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INTRODUCTION TO PFAS (PFAS-1)

ITRC Technical Resources For Addressing Environmental Releases Of Per- And Polyfluoroalkyl Substances

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- Federal Partners

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- ITRC Industry Affiliates Program
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Today's PFAS Trainers

Kristi Herzer, Vermont Department of Environmental Conservation

Mitch Olson, Ph.D., P.E., Trihydro

Sandra Goodrow, Ph.D. New Jersey Department of Environmental Protection

Andy Safulko, Brown and Caldwell

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Introduction to ITRC and PFAS Team

Kristi Herzer
Vermont Department of Environmental Conservation (VT DEC)

Topics for Today

Topic	**Speaker**
Introduction to ITRC and PFAS Team	Kristi Herzer
Naming Conventions and Sources	Mitch Olson
AFFF	Mitch Olson
Fate and Transport and Site Characterization	Sandra Goodrow
Q&A Break	
Sampling and Analysis	Kristi Herzer
Treatment Technologies	Andy Safulko
Q&A Break	

Who We Are

- State-led coalition (est. 1994) working to advance the use of innovative environmental technologies & approaches
- State, Federal, Stakeholder, Industry Members
- Funded through Federal Grants/ Industry Membership Fees

PFAS Experience Poll

- Which of the following best characterizes your experience with PFAS at environmental sites?
  - None
  - <1 year, 1-2 sites
  - 2-5 years, 10-20 sites
  - > 5 years, 20+ sites

ITRC PFAS Team

- Producing concise technical resources for project managers – regulators, consultants, responsible parties, and stakeholders

- Why: State and federal environmental regulators and others need easily accessible information to aid them in evaluating risks and selecting appropriate response actions at PFAS release sites

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Technical Resources

- ITRC PFAS: https://pfas-1.itrcweb.org/
- Guidance Document
  - First published April 2020
  - Updated December 2021
  - Next update September 2023
  - Small edits & reference additions November 2023
- 13 Fact Sheets
- Training Sessions
  - Video Modules
- Outreach

PFAS – Per- and Polyfluoroalkyl Substances

Welcome

Technical Resources for Addressing Environmental Releases of Per- and Polyfluoroalkyl Substances (PFAS)

PFAS HOME

This Interstate Technology and Regulatory Council (ITRC) online document includes the resources that the ITRC PFAS Team has developed since it began work in 2017.

- PFAS Fact Sheets
- PFAS Technical and Regulatory Guidance Document
  - External Data Tables
- Training Resources
  - Quick Explainer Videos
  - Longer PFAS Training Module Videos
  - Archived Roundtable Sessions
  - PFAS Training Page

You can reach this PFAS Home page from any of the pages on this web site with the Home button at the top of screen.

PFAS Technical and Regulatory Guidance Document

External Tables and Information

- Fact Sheets: PFAS Water and Soil Regulatory and Guidance Values Table Excel File
- Section 2: Figure 2-5 PFAS Family Tree PDF
- Section 2: USEPA Analytes List – PFAS Classifications PDF
- Section 3: AFFF Characteristics Excel File
- Section 3: AFFF Transition to F3 Case Studies Excel File
- Section 4: Physical and Chemical Properties Table 4-1 Excel File
- Section 5: Aquatic Organisms BCF-BAF Table 5-1 Excel File
- Section 5: Plants BCF-BAF Table 5-2 Excel File
- Section 8: PFAS Regulatory Programs Summary Excel File
- Section 11: Analytical Methods Excel File
- Section 11: PFAS Data Usability Table PDF
- Section 12: Treatment Technologies Table Excel File
- Section 12: Integrated Water Treatment Flow Chart PDF
- Section 14: Risk Communication Social Factors Vision Board PDF
- Section 15: Water Treatment Case Studies Excel File
- Section 17.2: Table 17-8 Toxicological Effects Excel File

13 PFAS Fact Sheets

Naming Conventions

Regulations

History and Use

Fate and Transport and Physical and Chemical Properties

Sampling Precautions and Laboratory Analytical Methods

Site Characterization and Media-Specific Occurrence

Treatment Technologies and Methods

Aqueous Film-Forming Foam

Human and Ecological Health Effects and Risk Assessment

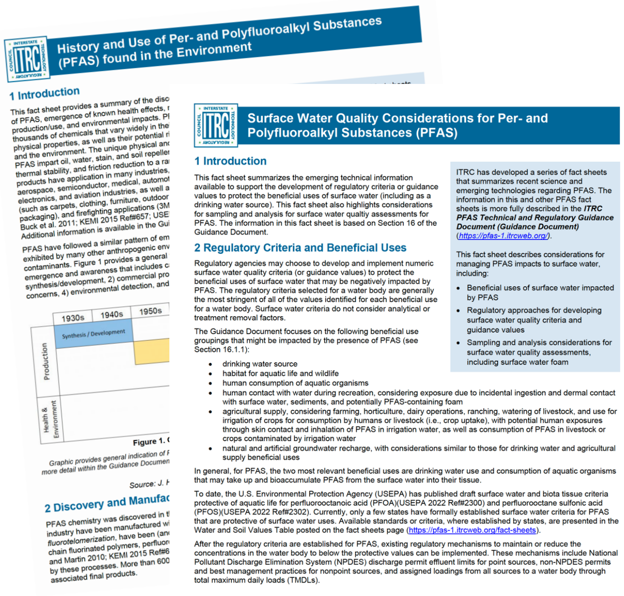
Risk Communication

Stakeholder Perspectives

Surface Water Quality

Biosolids

All updated September 2023



History and Use of Per- and Polyfluoroalkyl Substances (PFAS) found in the Environment

1 Introduction

Surface Water Quality Considerations for Per- and Polyfluoroalkyl Substances (PFAS)

1 Introduction

This fact sheet summarizes the emerging technical information available to support the development of regulatory criteria or guidance values to protect the beneficial uses of surface water (including as a drinking water source). This fact sheet also highlights considerations for sampling and analysis for surface water qualtiy assessments for PFAS. The information in this fact sheet is based on Section 16 of the Guidance Document.

ITRC has developed a series of fact sheets that summarizes recent science and emerging technologies regarding PFAS. The information in this and other PFAS fact sheets is more fully described in the ***ITRC PFAS Technical and Regulatory Guidance Document (Guidance Document)*** (https://pfas-1.itrcweb.org/).

This fact sheet describes considerations for managing PFAS impacts to surface water, including:

- Beneficial uses of surface water impacted by PFAS
- Regulatory approaches for developing surface water quality criteria and guidance values
- Sampling and analysis considerations for surface water quality assessments, including surface water foam

2 Regulatory Criteria and Beneficial Uses

Regulatory agencies may choose to develop and implement numeric surface water quality criteria (or guidance values) to protect the beneficial uses of surface water that may be negatively impacted by PFAS. The regulatory criteria selected for a water body are generally the most stringent of all of the values identified for each beneficial use for a water body. Surface water criteria do not consider analytical or treatment removal factors.

The Guidance Document focuses on the following beneficial use groupings that might be impacted by the presence of PFAS (see Section 16.1.1):

- drinking water source
- habitat for aquatic life and wildlife
- human consumption of aquatic organisms
- human contact with water during recreation, considering exposure due to incidental ingestion and dermal contact with surface water, sediments, and potentially PFAS-containing foam
- agricultural supply, considering farming, horticulture, dairy operations, ranching, watering of livestock, and use for irrigation of crops for consumption by humans or livestock (i.e., crop uptake), with potential human exposures through skin contact and inhalation of PFAS in irrigation water, as well as consumption of PFAS in livestock or crops contaminated by irrigation water
- natural and artificial groundwater recharge, with considerations similar to those for drinking water and agricultural supply beneficial uses

In general, for PFAS, the two most relevant beneficial uses are drinking water use and consumption of aquatic organisms that may take up and bioaccumulate PFAS from the surface water into their tissue.

To date, the U.S. Environmental Protection Agency (USEPA) has published draft surface water and biota tissue criteria protective of aquatic life for perfluorooctanoic acid (PFOA)(USEPA 2022 Ref#2300) and perfluorooctane sulfonic acid (PFOS)(USEPA 2022 Ref#2302). Currently, only a few states have formally established surface water criteria for PFAS that are protective of surface water uses. Available standards or criteria, where established by states, are presented in the Water and Soil Values Table posted on the fact sheets page (https://pfas-1.itrcweb.org/fact-sheets).

After the regulatory criteria are established for PFAS, existing regulatory mechanisms to maintain or reduce the concentrations in the water body to below the protective values can be implemented. These mechanisms include National Pollutant Discharge Elimination System (NPDES) discharge permit effluent limits for point sources, non-NPDES permits and best management practices for nonpoint sources, and assigned loadings from all sources to a water body through total maximum daily loads (TMDLs).

https://pfas-1.itrcweb.org/fact-sheets/

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Introduction to PFAS Naming Conventions and Sources

Mitch Olson, Ph.D., P.E., Trihydro

PFAS Technical and Regulatory Guidance Document Published

- Final web document PFAS-1: https://pfas-1.itrcweb.org
- PFAS Chemistry and Naming Conventions, History and Use of PFAS, and Sources of PFAS Releases to the Environment
  - Section 2.1 – Environmental Significance
  - Section 2.2 – Chemistry, Terminology, and Acronyms
  - Section 2.3 – Emerging Health and Environmental Concerns
  - Section 2.4 – PFAS Reductions and Alternative PFAS formulations
  - Section 2.5 – PFAS Uses and Products
  - Section 2.6 – PFAS Releases to the Environment

ITRC 2023. *PFAS Technical and Regulatory Guidance Document and Fact Sheets* PFAS-1. Washington, D.C.. https://pfas-1.itrcweb.org/.

PFAS Definitions and Nomenclature

- There is no universally accepted definition of PFAS
- In general, PFAS are characterized by carbon atoms linked to each other and bonded to fluorine atoms at most or all available carbon bonding sites
- References, definitions, and resources include:
  - Buck et al. (2011) - Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins
  - OECD (2018) - Toward a New Comprehensive Global Database of Per- And Polyfluoroalkyl Substances
  - OECD (2021) - Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances
  - USEPA CompTox Chemicals Dashboard - Publicly available PFAS structures and predicted properties (https://comptox.epa.gov/dashboard/)

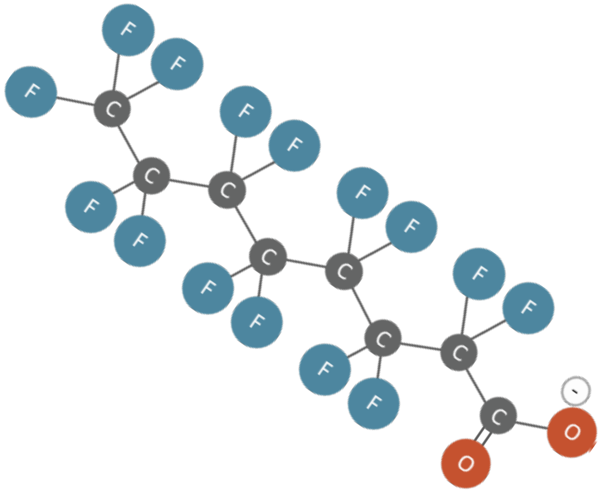


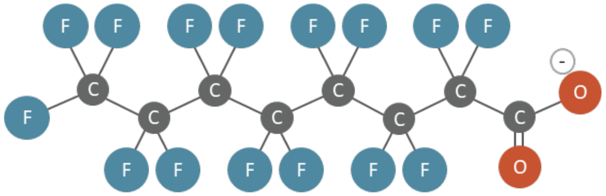
Table 2-1 Examples of PFAS definitions

PFAS-1, Section 2.2 Chemistry, Terminology, and Acronyms.
Source: M. Olson, Trihydro. Used with permission.

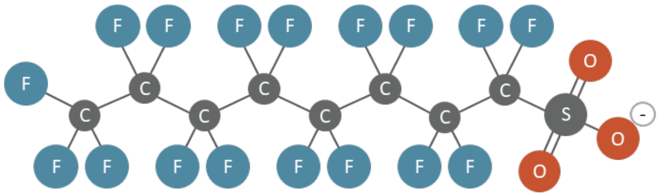
Key Terms and Acronyms

- PFAS (per- and polyfluoroalkyl substances)
- Perfluoroalkyl substances
  - PFAAs (perfluoroalkyl acids)
  - PFCAs (perfluoroalkyl carboxylates)
    - PFOA (perfluorooctane carboxylate)
  - PFSAs (perfluoroalkane sulfonates)
    - PFOS (perfluorooctane sulfonate)
- Polyfluoroalkyl substances
  - Precursors

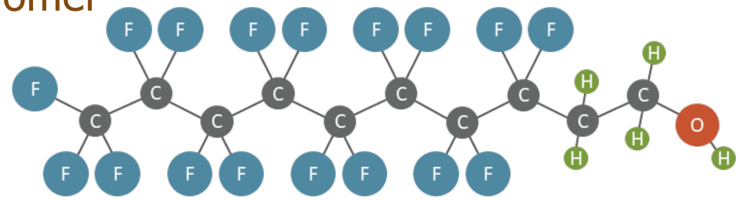
PFOA



PFOS



8:2 Fluorotelomer alcohol

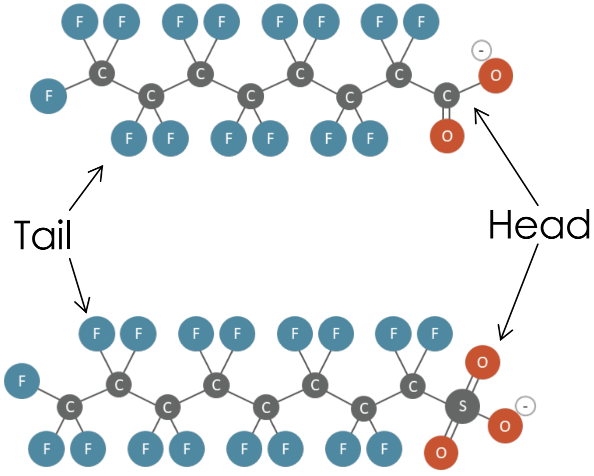


PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs) and Section 2.2.4 Polyfluoroalkyl Substances.
Source: M. Olson, Trihydro. Used with permission.

Basic PFAA Structure

- Perfluoroalkyl Acids (PFAAs)
  - Fully fluorinated chain (2 or more carbon “tail”)
    - Carbon-fluorine bond is very strong
    - Tail is lipid- and water-repelling
  - Functional group (“head”)
    - PFCAs: carboxylate group (COO^-)
    - PFSAs: sulfonate group (SO_3^-)

Perfluorooctane carboxylate (PFOA)



Perfluorooctane sulfonate (PFOS)

PFAS-1, Section 2.2. Figure 2-7, Tail and Head structure of PFOS and PFOA molecules. Source: M. Olson, Trihydro. Used with permission.

PFAA Naming System

- PFXY
  - PF = perfluoro
  - X = number of carbons
    - Same convention as hydrocarbons
    - Includes C in the carboxylate group
  - Y = functional group
    - S = sulfonate (R-SO_3^-)
    - A = carboxylate (R-COO^-)

4	B	(buta-)
5	Pe	(penta-)
6	Hx	(hexa-)
7	Hp	(hepta-)
8	O	(octa-)
9	N	(nona-)…..

PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs).

