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Fact Sheet

Interim Guidance on Sampling and Analysis for PFAS at Disposal Sites Regulated under the Massachusetts Contingency Plan

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Introduction

This Fact Sheet, prepared by the Massachusetts Department of Environmental Protection (MassDEP) Bureau of Waste Site Cleanup (BWSC), provides guidance regarding when and how to sample and analyze for Per- and Polyfluoroalkyl Substances (together, PFAS¹) at disposal sites regulated under the Massachusetts Contingency Plan (MCP). MassDEP recommends a specific list of target PFAS analytes and discusses appropriate quantitative and qualitative risk characterization approaches. The Fact Sheet also summarizes physical and chemical properties, potential environmental health effects, and current state and federal standards and guidelines for PFAS compounds.

PFAS may be present at MCP sites as a result of current or past releases associated with the manufacturing, use, or disposal of products containing these chemicals. PFAS are considered hazardous materials under MGL Chapter 21E and potential Contaminants of Concern (COCs).

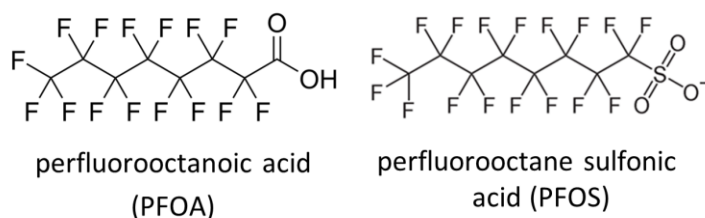
Background Information

What are PFAS?

PFAS are part of a large family of man-made fluorine-containing chemicals which have been used to impart unique properties when applied to materials, including resistance to water, grease and stains. They are also used for thermal stability, foaming control, flow control, leveling and wetting. For the purpose of this Fact Sheet, the substances of primary concern are the longer-chain perfluoroalkyl acids

¹ PFAS are sometimes referred to as polyfluorinated compounds or “PFCs” as well.

(C₆ to C₈)², such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), and products that can form these long-chain perfluoroalkyl acids.



As with any large family of structurally-similar compounds, PFAS can exhibit a wide range of physical, chemical and toxicological properties. This Fact Sheet focuses on those compounds and characteristics of greatest environmental concern while acknowledging that unique properties of individual PFAS may be considered on a case-by-case basis.

Some PFAS (e.g., PFOA, PFOS) can be very resistant to breakdown, migrate easily, and concentrate in the food chain (i.e., bioaccumulate). As a result, they may be found throughout the environment in groundwater, surface water, soil, and air, as well as in food, breast milk, and human blood serum. PFAS have been used for decades in many common products but their presence in the environment is still poorly understood as they have been subject to very limited testing.

Human Exposure and Potential Health Effects

Although our knowledge of the health risks posed by PFAS is still incomplete, exposures to these compounds have been associated with a wide range of adverse health effects in studies on laboratory animals and in people. These studies indicate that sufficient exposure to PFAS compounds, in particular PFOA and PFOS, may result in adverse effects on fetal and neonate development such as low birth weight, accelerated puberty, delayed mammary gland development and skeletal variations. Other adverse effects observed in adults include liver damage, effects on the immune system, thyroid, and cholesterol levels. There is also inconclusive evidence that they might cause testicular and kidney cancer in animals and humans. Some studies suggest that these chemicals function as endocrine disruptors and mimic fatty acids in the body. The chemicals are not easily excreted and remain in the human body for years (estimated 4 to 8 years), which can cause them to build up in the body following exposures.

While humans may be exposed to PFAS through a variety of pathways³, the most common and significant environmental exposure at disposal sites is through the consumption of drinking water from contaminated public or private water supplies. These chemicals have been found in a number of drinking water systems due to localized contamination from nearby manufacturing facilities that used PFAS or areas where the chemicals were used in firefighting foams. However, some PFAS are capable of traveling long distances through air and groundwater and may be found far from the locations where they were initially released into the environment.

Because these chemicals have been used in an array of consumer products, most people have been exposed to them. Since 1999, United States Centers for Disease Control and Prevention (US CDC) has

² The discussion in this Fact Sheet applies to both the acid and anion forms of PFAS.

