### Housekeeping

This event is being recorded; Event will be available On Demand after the event at the main training page

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

- If you have technical difficulties, please use the Q&A Pod to request technical support
- Need confirmation of your participation today?
  - Fill out the online feedback form and check box for confirmation email and certificate



Copyright 2020 Interstate Technology & Regulatory Council, 1250 H Street, NW Suite 850 | Washington, DC 20005



Advancing Environmental Solutions



# INTRODUCTION TO PFAS (PFAS-1)

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



**Sponsored by**: Interstate Technology and Regulatory Council (www.itrcweb.org) **Hosted by**: US EPA Clean Up Information Network (www.clu-in.org)<sup>2</sup>

## ITRC – Shaping the Future of Regulatory Acceptance

Host Organization



Network - All 50 states, PR, DC

**Federal Partners** 





**ITRC Industry Affiliates Program** 

Academia

**Community Stakeholders** 

https://pfas-1.itrcweb.org/about-itrc/#disclaimer

Disclaimer

Partially funded by the US government

ITRC nor US government warranty material

ITRC nor US government endorse specific products

ITRC materials available for your use – see <u>usage policy</u>





Itroweb



linkedin.com/ company/itrc



https://www.itrcweb.org/

### 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



Shalene Thomas, Battelle



Andy Safulko, Brown and Caldwell





Advancing Environmental Solutions



## Introduction to ITRC and PFAS Team

Kristi Herzer Vermont Department of Environmental Conservation (VT DEC)



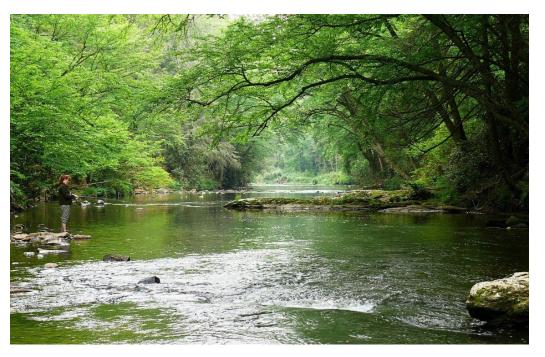
### Topics for Today

| Торіс   | Speaker        |
|---|----------------|
| Introduction to ITRC and PFAS Team              | Kristi Herzer  |
| Naming Conventions and Sources                  | Mitch Olson    |
| AFFF  | Shalene Thomas |
| Fate and Transport and Site<br>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



<u>This Photo</u> by Ken Thomas is licensed unde<u>CC BY-SA</u>.



#### 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



<u>A1C Kyle Gese</u>, Public domain, via Wikimedia Commons.

Ewan Munro from London, UK, CC BY-SA 2.0, via Wikimedia Commons.

> <u>This Photo</u> by Stephani Spitzer is licensed under CC BY 3.0.



### Technical Resources

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



#### PFAS — Per- and Polyfluoroalkyl Substances ENHANCED BY Google

#### 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**



HOME

PFAS

### External Tables and Information

- Fact Sheets: PFAS Water and Soil Regulatory and Guidance Values Table Excel File
- Fact Sheets: PFAS Air Criteria Table Excel FIle
- Section 2: Figure 2-5 PFAS Family Tree PDF
- <u>Section 2: USEPA Analytes List PFAS Classifications PDF</u>
- Section 3: AFFF Characteristics Excel File
- Section 3: AFFF Transition to F3 Case Studies Excel File
- <u>Section 4: Physical and Chemical Properties Table 4-1 Excel File</u>
- <u>Section 5: Aquatic Organisms BCF-BAF Table 5-1 Excel File</u>
- 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
- <u>Section 12: Treatment Technologies Table Excel File</u>
- Section 12: Integrated Water Treatment Flow Chart PDF
- Section 14: Risk Communication Social Factors Vision Board PDF
- <u>Section 15: Water Treatment Case Studies Excel File</u>
- Section 17.1: Table 17-1 A-C for Air PDF
- Section 17.1: Table 17-2 A-C forSoil, Sediments, and Biosolids PDF
- 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

ITRC has developed a series of fact sheets

that summarizes recent science and emerging technologies regarding PFAS. The

sheets is more fully described in the ITRC PFAS Technical and Regulatory Guidanc

This fact sheet describes considerations for

Beneficial uses of surface water impacte

Regulatory approaches for developing surface water quality criteria and

Sampling and analysis considerations for surface water quality assessments, including surface water foam

managing PFAS impacts to surface water,

information in this and other PFAS fact

Document (Guidance Document) (https://pfas-1.itrcweb.org/).

including

by PFAS

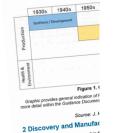
guidance values

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

#### 1 Introduction

1 Introduction This fact sheet provides a summary of the disc of PAS, emerginal environmental mediate, i-productions of chemicals that vary widely and the environment. The summary widely prefacil impact prefaces and an environment of PAS impact of uncertainty and an environment of the environment. The summary industry environment of the environment. The summary industry environment of the environment of t Vdditional information is available in the Gu

PFAS have followed a similar pattern of em PTAb have followed a similar pattern of em exhibited by many other anthropogenic env contaminants. Figure 1 provides a general contaminants. Figure 1 provides a general emergence and awareness that includes c synthesis/development, 2) commercial pro



PFAS chemistry was discovered in t PPAS chemistry was discovered in t industry have been manufactured wi *fluorotelomerization*, have been (any chain fluorinated polymers, perfluor and Martin 2010; KEMI 2015 Retet by these processes. More than 600 associated final products.

#### Surface Water Quality Considerations for Per- and ITRC 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 considerati for sampling and analysis for surface water gualtiy assessments for PEAS. The information in this fact sheet is based on Section 16 of the Guidance Document

#### 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 PAS-containing foam agricultural supply, considering farming, horticulture, dairy operations, ranching, watering of livestock, and use fo irrigation of crops for consumption by humans or livestock (i.e., crop untake) with potential human exposures ough 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 agricultura supply beneficial uses

n general, for PFAS, the two most relevant beneficial uses are drinking water use and consumption of aquatic organism 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 perfluorocctanoic acid (PFOA)(USEPA 2022 Ref#2300) and perfluorocctane 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-s

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).

12



Advancing Environmental Solutions



# 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: <u>https://pfas-1.itrcweb.org</u>
- PFAS Chemistry and Naming Conventions, History and Use of PFAS, and Sources of PFAS Releases to the Environment

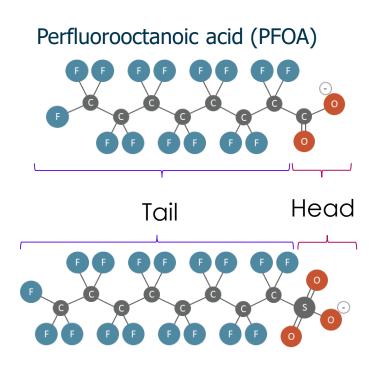
Section 2.1 – Environmental Significance

- 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



#### General Classification of Per- and Polyfluoroalkyl Substances (PFAS)

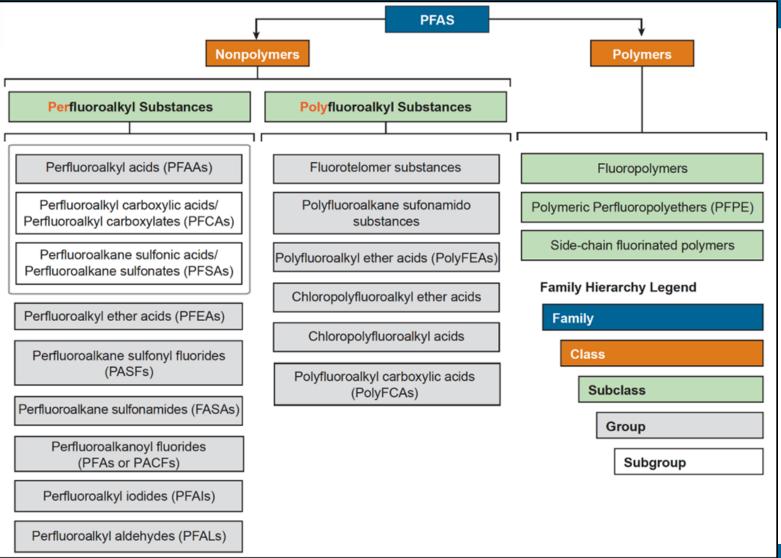


Perfluorooctane sulfonate (PFOS)