PFAA Naming System

- PFXY
  - PF = perfluoro
  - X = number of carbons
    - Same convention as hydrocarbons
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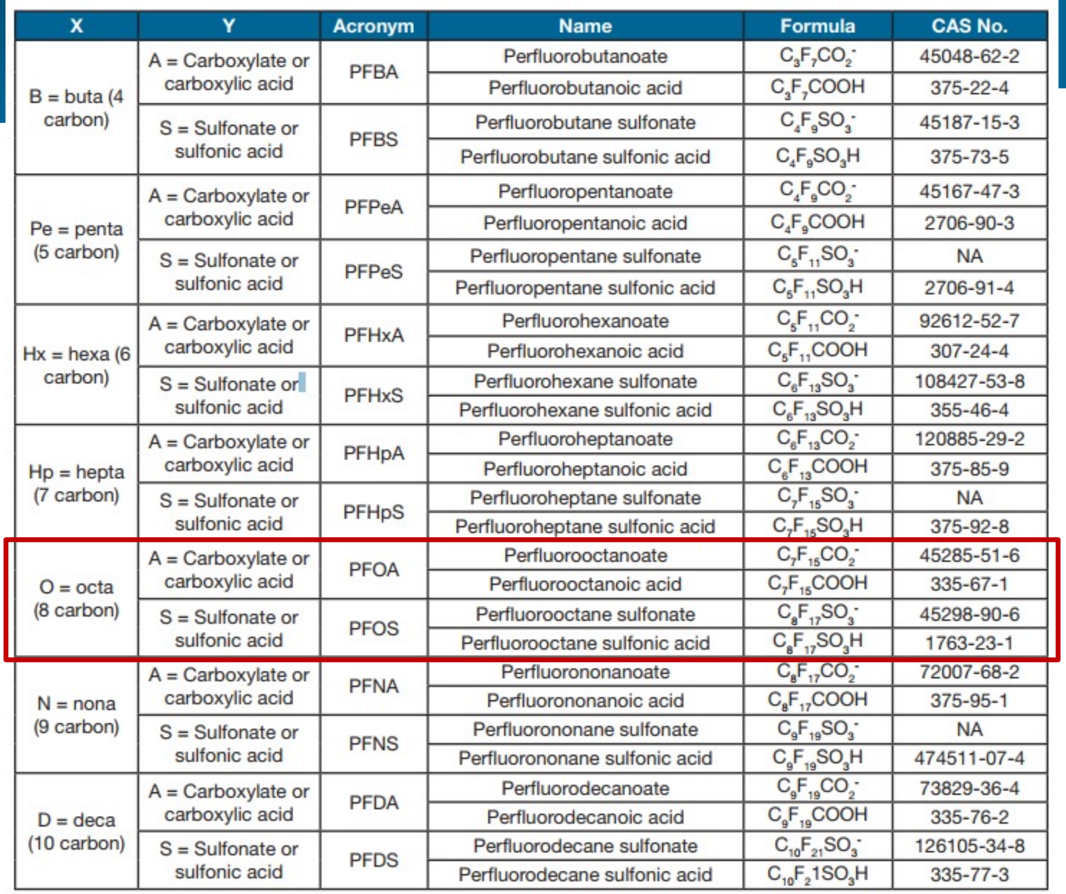
    - A = carboxylate (R-COO^-)

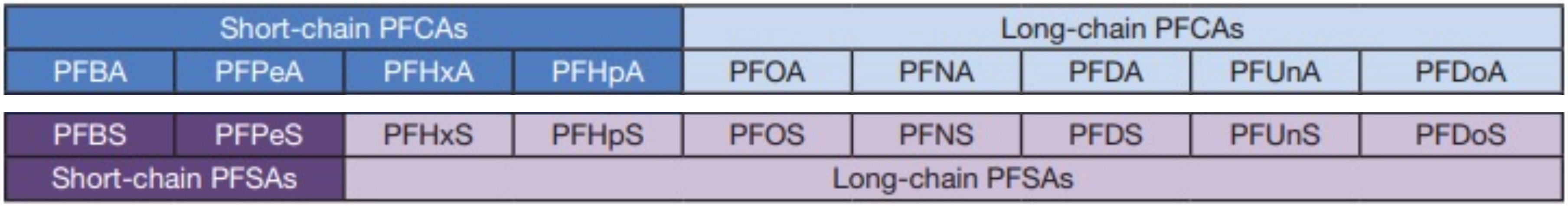


X	Y	Acronym	Name	Formula	CAS No.
B = buta (4 carbon)	A = Carboxylate or carboxylic acid	PFBA	Perfluorobutanoate	$C_3F_7CO_2^-$	45048-62-2
			Perfluorobutanoic acid	C_3F_7COOH	375-22-4
	S = Sulfonate or sulfonic acid	PFBS	Perfluorobutane sulfonate	$C_4F_9SO_3^-$	45187-15-3
			Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	375-73-5
Pe = penta (5 carbon)	A = Carboxylate or carboxylic acid	PFPeA	Perfluoropentanoate	$C_4F_9CO_2^-$	45167-47-3
			Perfluoropentanoic acid	C_4F_9COOH	2706-90-3
	S = Sulfonate or sulfonic acid	PFPeS	Perfluoropentane sulfonate	$C_5F_{11}SO_3^-$	NA
			Perfluoropentane sulfonic acid	$C_5F_{11}SO_3H$	2706-91-4
Hx = hexa (6 carbon)	A = Carboxylate or carboxylic acid	PFHxA	Perfluorohexanoate	$C_5F_{11}CO_2^-$	92612-52-7
			Perfluorohexanoic acid	$C_5F_{11}COOH$	307-24-4
	S = Sulfonate or sulfonic acid	PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_3^-$	108427-53-8
			Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	355-46-4
Hp = hepta (7 carbon)	A = Carboxylate or carboxylic acid	PFHpA	Perfluoroheptanoate	$C_6F_{13}CO_2^-$	120885-29-2
			Perfluoroheptanoic acid	$C_6F_{13}COOH$	375-85-9
	S = Sulfonate or sulfonic acid	PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_3^-$	NA
			Perfluoroheptane sulfonic acid	$C_7F_{15}SO_3H$	375-92-8
O = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
			Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
	S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
			Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1
N = nona (9 carbon)	A = Carboxylate or carboxylic acid	PFNA	Perfluorononanoate	$C_8F_{17}CO_2^-$	72007-68-2
			Perfluorononanoic acid	$C_8F_{17}COOH$	375-95-1
	S = Sulfonate or sulfonic acid	PFNS	Perfluorononane sulfonate	$C_9F_{19}SO_3^-$	NA
			Perfluorononane sulfonic acid	$C_9F_{19}SO_3H$	474511-07-4
D = deca (10 carbon)	A = Carboxylate or carboxylic acid	PFDA	Perfluorodecanoate	$C_9F_{19}CO_2^-$	73829-36-4
			Perfluorodecanoic acid	$C_9F_{19}COOH$	335-76-2
	S = Sulfonate or sulfonic acid	PFDS	Perfluorodecane sulfonate	$C_{10}F_{21}SO_3^-$	126105-34-8
			Perfluorodecane sulfonic acid	$C_{10}F_21SO_3H$	335-77-3

Table 2-2 Basic naming structure and shorthand for PFAAs

PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs).

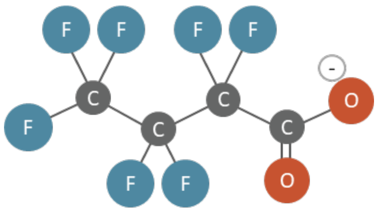
Long-Chain vs Short-Chain PFAAs



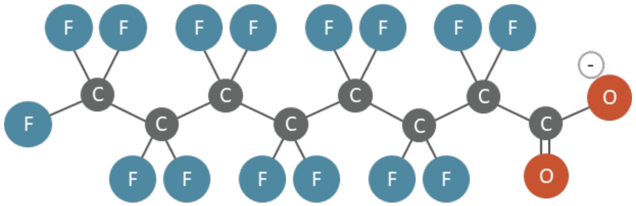
Short-chain PFCAs				Long-chain PFCAs				
PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA

PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
Short-chain PFSAs		Long-chain PFSAs						

Perfluorobutane carboxylate (PFBA)



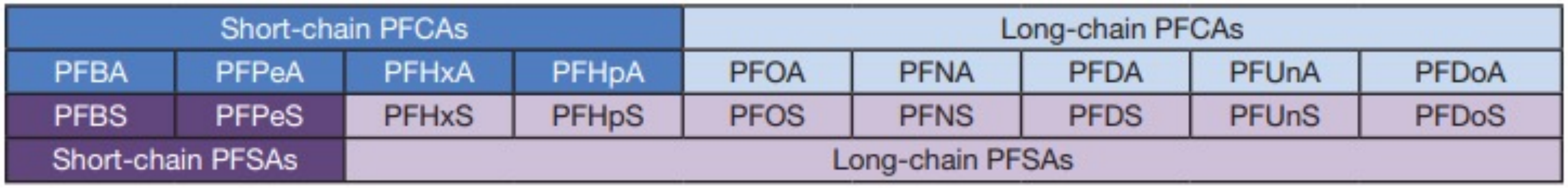
Perfluorooctane carboxylate (PFOA)



PFAS-1, Section 2.2. Table 2-3 Short-chain and long-chain PFCAs and PFSAs.
Figures Source: M. Olson, Trihydro. Used with permission.

Phase-Out of Long-Chain PFAS

- Potential health and environmental concerns, particularly for more bioaccumulative "long-chain" PFAS



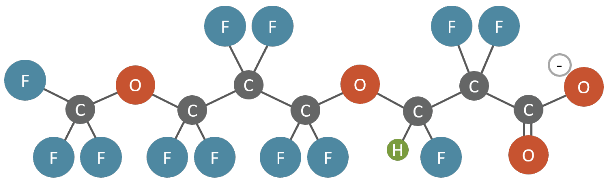
Short-chain PFCAs				Long-chain PFCAs				
PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
Short-chain PFSAs		Long-chain PFSAs						

- 2002-2008: 3M voluntarily phased out production of PFOS, PFHxS, PFOA, and related precursors
- 2010-2015: Most U.S. manufacturers eliminated production of PFOA and certain longer-chain PFCAs and related precursors
- Long-chain production shifted to parts of Asia and Eastern Europe

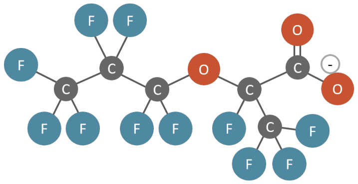
PFAS-1, Section 2.2. Table 2-3 Short-chain and long-chain PFCAs and PFSAs.

Replacement Chemistry

- Short-chain PFAS chemistries do not transform to longer PFAAs
- New applications, but not necessarily new chemicals
  - HFPO-DA (Hexafluoropropylene oxide dimer acid), a component of GenX processing aid technology used by one manufacturer (USEPA 2018)
  - Used for decades in fluoropolymer production
- ADONA and HFPO-DA (GenX) are replacement chemicals for PFOA
- For most replacement chemistries, limited information on toxicities, properties, fate and transport, and treatment options
  - USEPA released a toxicity assessment for GenX chemicals in October 2021



Chemical structure for ADONA

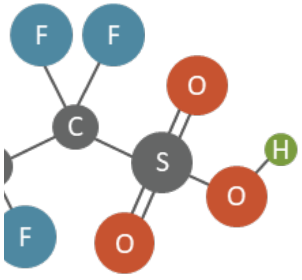


Chemical structure for GenX

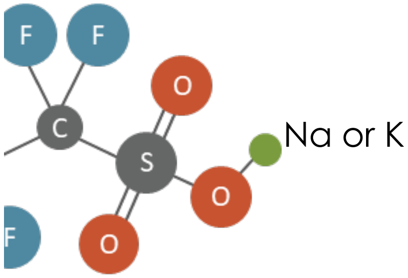
PFAS-1, Section 2.2. Figures 2-9 and 2-14 Chemical structures.

Which PFAA Are We Talking About?

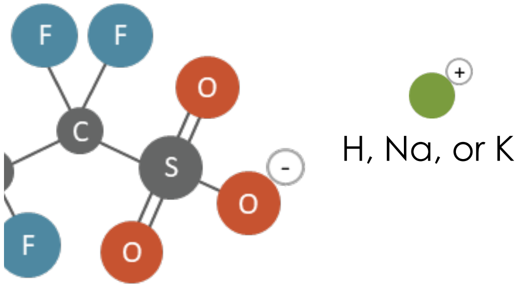
- Acid or Anion?
  - PFAAs may exists in various ionic states (acids, salt, anions)
    - In the environment, most PFAS exist in the anionic state (sulfonate, carboxylate, etc.)
    - Acid form of the name often used interchangeably (sulfonic acid and carboxylic acid)
    - Different CAS numbers & different chemical and physical properties



Acid



Salt

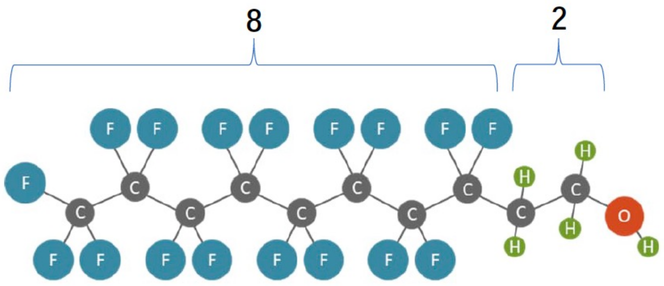


Anion

PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs).
Source: M. Olson, Trihydro. Used with permission.

Polyfluoroalkyl Substances

- Partially fluorinated
- Non-fluorine atom (usually H or O) attached to at least one, but not all, of the carbons in the alkane chain
- Theoretically creates a “weak link” that may be susceptible to biotic or abiotic transformation
- Fluorotelomers are often named using a “n:x” prefix (8:2 fluorotelomer alcohol, 8:2 FTOH)
    - n = number of fully fluorinated carbons
    - x = number of non-fully fluorinated carbons

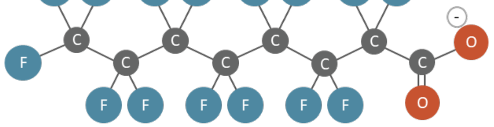


8:2 Fluorotelomer alcohol

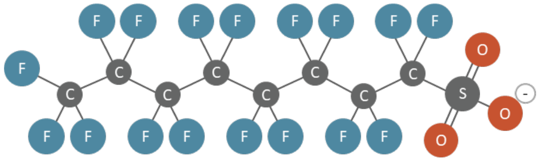
PFAS-1, Section 2.2.4.1. Figure 2-12 Example of a polyfluoroalkyl substance.
Source: M. Olson, Trihydro. Used with permission.

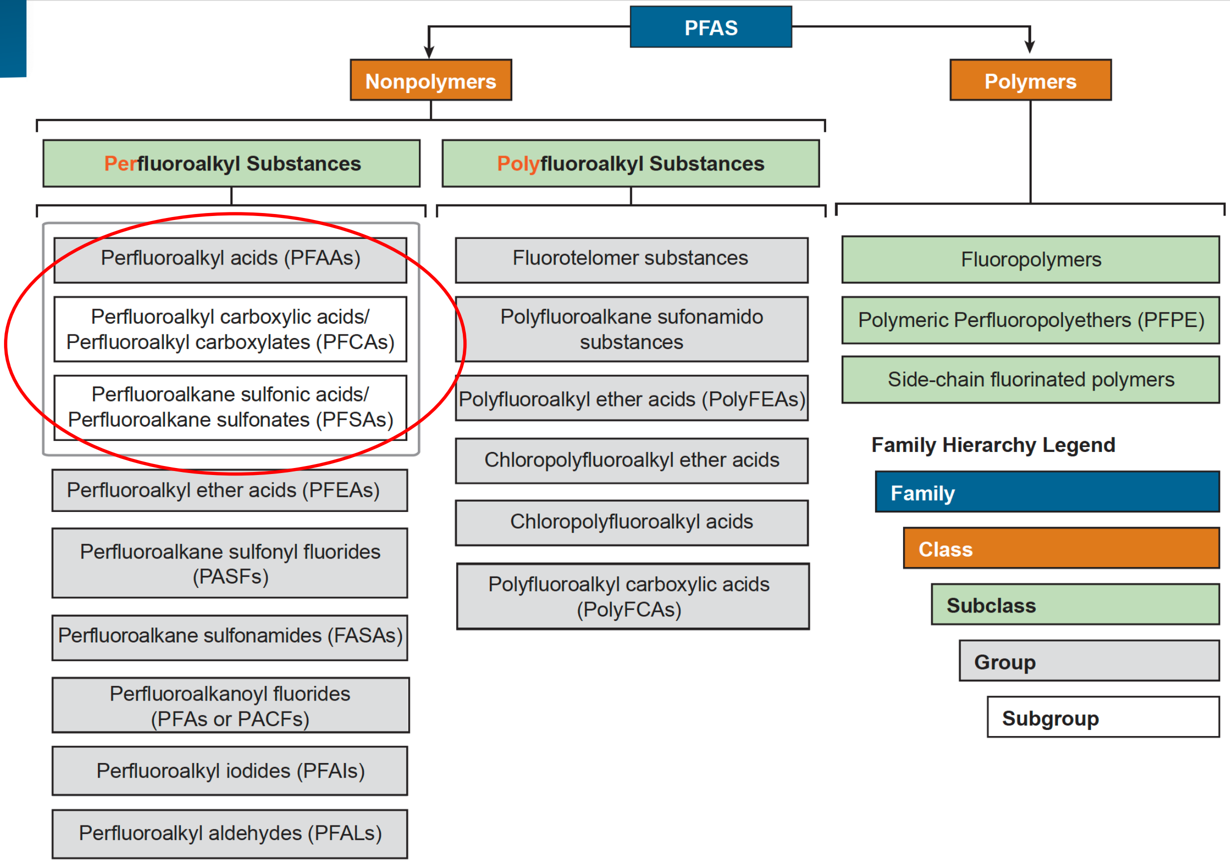
General Classification of Per- and Polyfluoroalkyl Substances (PFAS)

