

Perfluorinated Compounds

Treatment and Removal

What are PFCs?

The presence of perfluorinated compounds (PFCs) in source waters and drinking water is of growing concern to water professionals. This group of organic compounds, used for industrial and consumer applications such as nonstick coatings and firefighting foams, has potential health implications for humans and wildlife. PFCs are persistent in the environment and highly soluble in water. The U.S. Environmental Protection Agency (EPA) listed the following PFCs as suspected drinking water contaminants with presence in drinking water under the Unregulated Contaminant Monitoring Rule 3 (UCMR 3): perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS), perfluorohexanoic acid (PFHxA), perfluorobutanesulfonic acid (PFBS).

Current Regulation of PFCs

Currently there are no enforceable federal drinking water limits for PFCs. In May of 2016, EPA released Lifetime Health Advisories of 0.070 microgram per liter (µg/L) (70 ng/L) for PFOA and PFOS (individually or combined) for exposure from drinking water. These advisory levels are set at concentrations which EPA is certain are protective for the most sensitive individuals against reproductive and developmental impacts with a margin of safety. EPA has identified PFCs as an emerging contaminant because they have a pathway to enter the environment, may pose a human health or environmental risk, and do not have federal regulatory standards. In addition, individual states have begun to develop state PFC guidelines for monitoring and reducing PFCs in the environment.

Levels of PFCs above state guidance levels and the national lifetime health advisory should be reported to your state's primary agency to determine the course of action. EPA recommends that public health officials provide information on PFOA/PFOS exceedances to consumers with specific information regarding reproductive and developmental risks associated with elevated PFOA/PFOS levels.

Treatment Options for PFCs

Although the removal efficiency of PFCs from source waters depends on water treatment variables such as influent concentration and treatment conditions, several treatment methods have proven to remove up to 90% or greater of PFCs in finished water. Ultimately, systems facing a PFC treatment challenge will want to evaluate treatment strategies that best fit their source water, treatment objectives, and other system-specific considerations.



PFC Concentration Guidelines		
Agency	Matrix	Contaminant
U.S. EPA	Drinking Water	Lifetime Health Advisory: PFOA & PFOS (Combined or Individually) – 0.070 µg/L
State	Matrix	Contaminant
Illinois	Groundwater	PFOA – 0.400 µg/L PFOS – 0.200 µg/L
Maine	Groundwater	PFOA – 0.060 µg/L PFOS – 0.100 µg/L
Michigan	Surface Water	PFOA – 0.420 µg/L PFOS – 0.012 µg/L
Minnesota	Drinking Water + Fish Consumption	PFOA – 0.610 µg/L (Lake) PFOA – 0.720 µg/L (River) PFOS – 0.012 µg/L (Lake) PFOS – 0.006 µg/L (River)
New Jersey	Drinking Water	PFOA – 0.040 µg/L
North Carolina	Groundwater	PFOA – 2 µg/L
Vermont	Drinking Water	PFOA – 0.020 µg/L