ENVIRONMENTAL RESEARC

**REGULATORY** 

ЕСОЅ



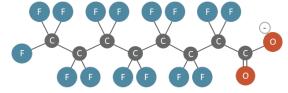
PFAS-1, Section 2.2. Figure 2-4 PFAS Family Tree and Figure 2-7 The tail and head structure of PFOS and PFOA molecules. Molecule Figures Source: M. Olson, Trihydro. Used with permission.

### Key Terms and Acronyms

- PFAS (per- and poly fluoroalkyl substances)
- <u>Perfluoroalkyl substances</u>

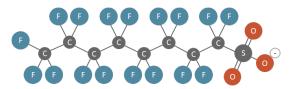
Perfluoroalkyl acids, or PFAAs

PFCAs (perfluoroalkyl carboxylates)



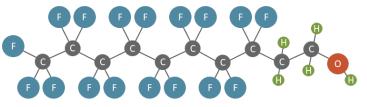
PFOA (perfluorooctane carboxylate)

PFSAs (perfluoroalkane sulfonates)



PFOS (perfluorooctane sulfonate)

- <u>Poly</u>fluoroalkyl substances
  - "Precursors"



8:2 Fluorotelomer alcohol (8:2 FTOH)



PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs) and Section 2.2.4 Polyfluoroalkyl Substances. 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<sub>3</sub><sup>-</sup>)
    - A = carboxylate (R-COO<sup>-</sup>)

(buta-) 4 В Pe 5 (penta-) Hx (hexa-) 6 Hp (hepta-) 7 8 Ο (octa-) 9 Ν (nona-).....



17

## 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<sub>3</sub><sup>-</sup>)
    - A = carboxylate (R-COO<sup>-</sup>)

Table 2-2 Basic naming structure and shorthand for PFAAs

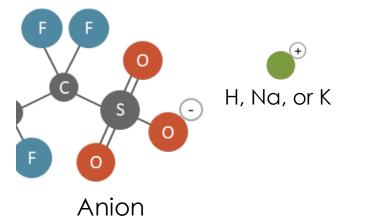
|         | Х                        | Y                                 | Acronym                   | Name  | Formula  | CAS No.     |
|---------|--------------------------|-----------------------------------|---------------------------|---|--|-------------|
|         |                          | A = Carboxylate or                |                           | Perfluorobutanoate                            | C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> <sup>-</sup>   | 45048-62-2  |
|         | B = buta (4              | carboxylic acid                   | PFBA                      | Perfluorobutanoic acid                        | C <sub>3</sub> F <sub>7</sub> COOH                           | 375-22-4    |
| carbon) | S = Sulfonate or         |                                   | Perfluorobutane sulfonate | C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> | 45187-15-3   |             |
| l       |                          | sulfonic acid                     | PFBS                      | Perfluorobutane sulfonic acid                 | C₄F <sub>9</sub> SO₃H  | 375-73-5    |
| ľ       |                          | A = Carboxylate or                | PFPeA                     | Perfluoropentanoate                           | C <sub>4</sub> F <sub>9</sub> CO <sub>2</sub> -              | 45167-47-3  |
|         | Pe = penta               | carboxylic acid                   |                           | Perfluoropentanoic acid                       | C₄F <sub>9</sub> COOH  | 2706-90-3   |
|         | (5 carbon)               | S = Sulfonate or                  | PFPeS                     | Perfluoropentane sulfonate                    | C5F11SO3-  | NA          |
|         |                          | sulfonic acid                     |                           | Perfluoropentane sulfonic acid                | C <sub>5</sub> F <sub>11</sub> SO <sub>3</sub> H             | 2706-91-4   |
| ľ       |                          | A = Carboxylate or                | PFHxA                     | Perfluorohexanoate                            | C <sub>5</sub> F <sub>11</sub> CO <sub>2</sub> -             | 92612-52-7  |
| l       | Hx = hexa (6             | carboxylic acid                   |                           | Perfluorohexanoic acid                        | C <sub>5</sub> F <sub>11</sub> COOH                          | 307-24-4    |
|         | carbon)                  | S = Sulfonate or<br>sulfonic acid | PFHxS                     | Perfluorohexane sulfonate                     | C <sub>6</sub> F <sub>13</sub> SO <sub>3</sub> <sup>-</sup>  | 108427-53-8 |
| l       |                          |                                   |                           | Perfluorohexane sulfonic acid                 | C <sub>6</sub> F <sub>13</sub> SO <sub>3</sub> H             | 355-46-4    |
| Ī       | Hp = hepta<br>(7 carbon) | A = Carboxylate or                | PFHpA                     | Perfluoroheptanoate                           | C <sub>6</sub> F <sub>13</sub> CO <sub>2</sub> -             | 120885-29-2 |
| l       |                          | carboxylic acid                   |                           | Perfluoroheptanoic acid                       | C <sub>6</sub> F <sub>13</sub> COOH                          | 375-85-9    |
|         |                          | S = Sulfonate or                  |                           | Perfluoroheptane sulfonate                    | C <sub>7</sub> F <sub>15</sub> SO <sub>3</sub> <sup>-</sup>  | NA          |
|         |                          | sulfonic acid                     | PFHpS                     | Perfluoroheptane sulfonic acid                | C <sub>7</sub> F <sub>15</sub> SO <sub>3</sub> H             | 375-92-8    |
| Π       |                          | A = Carboxylate or                | PFOA<br>PFOS              | Perfluorooctanoate                            | C <sub>7</sub> F <sub>15</sub> CO <sub>2</sub> -             | 45285-51-6  |
|         | O = octa<br>(8 carbon)   | carboxylic acid                   |                           | Perfluorooctanoic acid                        | C <sub>7</sub> F <sub>15</sub> COOH                          | 335-67-1    |
|         |                          | S = Sulfonate or                  |                           | Perfluorooctane sulfonate                     | C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> -             | 45298-90-6  |
| l       |                          | sulfonic acid                     |                           | Perfluorooctane sulfonic acid                 | C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> H             | 1763-23-1   |
| Ī       | N = nona<br>(9 carbon)   | A = Carboxylate or                | PENA                      | Perfluorononanoate                            | C <sub>8</sub> F <sub>17</sub> CO <sub>2</sub> -             | 72007-68-2  |
|         |                          | carboxylic acid                   | PENA                      | Perfluorononanoic acid                        | C <sub>8</sub> F <sub>17</sub> COOH                          | 375-95-1    |
|         |                          | S = Sulfonate or                  | PFNS                      | Perfluorononane sulfonate                     | C <sub>9</sub> F <sub>19</sub> SO <sub>3</sub> <sup>-</sup>  | NA          |
| l       |                          | sulfonic acid                     | FENO                      | Perfluorononane sulfonic acid                 | C <sub>9</sub> F <sub>19</sub> SO <sub>3</sub> H             | 474511-07-4 |
| ĺ       |                          | A = Carboxylate or                | PEDA                      | Perfluorodecanoate                            | C <sub>9</sub> F <sub>19</sub> CO <sub>2</sub> -             | 73829-36-4  |
|         | D = deca                 | carboxylic acid                   | FFUA                      | Perfluorodecanoic acid                        | C <sub>9</sub> F <sub>19</sub> COOH                          | 335-76-2    |
|         | (10 carbon)              | S = Sulfonate or                  | PFDS                      | Perfluorodecane sulfonate                     | C <sub>10</sub> F <sub>21</sub> SO <sub>3</sub> <sup>-</sup> | 126105-34-8 |
|         |                          | sulfonic acid                     | FFD3                      | Perfluorodecane sulfonic acid                 | C <sub>10</sub> F <sub>2</sub> 1SO <sub>3</sub> H            | 335-77-3    |