Perfluorooctane carboxylate (PFOA)



Perfluorooctane sulfonate (PFOS)





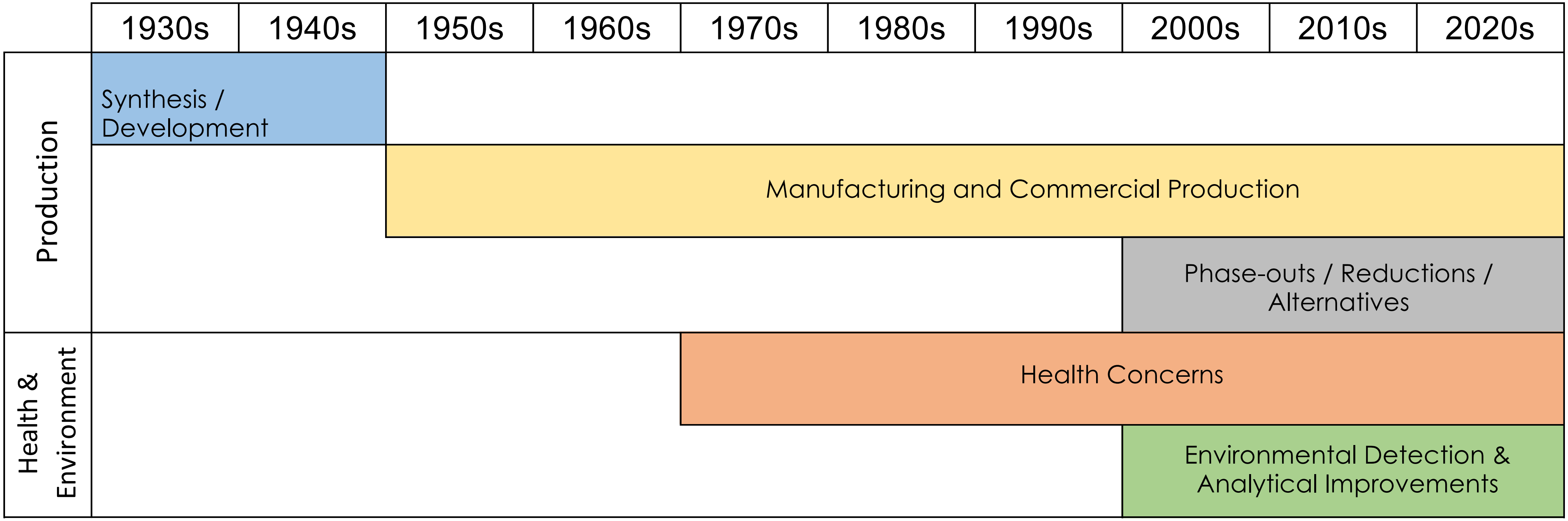
- **PFAS**
  - **Nonpolymers**
    - **Perfluoroalkyl Substances**
      - Perfluoroalkyl acids (PFAAs)
      - Perfluoroalkyl carboxylic acids/ Perfluoroalkyl carboxylates (PFCAs)
      - Perfluoroalkane sulfonic acids/ Perfluoroalkane sulfonates (PFSAs)
      - Perfluoroalkyl ether acids (PFEAs)
      - Perfluoroalkane sulfonyl fluorides (PASFs)
      - Perfluoroalkane sulfonamides (FASAs)
      - Perfluoroalkanoyl fluorides (PFAs or PACFs)
      - Perfluoroalkyl iodides (PFAIs)
      - Perfluoroalkyl aldehydes (PFALs)
    - **Polyfluoroalkyl Substances**
      - Fluorotelomer substances
      - Polyfluoroalkane sufonamido substances
      - Polyfluoroalkyl ether acids (PolyFEAs)
      - Chloropolyfluoroalkyl ether acids
      - Chloropolyfluoroalkyl acids
      - Polyfluoroalkyl carboxylic acids (PolyFCAs)
  - **Polymers**
    - Fluoropolymers
    - Polymeric Perfluoropolyethers (PFPE)
    - Side-chain fluorinated polymers

Family Hierarchy Legend

- **Family**
  - **Class**
    - **Subclass**
      - **Group**
        - **Subgroup**

PFAS-1, Section 2.2. Figure 2-4 PFAS Family and Figure 2-7 The tail and head structure of PFOS and PFOA molecules. Molecule Figures Source: M. Olson, Trihydro. Used with permission.

A Brief History of PFAS Discovery and Manufacture


PFAS Emergence Timeline

PFAS-1, Section 2.0. Figure 2-1 General timeline of PFAS emergence and awareness. Source: J. Hale, Kleinfelder. Used with permission.

A Brief History of PFAS Discovery and Manufacture

- Two major production processes
  - Electrochemical fluorination (ECF)
    - Contain a variable mixture of linear and branched perfluorinated isomers
  - Fluorotelomerization
    - Primarily used to produce even numbered, linear (straight-chain) PFAS isomers
    - Some sources indicate that the process can also produce compounds with odd number of carbons and branched chains

PFAS-1, Section 2.2.5 Chemical Manufacturing.

PFAS Use and Sources to the Environment

Aqueous Film Forming Foam (AFFF)
- Military installations & civil airports
- Petroleum refineries, terminals, & chemical facilities
- Firefighting - training and response areas

Industrial
- Primary manufacturing
- Surfactants, resins, molds, plastics
- Chrome plating and etching
- Textiles, coatings, leather, paper, carpet, etc.

Landfills
- Consumer products, industrial waste, biosolids from WWTP applied as cover
- Potential release via leachate or landfill gas

Wastewater Treatment Plants
- PFAS in influent (from industrial & domestic sources) may not be treated and end up in effluent
- Potential release via Liquid effluent or biosolids

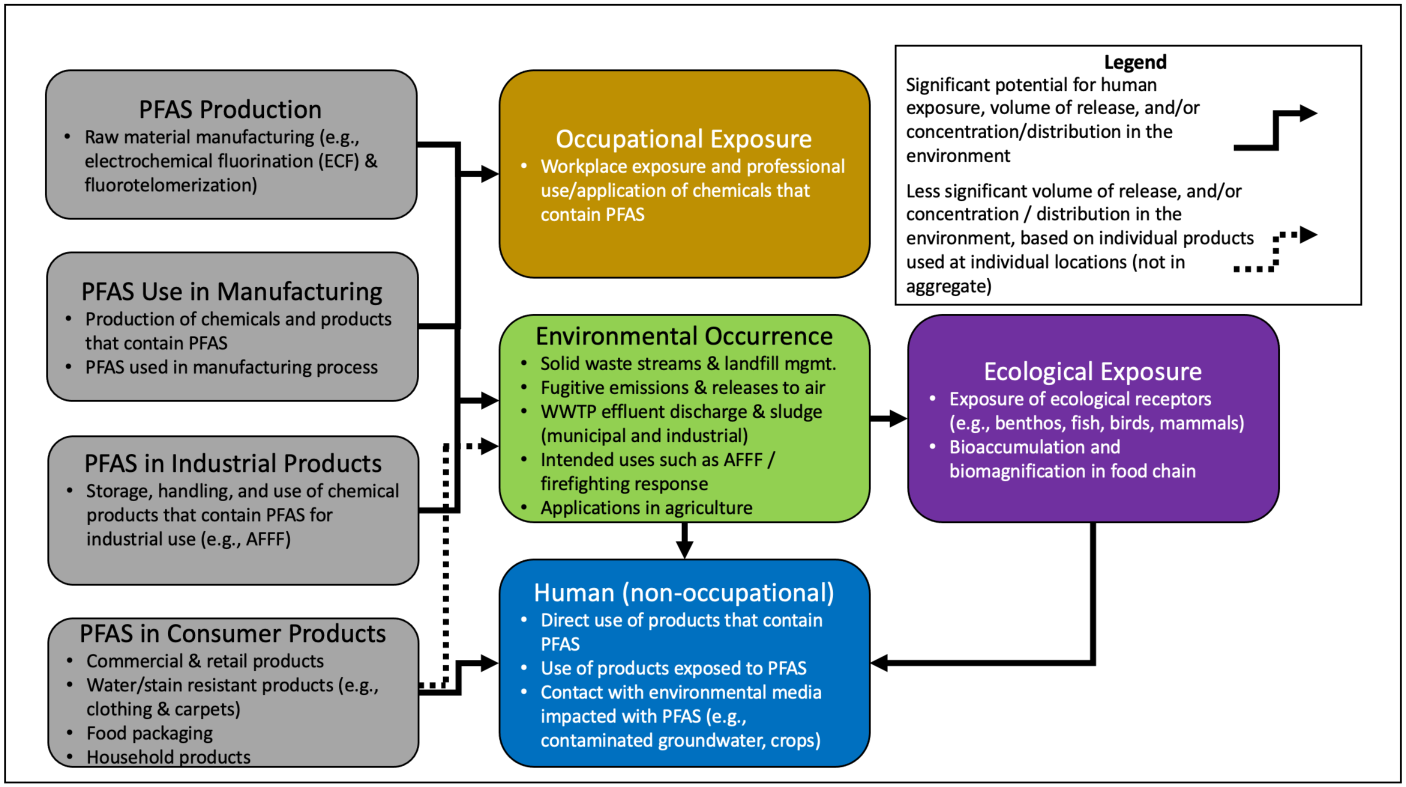

A1C Kyle Gese, Public domain, via Wikimedia Commons.


JJ Harrison, CC BY-SA 3.0, via Wikimedia Commons.


Iain Thompson / Cathkin Landfill Site, CC BY-SA 2.0, via Wikimedia Commons


Photo taken by Watzmann (c) Günter Seggebäing. CC BY-SA 3.0 Via Wikimedia Commons

Relative exposure and environmental impact due to PFAS manufacture and use



PFAS Production
- Raw material manufacturing (e.g., electrochemical fluorination (ECF) & fluorotelomerization)

PFAS Use in Manufacturing
- Production of chemicals and products that contain PFAS
- PFAS used in manufacturing process

PFAS in Industrial Products
- Storage, handling, and use of chemical products that contain PFAS for industrial use (e.g., AFFF)

PFAS in Consumer Products
- Commercial & retail products
- Water/stain resistant products (e.g., clothing & carpets)
- Food packaging
- Household products

Occupational Exposure
- Workplace exposure and professional use/application of chemicals that contain PFAS

Environmental Occurrence
- Solid waste streams & landfill mgmt.
- Fugitive emissions & releases to air
- WWTP effluent discharge & sludge (municipal and industrial)
- Intended uses such as AFFF / firefighting response
- Applications in agriculture

Human (non-occupational)
- Direct use of products that contain PFAS
- Use of products exposed to PFAS
- Contact with environmental media impacted with PFAS (e.g., contaminated groundwater, crops)

Ecological Exposure
- Exposure of ecological receptors (e.g., benthos, fish, birds, mammals)
- Bioaccumulation and biomagnification in food chain

Legend

Significant potential for human exposure, volume of release, and/or concentration/distribution in the environment

Less significant volume of release, and/or concentration / distribution in the environment, based on individual products used at individual locations (not in aggregate)

PFAS-1, Section 2.1. Figure 2-2 Generalized PFAS uses and relative exposure and environmental impact potential from PFAS life cycle.

Recent Claims of PFAS Use and Occurrence

- Food Packaging
- Fluorinated HDPE Containers
  - PFAS may form and then partly leach into the products in the containers
  - Degree of leaching relates to the brand of fluorinated containers and duration of liquid storage in container
- Synthetic Turf
  - No scientific evidence that detected PFAS originate from artificial turf itself
- Cosmetics and Personal Care Products
  - Dermal absorption of PFOA from sunscreen

PFAS-1, Section 2.5.2. Table 2-7 Summary of Recent Claims of PFAS Use and Occurrence.

PFAS Certification in Products

- Numerous labels and certifications related to reduction or elimination of PFAS in products exist in the marketplace but there is great variation in the terms used to indicate PFAS content in products.
- Commonly used PFAS-related terms for products include: PFAS-free, PFOS-free, PFOA-free and Fluorine-free.
- Many certifications allow a minimum limit to be present.
- Table 2-8 provides examples of some of the most commonly-used product labels and certifications for intentionally-added PFAS.

PFAS-1, Section 2.5.3. Table 2-8 Examples of Certifications – Intentionally Added PFAS.

Advancing
Environmental
Solutions

Aqueous Film Forming Foam (AFFF) and the Current Best Management Practices

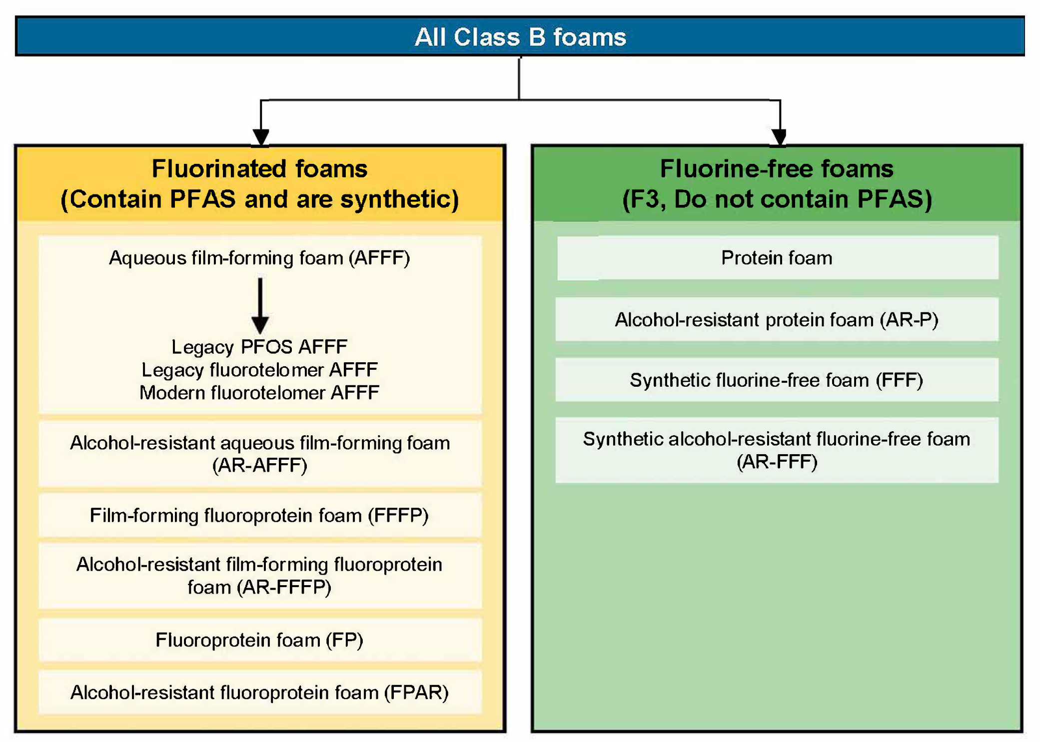
Mitch Olson, Ph.D., P.E., Trihydro

PFAS Technical and Regulatory Guidance Document Published

- Final web document PFAS-1: https://pfas-1.itrcweb.org
- Firefighting Foams, Section 3
- External Tables
  - AFFF Characteristics Excel File
  - AFFF Transition to fluorine-free foams (F3) Case Studies Excel File

ITRC 2023. *PFAS Technical and Regulatory Guidance Document and Fact Sheets* PFAS-1. Washington, D.C.. https://pfas-1.itrcweb.org/.

Classes of Firefighting Foams



All Class B foams

Fluorinated foams
(Contain PFAS and are synthetic)

- Aqueous film-forming foam (AFFF)
  - Legacy PFOS AFFF
  - Legacy fluorotelomer AFFF
  - Modern fluorotelomer AFFF
- Alcohol-resistant aqueous film-forming foam (AR-AFFF)
- Film-forming fluoroprotein foam (FFFP)
- Alcohol-resistant film-forming fluoroprotein foam (AR-FFFP)
- Fluoroprotein foam (FP)
- Alcohol-resistant fluoroprotein foam (FPAR)

Fluorine-free foams
(F3, Do not contain PFAS)

- Protein foam
- Alcohol-resistant protein foam (AR-P)
- Synthetic fluorine-free foam (FFF)
- Synthetic alcohol-resistant fluorine-free foam (AR-FFF)

- CLASS A Foams- Developed in the 1980s for fighting wildfires and used in structure fires. Do not contain PFAS
- CLASS B Foams- Used to fight fires involving flammable and combustible liquids and gases; petroleum greases, tars, oils and gasoline; and solvents and alcohols

Many Class B foams contain PFAS (due to Mil-Spec)

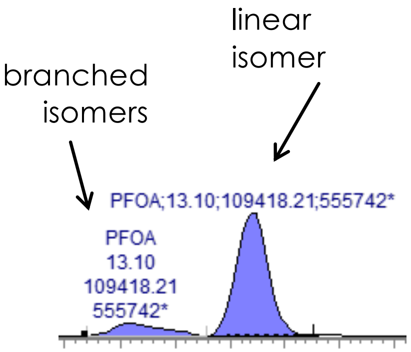
AFFF are the primary Class B foams that contain fluorosurfactants

PFAS-1, Figure 3-2 Types of Class B foams. Source: S. Thomas, Wood. Used with permission.

