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# 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)

# ITRC – Shaping the Future of Regulatory Acceptance





▶ Network - All 50 states, PR, DC







DOE

- ITRC Industry Affiliates Program
- Academia
- Community Stakeholders

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https://www.itrcweb.org/

### Today's PFAS Trainers



Kristi Herzer, Vermont Department of Environmental Conservation



Richard Spiese, Vermont Department of Environmental Conservation



Robert Burgess, Alaska Department of Environmental Conservation



Andy Safulko, Brown and Caldwell





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## Introduction to ITRC and PFAS Team

Kristi Herzer Vermont Department of Environmental Conservation (VT DEC)



## 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



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#### <u>Total Membership\* – 499</u>

- ► Active 239
- ► Interested Party 260



#### ► Other

- ► Academic 17
- Public Stakeholder 5
- Emeritus 2
- ► Tribal 1
- ► Federal Government
  - ▶ U.S. DOD 21
  - ▶ U.S. EPA 25
  - ▶ U.S. DOE 6
  - ► Other U.S. Agency 8
  - ► International Gov't 3

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\*\*Membership as of 3/14/2023

#### 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: <u>https://pfas-</u> 1.itrcweb.org/
- Guidance Document
  - ► First published April 2020
  - Updated December 2021
  - Small edits & reference additions June 2022
  - Next update September 2023
- ► 13 Fact Sheets
- Training Sessions
  - Video Modules
- Outreach



#### 1 Introduction

2 Naming Conventions and Use

3 Firefighting Foams

4 Physical and Chemical Properties

5 Fate and Transport>6 Occurrence>7 Health Effects>8 Basis of Regulations>9 Site Risk Assessment>10 Site<br/>Characterization>11 Sampling and<br/>Analysis>12 Treatment<br/>Technologies>

#### 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
- <u>External Data Tables</u>
  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

- <u>Fact Sheets: PFAS Water and Soil Regulatory and Guidance Values Table Excel</u>
  <u>File</u>
- Fact Sheets: Basis for PFOA and PFOS Regulatory Values in Drinking Water Table Excel File
- <u>Section 2: Figure 2-4 PFAS Family Tree PDF</u>
- Section 2: USEPA Analytes List-PFAS Classifications PDF
- <u>Section 3: AFFF Characteristics Excel File</u>
- <u>Section 3: AFFF Transition to F3 Case Studies Excel File</u>
- Section 4: Physical and Chemical Properties Table 4-1 Excel File
- <u>Section 5: Aquatic Organisms BCF-BAF Table 5-1 Excel file</u>
- Section 5: Plants BCF-BAF Table 5-2 Excel File
- <u>Section 7.2: Ecotoxicology Data Summary Excel File</u>

- Section 8: PFAS Regulatory Programs Summary Excel File
- <u>Section 11: Analytical Methods Excel File</u>
- Section 11: PFAS Data Usability Table PDF
- <u>Section 12: Table 12-1 Liquids Treatment Methods Table PDF</u>
- <u>Section 12: Table 12-2 Solids Treatment Methods Table PDF</u>
- <u>Section 12: Integrated Water Treatment Flow Chart PDF</u>
- Section 14: Risk Communication Social Factors Vision Board PDF
- <u>Section 15: Water Treatment Case Studies Excel File</u>
- Section 17.2: Table 17-8 Toxicological Effects Excel File



#### 13 Fact Sheets- Currently Online

Naming Conventions (published July 2022)

Regulations (published July 2022)

History and Use (published July 2022)

Fate and Transport and Physical and Chemical Properties (published July 2022) Sampling Precautions and Laboratory Analytical Methods (published July 2022)

Site Characterization and Media-Specific Occurrence (published July 2022)

Treatment Technologies and Methods (published July 2022)

Aqueous Film-Forming Foam (published July 2022)

Human and Ecological Health Effects and Risk Assessment (published July 2022)

Risk Communication (published July 2022)

Stakeholder Perspectives (published July 2022)

Surface Water Quality (published July 2022)

Biosolids and Per- and Polyfluoroalkyl Substances (published October 2022)

Note: The content in the **published** fact sheets has been through all reviews. The fact sheets will be updated to include newer **content** after that content has been through **full review**.