³ Depending upon the disposal site, other exposure pathways may be of concern, such as inhalation of contaminated air and contact with contaminated soil.

measured several types of PFAS in the US population as part of the National Health and Nutrition Examination Survey (NHANES). In particular, the survey has measured PFOS and PFOA. With the decrease in production and use of some PFAS, the national PFAS levels also have dropped over time. From 1999 to 2014, blood PFOA and PFOS levels declined by more than 60% and 80%, respectively⁴.

Sources of PFAS in the Environment

PFAS have been used since the 1940s as manufacturer-applied oil and water repellants on products such as clothing, upholstery, paper, and carpets, and were also used in making fluoropolymers for non-stick cookware (Table 1). Thus, these materials may be associated with many industries, including subsets of the aerospace, automotive, manufacturing, electronics, and textiles industries. PFAS surfactant qualities were also utilized in mist suppressants that can be added to metal plating baths to prevent air releases and to firefighting foams used to extinguish or prevent fires associated with flammable liquids.

Aqueous Film Forming Foams (AFFF) that contain PFOS have been used since the 1960s to prevent or extinguish highly flammable or combustible liquid Class B fires, such as fires involving gas tankers and oil refineries, and at military bases, airports, and firefighting training facilities. The foam has also been used by local fire departments in training and to extinguish (or prevent) motor vehicle fires at crash sites. AFFF containing PFOS has not been manufactured in the US since 2002 but stockpiles may remain at Department of Defense (DoD) bases, airports, local fire departments and other facilities.

PFOA has been used primarily as an aqueous dispersion agent in the manufacturing of fluoropolymers, which are substances with special properties that have thousands of manufacturing and industrial applications. While manufacturers are phasing out the use of PFOA in these applications, site investigations should consider the past use and past formulations when investigating possible PFAS releases.

PFOA and PFOS can also be created by the biotransformation of some fluorotelomers and other compounds (i.e., precursor compounds). Fluorotelomers are used in firefighting foams (as a replacement for PFOS) and as surface protection to provide soil, stain, grease, and water resistance in products such as tile, stone, textiles, and paper packaging.

PFOA and PFOS are no longer manufactured in the United States as a result of voluntary phase-outs, with a few exceptions for limited industrial uses. As part of the US Environmental Protection Agency's (USEPA) PFOA Stewardship Program⁵, eight major chemical manufacturers committed to eliminate the use of PFOA and PFOA-related chemicals in their facilities' emissions and product content by 2015. However PFOA and PFOS are still produced in other locations around the world and may continue to be imported into the US in consumer goods such as carpets, leather, apparel, textiles, paper and packaging, coatings, rubber, and plastics.

⁴ National Report on Human Exposure to Environmental Chemicals, www.cdc.gov/exposurereport

⁵ Fact Sheet: 2010/2015 PFOA Stewardship Program www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program

Table 1: Potential Processes, Uses & Sources of PFAS

Processes
Application of fluoropolymer coatings in manufacturing
Production of plastics/polymers
Application of oil and water repellent finishes/coatings
Firefighting and fire prevention activities using certain foams
Mist suppression in metal plating operations
Photo microlithography process to produce semiconductors
Photography and film production and processing

Product Uses/Sources
Some grease-resistant paper
Fast food containers/wrappers
Microwave popcorn bags
Pizza boxes
Candy wrappers
Non-stick cookware
Stain and/or water-resistant coatings used on carpets, upholstery, and other fabrics
Water-resistant clothing
Adhesives
Aviation hydraulic fluids
Paints, varnishes and sealants

As a consequence of the widespread use of PFAS in consumer products, the effluent from residential septic systems and wastewater treatments plants can contribute to environmental concentrations at a site. The presence of such sources may be documented and considered as a component of the Conceptual Site Model.

Standards and Guidelines

Federal Criteria

No federal drinking water standards have been established for PFOS and PFOA. USEPA is collecting drinking water data to determine if establishing a Maximum Contaminant Level (MCL) is warranted under the Safe Drinking Water Act based on PFOS and PFOA occurrence in drinking water, the number of people potentially being exposed, observed exposure levels, and costs for treatment to reduce levels.