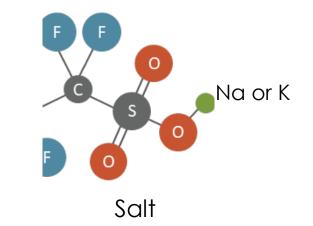
18

### Which PFAA Are We Talking About?

- Anion, Acid, or Salt?
  - PFAAs may exists in various states



Acid



In the environment, most PFAS exist in the anionic state (sulfonate/carboxylate)

Acid form of the name often used interchangeably (sulfonic acid/carboxylic acid) Different CAS numbers & physical/chemical properties

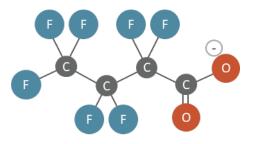


PFAS-1, Section 2.2.3.1 Perfluoroalkyl Acids (PFAAs). Source: M. Olson, Trihydro. Used with permission.

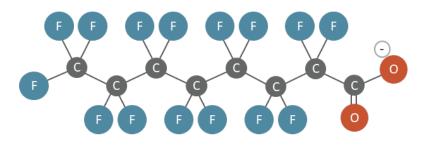
#### Long-Chain vs Short-Chain PFAAs

| 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-cha         | ain PFSAs |       |                  | Ŀ    | ong-chain PF | SAs  |       |       |

Perfluorobutane carboxylate (PFBA)



Perfluorooctane carboxylate (PFOA)

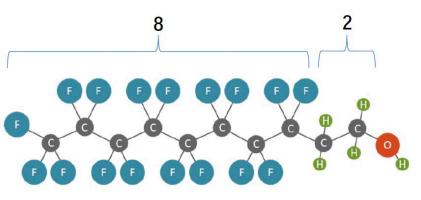




PFAS-1, Section 2.2. Table 2-3 Short-chain and long-chain PFCAs and PFSAs. <sup>20</sup> Figures Source: M. Olson, Trihydro. Used with permission.

### 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
- May be susceptible to biotic or abiotic transformation (not degradation)



8:2 Fluorotelomer alcohol

Fluorotelomers are often named using a "n:x" prefix (8:2 fluorotelomer alcohol, 8:2 FTOH)



PFAS-1, Section 2.2.4.1. Figure 2-12 Example of a polyfluoroalkyl substance. 21 Source: M. Olson, Trihydro. Used with permission.

### PFAA Precursors (under environmental conditions)

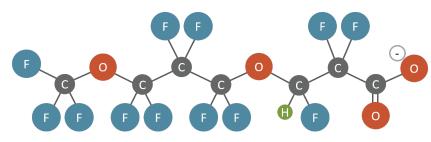
- Some PFAS can transform to PFAAs under environmental conditions
  - Referred to as "PFAA precursors"
  - Resulting PFAAs sometimes referred to as "terminal PFAAs"
- Perfluoroalkane sulfonamides (FASAs)
  - May transform to PFSAs and PFCAs
- Polyfluoroalkyl Substances
  - Fluorotelomers
    - Fluorotelomer alcohols (FTOH)
    - Fluorotelomer sulfonates (FTS)
    - Fluorotelomer carboxylates (FTCA)
    - May transform to <u>PFCAs</u>
  - Perfluoroalkyl sulfonamido ethanols (FASE) & acetic acids (FASAA)
    - May transform to PFCAs or PFSAs

As we learn more about transformation pathways, we may be able to use that information for site characterization – to determine sources, age, history, etc.

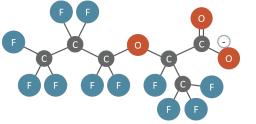


### Replacement Chemistry

- ADONA and HFPO-DA (GenX) are replacement chemicals for PFOA
- Generally limited info on toxicities, physical/chemical properties
- HFPO-DA (Hexafluoropropylene oxide dimer acid)
  - Component of GenX processing aid technology used by one manufacturer (USEPA 2018)
  - U.S. EPA proposed MCL for HFPO-DA; Health-Based Water Concentration = 10 ppt



Chemical structure for ADONA



Chemical structure for HFPO-DA (GenX) (hexafluoropropylene oxide dimer acid)



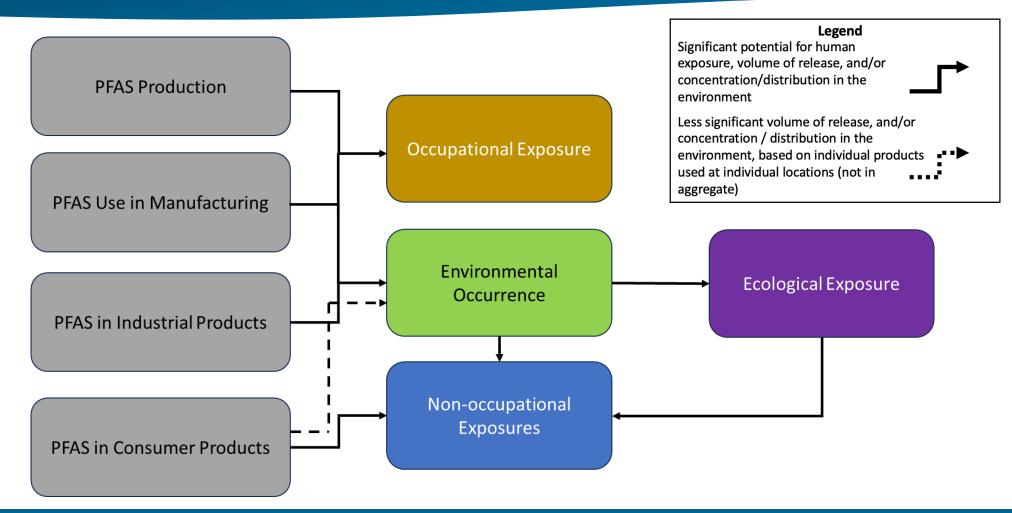
PFAS-1, Section 2.2. Figures 2-9 and 2-14 Chemical structures. Source: M. Olson, Trihydro. Used with permission.

|                         | 1930s                    | 1940s | 1950s | 1960s | 1970s | 1980s        | 1990s     | 2000s         | 2010s                         | 2020s |
|-------------------------|--------------------------|-------|-------|-------|-------|--------------|-----------|---------------|-------------------------------|-------|
| nc                      | Synthesis /<br>Developme | ent   |       |       |       |              |           |               |                               |       |
| Production              |                          |       |       |       | Manı  | ufacturing a | nd Commer | cial Producti | ion                           |       |
| Pr                      |                          |       |       |       |       |              |           |               | outs / Reduc<br>Alternatives  | -     |
| Health &<br>Environment |                          |       |       |       |       |              | Health C  | Concerns      |                               |       |
| Health<br>Environm      |                          |       |       |       |       |              |           |               | nmental Dete<br>tical Improve |       |

#### **PFAS Emergence Timeline**



# Relative exposure and environmental impact due to PFAS manufacture and use





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

25

### PFAS Use and Sources to the Environment

#### Aqueous Film Forming Foam (AFFF)

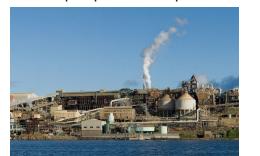
- Military installations & civil airports
- Petroleum refineries, terminals, & chemical facilities
- Firefighting training and response areas

#### Industrial

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



<u>A1C Kyle Gese</u>, Public domain, via Wikimedia Commons.



