA (ng/g or ppb) | PFOS (ng/g or ppb) | PFHxS (ng/g or ppb) |
|-----------|-------------------------|-----------------------|------------------------|-----------------------|------------------------|
| NC04 | RTP, NC | 31.7 | 12.4 | 2.55 | 0.527 |
| NC02 | RTP, NC | 15.6 | 5.36 | 0.606 | <0.51 |
| NC05 | Shinning Rock, NC | 8.40 | 5.62 | 1.47 | <0.51 |
| NC07 | Laurel Fork, NC | 1.35 | 0.945 | 2.52 | <0.51 |
| TX03 | Houston, TX | 2.66 | 2.96 | 2.16 | <0.51 |
| KY01 | Richmond, KY | 2.14 | 1.71 | 1.60 | <0.51 |
| IN01 | W. Lafayette, IN | 2.18 | 1.51 | <0.51 | 1.39 |
| MI01 | Michigan | <0.50 | <0.51 | <0.51 | <0.51 |
| MI02 | Michigan | 0.747 | 0.760 | <0.51 | <0.51 |
| GA03 | Georgia | 1.75 | 1.73 | <0.51 | <0.51 |

Table 9. Strynar et al. 2012 individual results for select PFAS for soil samples in the U.S.

Less than (<) values are reported at the LOQ

Rankin et al. 2016

In this study, 62 soil samples were obtained from 22 countries, representing all continents, and analyzed for 32 PFAS. Discrete samples were collected by various collectors throughout the world to a depth of about 10 cm. PFOS was detected in all samples except for one Estonian sample, and PFOA and PFHxA were detected in all samples. There were two samples collected in MN, which are reported in **Table 10**. Individual PFAS results for all samples are provided in Rankin et al. supplemental information.

| Sample ID | Location Description | PFOA (ng/g or ppb) | PFHxA (ng/g or ppb) | PFOS (ng/g or ppb) | PFHxS (ng/g or ppb) |
|-----------|--|-----------------------|------------------------|-----------------------|------------------------|
| NA01 | Between Chanhassen and Excelsior, MN 44.88312, -93.55454 | 0.158 | 0.0625 | 0.304 | 0.00378 |
| NA03 | Near Fertile, MN 47.5306, -96.3032 | 0.132 | 0.0600 | 0.112 | 0.00430 |

Scher et al. 2018

This study investigated the presence of PFAS in home gardens in an area with historical PFAS groundwater contamination. Soil and produce samples were collected from inside and outside of the Groundwater Contamination Area (GCA). For purposes of this review, samples collected outside of the GCA will be considered to represent ambient background conditions. One to three composite samples were collected at each site. Each composite was made up of five subsamples. **Table 11** provides summary statistics for samples inside and outside of the GCA.

| Location | PFAS | % Detects | Min (μg/kg or ppb) | 95 th PCTL (µg/kg or ppb) | Max (µg/kg or ppb) |
|--------------------------|-------|-----------|-----------------------|---|-----------------------|
| Location | | | | | |
| | PFBA | 100 | 0.037 | 3.4 | 13.0 |
| | PFHxA | 82 | ND | 0.65 | 0.66 |
| Incide CCA (24 complete) | PFOA | 100 | 0.11 | 2.7 | 3.0 |
| Inside GCA (34 samples) | PFBS | 9 | ND | 0.063 | 0.17 |
| | PFHxS | 71 | ND | 0.17 | 0.24 |
| | PFOS | 100 | 0.57 | 8.8 | 12.0 |
| | PFBA | 100 | 0.073 | 0.49 | 0.49 |
| | PFHxA | 100 | 0.029 | 0.088 | 0.088 |
| | PFOA | 100 | 0.29 | 0.54 | 0.54 |
| Outside GCA (6 samples) | PFBS | 17 | ND | 0.031 | 0.031 |
| | PFHxS | 100 | 0.028 | 0.11 | 0.11 |
| | PFOS | 100 | 0.93 | 2.1 | 2.1 |

Table 11. Scher et al. 2018 summary statistics for soil samples collected inside and outside of the GCA.