On May 19, 2016, USEPA released a Drinking Water Health Advisories (HA) of 70 parts-per-trillion (ppt) applicable to both the individual PFOA and PFOS chemical concentrations and when both PFOA and PFOS are found in drinking water, the 70 ppt HA level is applicable to the combined concentrations of PFOA and PFOS⁶. As published by USEPA, the HA level is non-enforceable/non-regulatory guidance intended to describe a concentration in drinking water offering a margin of protection for all Americans from adverse health effects throughout their life resulting from exposure to PFOA and PFOS⁷. Due to the concern over developmental toxicity, EPA recommends that the lifetime HA for PFOA and PFOS also apply to short-term (i.e., weeks to months) exposure scenarios during pregnancy and lactation.

Massachusetts Criteria

MassDEP has not published a drinking water standard for PFAS. On June 8, 2018, the Department published a drinking water guideline, known as an Office of Research and Standards Guideline, or “ORSG” (MassDEP, 2018). MassDEP’s ORSGs are usually developed when there are no federal standards or guidance. As noted above, the USEPA published a HA for the sum of two PFAS chemicals – PFOA and PFOS. Due to similar health concerns, MassDEP established its guideline to include the following three additional PFAS chemicals: perfluorononanoic acid (PFNA), perfluorohexanesulfonic acid (PFHxS), and perfluoroheptanoic acid (PFHpA). The ORSG is 70 ppt, and applies to the total summed level of all five compounds. Based on this ORSG, MassDEP recommends the following:

1. Consumers in sensitive subgroups (pregnant women, nursing mothers and infants) not consume water when the level of the five PFAS substances, individually or in combination, is above 70 ppt.
2. Public water suppliers take steps expeditiously to lower levels of the five PFAS, individually or in combination, to below 70 ppt for all consumers.

According to the Massachusetts Drinking Water Regulations [310 CMR 22.03(8)], if MassDEP finds on the basis of a health assessment that the level of any contaminant in drinking water at a Public Water System (PWS) poses an unacceptable health risk to consumers, the PWS must take actions to achieve safe levels and also to provide public notice.

The MassDEP Drinking Water Program (DWP) works closely with public water suppliers if PFAS is detected in a system at concentrations exceeding or approaching the ORSG. The DWP can assist with

⁶ Drinking Water Health Advisories for PFOS and PFOA: <https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos>

⁷ In developing the USEPA health advisory levels, the USEPA assumed that drinking water accounts for 20 percent of PFAS exposure.

technical support, public notice templates, fact sheets and development of treatment options or alternative sources if necessary.

Under the Waste Site Cleanup Program, no MCP Method 1 Standards have been established for PFAS⁸. A Method 2 and/or Method 3 Risk Characterization⁹ would apply to the characterization of risk at a disposal site with PFAS as a Contaminant of Concern (COC) in the absence of promulgated Method 1 Standards.

PFAS CONSIDERATIONS AT MCP SITES

Hazardous Materials Regulated Under M.G.L. Chapter 21E

Hazardous Material is defined (310 CMR 40.0006) to be a “material, including, but not limited to, any material in whatever form which, because of its quantity, concentration, chemical, corrosive, flammable, reactive, toxic, infectious or radioactive characteristics, either separately or in combination with any substance or substances, constitutes a present or potential threat to human health, safety, welfare, or to the environment, when improperly stored, treated, transported, disposed of, used, or otherwise managed...”

MassDEP has determined, pursuant to 310 CMR 40.0342, that the available toxicity information for PFOS, PFOA and related PFAS compounds indicates that these materials are “hazardous materials” subject to regulations under M.G.L. c.21E and the MCP.

Reportable Conditions for PFAS Compounds

There are no PFAS-specific Reportable Quantities (RQs) or Reportable Concentrations (RCs) established under the MCP in 310 CMR 40.1600 – the Massachusetts Oil and Hazardous Material List (“MOHML”). Therefore the reported presence of PFAS in soil or groundwater is not, by itself, a notifiable condition for those persons obligated to notify pursuant to M.G.L. Chapter 21E.

However, the MCP describes a 2-Hour notification condition that is applicable to any oil or hazardous material regardless of whether it is listed on the MOHML. Pursuant to 310 CMR 40.0311(7), “any release of any oil and/or hazardous material, in any quantity or concentration, that poses or could pose an Imminent Hazard, as described in 310 CMR 40.0321 and 40.0950” requires notification within two hours.

In addition, the MCP also requires that response actions be taken for any release of a hazardous material that poses a significant risk, even if the release itself is not notifiable (see 310 CMR 40.0370).