<u>JJ Harrison</u>, CC BY-SA 3.0, via Wikimedia Commons.

#### 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



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



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

26



#### Recent Claims of PFAS Use and Occurrence

- Cosmetics and Personal Care Products
- Fluorinated HDPE Containers
- Food Packaging
- Synthetic Turf



### PFAS Certification in Products

| Institution                               | Products  | Criteria   |
|---|---|--|
| USEPA Sustainable Marketplace             | Comprehensive web site of<br>multiple product categories  | Links to multiple Standards and Ecolabel   |
| USEPA – Safer Choice                      | Industrial and consumer products  | PFAS not specifically prohibited but EPA has determined that PFAS no<br>longer meet the Safer Choice standard; Exceptions allowed; will be<br>specifically called out as not meeting the standard in March of 2023<br>Other labels also listed |
| FDA                                       | Food-contact equipment & packaging  | Authorized limited PFAS use for certain categories of food contact products  |
| Green Screen                              | PFAS-free AFFF, cleaners and degreasers, furniture and fabrics, food service ware, and textiles | Separate limits for intentionally added PFAS (0-100 ppm) versus contamination as Total Organic Fluorine (1-100 ppm), which vary by product category.   |
| Biodegradable Products Institute<br>(BPI) | Compostable products and packaging  | No intentionally added PFAS; Limit of 100 ppm total fluorine; SDS review;<br>BPI-approved lab testing  |
| EWG                                       | EWG-Verified Program for consumer products  | Products cannot contain the PFAS that are on "Unacceptable" list of ingredients; Right to perform random testing   |
| PFAS-Central                              | Referrals to PFAS-free products   | Based on declared company policy, no independent verification  |





Advancing Environmental Solutions



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

#### Shalene Thomas, Battelle

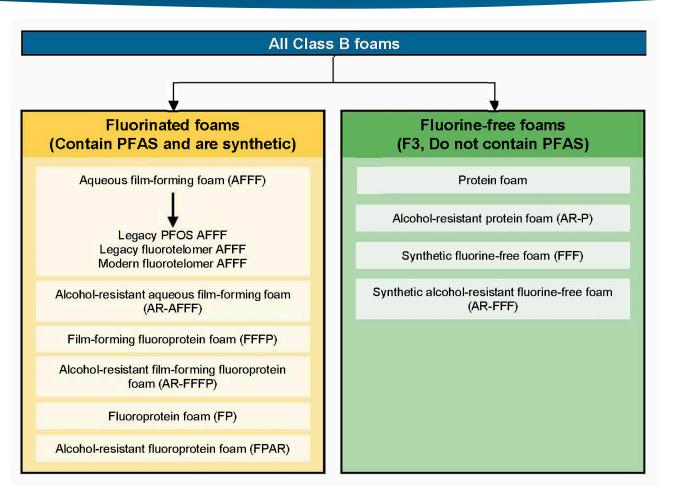


### PFAS Technical and Regulatory Guidance Document Published

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



# Classes of Firefighting Foams



- 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



### AFFF Classifications

#### • Legacy PFOS AFFF<sup>1,2</sup>

 ECF chemistry, (C2-C13), Branched & linear isomers (~1:4), PFAS composition (Mostly PFSAs, 89% (e.g., PFOS) in 3M Lightwater)

#### • Legacy Fluorotelomer AFFFs<sup>3, 4</sup>

 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

Note: PFAS composition of AFFF has changed over time



Photo courtesy of J. Field.

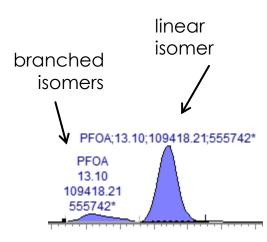


Figure courtesy C. Higgins, Colorado School of Mines.



#### PFAS-1, Section 3.1 Foam Formulations.

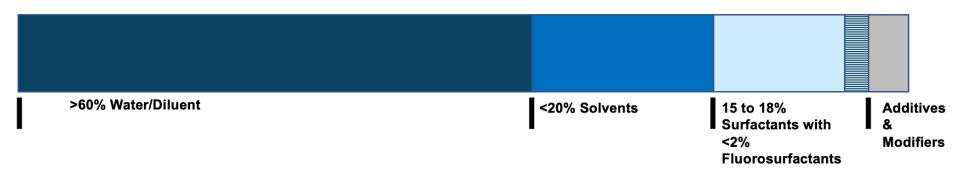
<sup>1</sup>Barzen-Hansen et al., 2015. *ES&T Letters* 2: 95-99; <sup>2</sup>Benskin, 2010. Rev Environ Contam Toxicol. <sup>3</sup>Place and Field, 2012. ES&T 46: 7120-7127; <sup>4</sup>Weiner et al., 2013. Environ Chem 10:486-493;

32

### 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

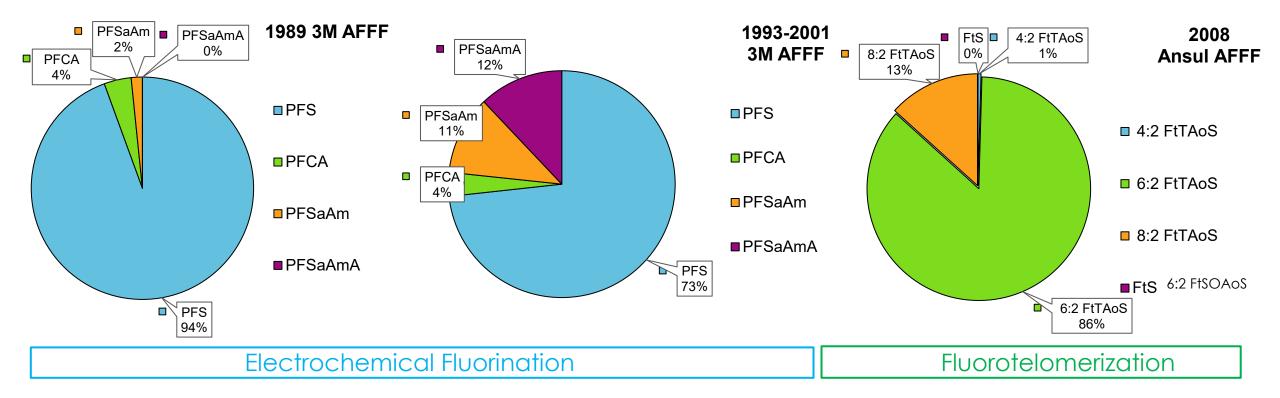
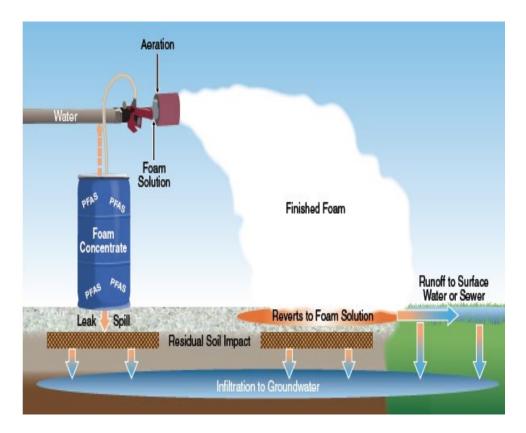


Table 3-1 of the ITRC PFAS Technical Regulatory Guidance document presents types of foam and composition.