ND = non-detect

MDLs ranged from 0.008 to 0.033 $\mu\text{g/kg}$ (ppb) depending on the analyte

Other studies

The following additional studies were reviewed:

• Xiao et al. 2015¹⁷ – Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in soils and groundwater of a U.S. metropolitan area: Migration and implications for human exposure

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¹⁷ Xiao et al. 2015. Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in soils and groundwater of a U.S. metropolitan area: Migration and implications for human exposure. Water Research 72: 64-74. <u>https://doi.org/10.1016/j.watres.2014.09.052</u>.

- Washington et al. 2018¹⁸ Determining global background soil PFAS loads and the fluorotelomer-based polymer degradation rates that can account for these loads
- Brusseau et al. 2020¹⁹ PFAS concentrations in soils: Background levels versus contaminated sites
- Sim et al. 2021²⁰ Characteristic distribution patterns of perfluoroalkyl substances in soils according to land-use types
- Kikuchi et al. 2018²¹ Analysis of per- and polyfluoroalkyl substances (PFASs) in soil from Swedish background sites

While these studies contain noteworthy information, they either did not provide any new data for U.S. locations (Washington et al. 2018 and Brusseau et al. 2020) or are from an area with historical PFAS contamination (Xiao et al. 2015).

Xiao et al. 2015 sampled soils in the Twin Cities Metro, extending from Cottage Grove to Big Lake, MN along U.S. Highway 10. Many of the samples were collected in the vicinity of Cottage Grove which is dealing with historic and ongoing PFAS contamination from a PFAS manufacturing facility as well as PFAS disposal sites. Xiao et al. report that the PFAS soil concentrations found in their study are generally higher than those reported in Strynar et al. 2012 (locations in NC, KY, TX, and IN) but comparable or lower than those reported for soils receiving municipal biosolids, at an Air Force Base, or near a PFAS manufacturing facility in China. Due to these findings, most samples collected by Xiao et al. would not represent ambient background concentrations.

Washington et al. 2018 used data from Rankin et al. 2016 to model global background PFAS soil loads to investigate whether environmental loads of long-chain PFCAs can be used to assess fluorotelomer-based polymers' half-lives. This publication did not contain any new data.

Brusseau et al. 2020 compiled data from various studies to compare PFAS soil concentrations at contaminated sites to background levels. The authors conducted a literature search primarily through the Web of Science, but also Google Scholar and Google using the following search terms: PFAS, Perfluor, Polyfluor, PFC, soil, vadose zone, and sediment. The authors provide summary tables presenting soil concentrations for the various types of locations considered – contaminated sites and background sites. Table 1 of the publication provides the maximum PFOS and PFOA soil concentrations of various "soil surveys", which the authors considered to be surveys of areas that are not directly impacted by PFAS sources and would therefore represent ambient background conditions. Of the studies reported in Table 1 of Brusseau et al. 2020, only seven studies contain samples collected in the U.S. Furthermore, the concentrations reported should be interpreted with caution and whenever possible confirmed in the original publication. For example, the maximum PFOS and PFOA concentrations reported for Scher et al. 2018 are for samples inside the GCA when samples outside the GCA would more closely represent ambient background conditions.

No additional U.S. studies were identified through a literature search using Google Scholar. Two additional recent studies, one in Sweden²² and the other in South Korea²³, investigating ambient background soil concentrations are of note and discussed briefly. The concentrations found in the two studies are summarized in **Table 12**. Kikuchi et al. 2018 data were subsequently used in a publication by Sörengård et al. 2022. Sim et al. 2021 did not provide results for individual samples, therefore, a 95th percentile concentration could not be calculated. This study also investigated soil samples from industrial areas and landfills and as expected, the concentrations in these areas are higher than for the other sites, which include farmland, mountain, and