Perfluorinated Compounds

Treatment and Removal

Treatment Method	Treatment Process	Documented PFC Removal Percentages	Relative Treatment Cost	Application	Treatment Considerations	
					Pros	Cons
Activated Carbon	Granulated activated carbon (GAC) or powdered activated carbon (PAC)	PFOA ≥ 90% PFOS ≥ 90% PFNA ≥ 90%	\$\$	Surface Water, Groundwater, PWSS, Households	<ul style="list-style-type: none"> Widely used for PFC removal, high removal rates possible GAC provides better removal than PAC PAC is useful for responding to spills In-house options are available for point-of-use or point-of-entry systems 	<ul style="list-style-type: none"> Conflicting results on which PFCs are removed most effectively Possibility of competitive adsorption with other compounds present, such as natural organic matter Slow GAC adsorption rates may extend operating time and require optimization Requires thermal regeneration of GAC Creates waste residuals to dispose of exhausted carbon Process optimization necessary (pH, temperature, contact time)
Anion Exchange	Special ion exchange material (commercial resins or petrochemical compounds) shaped as beads exchange anions and replace hydroxyl groups	PFOA = 10-90% PFOS = ≥ 90% PFNA = 67%	\$\$	Surface Water, Groundwater	<ul style="list-style-type: none"> PFOS removed well by anion exchange but sorption rates depend on polymer matrix and porosity Can partially remove PFOA, PFNA, PFOS 	<ul style="list-style-type: none"> Reject brine must be properly disposed of Costs are similar to activated carbon but depend greatly on resin and treatment system Rate of exchange will depend on many factors, including influent PFC concentration, design of the anion exchange, solution ionic strength and bead material Potential for competing anions Surface water supplies may need clarification/filtration before treatment Less effective at short-chain PFC removal
Membrane Filtration	Reverse Osmosis (RO): semi-permeable membrane to allow osmotic pressure to retain PFCs Nanofiltration (NF): uses filters with pore sizes around 0.001 micron and a high water flux to filter PFCs	PFOA = ≥ 90% PFOS = ≥ 90% PFNA = ≥ 90%	\$\$\$	Surface Water, Groundwater, PWSS, Households (RO)	<ul style="list-style-type: none"> Excellent PFC removal May be designed for under-sink or residential well water PFC treatment Can be successfully combined with GAC for higher PFC removal rates Multi-contaminant removal Reasonable for groundwater systems 	<ul style="list-style-type: none"> Reject water must be treated before discharging High capital expense with high energy demands Susceptible to fouling May require pre-treatment due to high fouling tendencies RO is preferable to NF due to higher removal efficiency
Advanced Oxidation Processes (AOP)	UV/H ₂ O ₂ UV/S ₂ O ₈ ²⁻	PFOA < 10% PFOS = 10 to 50% PFNA < 10%	\$\$\$	Surface Water, Groundwater	<ul style="list-style-type: none"> Can oxidize a multitude of contaminants to degradation products using reactive hydroxyl radicals 	<ul style="list-style-type: none"> Less effective at breaking down organic compounds such as PFCs No significant difference in removal of PFCs observed between different AOP methods Significant energy input is needed to achieve moderate PFAS oxidation with AOP

References

"Emerging Contaminants – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)," U.S. Environmental Protection Agency, Mar. 2014.

"Perfluorinated Chemicals (PFCs): Perfluorooctanoic Acid (PFOA) & Perfluorooctane Sulfonate (PFOS)," Association of State and Territorial Solid Waste Management Officials, 1101 17th Street, NW, Suite 707 Washington, DC 20036, Information Paper, Aug. 2015.

L. Cummings, A. Matarazzo, N. Nelson, F. Sickels, and C. Storms, "Recommendation on Perfluorinated Compound Treatment Options for Drinking Water," New Jersey Drinking Water Quality Institute, Treatment Subcommittee, Jun. 2015.

E. Dickenson and C. Higgins, "Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances," Water Research Foundation, 6666 West Quincy Avenue, Denver, CO 80235, Web Report 4322, 2016.

"Occurrence Data for the Unregulated Contaminant Monitoring Rule," U.S. Environmental Protection Agency, May 2016, [Online]. Available: <https://www.epa.gov/dwucmr/occurrence-data-unregulated-contaminant-monitoring-rule>. [Accessed 19-April-2016].

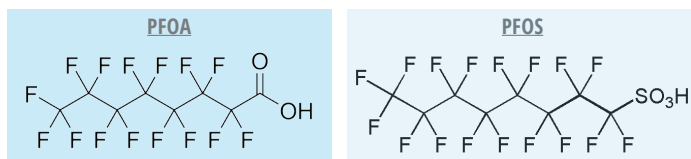
Perfluorinated Compounds

Prevalence and Assessment in Drinking Water

What are PFCs?

Perfluorinated Compounds (PFCs), also referred to as perfluorinated alkyl substances (PFASs), are a large group of environmentally persistent manufactured chemicals used in industrial applications and consumer products. PFCs are very stable, slow to degrade in the environment, and can lead to potential adverse health effects in humans and wildlife. Animal studies show that increased exposure to high concentrations of PFCs may cause abnormal endocrine activity, and reproductive and developmental problems.

Several compounds fall under the umbrella of PFCs, including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). The U.S. Environmental Protection Agency (EPA) and many states have provided guideline concentrations for PFOA and PFOS in source or drinking waters. In May of 2016, the EPA released lifetime health advisories for PFOA and PFOS that are based on adverse developmental health effects to the most sensitive populations: fetuses during pregnancy and breastfed infants. EPA recommends that drinking water containing PFOA or PFOS individually or in combination at concentrations greater than 0.070 µg/L (70 ng/L) should undergo further testing and efforts to limit exposure.