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



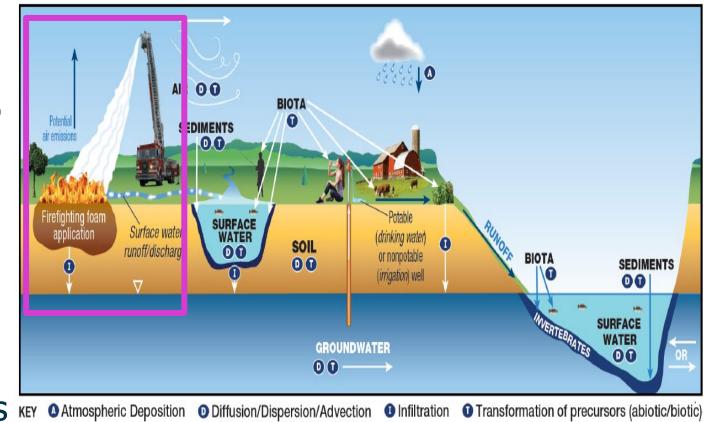
PFAS-1, Figure 3-4 Release of firefighting foam. Source: Adapted from figure by J. Hale, Kleinfelder, used with permission. Foam is released via various practices and mechanisms:

- 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)



### 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.



# AFFF Procurement and Inventory-BMP

#### 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, 5000gallon tanker truck, or suppression system
- Ensure proper secondary containment to avoid spills/mishaps



PFAS-1, Section 3.6 AFFF Procurement and Inventory. 37

**RISK** 

HAZARD X EXPOSURE =

#### Treatment and Disposal

- Consider USEPA Interim Guidance on Destroying and Disposing of Certain PFAS and PFAS-Containing Materials (Dec 2020)<sup>1</sup>
- 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  $^{\rm 1}$
  - 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.



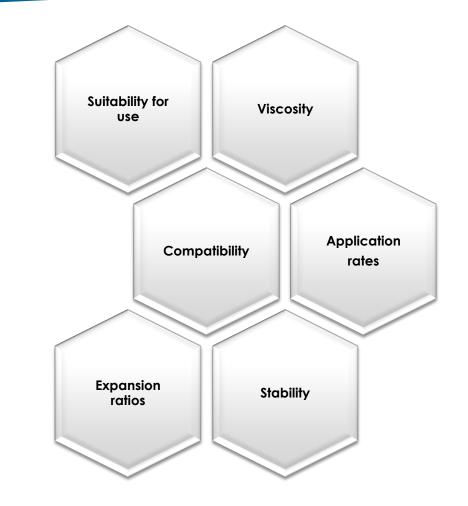
Photo from: http://clui.org/ludb/site/eastliverpool-hazardous-waste-incinerator.



<sup>1</sup>USEPA Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances <sup>38</sup> 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?





#### Foam Research and Development

- Research is being conducted on fluorine-free alternatives
- SERDP-ESTCP Research can be accessed online
  - <u>https://serdp-estcp.org/</u>
  - Table 3-8 includes a summary of some of these studies

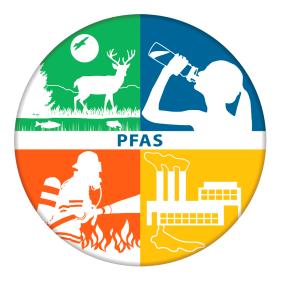




Advancing Environmental Solutions

#### Fate and Transport and Site Characterization

Sandra Goodrow, Ph.D., NJDEP





#### PFAS Technical and Regulatory Guidance Document Published

- Final web document PFAS-1: <u>https://pfas-1.itrcweb.org</u>
- 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



#### Sources of PFAS Release to the Environment



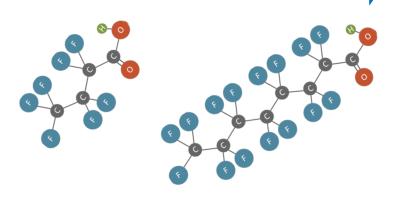
\*Landfills and WWTPs are receivers of PFAS materials from domestic and industrial sources. PFAS concentrations vary widely depending on the waste stream accepted by facilities.



43 PFAS-1, Section 2.6 Releases to the Environment.

# What is Fate and Transport?





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

PFAS Fate & Transport

Nature of release

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

Air

Soil

Groundwater

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.

Site Characteristics

Partitioning

+ Uptake (biota

+ Transformation

+ Leaching

(to soil and air-water interfa

and Applicatio

or Depositio

44

Partitioning (to air/aerosols)

- Transformation (photooxidation

Transformation

(hiotic/abiotic

+ Partitioning

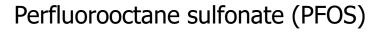
e, and foam form

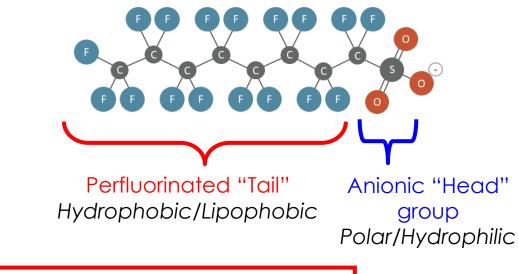
Uptake (bioto

Partitioning (to soil)

+ Transformation (biotic/abiotic) + Matrix Diffusion

#### The Heads and Tails of PFAS







#### Perfluoroalkyl acids (PFAAs) are extremely persistent in the environment

PFAAs preferentially partition at interfaces



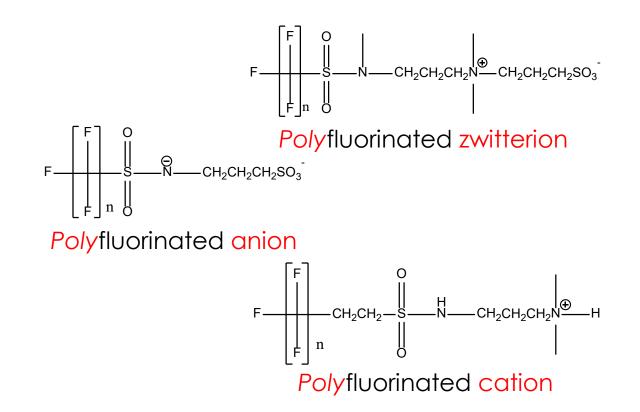
PFAS-1, Section 4.2 Physical Properties.

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

# Structural Implications

#### Functional Groups

- PFSAs tend to sorb more strongly than PFCAs of equal chain length
- Fluorination
  - Polyfluorinated can be transform to perfluorinated (PFAAs)



#### 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<sub>oc</sub> data from Guelfo, J.L., Higgins

| Analyte | # Carbons | K <sub>oc</sub> <sup>1</sup> | R <sub>f</sub> |
|---------|-----------|------------------------------|----------------|
| 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<sub>oc</sub> and K<sub>d</sub>) generally increases with number of carbons
- Retardation factor (R<sub>f</sub>) 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)

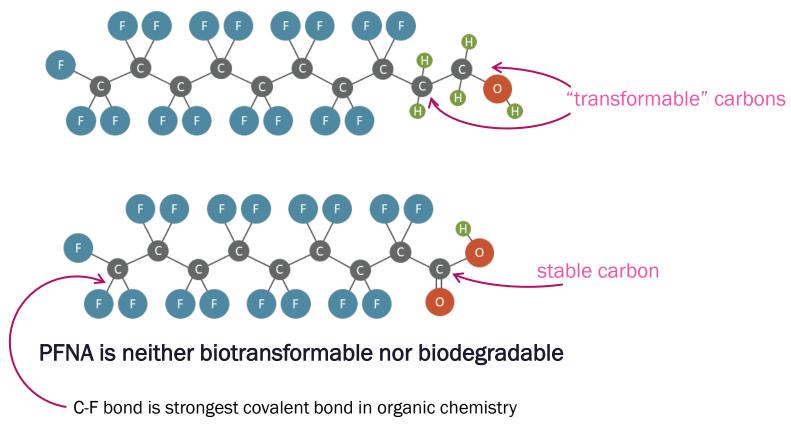
- Partitioning at interfaces may further slow transport and contribute to retardation
  - PFAS-NAPL interactions are complex