MassDEP may identify and notify Potentially Responsible Parties of their liability under M.G.L. c.21E for a release of oil or hazardous material to the environment, including releases without specific notification

⁸ Proposed standards and Reportable Concentrations (and supporting documentation) are expected to be published for public comment in the summer of 2018.

⁹ USEPA has established a Reference Dose of 0.00002 mg/kg/day, documented in the Drinking Water Health Advisory, which would serve as the basis of a MCP Risk Characterization.

criteria, pursuant to 310 CMR 40.0160. Such Notices of Responsibility would describe any actions the Department determines necessary to respond to the release.

PFAS Compounds as Contaminants of Concern

As hazardous materials, PFAS compounds must be included as COC if they are present at a disposal site being addressed under the MCP. MassDEP recognizes that the absence of RCs and the extensive list of PFAS compounds create uncertainty about which of the many PFAS compounds should be included in a 21E site investigation and how they may be evaluated.

In general, MassDEP recommends that the 14 analytes specified in EPA Method 537 Rev. 1.1 and listed in Table 3 should be the focus of MCP site investigations. (See also the following discussion of analytical methods and reporting limits.) However, specific knowledge of site history/operations, the results of past analyses and other relevant information may be considered, consistent with MassDEP sampling and analysis guidance, to expand or narrow the list of target analytes. For example, if past industrial operations at the site indicate the likely presence of other PFAS compounds at toxicologically significant concentrations, then those compounds would also be included in the investigation.

PFAS in MCP Risk Characterizations

In the absence of promulgated Method 1 soil and groundwater standards for PFAS, these COCs must be addressed using either a Method 2 (310 CMR 40.0980) or Method 3 (310 CMR 40.0990) Risk Characterization, as applicable.

MassDEP has conducted a preliminary review of the toxicity information available for PFAS and recommends that these compounds be addressed using a toxicity equivalency approach¹⁰ to quantitatively and qualitatively address mixtures of PFAS present at a disposal site.

Quantitatively Evaluate Five PFAS Compounds

Table 2 lists five PFAS compounds for which the available information indicates that the toxicity of each compound is approximately equivalent to that of PFOA.

Using an MCP Method 2 Risk Characterization, the concentrations of these five PFAS compounds (if present) would be summed and compared to a single calculated Method 2 PFAS-equivalent standard. For the purpose of conducting a Method 2 risk characterization for PFAS in drinking water, or in groundwater protected for its current or future use as drinking water (i.e., Category GW-1 groundwater), the ORSG of 0.07 µg/L may be cited as a Method 2 GW-1 Groundwater Standard pursuant to 310 CMR 40.0982(7).

Using an MCP Method 3 Risk Characterization, the concentrations of these five PFAS compounds (if present) would be summed and used to calculate an Exposure Point Concentration to be used to estimate the Cumulative Receptor Risk.

¹⁰ For example, MassDEP uses a similar toxicity equivalency factor (“TEF”) approach to develop MCP Method 1 standards and to conduct Method 3 risk characterizations for dioxin mixtures.

Qualitatively Evaluate Other PFAS Compounds

For other PFAS compounds not listed in Table 2, the toxic equivalency is assumed to be zero (0) for the purposes of an MCP risk characterization. The concentrations of these PFAS compounds at the disposal site should be discussed as part of the overall site assessment, but – *at this time* - these PFAS need not be summed and compared to a Method 2 Standard nor included in a Method 3 Cumulative Receptor Risk estimate.

PFAS SAMPLING AND ANALYSIS CONSIDERATIONS

When/Where to Sample for PFAS

Under the MCP, many factors are considered by the Licensed Site Professional (LSP) to determine the sampling strategy – including likely COCs - at a disposal site. The need to sample for PFAS will depend on the disposal site Conceptual Site Model and case-specific information, including the specific nature of operations at a site, the time period (relative to PFAS availability) of operations and the proximity to current or future drinking water sources (GW-1 areas).

The need for drinking water samples (i.e., from a public or private drinking water well or tap) would be indicated where plume delineation shows potential for contamination of a drinking water supply well.

For example, sampling for PFAS should be considered at locations in or near GW-1 areas where the following activities may have occurred or where related wastes have come to be located:

Facilities where PFAS have been manufactured (i.e., chemical facilities) or applied (see the list of process/product uses/sources in Table 1) and may have resulted in releases to the environment (including air emissions and subsequent air distribution).