PFCs can be clustered into two groups – “long-chain” and “short-chain” PFCs. “Long-chain” PFCs, which include PFOA and PFOS, typically are designated as perfluoroalkyl sulfonic acids containing ≥6 carbons and perfluoroalkyl carboxylic acids with ≥8 carbons. Short-chain PFCs, which have less than 6 carbon molecules, can be degradation by-products of long-chain PFCs or independent PFC compounds. Long- and short-chain PFCs have been identified in drinking water and are categorized as contaminants that should be monitored. “Long-chain” PFCs are of particular concern because they are more difficult to degrade and more likely to persist in the environment.

Currently there are no enforceable federal drinking water limits for PFCs. Elevated levels of PFCs should be reported to your state’s primary agency to determine the course of action. While there are numerous PFCs identified to date, the EPA has only required monitoring of the following PFCs as contaminants with suspected presence in drinking water under the Unregulated Contaminant Monitoring Rule 3 (UCMR 3).

Primary PFCs Found in Drinking Water	Source of PFC
Long-Chain	
Perfluorooctanoic acid (PFOA)	Nonstick Surfaces
Perfluorooctane sulfonate (PFOS)	Fabric Protection , Firefighting Foam
Perfluorononanoic acid (PFNA)	Surfactant Used for Plastic Production
Short-Chain	
Perfluorohexane Sulfonic Acid (PFHxS)	Firefighting Foam
Perfluorohexanoic Acid (PFHxA)	Degradation Product of PFHxS
Perfluorobutanesulfonic Acid (PFBS)	Stain Repellent; Replacement for PFOS

Presence of PFCs in Drinking Water Supplies

PFCs are highly soluble in aquatic environments and can dissolve into water from various sources. Due to their chemical and biological stability, PFCs are difficult to degrade via biodegradation, photolysis, or hydrolysis. They are most often found near industry discharge points where they have been used. Surface water sources of PFCs include aqueous film forming foam (AFFF) runoff from firefighting activities, industrial factory runoff, and wastewater treatment plant discharges. Groundwater sources include landfill leachate, plumes from AFFF use, and runoff from land application of wastewater biosolids.

In the United States, source waters including lakes, rivers, tributaries, and groundwater have been found to have low ng/L levels of PFCs. The chemical species of PFC present in source waters is also of interest to water researchers since the toxicity is closely related to the form of PFC found. Data collected as part of the EPA’s UCMR 3 illustrates that PFOS and PFOA are the most frequently detected PFC compounds in finished drinking waters .

Removal of PFCs from source waters depends on water treatment variables such as influent concentration and treatment techniques. Conventional treatment has been shown to be largely ineffective at removal of PFCs, but studies show up to a 90% removal of PFCs is possible with certain advanced treatment techniques like activated carbon filtration, high pressure membrane filtration, or anion exchange.

Perfluorinated Compounds

Prevalence and Assessment in Drinking Water

Occurrence of PFCs in Public Water Systems (PWSs)

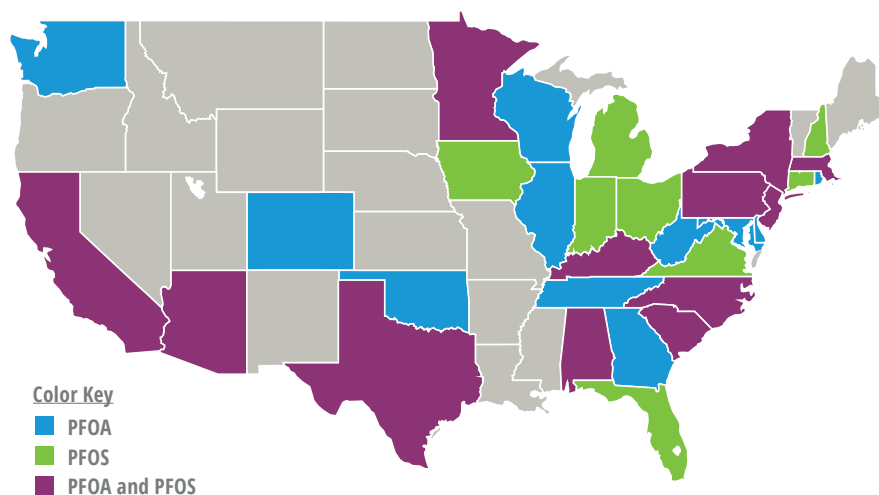
Compound	EPA Lifetime Health Advisory (LHA) Concentration (µg/L)* (2016)	UCMR 3 Minimum Reporting Level (MRL) (µg/L)*	% of PWSs with Results ≥ MRL*	% of PWSs with Results > LHA*
PFOS	0.070	0.040	0.30%	0.90%
PFOA	0.070	0.020	0.09%	0.30%
PFNA	N/A	0.020	--	--
PFHxS	N/A	0.030	--	--
PFHpA	N/A	0.010	--	--
PFBS	N/A	0.090	--	--