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, not biodegradable



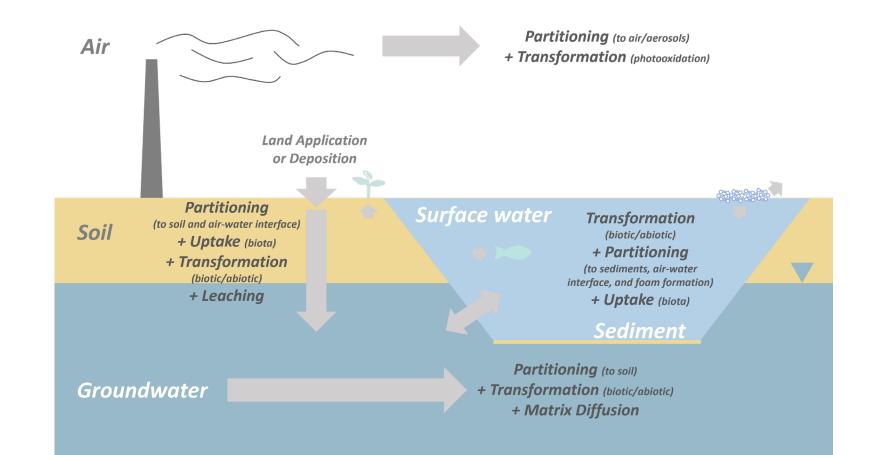


PFAS-1, Section 5.4.2 PFAA Precursors. PFAS figure source: M. Olson, Trihydro. Used with permission.

49

#### PFAS Occurrence in Environmental Media

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





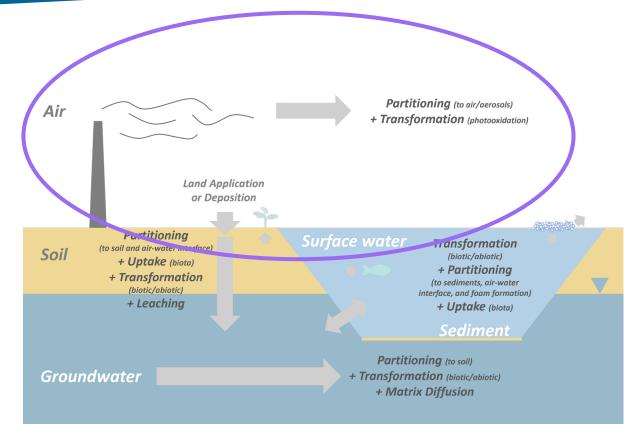
PFAS-1, Section 6 Media-Specific Occurrence.

50

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





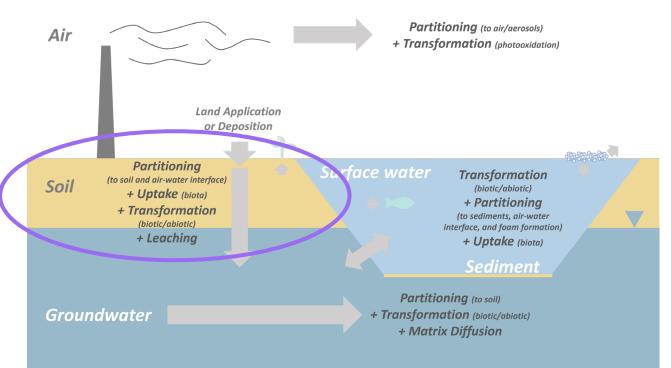
PFAS-1, Section 5.3.2 PFAS Transport via Air.

51

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



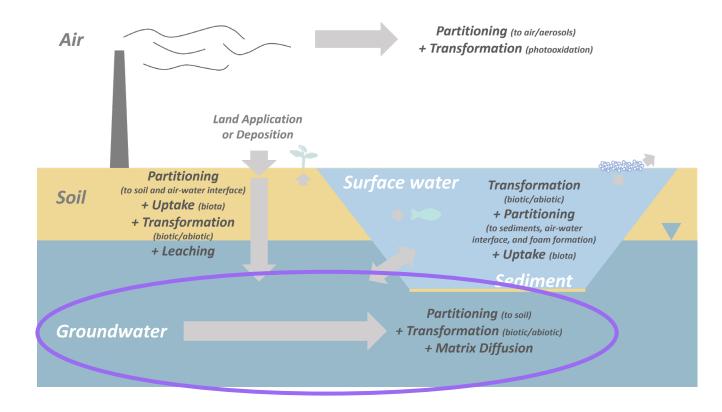


52 PFAS-1, Section 5.3.3 Leaching.

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<sub>oc</sub> 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

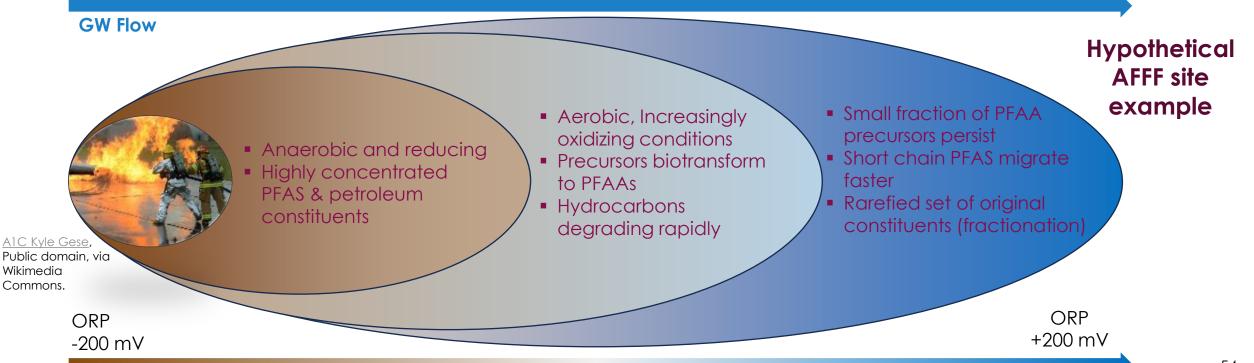




53 PFAS-1, Section 5 Environmental Fate and Transport Processes. PFAS-1, Figure 5-1. Fate and transport processes relevant for PFAS. Source: D. Adamson, GSI. used with permission.

#### Conceptual PFAS Fate and Transport at an AFFF site

- Differential transport and precursor transformation lead to environmental fractionation
- As PFAS move downgradient from source area, composition of PFAS changes
- Source type and hydrogeochemical parameters influence type and rates of change



#### 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)



55

#### 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, offsite contributions)



56

# 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)





Please use the Q&A Pod to ask questions.







Advancing Environmental Solutions



# 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: <u>https://pfas-1.itrcweb.org</u>
- 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



# 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



#### 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 USEPA 1633, request laboratory screen all samples prior to sample preparation (additional containers for aqueous samples needed)



# 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





# Sample Considerations

- USEPA Methods 537.1 and 533, and USEPA 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



#### 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.



#### 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



### 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 sitespecific work plan and data quality objectives



68

#### 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 drinkingwater programs (minimum of 1/event).



## 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



70



Advancing Environmental Solutions

# PFAS Analysis



PFAS-1, Section 11.2 Analytical Methods/Techniques.