## Highlights of New Content - to be published Fall 2023

- ► Team is working on updates and additions
  - ► Still in the review process
- Content includes
  - Common chemical structures of PFAS
  - Recent news about uses of PFAS
  - PFAS in AFFF chemical profiles, updated information about fluorine-free foams
  - PFAS in Biosolids management approaches, occurrence, analytical methods
  - PFAS in Air occurrence, transport, modeling, inhalation toxicity
  - ► Grouping PFAS to inform risk assessment

- Effluent limitations for discharges of PFAScontaining wastewater to surface water
- Site Investigations sampling porewater, passive groundwater sampling, analytical methods, analytical data usability, IDW
- Fate and Transport partitioning to solid phases, modeling vadose zone leaching, retention, attenuation, assessing plume stability in groundwater
- Forensics and source identification, update to multivariate statistical tools
- ► Treatment methods updates
- New case studies treatment success stories, PFAS-containing surface water foam





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# Introduction to PFAS Sources, Physical and Chemical Properties



#### 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
  - Section 2.6 PFAS Releases to the Environment



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## Learning Objectives

- Understand timeline of PFAS history and use
- Understand major uses of PFAS and potential for releases to the environment
- Understand introductory information about PFAS chemistry



<b>PFAS Eme</b>	rgence	Timeline
-----------------	--------	----------

	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s	2010s	2020s
nc	Synthesis / Developme	ent								
Production					Manu	ufacturing ar	nd Commer	cial Producti	ion	
Pr			Phase-outs / Reductions / Alternatives							
Health & Environment			Health Concerns							
Health Environm									nmental Dete tical Improve	



## 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



# Emerging awareness and emphasis on PFAS occurrence in the environment



not a greater quantity by mass, concentration, or frequency of detection.



PFAS-1, Section 2.3. Figure 2-16 Emerging awareness and emphasis on PFAS occurrence in the environment. Source : J. Hale, Kleinfelder, 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-cha	ain 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



## Replacement Chemistry

Short chain PFAS chemistries do not degrade 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

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

$$\mathsf{H}_{\mathsf{I}}^{\mathsf{H}} \mathsf{F}_{3}\mathsf{C}\text{-}\mathsf{O}\text{-}\mathsf{C}\mathsf{F}_{2}\text{-}\mathsf{C}\mathsf{F}_{2}\text{-}\mathsf{C}\mathsf{F}_{2}\text{-}\mathsf{C}\mathsf{F}_{2}\text{-}\mathsf{C}\mathsf{O}\mathsf{O}^{-} + \mathsf{N}\mathsf{H}_{4}^{+}$$

Chemical structure for ADONA



Chemical structure for GenX Ammonium Salt



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## Major Uses of PFAS

Industrial (primary production and secondary manufacturing)

- Surfactants, resins, molds, plastics
- Plating and etching (esp., chrome)
- Coatings (textiles, leather, paper, carpets)
- Aqueous Film Forming Foam (AFFF) to fight fires involving flammable, combustible liquids and gases; petroleum greases, tars, oils and gasoline; and solvents and alcohols
  - Military installations and civil airports
  - Petroleum refineries and chemical facilities
  - ► Fire fighting training and response areas



### Sources of PFAS Releases to the Environment

#### Aqueous Film Forming Foam (AFFF)

- Military installations & civil airports
- Petroleum Refineries & Chemical Facilities
- ► Fire Fighting Training Areas and Response Areas

#### Industrial (primary production & secondary manufacturing)

- Surfactants, resins, molds, plastics
- Plating and etching (esp. chrome)
- Coatings (textiles, leather, paper, carpet, etc.)