AFFF Classifications

- **Legacy PFOS AFFF**[1,2]
  - ECF chemistry, (C2-C13), Branched & linear isomers (˜1:4), PFAS composition (Mostly PFSAs, 89% (e.g., PFOS) in 3M Lightwater)
- **Legacy Fluorotelomer AFFFs**[3, 4]
  - Contain polyfluorinated PFAS which can transform to PFCAs, Contain no PFOS and cannot transform to PFOS, Fluorotelomers not listed on UCMR or Method 537 lists
- **Modern Fluorotelomer AFFFs**
  - Developed in response to PFOA/PFOS phaseout, contains short chain PFAS (C6), may have trace amounts (ppb) PFOA, may transform to PFCAs

Photo courtesy of J. Field.



Note: PFAS composition of AFFF has changed over time

Figure courtesy C. Higgins, Colorado School of Mines.

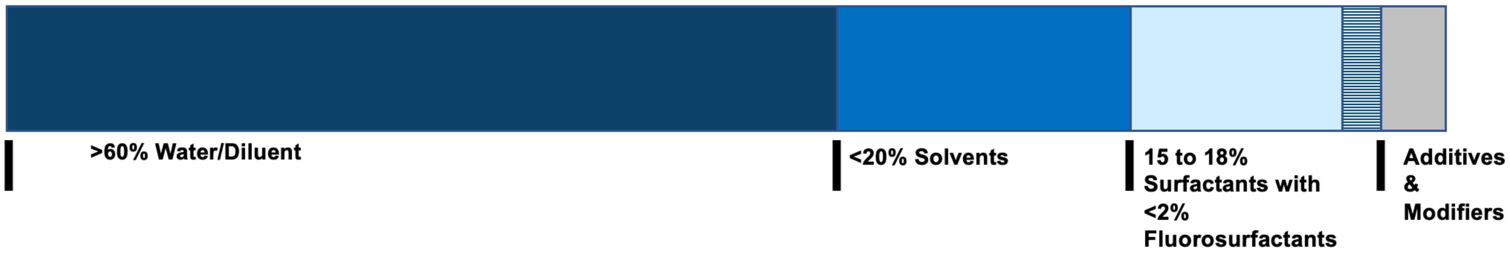
PFAS-1, Section 3.1 Foam Formulations.

[1]Barzen-Hansen et al., 2015. *ES&T Letters* 2: 95-99; [2]Benskin, 2010. Rev Environ Contam Toxicol.
[3]Place and Field, 2012. ES&T 46: 7120-7127; [4]Weiner et al., 2013. Environ Chem 10:486-493;

Typical Composition of AFFF

AFFF products contain other surfactants, solvents, additives

- 3% AFFF concentrate contains:
  - More than 60% water/diluent
  - Up to 20% is solvents
  - As much as 18% is surfactants ***of which less than 2% is fluorosurfactants.***

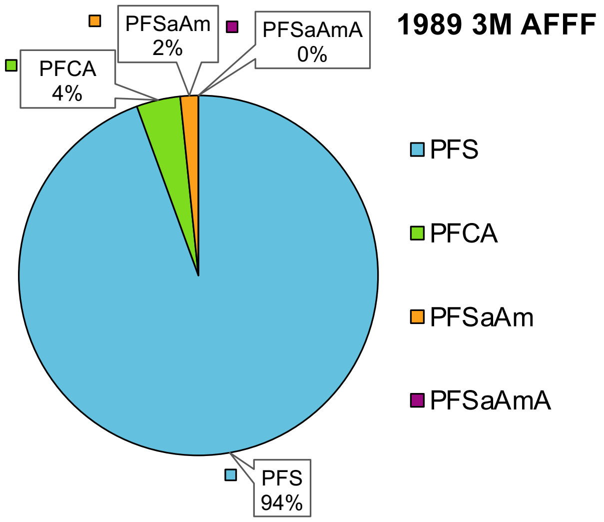


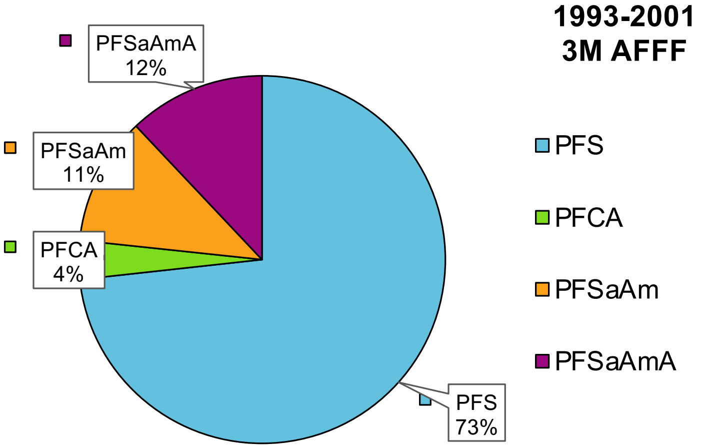
PFAS-1, Section 3.1. Figure 3-3 Typical composition of 3% AFFF concentrate

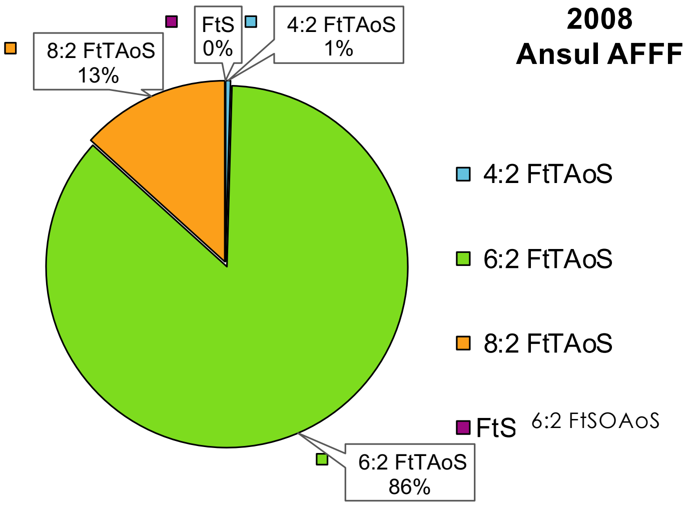
Source: S. Thomas, Wood. Adapted from Kempisty, Xing and Racz 2018. Used with permission.

AFFF Contains Highly Diverse Mixtures

AFFF product chemistry has changed over time


1989 3M AFFF


1993-2001 3M AFFF


2008 Ansul AFFF

Electrochemical Fluorination

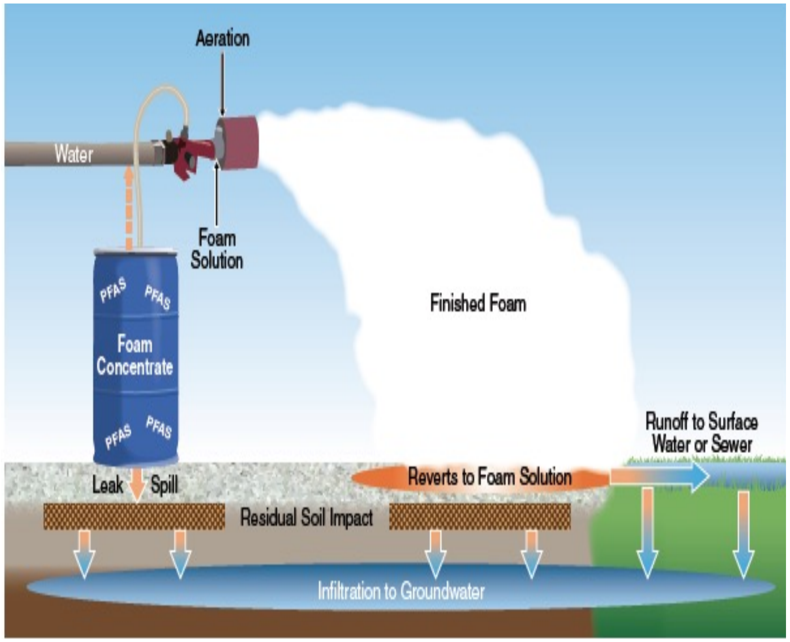
Fluorotelomerization

Table 3-1 of the ITRC PFAS Technical Regulatory Guidance document presents types of foam and composition.

Barzen-Hanson et al. 2017. Environ Sci Technol 51: 2047-2057.

Figures used with permission from J. Field, Oregon State.

Mechanisms for Application and Release to Environment



PFAS-1, Figure 3-4 Release of firefighting foam.
Source: Adapted from figure by J. Hale, Kleinfelder, used with permission.

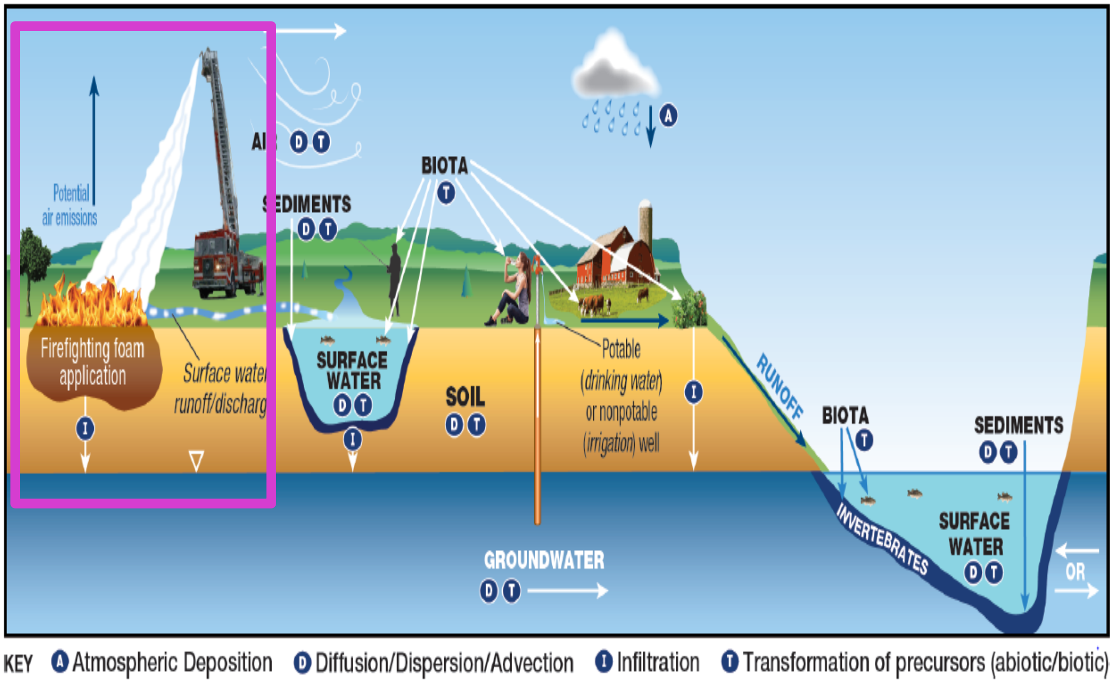
Foam is released via various practices and mechanisms:

- Low volume releases of foam concentrate (Spills)
- Accidental leaks
- Moderate volume discharge of foam solution (Firefighting operations)
- Infrequent high-volume, broadcast discharge (Firefighting operations)
- Periodic, high volume, broadcast discharge (historic training operations, equipment checks)

PFAS-1, Section 3.3 Mechanisms for Release to the Environment.

AFFF Fate and Transport

- Used to address potential risk, development of CSM, and identification of treatment options.
- Affected by several physical and chemical properties.
- Abiotic transformation of precursors by hydrolysis, photolysis, and oxidation can produce PFCAs and PFSAs.
- Biotransformation of precursors to PFAA over time can produce PFAAs such as PFOA.



PFAS-1, Figure 2-21 CSM for fire training areas. Figure Adapted from figure by L. Trozzolo, TRC, used with permission.

PFAS-1, Section 3.4 AFFF Fate and Transport.

AFFF Procurement and Inventory-BMP

HAZARD X EXPOSURE = RISK

Foam Selection and Requirements

- Document all procurement and inventory
- Understand performance specification requirements

(e.g., Mil-Spec MIL-PRF-24385, MIL-PRF-32725; UL Standard 162)

- Concentrate mixtures of 1,3, or 6 percent solution in water

Foam Storage and Handling

- Stored in 5-gallon bucket, 55-gallon drum to 256-gallon tote container, 5000-gallon tanker truck, or suppression system
- Ensure proper secondary containment to avoid spills/mishaps

PFAS-1, Section 3.6 AFFF Procurement and Inventory.

Figure Adapted from https://worksmart.org.uk/health-advice/health-and-safety/hazards-and-risks/what-difference-between-hazard-and-risk.

Treatment and Disposal

- Consider USEPA Interim Guidance on Destroying and Disposing of Certain PFAS and PFAS-Containing Materials (Dec 2020)[1]
- Fire and flush water containing AFFF should be disposed of as a generated waste, when possible
  - PFAS in water can be processed to concentrate PFAS prior to disposal to reduce treatment costs
  - Concentrated waste can be stored, incinerated, landfilled, or stabilized [1]
  - Incineration of AFFF concentrate should be performed at certified facilities
- Best management practices include accounting for all volumes of AFFF and weights of system components for disposal certificates.

Photo from: http://clui.org/ludb/site/east-liverpool-hazardous-waste-incinerator.

[1] USEPA Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials (USEPA2020)

PFAS-1, Section 3.10 AFFF Disposal.

Firefighting Foam and Foam System Replacement

- Consider performance specifications, system modifications, decontamination and disposal
- Consider clean-out vs replacement options
- Consider alternatives to using fire foam for specific hazards such as: Water Mist; Dry Chemical; Containment flooring systems; separation and exposure protection
- Factors to consider:
  - What are the current performance requirements for the foam?
  - What application techniques are anticipated?
  - How Clean does the System need to be for future use?

Suitability for use

Viscosity

Compatibility

Application rates

Expansion ratios

Stability

PFAS-1, Section 3.11.3 AFFF Transition Planning. Table 3-5 Example Case Studies.

Foam Research and Development

SERDP-ESTCP Research (https://serdp-estcp.org/)

Representative projects that have been completed around AFFF:

- Novel Fluorine-free Replacement for AFFF - NRL (completion August 2018)
- Fluorine-free Foam - National Foam (completion September 2019)
- Fluorine-free Foams with Oleophobic Surfactants and Additives for Effective Pool Fire Suppression - NRL (completion December 2020)

Advancing
Environmental
Solutions

Fate and Transport and Site Characterization

Sandra Goodrow, Ph.D. NJDEP

ECOS

ERIS
ENVIRONMENTAL RESEARCH
INSTITUTE OF THE STATES

PFAS Technical and Regulatory Guidance Document Published

- Final web document PFAS-1: https://pfas-1.itrcweb.org
- PFAS Releases to the Environment, Section 2.6
- Physical and Chemical Properties, Section 4
  - Physical and Chemical Properties Table 4-1
- Fate and Transport, Section 5
- Media-Specific Occurrence, Section 6
  - Additional Information for Media-Specific Occurrence, Section 17.1
- Site Characterization, Section 10

ITRC 2023. *PFAS Technical and Regulatory Guidance Document and Fact Sheets* PFAS-1. Washington, D.C.. https://pfas-1.itrcweb.org/.

Sources of PFAS Release to the Environment

Fire Training/Fire Response Sites

Industrial Sites

Landfills*

BIOSOLIDS

LEACHATE

WWTPs/Biosolids*

*Landfills and WWTPs are receivers of PFAS materials from domestic and industrial sources. PFAS concentrations vary widely depending on the waste stream accepted by facilities.

PFAS-1, Section 2.6 Releases to the Environment.

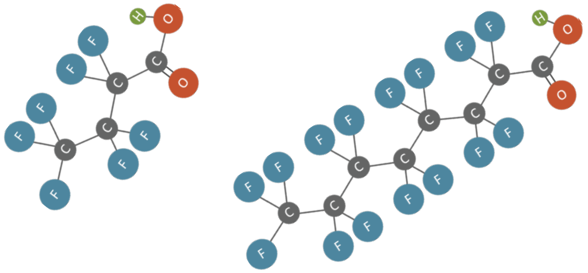
What is Fate and Transport?