 ¹⁸ Washington et al. 2018. Determining global background soil PFAS loads and the fluorotelomer-based polymer degradation rates that can account for these loads. Science of the Total Environment 651(2): 2444-2449. <u>https://doi.org/10.1016/j.scitotenv.2018.10.071</u>.
 ¹⁹ Brusseau et al. 2020. PFAS concentrations in soils: Background levels versus contaminated sites. Science of the Total Environment 740: 140017. <u>https://doi.org/10.1016/j.scitotenv.2020.140017</u>

²⁰ Sim et al. 2021. Characteristic distribution patterns of perfluoroalkyl substances in soils according to land-use types. Chemosphere 276: 130167. <u>https://doi.org/10.1016/j.chemosphere.2021.130167</u>.

²¹ Kikuchi et al. 2018. Analysis of per- and polyfluoroalkyl substances (PFASs) in soil from Swedish background sites. Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences. Uppsala, April 2018. <u>https://pub.epsilon.slu.se/15902/</u>.

²² Sörengård et al. 2022. Spatial distribution and load of per- and polyfluoroalkyl substances (PFAS) in background soils in Sweden. Chemosphere 295: 133944. <u>https://doi.org/10.1016/j.chemosphere.2022.133944</u>.

²³ Sim et al. 2021. Characteristic distribution patterns of perfluoroalkyl substances in soils according to land-use types. Chemosphere 276: 130167. <u>https://doi.org/10.1016/j.chemosphere.2021.130167</u>.

woodland. Therefore, only data for the other sites are reported in **Table 12** as these more closely represent ambient background.

| Sim et al. 2021 (South Korea) | | | | | | | | |
|-------------------------------|-----------------------|-------|-------|--------|--------|--------|--|--|
| | | PFHxA | PFOA | PFBS | PFHxS | PFOS | | |
| Farmland n = 4 | Mean | 0.028 | 0.262 | <0.063 | <0.060 | <0.200 | | |
| | 95 th PCTL | - | - | - | - | - | | |
| | Max | 0.112 | 0.408 | - | - | - | | |
| Mountain n = 8 | Mean | 0.008 | 0.252 | 0.014 | <0.060 | 0.326 | | |
| | 95 th PCTL | - | - | - | - | - | | |
| | Max | 0.065 | 0.986 | 0.114 | - | 1.051 | | |
| Woodland | Mean | 0.038 | 0.399 | <0.063 | <0.060 | 0.142 | | |
| | 95 th PCTL | - | - | - | - | - | | |
| n = 4 | Max | 0.162 | 0.722 | - | - | 0.567 | | |
| Kikuchi et al. 2018 (Sweden) | | | | | | | | |
| | | PFHxA | PFOA | PFBS | PFHxS | PFOS | | |
| Forested land n = 31 | Mean | <8.8 | 0.061 | 0.30 | 0.075 | 0.43 | | |
| | 95 th PCTL | - | 0.22 | 0.91 | 0.15 | 1.3 | | |
| | Max | - | 0.57 | 0.96 | 0.4 | 1.7 | | |

 Table 12. Summary statistics in ng/g (ppb) for select PFAS from Sim et al. 2021 and Kikuchi et al. 2018.

Less than (<) values are reported at the MDL

- = no data available or could not be calculated

Conclusion

Table 13 provides a summary and comparison of MPCA 2024 PFAS SRVs to the PFAS soil concentrations obtained from the various published studies discussed above. While MPCA has developed an SRV for HFPO-DA (66 ppb for the residential/recreational land use), only one study (Santangelo et al. 2022) contained usable data on HFPO-DA, therefore, it is not included in the table. Xiao et al. 2015 data are provided for comparison purposes only, as an example of an area with historic PFAS contamination and are not considered representative of ambient background. Many of the soils sampled by Xiao et al. are close to PFAS point sources and the calculated 95th percentiles are therefore much higher than would be expected for ambient background. An attempt was made to report the 95th percentile of PFAS soil concentrations for all studies, however, not all studies provided individual sample results which would allow for this calculation or summary statistics that contained a 95th percentile concentration. Because the authors of the Vermont and Maine soil surveys already calculated BTVs based on UTLs, the UTLs are provided instead of 95th percentile concentrations.