#### Landfills\*

- Consumer products, industrial waste, demolition debris
- Biosolids from WWTP applied as cover

#### Wastewater Treatment Plants\*

- > PFAS in influent (from industrial & domestic sources) may not be treated and end up in effluent
- Biosolids created in treatment process may contain PFAS



\*PFAS composition and concentrations vary widely depending on the waste streams accepted by facilities



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



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

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# 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.

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### 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 (<u>https://comptox.epa.gov/dashboard/</u>)



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







#### **Basic PFAA Structure**

#### Perfluoroalkyl Acids (PFAAs)

- ► Fully fluorinated chain (2 or more carbon "tail")
- ► Functional group ("head")
  - ► PFCAs: Carboxylate group (COO<sup>-</sup>)
  - ► PFSAs: Sulfonate group (SO<sub>3</sub><sup>-</sup>)





# 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-).....

#### ► Example:

► X: 8 carbons = "octa"

► Y: S = sulfonate





#### PFAA Naming System

	X	Y		Acronym	Name	Formula	CAS No.			
B = buta (4		A = Carboxylate or carboxylic acid		PFBA	Perfluorobutanoate	C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> <sup>-</sup>	45048-62-2			
				PFBA	Perfluorobutanoic acid	C <sub>3</sub> F <sub>7</sub> COOH	375-22-4			
	carbon)	S = Sulfonate	e or	DEDO	Perfluorobutane sulfonate	C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> -	45187-15-3			
		sulfonic ac	id	PFBS	Perfluorobutane sulfonic acid	C₄F <sub>9</sub> SO₃H	375-73-5			
		A = Carboxyla	te or	DED.A	Perfluoropentanoate	C <sub>4</sub> F <sub>9</sub> CO <sub>2</sub> -	45167-47-3			
	Pe = penta	carboxylic a		PFPeA	Perfluoropentanoic acid	C₄F <sub>9</sub> COOF	2706-90-3			
	(5 carbon)	S = Sulfonate	e or	PFPeS	Perfluoropentane sulfonate	C <sub>5</sub> F <sub>11</sub> SO <sub>3</sub>	NA	1		
		sulfonic ac	id	PFPe5	Perfluoropentane sulfonic acid	C <sub>5</sub> F <sub>11</sub> SO <sub>3</sub> H	2706-91-4			
		A = Carboxyla	te or	PFHxA	Perfluorohexanoate	C <sub>5</sub> F <sub>11</sub> CO <sub>2</sub> -	92612-52-7	1		
	Hx = hexa (6	a sub-security sector		PFHXA	Perfluorohexanoic acid	C <sub>5</sub> F <sub>11</sub> COO	H 307-24-4			
	carbon)	S = Sulfonate or		PFHxS	Perfluorohexane sulfonate	C <sub>6</sub> F <sub>13</sub> SO <sub>3</sub>	108427-53-8			
		sulfonic ac	id	FTTIAS	Perfluorohexane sulfonic acid	C <sub>6</sub> F <sub>13</sub> SO <sub>3</sub> H				
		A = Carboxyla		PFHpA	Perfluoroheptanoate	C <sub>6</sub> F <sub>13</sub> CO <sub>2</sub> -				
	Hp = hepta	carboxylic a	cid		Perfluoroheptanoic acid	C <sub>6</sub> F <sub>13</sub> COO				
_	(7 carbon)	S = Sulfonat	e or		Perfluoroheptane sulfonate	C <sub>7</sub> F <sub>15</sub> SO <sub>3</sub>	NA			
	A = Carb	oxylate or			Perfluorooctanoate	)	C <sub>7</sub> F <sub>15</sub> CO <sub>2</sub> -	45285-51-6		
O = octa	carbox	ylic acid	ic acid		Perfluorooctanoic acid		C <sub>7</sub> F <sub>15</sub> COOH	335-67-1		
(8 carbon)	S = Sulf	onate or	onate or DEC		PFOS		Perfluorooctane sulfonate		C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> -	45298-90-6
	sulfoni		ic acid		Perfluorooctane sulfonic acid		C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> H	1763-23-1		
	N = nona	carboxylic a	cid	PFNA	Perfluorononanoic acid	C <sub>8</sub> F <sub>17</sub> COOF	H 375-95-1			
	(9 carbon)		S = Sulfonate or		Perfluorononane sulfonate	C <sub>9</sub> F <sub>19</sub> SO <sub>3</sub>				
		sulfonic ac	sulfonic acid		Perfluorononane sulfonic acid	C <sub>9</sub> F <sub>19</sub> SO <sub>3</sub> H	474511-07-4			
	D = deca		A = Carboxylate or		Perfluorodecanoate	C <sub>9</sub> F <sub>19</sub> CO <sub>2</sub>				
			cid	PFDA	Perfluorodecanoic acid	C <sub>9</sub> F <sub>19</sub> COO				
	(10 carbon)	carbon) S = Sulfonate or		PFDS	Perfluorodecane sulfonate	C <sub>10</sub> F <sub>21</sub> SO <sub>3</sub>				
		sulfonic ac	id		Perfluorodecane sulfonic acid	C <sub>10</sub> F <sub>2</sub> 1SO <sub>3</sub>	H 335-77-3			