71

# 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 <sup>72</sup> Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. EPA/815-B-19-20.

#### USEPA PFAS DW Analytical Methods

| Method 537.1 Only |          | Bo    | th 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           | 9CI-PF3ONS   | PFBA            | PFHpS   | PFPeS   |  |  |
|                   |          | PFHxA | PFUnA           | ADONA        | PFPeA           | PFMBA   | PFMPA   |  |  |
|                   |          | PFBS  | PFHpA           | HFPO-DA      | PFEESA          | NFDHA   |         |  |  |
|                   |          | PFHxS | PFNA            |              |                 |         |         |  |  |

Table 2-5, separate PDF, categorizes the PFAS analytes according to the family tree hierarchy



73

#### USEPA Method 1633

- USEPA Method 1633 (January 2024)
- Isotope dilution method
  - Compound-Specific Analyses (targeting 40 PFAS)
  - GW, SW, WW, Leachate, Biosolid, Tissue, Sediment, Soil



#### 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



75



#### 76

# INTERSTATE THE SEARCH

# Media; Limit of Detection & Quantitation; Analytes (individual and isomeric profile) Sample preparation processes

Key Method Differences

- Whole sample vs Aliquot; Solid Phase Extraction vs solvent dilution; Clean-up vs no clean-up
- Quantitation Scheme

Method Scope

- 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



#### 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)



77

#### 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





Advancing Environmental Solutions



## Treatment Technologies

#### Andy Safulko, Brown and Caldwell

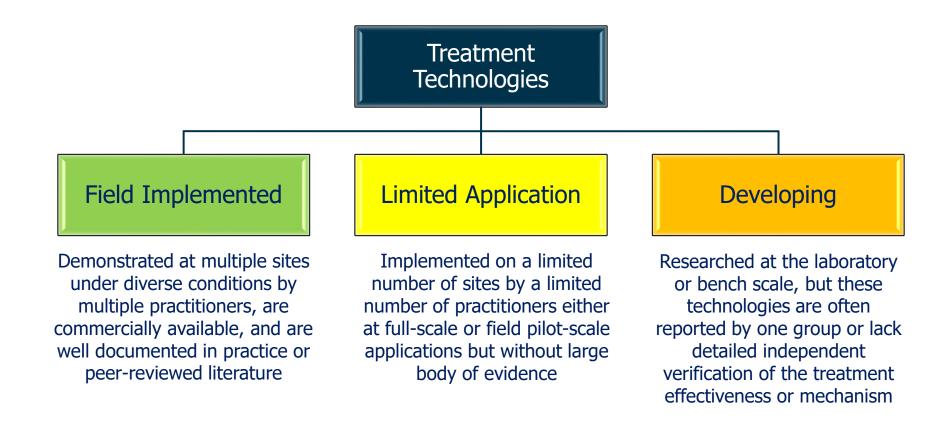


#### PFAS Technical and Regulatory Guidance Document Published

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



#### Treatment Technology Maturity





PFAS-1, Section 12 Treatment Technologies.

#### Treatment Technologies Table

| Technology                     |   |                                   |                                    |  |              |      |                  |                           |                |                         |
|--------------------------------|---|-----------------------------------|------------------------------------|--|--------------|------|------------------|---------------------------|----------------|-------------------------|
|                                | Treatment Treatment Case<br>Technologies Studies Section<br>Section 12 15.2 |                                   | Description (brief,                | Stage of                               | Phase        |      | Applicable Media |                           |                |                         |
|                                |   |                                   |                                    | Development: Field<br>Implemented (F); |              |      |                  |                           |                |                         |
| Technology Name                | https://pfas-   | https://pfas-                     | include in/ex situ)                | Limited Application                    | Liquid Solid |      |                  | soil/                     | liquid         |                         |
|                                | 1.itroweb.org/12-<br>treatment-   | <u>1.itroweb.org/15-</u><br>case- |                                    | (L); Developing (D)                    |              |      | water            | sedime                    | Waste<br>(Note | waste<br>(Note          |
|                                | technologies/   | studies/#15_2                     |                                    |  |              |      | nt               |                           | 2)             | 31                      |
| Name 🖵                         | Section 🚽   | Case Study 👻                      | Description 🚽                      | Stage 🚽                                | Liq 🖵        | Sc 👻 | wa 🚽             | soi <sup>u</sup><br>sedii | liq:⊐<br>wa:▼  | so <sup>t</sup> J<br>wa |
| Activated Persulfate           | <u>12.6.3.3</u>   |                                   | Oxidation<br>(ex situ, in situ)    | D                                      | Yes          | No   | ×                |                           | ×              |                         |
| Alkaline Hydrothermal Reaction | <u>12.6.5</u>   |                                   | Chemical<br>Treatment<br>(ex situ) | D                                      | Yes          | No   | ×                |                           | ×              |                         |
| Hikalite Hydrottermal treactor |   |                                   |                                    |  |              |      |                  |                           |                |                         |
|                                | 12.6.3.10   |                                   | Reduction<br>(ex situ)             | D                                      | Yes          | No   | ×                |                           | ×              |                         |
| Alkaline Metal Reduction       |   |                                   | (en sila)                          |  |              |      |                  |                           |                |                         |
| Biochar                        | 12.6.1.3  |                                   | Adsorption<br>(in situ, ex situ)   | D                                      | Yes          | No   | ×                |                           | ×              |                         |
| Biodegradation                 | 12.6.4  |                                   | Transformation<br>(in situ)        | D                                      | Yes          | No   | ×                |                           |                |                         |
| Diodegradation                 |   |                                   |                                    |  |              |      |                  |                           |                |                         |
| Catalyzed Hydrogen Peroxide    | 12.6.3.2  |                                   | Oxidation<br>(ex situ, in situ)    | D                                      | Yes          | No   | ×                |                           | ×              |                         |
| Coated Sand                    | 12.6.1.1  |                                   | Adsorption<br>(in situ, ex situ)   | D                                      | Yes          | No   | ×                |                           | ×              |                         |
| Colloidal Activated Carbon     | 12.2.4  | <u>15.2.3</u>                     | Adsorption<br>(in situ)            | L                                      | Yes          | No   | ×                |                           |                |                         |





Advancing Environmental Solutions

# 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





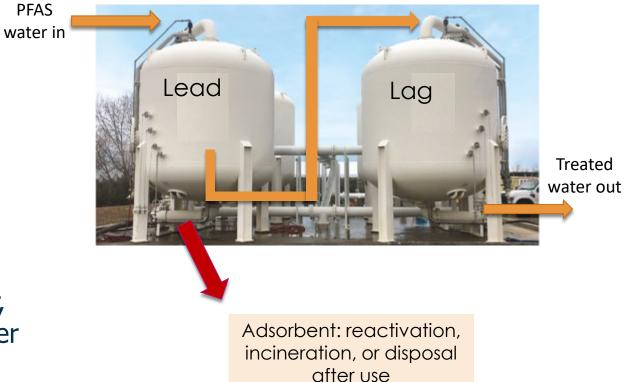




84

#### Adsorption Systems

- 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



Field

Implemented



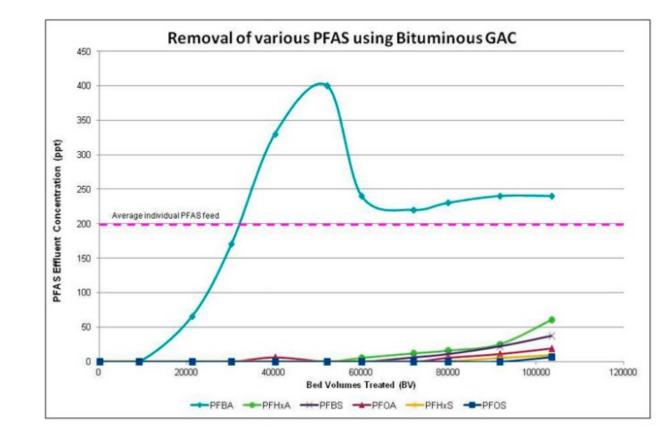
Graphic used with permission, Scott Grieco, adapted from Stew Abrams and Purolite. Photo used with permission, Francis Boodoo, Purolite.