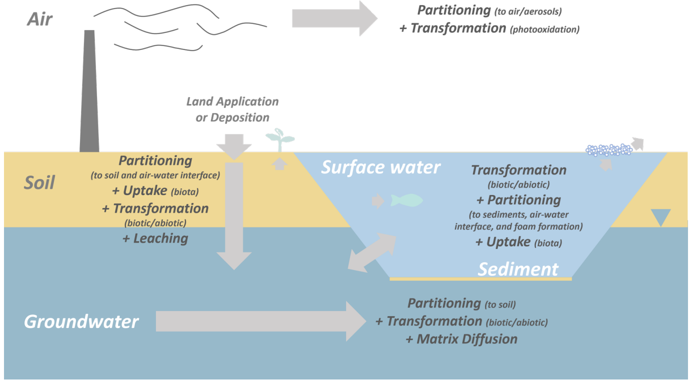
PFAS Characteristics

PFAS
Fate & Transport

Nature of release

Site Characteristics





- *Perfluorinated* vs. *poly*fluorinated
- *Fluorinated tail:* chain length
- *Non-fluorinated head:* functional group and charge state

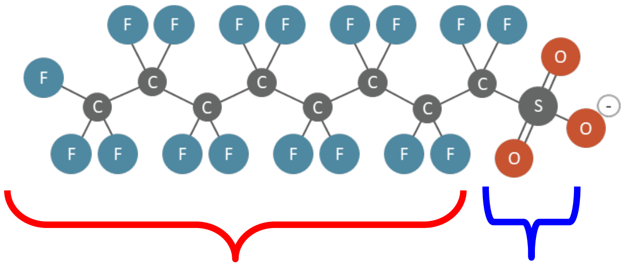
- Soil properties
- Groundwater depth/velocity
- Groundwater geochemistry
- Prevailing atmospheric conditions
- Co-contaminants

PFAS figure source: M. Olson, Trihydro. Used with permission.

PFAS-1, Section 5.1. Figure 5-1 Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

The Heads and Tails of PFAS

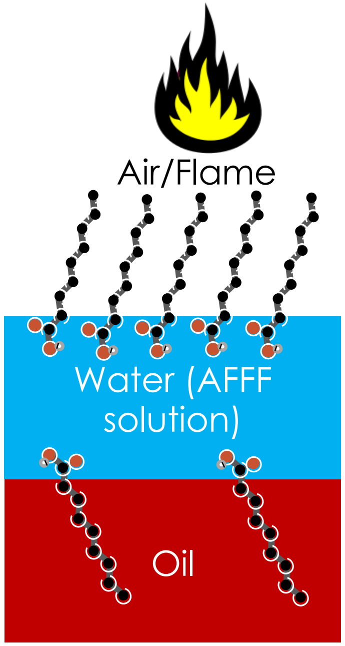
Perfluorooctane sulfonate (PFOS)



Perfluorinated "Tail"
Hydrophobic/Lipophobic

Anionic "Head" group
Polar/Hydrophilic

Perfluoroalkyl acids (PFAAs) are extremely persistent in the environment



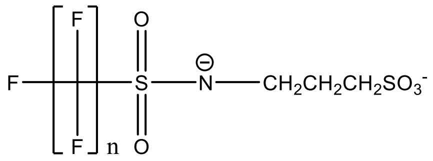
PFAAs preferentially partition at interfaces

PFAS-1, Section 4.2 Physical Properties.

PFAS images used with permission from Mitchell Olson, Trihydro.
Flame image credit: https://commons.wikimedia.org/wiki/File:Flames_by_mimooh.svg.

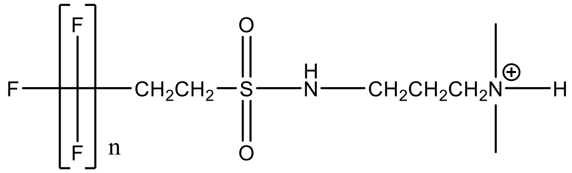
Structural Implications

- Diversity of PFAS structures has important implications for fate and transport processes



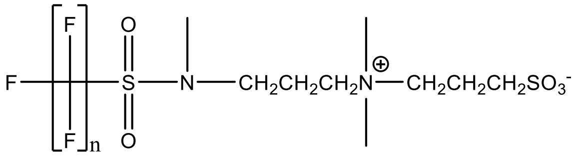
$$\mathrm{F}-\left[\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mid}}\right]_n-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\overset{\|}{\underset{\|}{\mathrm{S}}}}}-\overset{\ominus}{\mathrm{N}}-\mathrm{CH_2CH_2CH_2SO_3^-}$$

*Poly*fluorinated anion



$$\mathrm{F}-\left[\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mid}}\right]_n-\mathrm{CH_2CH_2}-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\overset{\|}{\underset{\|}{\mathrm{S}}}}}-\overset{\mathrm{H}}{\mathrm{N}}-\mathrm{CH_2CH_2CH_2}\overset{\mid}{\underset{\mid}{\mathrm{N}}}{}^{\oplus}-\mathrm{H}$$

*Poly*fluorinated cation



$$\mathrm{F}-\left[\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mid}}\right]_n-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\overset{\|}{\underset{\|}{\mathrm{S}}}}}-\overset{\mid}{\mathrm{N}}-\mathrm{CH_2CH_2CH_2}\overset{\mid}{\underset{\mid}{\mathrm{N}}}{}^{\oplus}-\mathrm{CH_2CH_2CH_2SO_3^-}$$

*Poly*fluorinated zwitterion

PFAS-1, Section 4.3 Chemical Properties.

Figures Source: J. Field, Oregon State University. Used with permission.

Properties of PFAAs

- Negatively charged at typical environmental and physiological pH (i.e., 4-10)
- Water soluble
- Surfactants
- Low vapor pressure and Henry's Law coefficients

Table 4-1 Physical and Chemical Properties Excel Table

Anion Sorption and Transport

K_{OC} data from Guelfo, J.L., Higgins

Analyte	# Carbons	$K_{oc}{}^1$	R_f
PFBA	4	76	2.6
PFPeA	5	23	1.5
PFHxA	6	20	1.4
PFHpA	7	43	1.9
PFOA	8	78	2.7
PFNA	9	229	5.9
PFDA	10	912	21
PFUnA	11	3,600	78
PFBS	4	62	2.3
PFHxS	6	112	3.4
PFOS	8	631	15

Note: these results represent one study of many summarized in the physical/chemical properties in Section 4

- Sorption (K_{oc} and K_d) generally increases with number of carbons
- Retardation factor (R_f) calculations illustrate potential variability

$$R_f = 1 + K_d \frac{\text{Bulk density}}{\text{Porosity}}$$

where $K_d = K_{oc} * f_{oc}$

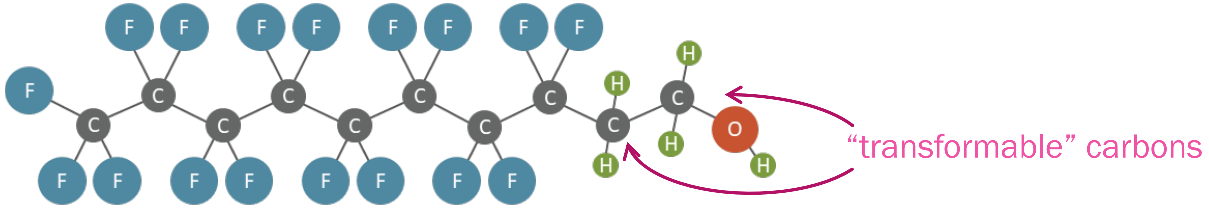
and f_{oc} = fraction of organic carbon (0.01)

- Partitioning at interfaces may further slow transport and contribute to retardation
- PFAS-NAPL interactions are complex

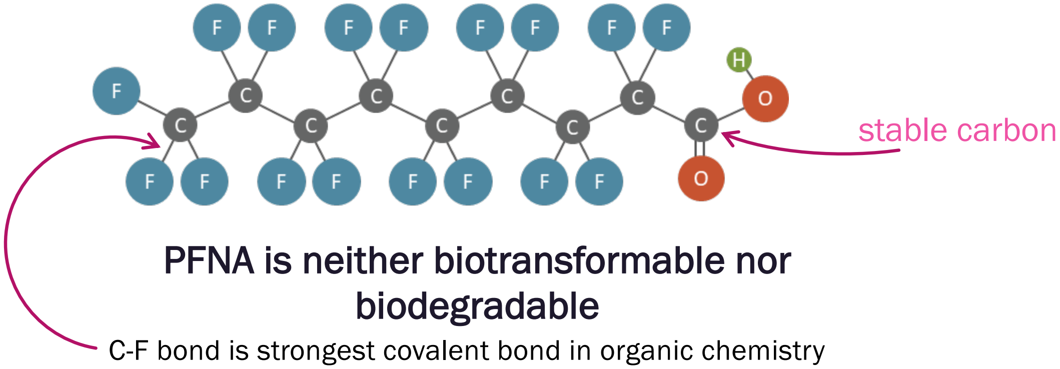
PFAS-1, Section 5.3 Media-Specific Migration Processes. Guelfo, J.L., Higgins, C.P. Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. Environ. Sci. Technol. 2013. 47, 4164–4171.

Transformation of Precursors to PFAAs

8:2-fluorotelomer alcohol (8:2-FTOH) is biotransformable, <u>not biodegradable</u>



“transformable” carbons



stable carbon

PFNA is neither biotransformable nor biodegradable

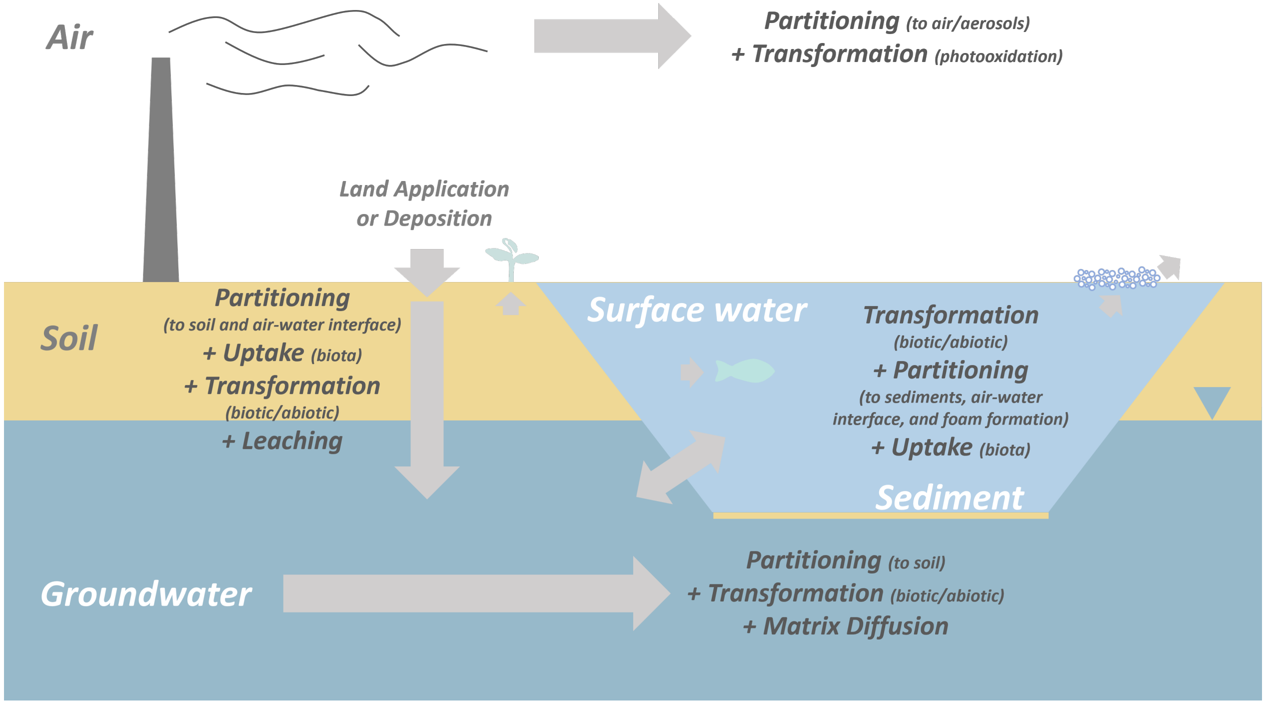
C-F bond is strongest covalent bond in organic chemistry

PFAS-1, Section 5.4.2 PFAA Precursors.

PFAS figure source: M. Olson, Trihydro. Used with permission.

PFAS Occurrence in Environmental Media

- Air
- Soil
- Groundwater
- Surface water
- Sediment
- Biota



Air

Partitioning (to air/aerosols)
+ Transformation (photooxidation)

Land Application or Deposition

Soil

Partitioning (to soil and air-water interface)
+ Uptake (biota)
+ Transformation (biotic/abiotic)
+ Leaching

Surface water

Transformation (biotic/abiotic)
+ Partitioning (to sediments, air-water interface, and foam formation)
+ Uptake (biota)

Sediment

Groundwater

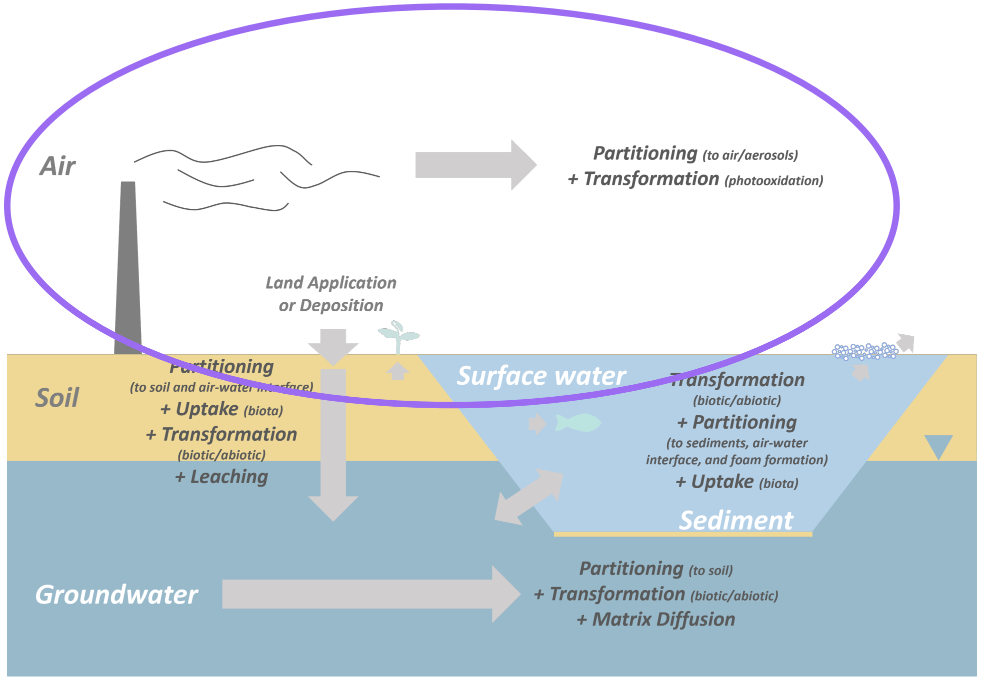
Partitioning (to soil)
+ Transformation (biotic/abiotic)
+ Matrix Diffusion

PFAS-1, Section 6 Media-Specific Occurrence.

PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

Atmospheric Transport

- Regional/global scale
- Sources: stack emissions, incineration, fire suppression
- Some PFAA precursors are volatile: fluorotelomer alcohols (FTOHs)
  - Precursors may transform into PFAAs
  - PFAAs (PFOA, PFOS) may transport via aerosols/particulates
- Atmospheric deposition = large impacted areas around industrial sites

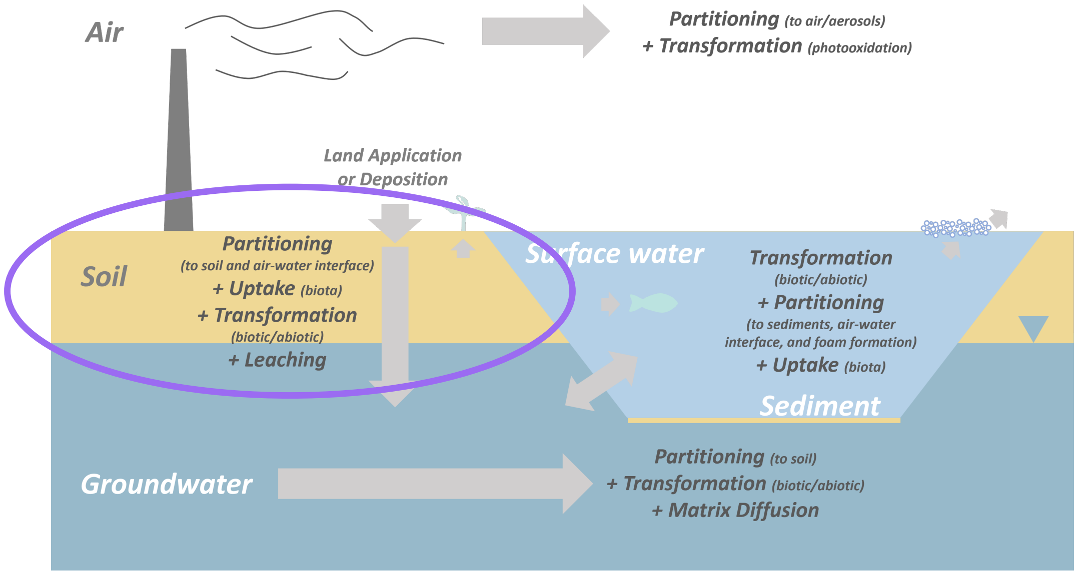


PFAS-1, Section 5.3.2 PFAS Transport via Air.

PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

Transport in the Vadose Zone

- PFAS source areas: vadose-zone retention may be significant
  - Cationic/zwitterionic precursors may strongly sorb
  - Long-chain PFAA sorption
  - PFAAs accumulate at air/water interfaces (may retard transport)
- Low volatility for most PFAS
- Leaching may provide long-term source to groundwater

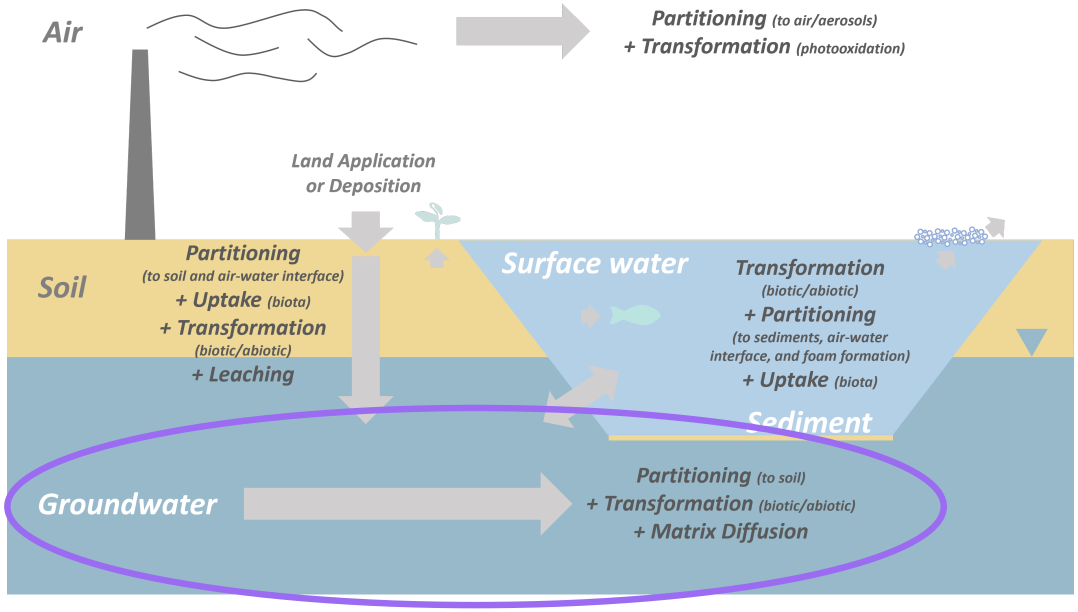


PFAS-1, Section 5.3.3 Leaching.

PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

Transport in Groundwater

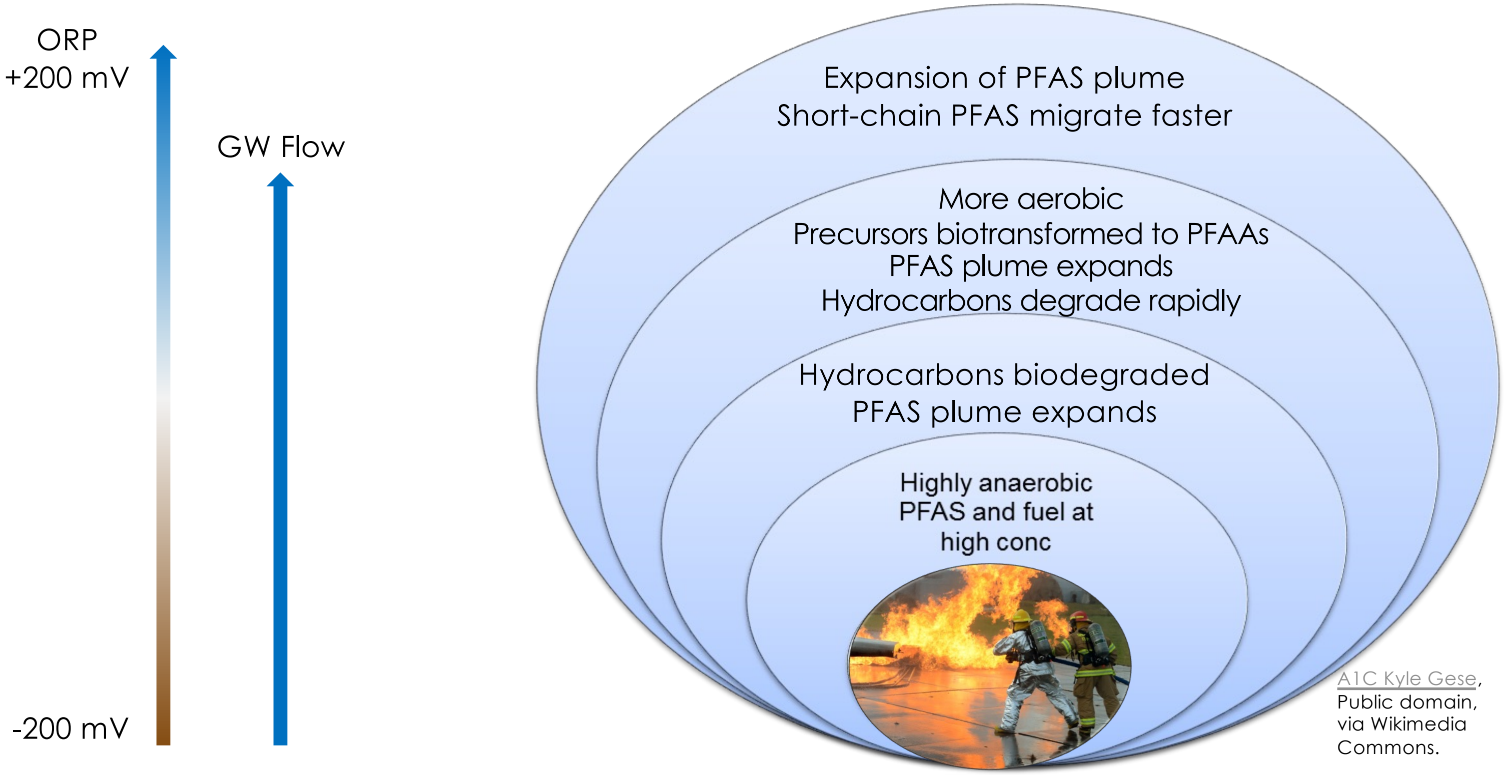
- Readily transported once in groundwater
  - Chain-length dependent
  - K_{OC} important, but not sufficient
  - Biotransformation vs. biodegradation
- Potential impacts of remedial activities/biotransformation
  - Precursor transformation may cause PFOA/PFOS (and other PFAAs) concentrations to increase



PFAS-1, Section 5 Environmental Fate and Transport Processes.

PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

Conceptual PFAS Fate and Transport at an AFFF site



ORP
+200 mV

-200 mV

GW Flow

Expansion of PFAS plume
Short-chain PFAS migrate faster

More aerobic
Precursors biotransformed to PFAAs
PFAS plume expands
Hydrocarbons degrade rapidly

Hydrocarbons biodegraded
PFAS plume expands

Highly anaerobic
PFAS and fuel at
high conc

A1C Kyle Gese,
Public domain,
via Wikimedia
Commons.

PFAS-1, Section 5 Environmental Fate and Transport Processes.

Site Characterization: Issues Relevant to PFAS

- Evolving science and regulations
  - State of the science
  - Analytical methodologies (detection and reporting limits, expanding parameter lists)
  - Sampling methodologies (potential for cross-contamination)
  - Regulatory environment (changing regulatory limits, sampling procedures, and compounds of interest)

PFAS-1, Section 10 Site Characterization.

Site Characterization: Issues Relevant to PFAS

- Groundwater significant due to its source as drinking water
- Plumes may be quite extensive
- Compound suite and possible precursors
- Identification of PFAS-specific data analysis and interpretation approaches, models, and tools
- Need historical view to understand site
- Widespread use (potential for multiple releases in a given area, off-site contributions)

PFAS-1, Section 10 Site Characterization.

Site Characterization: Issues Relevant to PFAS

- Site characterization concerns arise due to unique source, fate and transport properties
  - Atypical sources
    - Broad variety of unusual primary sources
    - Secondary sources created from movement of contaminated media into a previously uncontaminated area
    - Precursor transformation
  - Atypical pathways (e.g., air deposition resulting in groundwater impacts with no direct on-site release)
  - Complex transitions between media (e.g., vadose zone, groundwater and surface water interactions)
  - Partitioning (e.g., sorption through hydrophobic, electrostatic, and interphase partitioning mechanisms)

PFAS-1, Section 10 Site Characterization.

Questions

Please use the Q&A Pod to ask questions.

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PFAS Sampling and Analysis

Kristi Herzer
Vermont Department of Environmental Conservation
(VT DEC)

PFAS Technical and Regulatory Guidance Document Published

- Final web document PFAS-1: https://pfas-1.itrcweb.org
- Sampling and Analytical Methods, Section 11
- Analytical methods Excel file
  - Table 11-2 Published methods basics
  - Table 11-3 Published methods specifics
  - Table 11-4 Analyte lists
  - Table 11-5 Draft published methods

ITRC 2023. *PFAS Technical and Regulatory Guidance Document and Fact Sheets* PFAS-1. Washington, D.C.. https://pfas-1.itrcweb.org/.

General Sampling Guidelines

- Site-specific QAPP or work plan
- Refer to 11.1.2 for materials to avoid during sampling event
- Pretesting sampling equipment or materials
  - Equipment Rinse Blanks (ERBs/EBs)
  - Documentation during sampling event for any potential causes for bias

Sampling Event Preparation

The overarching objectives of the project and conceptual site model will influence the fundamentals of any sampling and analysis program

- Site history (e.g., potential sources, quantities used) as an indicator of potential level of PFAS
- Project Action Levels

Develop a project-specific sampling and analysis plan (SAP) which addresses the increased risk of contamination and project-specific considerations

PFAS-1, Section 11.1 Sampling.

Planning Laboratory Analysis

- Project team discusses with the laboratory:
  - the PFAS to be analyzed and project reporting levels
  - the volume of sample required to achieve the lab reporting levels
  - project sample preparation requirements
  - the number of bottles needed, including QC samples

- Provide laboratory information on high concentration samples
- For Draft 1633, request laboratory screen all samples prior to sample preparation (additional containers for aqueous samples needed)

PFAS-1, Section 11.1 Sampling.

What To Do If You Are Unsure If Item Contains PFAS Or Not?

- Review the Safety Data Sheets and consult with the manufacturer of the item
- Consult:
  - PFAS sampling guidance documents
  - PFAS resources within your organization
  - An analytical chemist with PFAS experience
- Collect equipment blank(s) from a specific item in question or send a section or piece of the equipment (if practical) to the laboratory for a more vigorous leachate analysis
- Tiered approach
  - 1st: Restrictions on sampling materials in direct contact with samples
  - 2nd: Restrictions on materials allowed on personnel and staging area

ERR ON THE SIDE OF BEING CAUTIOUS
RATHER THAN BEING UNSURE AND RISK CROSS-CONTAMINATION

PFAS-1, Section 11.1.2 Equipment and Supplies.

Sample Considerations

- USEPA Methods 537.1 and 533, and USEPA Draft Method 1633 all require the laboratory to prepare the entire sample collected, including sample container rinsate(s)
- DOD AFFF01 requires the container holding the diluted AFFF concentrate be prepared in its entirety, including a rinse of the container

PFAS-1, Section 11.1 Sampling.

Laboratory Supplied Sampling Materials

Sample containers (polypropylene or HDPE), solvents (such as methanol), and water used for blanks in the field and for final rinse of equipment should:

- be supplied by the lab performing the analysis, and
- be verified as being PFAS-free (as defined by the project) prior to use

If site water is used in the field for any blanks or final rinse, a sample of this water should be sent to the laboratory for analysis.

PFAS-1, Section 11.1 Sampling.

Field Decontamination

- Reusable field equipment cleaned between samples
- The SDSs of detergents or soaps used in decontamination procedures should be reviewed to ensure fluorosurfactants are not listed as ingredients
- Heavy equipment best cleaned at decontamination facility or other containment method
- Use laboratory-verified PFAS-free water in final rinse of decontamination of sampling equipment

PFAS-1, Section 11.1.5 Decontamination Procedures.

Field Quality Control

- Table 11-1 lists typical field QC samples
- USEPA 537.1 and 533 have additional requirements
  - Minimum of one field reagent blank for each set of samples per site and field duplicates
  - Both methods specify the frequency of the field duplicate in terms of extraction batch (one per extraction batch, not to exceed 20 field samples), not collection frequency
- Additional quality control samples may be needed based on site-specific work plan and data quality objectives

PFAS-1, Section 11.1.6 Field QC Samples.

QA/QC Sample Collection

Using blanks to evaluate composition or suitable nature of equipment/supplies for sampling, and to assess possibility of cross-contamination during sampling/transport/storage

- **Pre-investigation equipment blanks** (decon water, methanol, new equipment, plastic bags as sample containers, anything you are unsure of)
- **Equipment blanks** to assess adequacy of decontamination process and/or evaluate potential contamination from equipment.
- **Field blanks** to assess contamination from field conditions.
  - Recommended frequency: one blank/day/matrix or one blank/20 samples/matrix, whichever more frequent.
  - **Field reagent blanks** (USEPA Method 537.1, 533) should originate from the laboratory for all drinking-water programs (minimum of 1/event).

PFAS-1, Section 11.1.6. Table 11-1 Typical field QC Samples.

Filtering of Water Samples

- Evidence that PFAS may sorb onto various filters (e.g., glass fiber filters)
- Data may be misinterpreted as PFAS sorbed to soil or sediment in the water sample when the reduction may actually reflect PFAS sorbed onto the glass fiber filter
- Consider use of low flow sampling
- Laboratory centrifugation is a good alternative

PFAS-1, Section 11.2.1.2. Sample Preparation.

PFAS Analysis

PFAS-1, Section 11.2 Analytical Methods/Techniques.

USEPA 537.1 & 533 PFAS Drinking Water Methods

Similarities

- Sample preparation via Solid Phase Extraction (SPE)
- Compound-Specific Analysis by LC-MS/MS
- Laboratories allowed some modifications, but not:
  - Sample collection/preservation
  - Extraction
  - Quality control
- Multi-laboratory validated method

Differences

- Sample collection - chemical preservation
- Analysis
  - Quantification scheme
  - Analyte Lists
  - Holding time

USEPA. 2020. Method 537.1 Determination of Selected PFAS in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Revision 2.0.

USEPA. 2019. Method 533: Determination of PFAS in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. EPA/815-B-19-20.

USEPA PFAS DW Analytical Methods

Method 537.1 Only		Both Methods 537.1 and 533			Method 533 Only		
NEtFOSAA	NMeFOSAA	PFOA	PFOS	11Cl-PF3OUdS	4:2 FTS	6:2 FTS	8:2 FTS
PFTA	PFTrDA	PFDA	PFDoA	9Cl-PF3ONS	PFBA	PFHpS	PFPeS
		PFHxA	PFUnA	ADONA	PFPeA	PFMBA	PFMPA
		PFBS	PFHpA	HFPO-DA	PFEESA	NFDHA	
		PFHxS	PFNA				

Table 2-4, separate PDF, categorizes the PFAS analytes according to the family tree hierarchy

PFAS-1, Section 11.2. External Table 11-4 Analyte Lists, see also Section 2.3.2. Table 2-5.

USEPA Draft Method 1633

- Fourth Draft published USEPA Method 1633 (July 2023)
  - Single-laboratory validated August 2021
  - Wastewater section multi-lab validated in Fourth Draft Method 1633
- Isotope dilution method
  - Compound-Specific Analyses (targeting 40 PFAS)
  - GW, SW, WW, Leachate, Biosolid, Tissue, Sediment, Soil

PFAS-1, Section 11.2.1 Quantitative Techniques.