The following are general observations based on data presented in Table 13:

- Ambient background soil concentrations for PFOS and PFOA may be in the range of approximately 0.5 2 ppb (some areas may be lower or higher than this range).
- Ambient background soil concentrations for PFHxS may be in the range of approximately 0.05 0.2 ppb (some areas may be lower or higher than this range).
- Data for PFBA and PFBS are sparse, therefore, it is not possible to reasonably assess potential ambient background concentrations. However, the SRVs for PFBA and PFBS are orders of magnitude higher than for PFOS and PFOA and are not expected to drop below ambient background concentrations.
- Similarly, the SRV for PFHxA is two orders of magnitude higher than for PFOS and is also not expected to drop below ambient background concentrations.

To reiterate, it is *not* recommended that the values provided here be used for any site cleanup decisions. Rather, they should serve as a preliminary guide of the possible range of ambient background concentrations that may exist. Where possible and needed, site-specific ambient background should be derived when making site cleanup decisions.

Table 13. Comparison of MPCA residential/recreational SRVs to PFAS soil concentrations from published studies.

| Author Location Value type | MPCA 2024 Minnesota Res/Rec SRV ¹ | Zhu et al. 2019 Vermont (n = 66) UTL ² | Maine DEP Study 2022 Maine (n = 63) UTL ² | Santangelo et al. 2022 New Hampshire (n = 112) 95 th PCTL | Rankin et al. 2016 MN sites (n = 2) 95 th PCTL | Rankin et al. 2016 All NA ³ sites (n = 33) 95 th PCTL | Strynar et al. 2012 U.S. sites ⁴ (n = 8) 95 th PCTL | Scher et al. 2018 MN outside GCA ⁵ (n = 6) 95 th PCTL | Sim et al. 2018 South Korea (n = 16) Mean | Kikuchi et al. 2018 Sweden (n = 31) 95 th PCTL | Xiao et al. 2015 (not representative of ambient background) All sites ⁶ (Cottage Grove to Big Lake, MN; n = 46) 95 th PCTL |
|----------------------------------|--|---|--|--|---|---|---|---|---|---|---|
| Units | ppb | ppb | ppb | ppb | ppb | ppb | ppb | ppb | ppb | ppb | ppb |
| PFAS | | | | | | | | | | | |
| PFBS | 1,100 | N/A | N/A | 0.16 | N/A | N/A | N/A | ND | 0.045 | 0.91 | N/A |
| PFBA | 49,000 | N/A | 0.43 | 1.1 | N/A | N/A | N/A | 0.49 | N/A | N/A | N/A |
| PFOS | 13 | 3.4 | 3.04 (urban) 0.55 (non-urban) | 2.6 | 0.29 | 1.4 | 2.4 | 2.1 | 0.22 | 1.3 | 72 |
| PFOA | 0.36 | 1.6 | 2.2 | 2.2 | 0.16 | 1.5 | 6.4 | 0.54 | 0.30 | 0.22 | 28 |
| PFHxS | 130 | 0.38 | N/A | 0.13 | 0.0043 | 0.034 | 1.1 | 0.11 | ND | 0.15 | N/A |
| PFHxA | 1,900 | 0.87 | 1.5 | 0.60 | 0.062 | 0.87 | 4.7 | 0.088 | 0.025 | N/A | N/A |

1 – Res/Rec SRV = Residential/Recreational soil reference value

2 – UTL = Upper tolerance limit

3 – NA = North America (includes US, Canada, Mexico, Puerto Rico)

4 – The RTP, NC sites were excluded from the calculation. The higher PFOA and PFHxA concentrations at the RTP sites suggest that there may be a potential local PFAS source.

5 – GCA = Groundwater Contamination Area

6 – Includes all soil samples; deeper soil increments (up to 91 cm below ground surface) were collected at some sites.

N/A = not applicable or data not provided

ND = non-detect