Landfills¹¹ where uncontrolled leaching from disposal of waste materials from PFAS manufacturing facilities may have occurred.

Junkyards and other locations where auto fluff may have been disposed.

Former or Current DoD sites where there has been (or likely has been) historic use of AFFF.

Airport hangars, rail yards and other facilities (e.g., petrochemical) where quantities of AFFF may have been applied or stored.

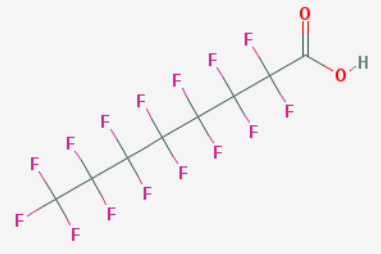
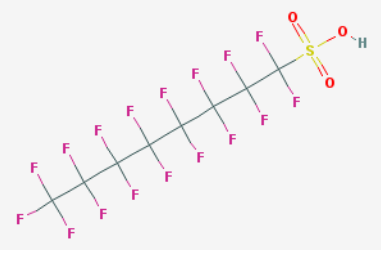
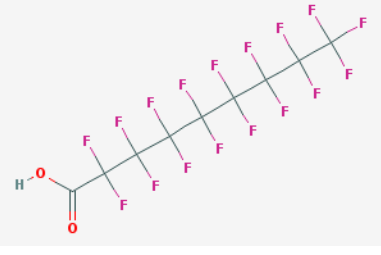
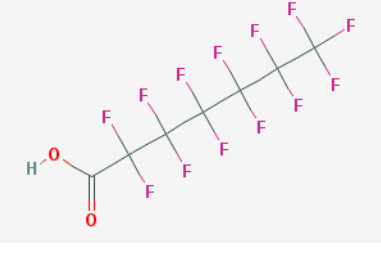
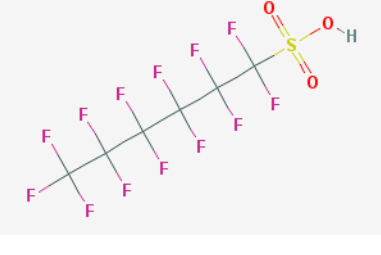
Firefighting training and equipment test areas where AFFF has been (or likely has been) used.

Crash sites, including aircraft, rail and motor vehicle sites where AFFF may have been used.

Metal coating and plating facilities.

¹¹ This guidance is applicable to landfills and other solid waste facilities for which assessments are conducted in whole or in part under the MCP. Facilities regulated under 310 CMR 16.00: Site Assessment for Solid Waste Facilities may also be required to sample for PFAS as a permit requirement.

Table 2 - PFAS Compounds with Sufficient Toxicity Information to be Quantified in MCP Risk Characterizations

Compound	CAS	Carbon Chain Length	Structure
Perfluorooctanoic acid	PFOA 335-67-1	8	
Perfluorooctanesulfonic acid	PFOS 1763-23-1	8	
Perfluorononanoic acid	PFNA 375-95-1	9	
Perfluoroheptanoic acid	PFHpA 375-85-9	7	
Perfluorohexanesulfonic acid	PFHxS 355-46-4	6	

How to Sample for PFAS

Because of the potential presence of PFAS in common consumer products and in equipment typically used to collect soil, groundwater, surface water, sediment, and drinking water samples as well as the need for very low reporting limits, special handling and care must be taken when collecting samples for PFAS analysis to avoid sample contamination. In general, items that are specifically identified as waterproof, water resistant or stain-resistant should be avoided or examined for the potential presence of PFAS. There is extensive guidance available online¹² and it is not MassDEP's intent to the use and avoidance of certain products, particularly as formulations may change over time.

Specific recommendations are less important than the LSP's awareness and consideration of how product formulation or analytical methodologies may affect the results at a site.

Sample collection method/sequence

Using new nitrile gloves, collect the sample for PFCs prior to collecting samples for any other analysis to avoid contact with other types of sample containers, bottles or package materials.

As with all samples, do not place the sample bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap.