Key Method Consistencies

- Use liquid chromatography tandem mass spectrometry (LC-MS/MS)
- Do not address neutral/volatile PFAS (i.e., fluorotelomer alcohols and derivatized PFCAs)
- Standards must be analyzed in order to identify and quantify individual PFAS
- Same equipment and supply concerns associated with field sampling apply to sample preparation and analysis

PFAS-1, Section 11.2.1 Quantitative Techniques.

Key Method Differences

- Method Scope
  - Media; Limit of Detection & Quantitation; Analytes (individual and isomeric profile)
- Sample preparation processes
  - Whole sample vs Aliquot; Solid Phase Extraction vs solvent dilution; Clean-up vs no clean-up
- Quantitation Scheme
  - External standard
    - Surrogates added prior to sample preparation; Quantitation does not account for bias associated with sample preparation or instrumentation; Data review must include evaluation of surrogate recoveries
  - Internal standard
    - Surrogates added before sample preparation and internal standards added to aliquot of extract prior to analysis; Quantitation does not account for bias associated with sample preparation but DOES account for instrumentation bias; Internal standard recoveries matter
  - Isotope standard quantitation
    - Isotopically labeled standards added before sample preparation; Quantitation accounts for bias associated with sample preparation AND instrumentation; Isotopically labeled standard recoveries matter

PFAS-1, Section 11.2.1 Quantitative Techniques.

Data Review and Validation

- Published Data Review and Validation Guidelines
  - Drinking Water Data Validation Guidance (*Data Review and Validation Guidelines for Perfluoralkyl Substances (PFASs) Analyzed Using EPA Method 537* (EPA 910-R-18-001, November 2018)
  - Data Review Guidance (USEPA Technical Brief "Per-and Polyfluoroalkyl Substances (PFAS): Reviewing Analytical Methods Data for Environmental Samples." April 2019)
  - DOD Validation Guidance (*Data Validation Guidelines Module 6: Data Validation Procedure for Per- and Polyfluoroalkyl Substances Analysis by QSM Table B-24*, 2022)

PFAS-1, Section 11.3 Data evaluation. Table 11-6 PFAS Analytical Data Usability Table.

Less-Standardized Analytical Techniques

- Particle-Induced Gamma Emission (PIGE) spectroscopy measures elemental fluorine from a sample isolated on a thin surface
- Precursor Analysis by Total Oxidizable Precursor (TOP) Assay measures PFAA precursors or polyfluorinated compounds that can be converted to PFAAs
- LC quadrupole time-of-flight mass spectrometry (LC-QToF-MS) tentatively identifies PFAS structures through library matches
- Extractable/Absorbable Organic Fluorine (EOF/AOF) measures fluorine in a sample as fluoride

PFAS-1, Section 11.2.2 Qualitative Techniques.

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Treatment Technologies

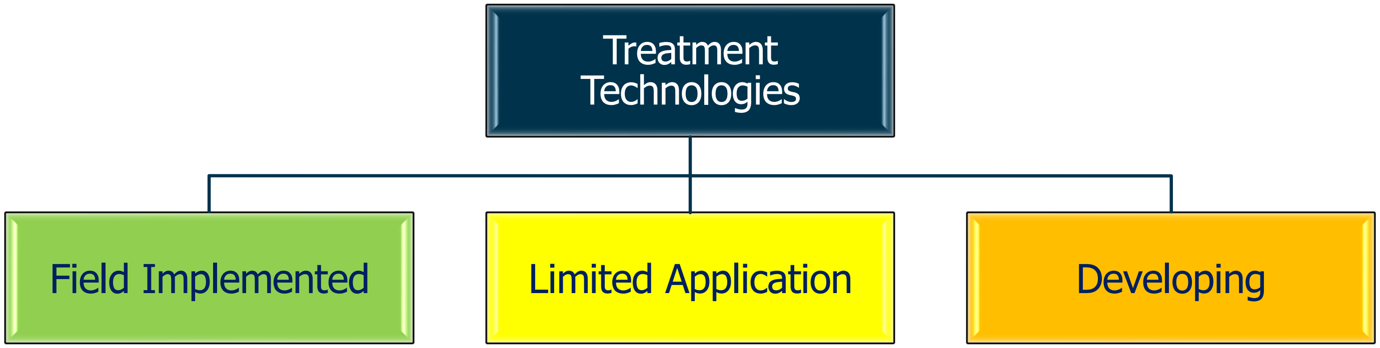
Andy Safulko, Brown and Caldwell

PFAS Technical and Regulatory Guidance Document Published

- Final web document PFAS-1: https://pfas-1.itrcweb.org
- Treatment Technologies, Section 12
- Table 12-1 Treatment Technologies Table
- Treatment Case Studies, Section 15.2

ITRC 2023. *PFAS Technical and Regulatory Guidance Document and Fact Sheets* PFAS-1. Washington, D.C.. https://pfas-1.itrcweb.org/.

Treatment Technology Maturity



Treatment Technologies

Field Implemented

Demonstrated at multiple sites under diverse conditions by multiple practitioners, are commercially available, and are well documented in practice or peer-reviewed literature

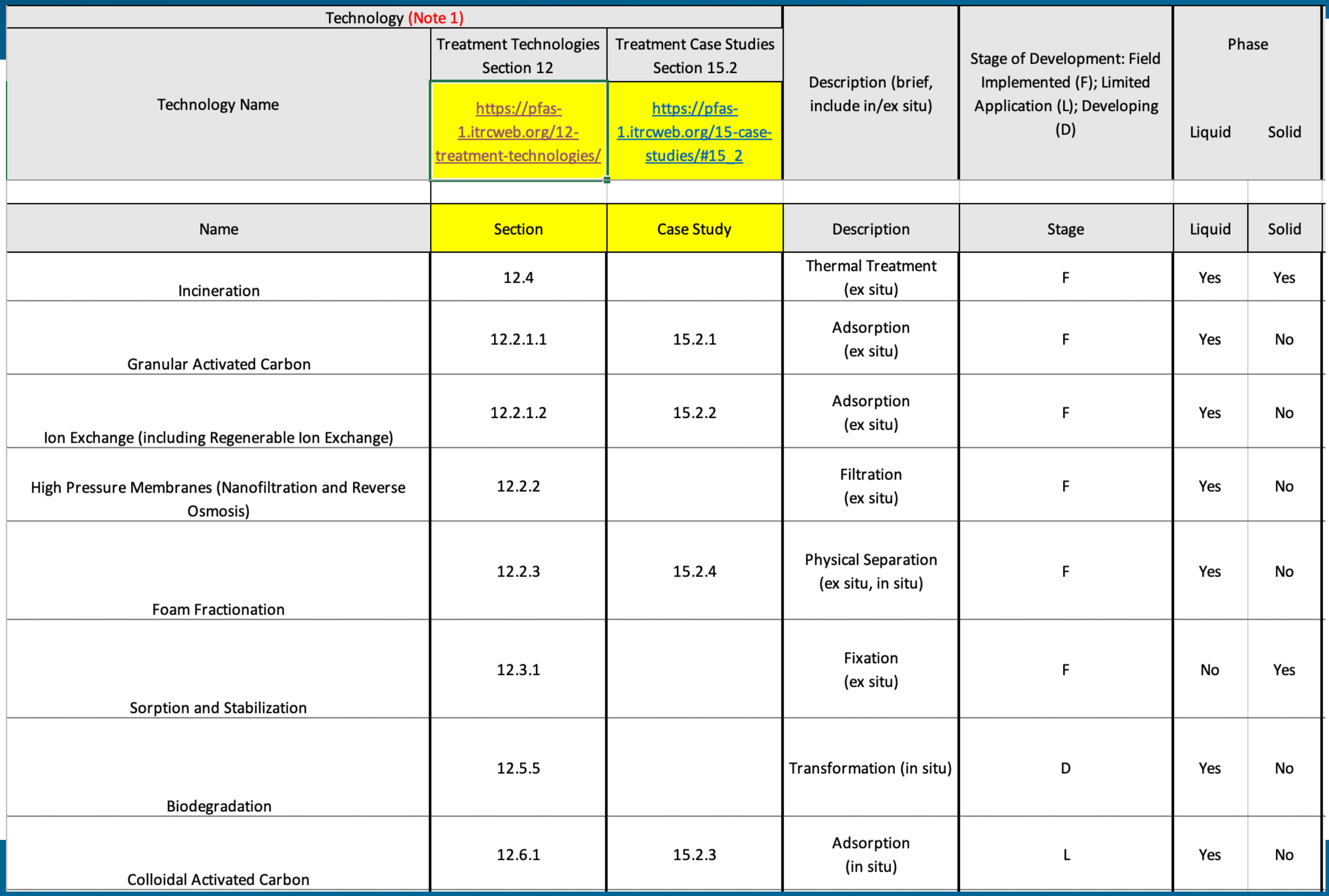
Limited Application

Implemented on a limited number of sites by a limited number of practitioners either at full-scale or field pilot-scale applications but without large body of evidence

Developing

Researched at the laboratory or bench scale, but these technologies are often reported by one group or lack detailed independent verification of the treatment effectiveness or mechanism

Treatment Technologies Table



Technology (Note 1)			Description (brief, include in/ex situ)	Stage of Development: Field Implemented (F); Limited Application (L); Developing (D)	Phase	
Technology Name	Treatment Technologies Section 12 https://pfas-1.itrcweb.org/12-treatment-technologies/	Treatment Case Studies Section 15.2 https://pfas-1.itrcweb.org/15-case-studies/#15_2			Liquid	Solid
Name	Section	Case Study	Description	Stage	Liquid	Solid
Incineration	12.4		Thermal Treatment (ex situ)	F	Yes	Yes
Granular Activated Carbon	12.2.1.1	15.2.1	Adsorption (ex situ)	F	Yes	No
Ion Exchange (including Regenerable Ion Exchange)	12.2.1.2	15.2.2	Adsorption (ex situ)	F	Yes	No
High Pressure Membranes (Nanofiltration and Reverse Osmosis)	12.2.2		Filtration (ex situ)	F	Yes	No
Foam Fractionation	12.2.3	15.2.4	Physical Separation (ex situ, in situ)	F	Yes	No
Sorption and Stabilization	12.3.1		Fixation (ex situ)	F	No	Yes
Biodegradation	12.5.5		Transformation (in situ)	D	Yes	No
Colloidal Activated Carbon	12.6.1	15.2.3	Adsorption (in situ)	L	Yes	No

PFAS-1, Table 12-1 Treatment Technologies Table.

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Liquids Treatment Technologies

Liquids Treatment

- Field Implemented (Section 12.2)
  - Granular activated carbon (GAC) adsorption
  - Ion exchange (IX) resin adsorption
  - High-pressure membrane filtration
  - Foam fractionation
  - In-situ colloidal activated carbon
- Limited Applications (Section 12.6)
  - Examples include - surface modified clay
- Developing Technologies (Section 12.6)
  - Examples include – alternative adsorbents, bioremediation, advanced chemical oxidation/reduction, plasma, others

Field Implemented

Limited Application

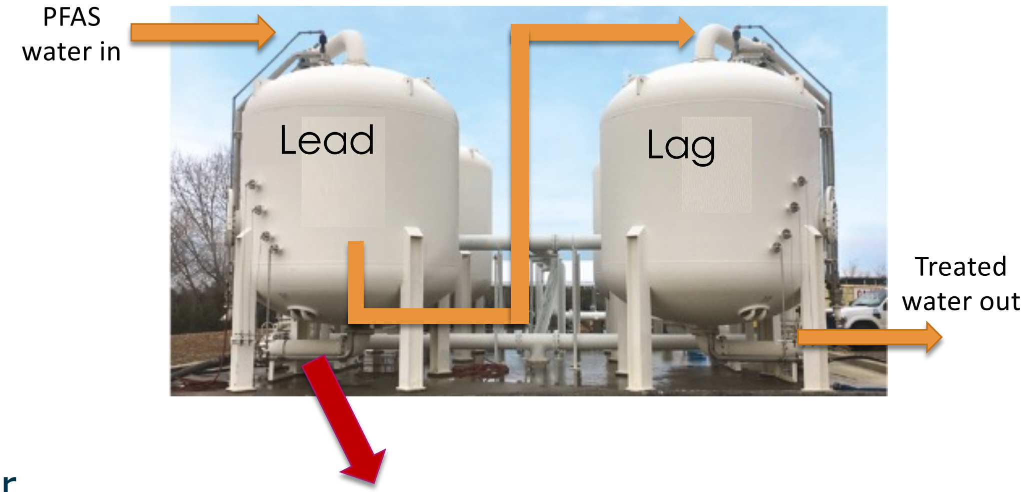
Developing

PFAS-1, Section 12 Treatment Technologies
PFAS-1, Table 12-1 Treatment Technologies Table

Adsorption Systems

Field Implemented

- Technologies: granular activated carbon (GAC), single use ion exchange resin (IX), regenerable IX
- PFAS are not destroyed
- Pre-Treatment needed
- Monitoring - Influent, mid-point, effluent
- Media Change Out: Lag to lead, new to lag
- Post treatment/polish (optional)
- Spent Media Management
- Field implemented applications for Drinking water, Groundwater, Surface Water, Industrial Wastewater



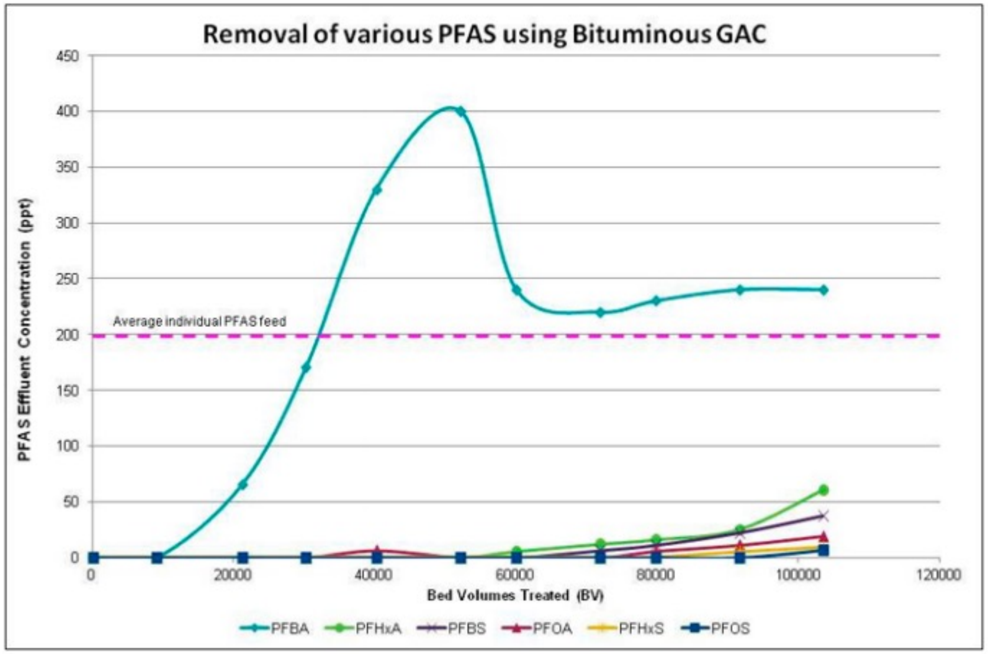
Adsorbent: reactivation, incineration, or disposal after use

Graphic used with permission, Scott Grieco, adapted from Stew Abrams and Purolite.
Photo used with permission, Francis Boodoo, Purolite.

Activated Carbon

Field Implemented

- Granular Activated Carbon (GAC) field implemented for PFAS treatment for >10 years.
- GAC performance varies based on site-specific conditions, carbon source types, GAC manufacturing methods, and target PFAS.
- Sizing and Design Issues
    - Vessel size based on 10 to 15 minute "Empty Bed Contact Time" (EBCT).
    - GAC usage rates are site specific
- Pretreatment processes – fouling mitigation

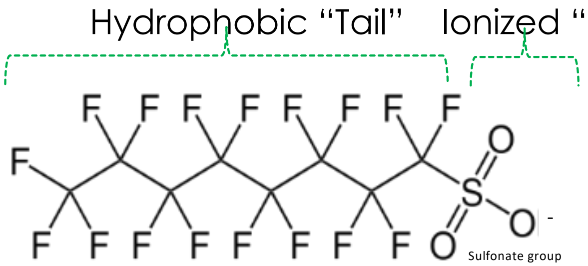


PFAS-1, Section 12.2.1.1 Figure 12-1. Example GAC removal curves at specific influent concentration . Source: Calgon Carbon Corporation. Used with permission.