PFAS-1, Section 2.2.3.1. Table 2-1 Basic naming structure for PFAAs.

### Which PFAA Are We Talking About?

#### ► Acid or Anion?

- ▶ PFAS may exists in various ionic states (acids, anions, cations, zwitterions)
  - ▶ 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 & very different chemical and physical properties
- ► What Is My Lab Really Testing For?
  - ► Some labs report some or all of their PFAAs in the acid form
  - ▶ Depends on the standards used, which may be acids or salts of PFAAs (typically Na<sup>+</sup> or K<sup>+</sup>)
  - ▶ The lab performs a calculation to account for the mass of the cation
    - ► For H+ in acids, this is essentially irrelevant in terms of the results
    - ► For salts, confirm the lab is accurately accounting for the cation mass (Section 7.2.3 of EPA Method 537.1)



## 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 degradation
- Fluorotelomers are often named using a "n:x" prefix
  - ► n = number of fully fluorinated carbons
  - ightarrow x = number of non-fully fluorinated carbons



## PFAA Precursors (under environmental conditions)

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



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## Proposed PFAS National Primary Drinking Water Regulation

- ► USEPA Announcement 3/14/23
- Requesting public comment
- Plan to finalize the regulation by the end of 2023

Maximum Contaminant Level (MCL): highest concentration of a contaminant allowed in drinking water

Maximum Contaminant Level Goal (MCLG): non-enforceable public health goal

Compound	Proposed MCLG	Proposed MCL (enforceable levels)	
PFOA	Zero	4.0 parts per trillion (also expressed as ng/L)	
PFOS	Zero	4.0 ppt	
PFNA			
PFHxS			
PFBS	1.0 (unitless)	1.0 (unitless)	
HFPO-DA (commonly referred to as GenX Chemicals)	Hazard Index	Hazard Index	

Table Source: https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas





Advancing Environmental Solutions



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

Richard Spiese, Vermont Department of Environmental Conservation



## Learning Objectives

- Understand Class of Foams
- Understand the Types of AFFF
- Become familiar with best management practices (BMPs) for:
  - ✓ Procurement and Storage
  - ✓ Use and Replacement
  - ✓ Treatment and Disposal





# 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 Milspec)

AFFF are the primary Class B foam that contain fluorosurfactants


## AFFF Classifications

#### Legacy PFOS AFFF

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

#### Legacy Fluorotelomer AFFFs<sup>2</sup>

Polyfluorinated forms, no PFOS or degrade to PFOS, no UCMR3 or Method 537 lists, degrades to PFCAs

#### Modern Fluorotelomer AFFFs

Developed in response to PFOA/PFOS phaseout, contains short chain PFAS (C6), may have trace amounts (ppb) PFOA, may degrade to PFCAs



Photo courtesy of J. Field.