*4,864 reporting PWSs - Data from EPA UCMR 3

Preferred PFC Analytical Method

Standard Name	EPA 537 Rev. 1.1
Method Name	LC/MS/MS
Interferences	<ul style="list-style-type: none"> • Humic and/or fulvic materials • Laboratory supplies containing PFCs • Chlorine
Sampling Equipment	250 mL Polypropylene bottles with polypropylene screw caps, nitrile gloves
Sample Preservation	A preservation reagent, Trizma® is recommended for buffering and removal of free chlorine
Sample Standardization	A field blank sample is required per site
Sample Holding Time	14 days with sample chilling as described in Section 8.4
Extract Holding Time	28 days with described preservation and storage in Section 8.5
Reporting Limit	0.5 to 1 ng/L for primary PFCs

PFOA and PFOS Occurrence



Source: Map created from data collected by Eurofins Eaton Analytical

Sampling and Measurement of PFCs

While no special equipment is required for sampling stable PFC compounds in water, special care should be taken during the sampling and transport process to avoid contamination from PFC coated clothing, sampling materials and storage containers. Grab samples are collected in polypropylene bottles and shipped in coolers with ice packs to the selected laboratory for PFC measurement. The analysis typically costs \$300 - \$350 per sample when completed by a commercial laboratory.

Sampling location should be based on the water utility's source waters and distribution system design. In general, samples should be gathered from multiple surface waters, unconfined wells,

or semi confined groundwater wells. Occurrence of PFCs should be examined first in finished water sources to confirm presence of PFCs. If PFCs are detected in finished water, raw water should be screened. Treatment of PFCs through conventional water treatment has not been shown to be very effective, but blending of water sources may reduce the amount of PFCs measured in finished waters. The presence of chlorine, other PFCs, humic acids, fulvic acids, or organic acids in the water sample may cause measurement interference, but interferences can be removed through sample preparation.

The analytical method for measuring PFCs is EPA 537 Rev. 1.1 which uses solid phase extraction

followed by liquid chromatography with tandem mass spectrometry (LC/MS/MS). This approach, also cited by the International Standards Organization (ISO) and the American Society for Testing and Materials (ASTM), has proven highly accurate for a range of fourteen PFCs, including the PFCs listed above.

While most PFCs show a single concentration peak on an LC/MS/MS chromatogram, PFOS produces linear and branched isomers, showing two concentration peaks. The method combines the isomers for quantification. There is speculation that this phenomenon exists for PFHxS and PFBS, but this has not been confirmed to date.

References

*Emerging Contaminants – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA). U.S. Environmental Protection Agency, Mar. 2014.

*Perfluorinated Chemicals (PFCs): Perfluorooctanoic Acid (PFOA) & Perfluorooctane Sulfonate (PFOS). Association of State and Territorial Solid Waste Management Officials, 1101 17th Street, NW, Suite 707 Washington, DC 20036, Information Paper, Aug. 2015.

L. Cummings, A. Matarazzo, N. Nelson, F. Sicksel, and C. Storms, "Recommendation on Perfluorinated Compound Treatment Options for Drinking Water," New Jersey Drinking Water Quality Institute, Treatment Subcommittee, Jun. 2015.

E. Dickenson and C. Higgins, "Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances," Water Research Foundation, 6666 West Quincy Avenue, Denver, CO 80235, Web Report 4322, 2016.

L. Bonnette, B. J. Boros-Russo, A. Dillon, E. Apalinski, J. Berchtold, K. Fell, B. Hamill, M. Ferko, and B. Wilk, "Determination of Perfluorooctanoic Acid (PFOA) in Aqueous Samples," New Jersey Department of Environmental Protection Division of Water Supply, Trenton, N.J., Jan. 2007.