Ion Exchange (IX) Resin

Field Implemented

- Field-demonstrated
- Selective IX Resin removed by both <u>ion exchange</u> (head) and <u>adsorption</u> (tail)
- High removal efficiency
- Shorter EBCT and small footprint relative to GAC
- High operating capacity
  - 100,000 to 350,000 bed volumes for low concentration drinking water
- Operation costs dependent on water quality and pretreatment needs
- Single use or regenerable options



Adsorbent: incineration or disposal after use

Short Contact Time ~3 mins

PFAS-1, Section 12.2.1.2 Ion Exchange Resin.

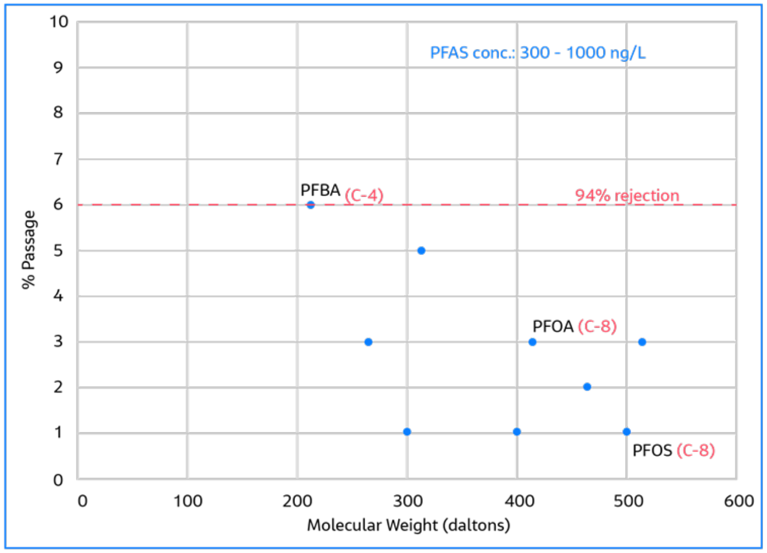
Graphic used with permission, Scott Grieco, adapted from Stew Abrams and Purolite. Photo used with permission, Francis Boodoo, Purolite.

High-Pressure Membranes

Field Implemented

- Reverse Osmosis (RO) is effective for long- and short-chain PFAS
- Nanofiltration (NF) is molecule size/charge dependent
- Advantages
  - Effective barrier for PFAS of concern
  - Provide dual role for softening/ inorganics removal
  - Can be effective for polar organics
- Concerns
  - Expense/energy use
  - Pretreatment requirements
  - Managing liquid concentrate

PFAS Passage through Dow NF-270 (polypiperzazineamide) membrane (MWCO = 200 daltons)



Adapted from Appleman et al., 2013

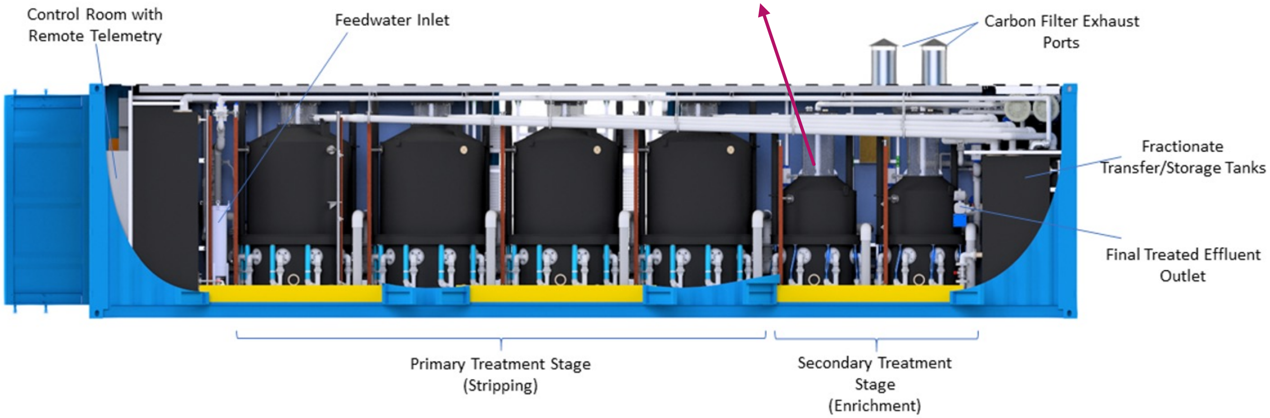
PFAS-1, Section 12.2.2 High-Pressure Membranes.
Photo and graph source: Scott Grieco, Jacobs. Used with permission.

Foam Fractionation

Field Implemented

- PFAS partition to the air-water interface of the bubble surfaces and accumulate as foam
- Sequential fractionation steps concentrate PFAS into highly concentrated waste foam
- Foam concentrate needs management or destruction
- Standalone technology or combined with other technologies to improve PFAS removal

PFAS concentrated foam



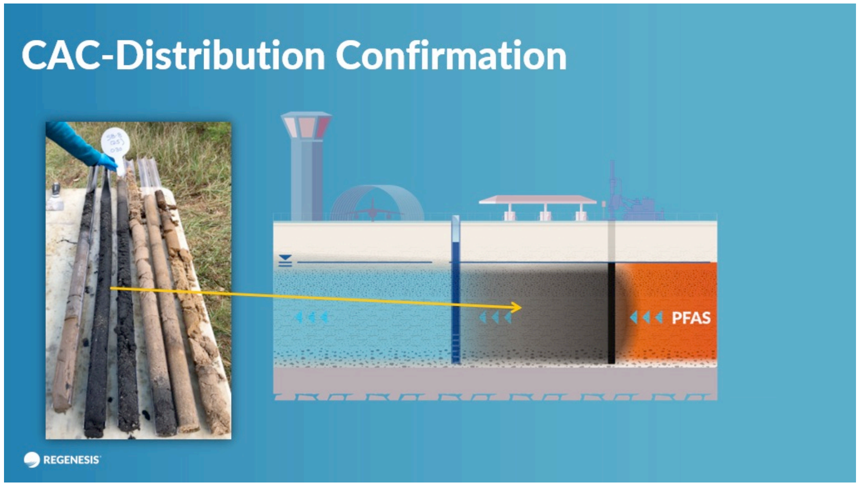
Source: Photos used with permission from D. Burns, EPOC Enviro LLC a subsidiary of OPEC Systems Pty Ltd.

PFAS-1, Section 12.2.3 Foam Fractionation.

Colloidal Activated Carbon (CAC) [in situ]

Field Implemented

- Injection (direct-push) of CAC into flux zones of an aquifer immobilizes contaminants to prevent further horizontal and vertical migration
- Colloidal size = ~2 microns in diameter
    - Small enough to move through soil pores
    - Adsorption kinetics much faster than with traditional GAC
- Longevity of performance dependent on many factors
    - Modeling indicates it could be on the order of decades
- New case study added to Section 15



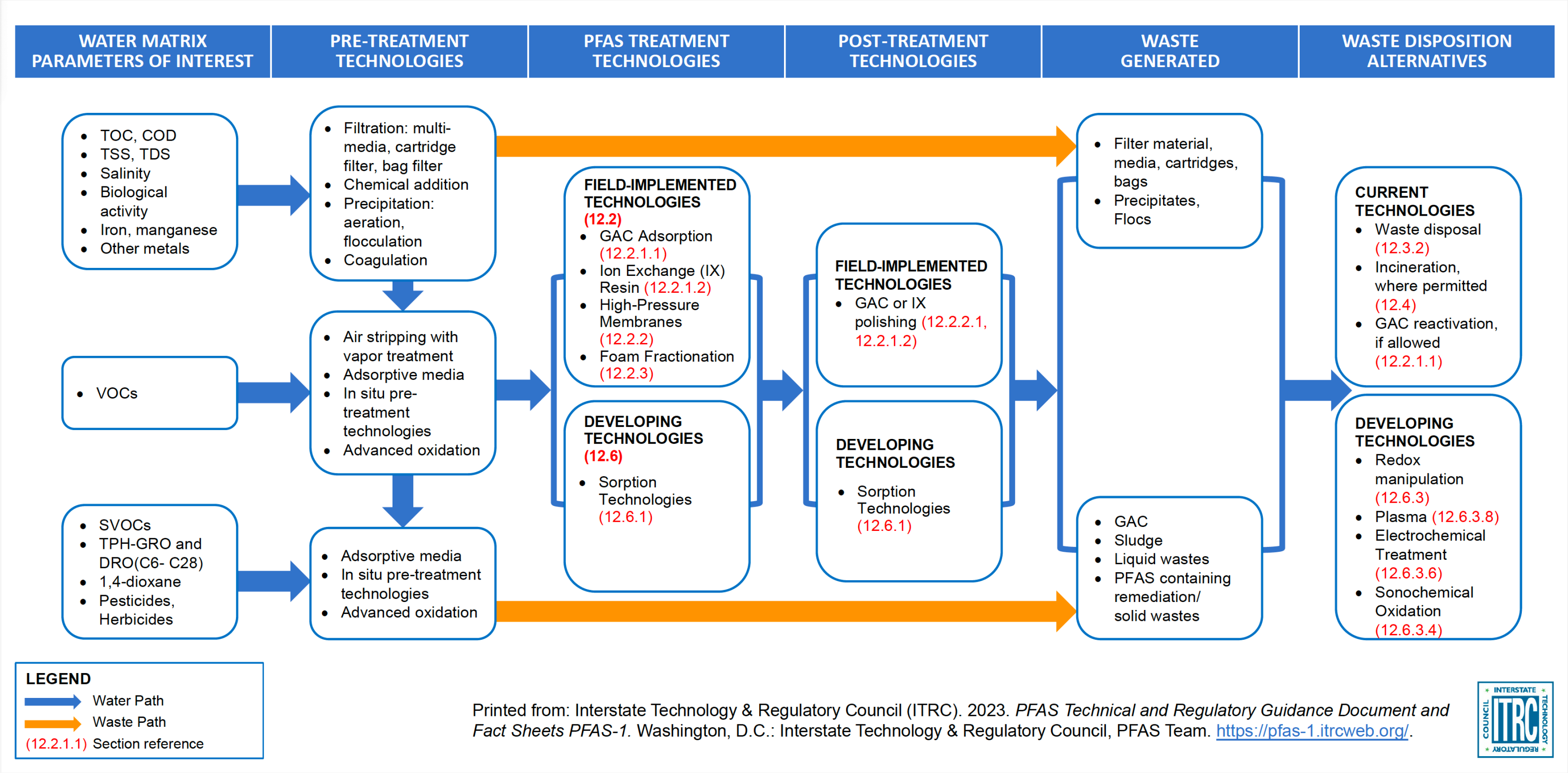
CAC-Distribution Confirmation

Vertical sections of a "searcher core" to verify presence of CAC at the desired interval

Source: Photos used with permission from S. Wilson, Regenesis

PFAS-1, Section 12.2.4 In Situ Remediation with Colloidal Activated Carbon.

Integrated Remedial Solutions - Flowchart



WATER MATRIX PARAMETERS OF INTEREST

- TOC, COD
- TSS, TDS
- Salinity
- Biological activity
- Iron, manganese
- Other metals

- VOCs

- SVOCs
- TPH-GRO and DRO(C6- C28)
- 1,4-dioxane
- Pesticides, Herbicides

PRE-TREATMENT TECHNOLOGIES

- Filtration: multi-media, cartridge filter, bag filter
- Chemical addition
- Precipitation: aeration, flocculation
- Coagulation

- Air stripping with vapor treatment
- Adsorptive media
- In situ pre-treatment technologies
- Advanced oxidation

- Adsorptive media
- In situ pre-treatment technologies
- Advanced oxidation

PFAS TREATMENT TECHNOLOGIES

FIELD-IMPLEMENTED TECHNOLOGIES (12.2)

- GAC Adsorption (12.2.1.1)
- Ion Exchange (IX) Resin (12.2.1.2)
- High-Pressure Membranes (12.2.2)
- Foam Fractionation (12.2.3)

DEVELOPING TECHNOLOGIES (12.6)

- Sorption Technologies (12.6.1)

POST-TREATMENT TECHNOLOGIES

FIELD-IMPLEMENTED TECHNOLOGIES

- GAC or IX polishing (12.2.2.1, 12.2.1.2)

DEVELOPING TECHNOLOGIES

- Sorption Technologies (12.6.1)

WASTE GENERATED

- Filter material, media, cartridges, bags
- Precipitates, Flocs

- GAC
- Sludge
- Liquid wastes
- PFAS containing remediation/ solid wastes

WASTE DISPOSITION ALTERNATIVES

CURRENT TECHNOLOGIES

- Waste disposal (12.3.2)
- Incineration, where permitted (12.4)
- GAC reactivation, if allowed (12.2.1.1)

DEVELOPING TECHNOLOGIES

- Redox manipulation (12.6.3)
- Plasma (12.6.3.8)
- Electrochemical Treatment (12.6.3.6)
- Sonochemical Oxidation (12.6.3.4)

LEGEND

➡	Water Path
➡	Waste Path
(12.2.1.1)	Section reference

Printed from: Interstate Technology & Regulatory Council (ITRC). 2023. *PFAS Technical and Regulatory Guidance Document and Fact Sheets PFAS-1*. Washington, D.C.: Interstate Technology & Regulatory Council, PFAS Team. https://pfas-1.itrcweb.org/.

PFAS-1, Figure 12-7. Section 12.8 Integrated Water Treatment Solutions.

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Solids Treatment Technologies

Solids Treatment

- Field Implemented conventional approaches, with limitations:
  - Excavation and incineration or disposal (Section 12.3.2)
  - Activated carbon based in situ or ex situ stabilization (Section 12.3.1)
  - Soil washing (Section 12.3.3)
- Limited applications and developing technologies
  - Alternative sorption, stabilization/solidification (12.7.1)
  - Thermal treatment (12.7.2)

Soil Remedial Technologies

Field Implemented

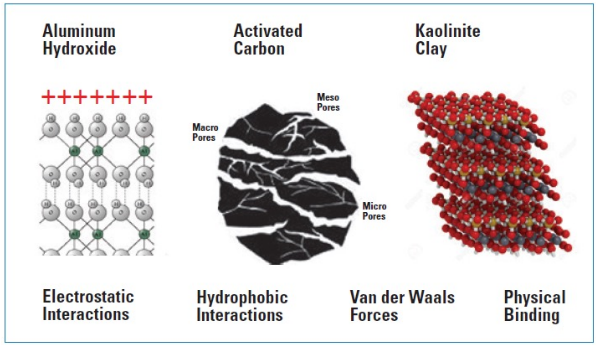
- Excavation with offsite disposal in a permitted landfill, where allowed
  - Some landfills no longer will accept PFAS soils
  - Do not assume this is straightforward
- Excavation with offsite incineration
  - Destruction assumed but not well documented
  - USEPA, USDOD and other research programs looking closely at destruction
- Pending CERCLA hazardous substances designation likely to impact these options

Photo courtesy of CH2M/Jacobs. Used with permission.

Soil Stabilization

Field Implemented

- In-situ or ex-situ stabilization/immobilization via sorption
- Combination of powder-based reagents with high surface area and various binding methods:
  - For example: powdered activated carbon, aluminum hydroxide, kaolin clay
  - Added from 1-5% by weight to soil
  - Fully commercial & demonstrated in Australia
  - Extensive testing, research and demonstration in Europe
- Implementation in situ with large diameter augers possible



Images courtesy of Ziltek™ and AquaBlok Ltd.
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PFAS-1, Section 12.3.1 Sorption and Stabilization.

Soil Washing

Field Implemented

- Full-scale systems operating in Australia and Canada, some US pilot testing
- Can be enhanced specifically to keep PFAS in solution longer
- PFAS treated with GAC and/or IX resins, yielding these wastes
- Results in >99.4% mass reduction
- Lower throughput for clay-rich soils as compared to sandy soils (10 tons/hour vs 25 tons/hour)

PFAS-1, Section 12.3.3 Soil Washing.

Incineration for PFAS-Contaminated Media

- Incineration has the potential to destroy PFAS
  - Vaporized combustion products can be further oxidized and/or captured (precipitation, wet scrubbing)
- Solids
  - soil/sediment/spent adsorbents/waste
- Liquids
  - water/wastewater/leachate/chemicals
- Questions remain
  - Products of incomplete combustion, stack gas analysis, fallout onto land adjacent to the incinerator and other risk factors
  - USEPA and others are currently conducting research to help answer these questions
- Considerations for using different facilities – transportation costs, energy costs, final disposition of process waste residues, state or local regulatory program

PFAS-1, Section 12.4 Incineration.

Questions

Please use the Q&A Pod to ask questions.

Web Sites

- Published Guidance Document, Fact Sheets, Videos, Training
  - https://pfas-1.itrcweb.org
- PFAS Team Public page
  - https://itrcweb.org/teams/active/pfas

Thank you!

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