When the sample is collected and capped, place the sample bottle(s) in an individual sealed plastic bag, separate from all other sample parameter bottles, and place in shipping container packed only with ice

Groundwater, surface water, or drinking water samples should not be field filtered as the glass fiber on the filter can potentially absorb PFAS, resulting in underestimates of PFAS concentration. No sub-sampling/sample transfer should occur in the field. Water samples should be placed in sealed plastic bags to avoid contamination during transport.

Field/Equipment Blanks

When sampling for PFAS, it is recommended that additional and/or more frequent field/equipment blanks be collected prior to and during sampling to check for residual PFAS on sampling equipment due to the potential for cross-contamination issues and the need for very low reporting limits. Source water for blank samples and decontamination fluids should be certified PFAS-free by the analytical laboratory.

Analytical Methods and Reporting Limits

Chemical and physical properties of PFAS prevent the use of conventional analysis (e.g., gas chromatography/mass spectrometry [GC/MS]) to measure them in the environment. EPA's Method 537,

¹² Sources of sampling information include:

- USEPA's "Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS), Methods and guidance for sampling and analyzing water and other environmental media", https://www.epa.gov/sites/production/files/2018-04/documents/pfas_methods_tech_brief_02apr18_revison.pdf
- ITRC's "Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)" https://pfas-1.itrcweb.org/wp-content/uploads/2018/03/pfas_fact_sheet_site_characterization_3_15_18.pdf

Rev. 1.1¹³, published in September 2009, is a liquid chromatography and tandem mass-spectrometry (LC/MS-MS) method is a standard approach for analyzing PFAS in drinking water samples. This type of analysis has allowed for more sensitive determination of PFAS. The method, as written, is intended for analyzing selected perfluorinated alkyl acids in drinking water using solid phase extraction with LC/MS-MS; however, this method has been modified by analytical laboratories to accommodate other matrices. This method has been validated for 14 different perfluorinated alkyl acids and has minimum reporting limits of 2.9 ppt to 14 ppt in drinking water. The EPA method and the September 2016 *Technical Advisory - Laboratory Analysis of Drinking Water Samples for Perfluorooctanoic Acid (PFOA) Using EPA Method 537 Rev. 1.1*¹⁴ provide guidance to ensure that both branched and linear isomers of select PFAS are properly quantified during analysis. Close coordination and advance planning with a qualified laboratory is strongly recommended, particularly if sampling matrices other than water.

A “modified” Method 537 or other analytical method may also be considered, particularly for sampling media other than drinking water. Under the MCP, results from the use of an alternative to EPA Method 537 may be acceptable for site assessment and remedial decisions if the results meet data quality objectives and the supporting QA/QC information is provided. **Note, however, that the use of a method other than Method 537 may not be acceptable for the evaluation of Public Drinking Water Supplies regulated pursuant to 310 CMR 22.00.** It is important to confirm the acceptability of using results from an alternative method before samples are analyzed.

The USEPA, MassDEP and others are currently reviewing the analytical methods available for PFAS. MassDEP is planning to include a PFAS analysis in the Compendium of Analytical Methods (CAM)¹⁵. In addition, the USEPA is in the process of updating Method 537.

The 14 analytes specified in EPA Method 537 Rev. 1.1 and listed below (Table 3) should be the focus of MCP site investigations at this time.

¹³ www.epa.gov/water-research/epa-drinking-water-research-methods

¹⁴ www.epa.gov/sites/production/files/2016-09/documents/pfoa-technical-advisory.pdf

¹⁵ www.mass.gov/guides/compendium-of-analytical-methods-cam

Table 3 - EPA Method 537 Rev. 1.1 Analyte List

Analyte	Acronym
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA
Perfluorobutanesulfonic acid	PFBS
Perfluorodecanoic acid	PFDA
Perfluorododecanoic acid	PFDoA
Perfluoroheptanoic acid	PFHpA
Perfluorohexanesulfonic acid	PFHxS
Perfluorohexanoic acid	PFHxA
Perfluorononanoic acid	PFNA
Perfluorooctanesulfonic acid	PFOS
Perfluorooctanoic acid	PFOA
Perfluorotetradecanoic acid	PFTA
Perfluorotridecanoic acid	PFTTrDA
Perfluoroundecanoic acid	PFUnA

Before September 2009, there were no validated test methods or standardized data quality criteria. As a result, most PFAS data generated and used in earlier publications and assessments have limitations and should be used, if necessary, with caution.

REFERENCES

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