*Occurrence Data for the Unregulated Contaminant Monitoring Rule," U.S. Environmental Protection Agency, May 2016, [Online]. Available: <https://www.epa.gov/dwucmr/occurrence-data-unregulated-contaminant-monitoring-rule>. [Accessed 19-April-2016].

EPA, "Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)." [Online]. Available: https://pub.epa.gov/si/public_record_report.cfm?dirEntryID=198984&sampleSearch=1&searchAll=EPAN%25F000%25FR-08%25F002+ [Accessed 06-May-2016].

Perfluorinated Compounds

Resources for Identifying and Managing PFCs

Perfluorinated Compounds (PFCs) are a group of persistent organic chemicals that have been used in industrial and consumer product applications for their nonstick properties. As industry understanding of PFCs continues to grow, regulatory agencies and industry researchers have developed tools for assessing, measuring, and treating PFCs in water to prevent human health implications. PFCs are very stable in aqueous solutions and are not easily removed through conventional water treatment. As a result, advanced treatment processes may be necessary to prevent PFCs from reaching consumers. Several helpful guides have been assembled to assist water utility staff with addressing PFCs. Additional resources include but are not limited to:

U.S. Environmental Protection Agency (EPA) Resources:

- EPA's Health Advisories for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS): www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos
- EPA's Perfluorooctanoic Acid (PFOA) and Other Perfluorinated Chemicals (PFCs) resource page: www.epa.gov/chemical-research/research-perfluorooctanoic-acid-pfoa-and-other-perfluorinated-chemicals-pfcs
- EPA's Third Unregulated Contaminant Monitoring Rule: www.epa.gov/dwuicmr/third-unregulated-contaminant-monitoring-rule

Analytical Methods for Measuring PFCs:

- EPA Method 537 Rev. 1.1. Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS): www.epa.gov/water-research/epa-drinking-water-research-methods
- List of Laboratories Approved by EPA for the Third Unregulated Contaminant Monitoring Rule (UCMR 3): www.epa.gov/dwuicmr/list-laboratories-approved-epa-third-unregulated-contaminant-monitoring-rule-ucmr-3
- ISO 25101:2009 - Water quality - Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) - Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry: www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=42742
- ASTM D7979 - 15e1 - Standard Test Method for Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS): www.astm.org/Standards/D7979.htm

Research Reporting on PFCs:

- Water Research Foundation Report #4322 – Treatment Mitigation Strategies for Poly- and Perfluorinated Chemicals: www.waterrf.org/Pages/Projects.aspx?PID=4322
- Water Research Foundation Report #4344 – Removal of Perfluoroalkyl Substances by PAC Adsorption and Anion Exchange: www.waterrf.org/Pages/Projects.aspx?PID=4344
- New Jersey Drinking Water Quality Institute – Recommendation on Perfluorinated Compound Treatment Options for Drinking Water Report: www.nj.gov/dep/watersupply/pdf/pfna-pfc-treatment.pdf

Treatment & Decision Making Guides for PFCs

- State of Minnesota – Minnesota Department of Health - Performance Evaluation Removal of Perfluorochemicals (PFC's) with Point-of-Use (POU) Water Treatment Devices: <http://www.health.state.mn.us/divs/eh/wells/waterquality/poudevicefinal.pdf>
- Remediation of Perfluorinated Alkyl Chemicals at a Former Fire-Fighting Training Area: www.esaa.org/wp-content/uploads/2015/06/08-Paper-34.pdf
- ESTCP – DOD's Environmental Research Programs - Remediation of Perfluoroalkyl Contaminated Aquifers using an In Situ Two-Layer Barrier: Laboratory Batch and Column Study: [https://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2127/ER-2127/\(language\)/eng-US](https://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-2127/ER-2127/(language)/eng-US)

Additional Resources on PFCs

- American Water Works Association's DrinkTap General Resource on Drinking Water: www.drinktap.org/water-info/whats-in-my-water/perfluorinated-compounds.aspx
- Center for Disease Control and Prevention – PFOA Fact Sheet: www.cdc.gov/biomonitoring/PFOA_FactSheet.html
- National Institute of Environmental Health Services PFC Fact Sheet: www.niehs.nih.gov/health/materials/perfluorinated_chemicals_508.pdf