Note: PFAS composition has changed over time

#### 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. +Place and Field, 2012. ES&T 46: 7120-7127; 2Weiner et al., 2013. Environ Chem 10:486-493;

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## 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.





#### 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.
- Biodegradation of precursors to PFAA over time can produce PFAAs such as PFOA.



PFAS-1, Figure 2-19, 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, 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



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

HAZARD X EXPOSURE =

**RISK** 

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#### Treatment and disposal

- Consider EPA 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 <sup>1</sup>
  - 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>EPA Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and <sup>43</sup> 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

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

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

Robert Burgess, AK DEC





#### 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



## Learning Objectives

- Fate and transport: unique characteristics of PFAS
- PFAS occurrence and behavior in environmental media
- Site characterization: where to look, how to sample, what to analyze for





#### Sources of PFAS Release to the Environment



\*PFAS composition and concentrations vary widely depending on the waste streams accepted by facilities



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

Soi

Groundwater

Site Characteristics

Partitionin

+ Uptake (biota)

+ Transformation (biotic/abiotic) + Leaching

(to soil and air-water inter

and Applicatio

or Denositi

Co-contaminants

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

Partitioning (to air/aerosols)

- Transformation (photooxidation

Transformation

+ Partitioning

Uptake (biot

Partitioning (to soil)

+ Transformation (biotic/abiotic

Matrix Diffusion

Surface water

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

#### The Heads and Tails of PFAS





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





Polyfluorinated anion

Polyfluorinated cation



Polyfluorinated zwitterion



#### Properties of Anionic 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



PFAS-1, Section 4 Physical and Chemical Properties.

## 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.

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#### PFAS Occurrence in Environmental Media





#### 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





#### 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





#### 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





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





#### 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)



#### 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)



## 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 a 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.







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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: <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



## Learning Objectives

- Understand key elements that make PFAS sampling different from other sampling events
- Understand best practices for preparing for and conducting a PFAS sampling event
- Understand current state of PFAS analytical methods
- Understand basics of compound-specific PFAS analysis
- Understand alternative analytical techniques and how they can be useful



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



## Equipment & Supplies

- There are some materials that should be avoided due to contamination and possible adsorption issues that if used and contacted sample may introduce bias
  - polytetrafluoroethylene (PTFE)
  - waterproof coatings containing PFAS
  - fluorinated ethylene-propylene (FEP)
  - ethylene tetrafluoroethylene (ETFE)
  - Iow-density polyethylene (LDPE) [adsorption]
  - polyvinylidene fluoride (PVDF)
  - ▶ pipe thread compounds and tape



## 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 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



## 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



## 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





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## PFAS Analysis



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PFAS-1, Section 11.2 Analytical Methods/Techniques.

## USEPA PFAS Drinking Water Methods

#### ► USEPA 537.1

- ► Finalized Method (Version 2.0 published 2020)
- Compound-Specific Analyses (18 PFAS)

### ► USEPA Method 533

- ► Finalized Method (published 2019)
- Compound-Specific Analyses (25 PFAS)
- Addresses some compounds that were not included in Method 537.1 due to poor performance



USEPA. 2020. Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water <sup>80</sup> by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Revision 2.0. Washington, D. C.

## 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. 2019. Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry. EPA/815-B-19-20. Cincinnati, OH.