PFAS

#### Activated Carbon

Field Implemented

- Granular Activated Carbon (GAC) field implemented for PFAS treatment for >10 years.
- GAC performance varies based on sitespecific 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

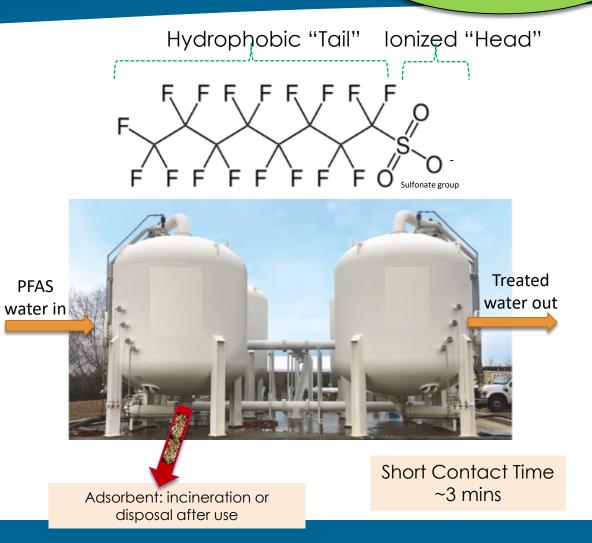




PFAS-1, Section 12.2.1.1 Figure 12-1. Example GAC removal curves at specific influent concentration . Source: Calgon Carbon Corporation. Used with permission.

### Ion Exchange (IX) Resin

- Field-demonstrated
- Selective IX Resin removed by both <u>ion</u> <u>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



Field Implemented

87



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.

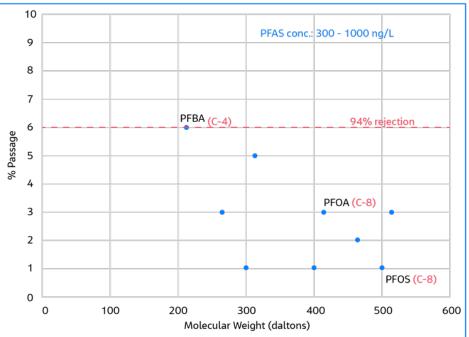
# 0 100 200 300 400 0 100 200 300 400 Molecular Weight (daltons) Adapted from Appleman et al., 2013

#### High-Pressure Membranes

- 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)



Field

Implemented



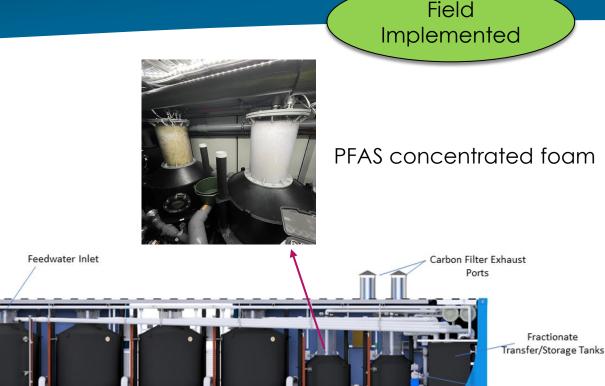
#### Foam Fractionation

- 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

Control Room with

Remote Telemetry

- Foam concentrate needs management or destruction
- Standalone technology or combined with other technologies to improve PFAS removal



Final Treated Effluent Outlet

Fractionate

Primary Treatment Stage (Stripping)

Secondary Treatment Stage (Enrichment)



Source: Photos used with permission from D. Burns, EPOC Enviro 89 LLC a subsidiary of OPEC Systems Pty Ltd.

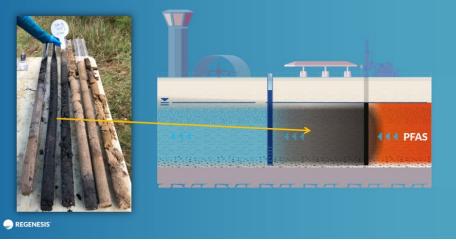
PFAS-1, Section 12.2.3 Foam Fractionation.

### 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 =  $\sim$ 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**

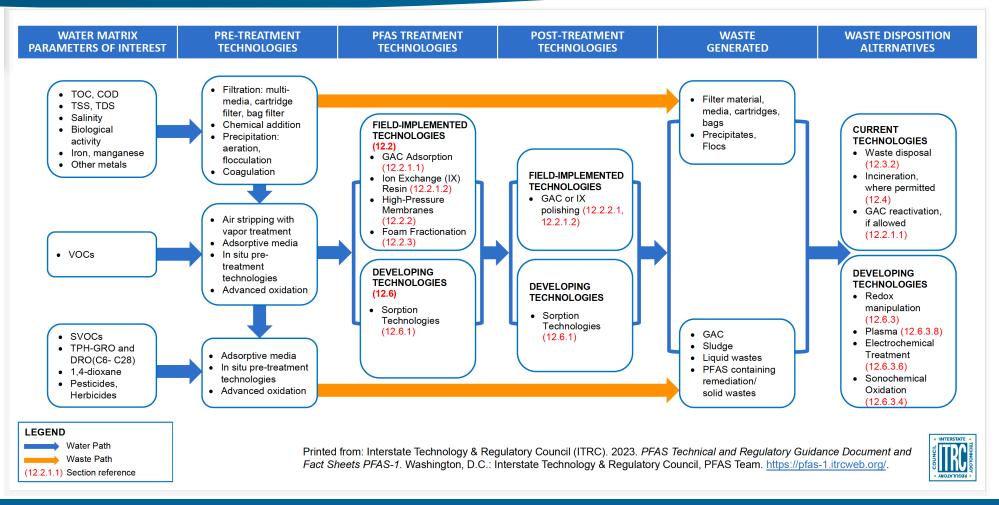


Vertical sections of a "searcher core" to verify presence of CAC at the desired interval

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







Advancing Environmental Solutions

# 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)



93

### Soil Remedial Technologies

- 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



Field

Implemented

Photo courtesy of CH2M/Jacobs. Used with permission.



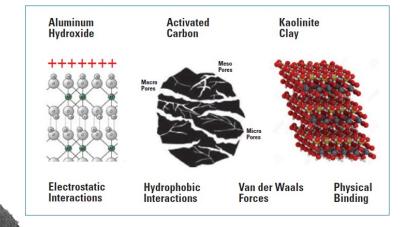
#### Soil Stabilization

- 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

Field Implemented







Images courtesy of Ziltek<sup>™</sup> and AquaBlok Ltd. Used with permission.



### 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)



#### 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





#### Please use the Q&A Pod to ask questions.







#### Published Guidance Document, Fact Sheets, Videos, Training

https://pfas-1.itrcweb.org

#### PFAS Team Public page

https://itrcweb.org/teams/active/pfas



# Thank you!

#### PFAS Team Leaders:

Ted Campbell - <u>ted.campbell@deq.nc.gov</u> Kristi Herzer - <u>Kristi.Herzer@vermont.gov</u> Jeff Wenzel - <u>Jeff.Wenzel@health.mo.gov</u>

PFAS Team Program Advisors: Lesley Hay Wilson - <u>Ihay\_wilson@sagerisk.com</u> Jim Rocco - <u>jrocco@sagerisk.com</u> facebook.com/itrcweb