### USEPA PFAS Analytical Methods

7.1 Only	Во	th Methods 537.	1 and 533	Method 533 Only			
NMeFOSAA	PFOA	PFOS	11CI-PF3OUdS	4:2 FTS	6:2 FTS	8:2 FTS	
PFTrDA	PFDA	PFDoA	9CI-PF3ONS	PFBA	PFHpS	PFPeS	
	PFHxA	PFUnA	ADONA	PFPeA	PFMBA	PFMPA	
	PFBS	PFHpA	HFPO-DA	PFEESA	NFDHA		
	PFHxS	PFNA					
	NMeFOSAA	NMeFOSAA PFOA PFTrDA PFDA OPFHxA PFBS	NMeFOSAAPFOAPFOSPFTrDAPFDAPFDoAImage: Strain of the st	NMeFOSAAPFOAPFOS11Cl-PF3OUdSPFTrDAPFDAPFDoA9Cl-PF3ONSOPFHxAPFUnAADONAOPFBSPFHpAHFPO-DA	NMeFOSAAPFOAPFOS11Cl-PF3OUdS4:2 FTSPFTrDAPFDAPFDoA9Cl-PF3ONSPFBAOPFHxAPFUnAADONAPFPeAOPFBSPFHpAHFPO-DAPFESA	NMeFOSAAPFOAPFOS11Cl-PF3OUdS4 4:2 FTS6:2 FTSPFTrDAPFDAPFDoA9Cl-PF3ONS4 PFBAPFHpSPFHxAPFUnAADONA4 PFPeAPFMBAPFBSPFHpAHFPO-DA4 PFESANFDHA	

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



## USEPA Draft Method 1633

► Third Draft published USEPA Method 1633 (Dec 2022)

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



## USEPA Draft Other Test Method 45 (OTM-45)

- ► January 2021
  - Single-laboratory validated
- Compound-Specific Analyses by LC-MS/MS (50 PFAS analytes)
- Semivolatile and nonvolatile polar PFAS in air emissions (stationary sources)
- Includes sampling, sample preparation, and analytical procedures



### DOD AFFF01

- December 2021
  - Multi-laboratory validated
- ► LC-MS/MS (PFOA and PFOS only)
- AFFF concentrates
  - Compliance for military specifications MIL-PRF-24385



## 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



## 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





## 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)



## 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





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## Treatment Technologies

### Andy Safulko, Brown and Caldwell



## Outline

Introduction

### Liquids Treatment

- ► Field implemented technologies
- Limited applications, developing technologies

#### Solids Treatment

- Field implemented technologies
- Limited applications, developing technologies
- ► Incineration



### Treatment Technology Maturity





### Treatment Technologies Table

Remediation Technology Group	Remediation Technology Document Sections included	What PFAS Demonstrated On? What Concentrations/Re moval Reported?	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)		Future Data Needs	PFAS Demonstration Maturity (Lab, Field Pilot, Full- Scale, Commercialized)	References
Sorption (Separation)	12.2.1.1 Granular activated carbon (GAC)	Demonstrated for all PFAS tested to date at parts per trillion to parts per billion concentrations for aboveground activated carbon treatment	Treats all tested PFAS to date with high removals prior to breakthrough. Design flexibility to increase removal. Simple to operate. Multiple vendors. Off-site reactivation/regener ation available for PFAS.	Possible faster breakthrough times for shorter chain versus longer chain PFAS under certain influent and other conditions. Becomes less economical at higher influent concentrations (for example, >10–100 ppb). Competitive adsorption w/ other species. Precursors and other PFAS not analyzed for can increase GAC loading and accelerate changeout frequencies. No destruction of PFAS, unless it is reactivated or incinerated at high temperature (>1,100°C). <b>Pretreatment may be</b> <b>necessary.</b>	Spent activated carbon must be removed for offsite disposal, or reactivation/regeneration.	More comprehensive shorter chain adsorption capacity data. Competition with other contaminants and aqueous species. Regulation of individual PFAS in addition to PFOA and PFOS. Impact on PFAS precursors.	FI	(Dickenson and Higgins 2016; Brewer 2017; Cummings et al. 2015; Appleman et al. 2013; Szabo et al. 2013; Szabo et al. 2017; Burdick et al. 2016; Woodard, Berry, and Newman 2017; Hohenstein 2016; Xiao et al. 2017; AWWA 2016; Mimna 2017; McNamara et al. 2018; Westreich et al. 2018; Liu, Werner, and Bellona 2019)



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



Advancing Environmental Solutions

# Liquids Treatment Technologies



## Liquids Treatment

### Field Implemented (Section 12.2)

- ► Granular activated carbon (GAC) adsorption
- ► Ion exchange (IX) resin adsorption
- ► Reverse osmosis (RO) / membrane filtration
- ► Foam fractionation\*
- In-situ colloidal activated carbon\*
- Limited Applications (Section 12.5)
  - Examples include surface modified clay, foam fractionation\*, in-situ colloidal activated carbon\*
- Developing Technologies (Section 12.5)
  - Examples include coated sand, biochar, precipitation/coagulation/flocculation, nanofiltration alternative adsorbents, bioremediation, advanced chemical oxidation, chemical reduction, thermal desorption, electrochemical, others









## Adsorption Systems

Technologies: granular activated carbon (GAC), single use ion exchange resin (IX), regenerable IX

PFAS

- 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, Ground Water, 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.

## 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 and manufacturing methods.
- Shorter-chain PFAS breakthrough faster than longer chain, but generally still within the range considered feasible.
- PFCAs generally break through faster than PFSAs





PFAS-1, Section 12.2.1 Figure 12-1. Example GAC removal curves at specific influent concentration . Source: Calgon Carbon Corporation. Used with permission.

## GAC Design/Operation Considerations

### 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
  - Mitigating potential clogging of GAC units typically required. These can include pH adjustment, filtration, or dissolved iron treatment.
- Start-up volume
  - ► GAC: pH stabilization, arsenic rinsing
- Backwash provisions



Field

Implemented



PFAS-1, Section 12.2.1 Figure 12-2. Typical GAC treatment system process flow diagram. Source: Calgon Carbon Corporation. Used with permission.

## Single-Use IX

Field-demonstrated

- Selective IX Resin removed by both ion exchange (head) and adsorption (tail)
- High removal efficiency
- Shorter EBCT and small footprint relative to GAC
- High operating capacity
  - 100,000 to 350,000 BV for low concentration drinking water
- Operation costs dependent on water quality and pretreatment needs



Field

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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.

### Regenerable IX Resin Process

Field Implemented





PFAS-1, Section 15.2 Figure 15-10. Block flow diagram of full-scale treatment system. Source: S. Woodward, ECT2 and N. Hagelin, Wood. Used with permission.

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## Membrane Systems

- ► RO is effective for long- and short-chain PFAS
- ► 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 for high concentrations of organic solvents and strong oxidants
- Managing liquid concentrate







Field

Implemented



PFAS-1, Section 12.2.2 Reverse Osmosis (RO). Photo and graph source: Scott Grieco, Jacobs. Used with permission.

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Adapted from Appleman et al., 2013

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





Source: Photos used with permission from D. Burns, EPOC Enviro LLC a subsidiary of OPEC Systems Pty Ltd. 102

PFAS-1, Section 12.5.7 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 12.6.1.1 In Situ Remediation with Colloidal Activated Carbon.



## Integrated Remedial Solutions -Flowchart



Printed from: Interstate Technology & Regulatory Council (ITRC). 2021. *PFAS Technical and Regulatory Guidance Document and Fact Sheets PFAS-1*. Washington, D.C.: Interstate Technology & Regulatory Council, PFAS Team. <u>https://pfas-1.itrcweb.org/</u>.





Waste Path

(12.2.1.1) Section reference



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# Solids Treatment Technologies



## Solids Treatment

Field Implemented conventional approaches, with limitations:

- ► Excavation and disposal (Section 12.3.2)
- ▶ In situ or ex situ stabilization (Section 12.3.1)
- ► Soil washing (Section 12.7.3)
- Limited applications and developing technologies
  - ► Sorption, stabilization/solidification (12.7.1)
  - ► Thermal treatment (12.7.2)



## 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
  - US EPA, US DOD and other research programs looking closely at destruction



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









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 <0.6% waste mass
- 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!

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