INTRODUCTION TO PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs)

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State Agencies Liaison, Brown SRP
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Brown University Superfund Research Program

Toxicant Exposures In Rhode Island: Past, Present & Future

Project 1: Molecular Biomarkers for Assessing Testicular Toxicity
PI: Boekelheide

Project 2: Adverse Health Impacts of Nanomaterials
PI: Kane

Project 3: Indoor Air Concentration Dynamics & Vapor Intrusion
PI: Suuberg

Project 4: Nanomaterial Design for Environmental Health & Safety
PI: Hurt

Integrated Biomedical & Engineering Solutions to Regulatory Uncertainty

Vapor Intrusion Modeling & Health Monitoring

Biomarkers & Toxicity Testing

Nanotechnology Applications & Safety

Biomedical projects
Engineering projects

Partnerships

Academic
Community
Government

Administrative Core • Research Translation Core • Community Engagement Core
Training Core • Molecular Pathology Core

NIH National Institute of Environmental Health Sciences
Superfund Research Program
INTRODUCTION: ROLE OF RESEARCH TRANSLATION

The goal of the survey is to identify key site characteristics associated with PFAS sites, and to recognize real and perceived challenges to managing sites. We also seek to identify stakeholders’ knowledge and experiences with treatment approaches.

Survey link: goo.gl/zakRX3

Thank you!
PFAS Overview

- Terminology
- Manufacturing Processes
- Chemistry
PFAS OVERVIEW: TERMINOLOGY & STRUCTURE

**Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)**

**Non-Polymers**

- **Perfluoroalkyl Substances**
  - Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines
  - (Aliphatic) perfluorocarbons (PFCs)
  - Perfluoroalkyl acids
  - Perfluoroalkane sulfanyl fluorides
  - Perfluoroalkane sulfonamides
  - Perfluoroalkyl iodides
  - Perfluoroalkyl aldehydes

- **Polyfluoroalkyl Substances**
  - Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines
  - Perfluoroalkane sulfonamido derivatives
  - Fluorotelomer-based compounds
  - Semifluorinated n-alkanes and alkenes

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**Polymers**

- **Fluoropolymers**
  - Carbon-only polymer backbone with fluorines directly attached

- **Perfluoropolyethers**
  - Carbon and oxygen polymer backbone with fluorines directly attached to carbon

- **Side-chain Fluorinated Polymers**
  - Variable composition non-fluorinated polymer backbone with fluorinated side chains
    - Fluorinated acrylate and methacrylate polymers
    - Fluorinated urethane polymers
    - Fluorinated oxetane polymers

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**PFAS OVERVIEW: TERMINOLOGY & STRUCTURE**

**Perfluoroalkyl carboxylates (PFCAs):**

Examples:
- m=2 PFBA
- m=4 PFHxA
- m=6 PFOA

**Perfluoroalkane sulfonates (PFSAs):**

Examples:
- m=3 PFBS
- m=5 PFHxS
- m=7 PFOS

*Per = fully fluorinated alkyl tail.*
**PFAS OVERVIEW: TERMINOLOGY & STRUCTURE**

**Perfluoroalkyl carboxylates (PFCAs):**

Examples:
- $m=2$ PFBA
- $m=4$ PFHxA
- $m=6$ PFOA

**Perfluoroalkane sulfonates (PFSAs):**

Examples:
- $m=3$ PFBS
- $m=5$ PFHxS
- $m=7$ PFOS

Poly = partially fluorinated alkyl tail.

**Polyfluoroalkyl substances:**

- $m=5$ 6:2 FtS
- $m=7$ 8:2 FtS
**PFAS OVERVIEW: TERMINOLOGY & STRUCTURE**

**Perfluoroalkyl carboxylates (PFCAs):**
- Examples:
  - m=2 PFBA
  - m=4 PFHxA
  - m=6 PFOA

**Perfluoroalkane sulfonates (PFSAs):**
- Examples:
  - m=3 PFBS
  - m=5 PFHxS
  - m=7 PFOS

**Per** + **Poly** = **Per & polyfluoro alkyl substances (PFAS)**

**Polyfluoroalkyl substances:**
- m=5 6:2 FtS
- m=7 8:2 FtS
What is a precursor?

**Poly**fluoroalkyl substances that can undergo transformation to form **per**fluoroalkyl acids

8:2 FtTAoS (precursor)  
8:2 FtS (intermediate)  
PFOA (terminal endpoint)

Figure adapted from Ref. 2

PFAS OVERVIEW: MANUFACTURING

Electrochemical fluorination

$2H^+ + 2e^- \rightarrow H_2$

PFAS OVERVIEW: MANUFACTURING

Electrochemical fluorination

$\text{H}_2$  

Anode

-  

+  

Liquid hydrogen fluoride (HF)  

Organic raw material  

$\text{CH}_3$  

$\text{CH}_4$  

$\text{CH}_2\text{F}_2$  

$\text{CHF}_3$  

$\text{CF}_4$  

**PFAS OVERVIEW: MANUFACTURING**

![Electrochemical fluorination diagram](image)

- **H₂**
- **-**
- **+**
- **Liquid hydrogen fluoride (HF)**
- **Organic raw material**

### Electrochemical fluorination

- **C₈H₁₇SO₂F**
  - Octane sulfonyl fluoride

- **C₈F₁₇SO₂F**
  - Perfluoroctane sulfonyl fluoride

- **C₈F₁₇SO₂F**
  - Perfluoroctane sulfonyl fluoride

- **C₈F₁₇SO₂H**
  - Perfluoroctane sulfonic acid (PFOS)

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PFAS OVERVIEW: MANUFACTURING

Telemorization$^{1,4}$

\[ YZ + nA \rightarrow Y - (A)_n - Z \]

Telogen  Taxogen  Telomer
**PFAS OVERVIEW: MANUFACTURING**

**Telemorization**

\[
YZ + nA \rightarrow Y - (A)_n - Z
\]

Telogen  \hspace{1cm} Taxogen  \hspace{1cm} Telomer

\[
F(CF_2)_2I + \frac{n - 2}{2} CF_2=CF_2 \rightarrow F(CF_2)_nI
\]

Perfluoroalkyl iodide, e.g. pentafluoroethyl iodide

Tetrafluoroethylene

n=desired chain length

Perfluoroalkyl iodide
**PFAS OVERVIEW: MANUFACTURING**

Telemorization\(^1,^4\)

\[
YZ + nA \rightarrow Y - (A)_n - Z
\]

Telogen \hspace{2cm} Taxogen \hspace{2cm} Telomer

\[\text{Perfluoroalkyl iodide, e.g. pentafluoroethyl iodide}\]

\[F(CF_2)_2I + \frac{n-2}{2} \text{CF}_2=\text{CF}_2 \rightarrow F(CF_2)_nI\]

Tetrafluoroethylene \hspace{2cm} n=desired chain length

**Ex. 1**

\[F(CF_2)_nI + \text{CH}_2=\text{CH}_2 \rightarrow F(CF_2)_n\text{CH}_2\text{CH}_2I\]

Perfluoroalkyl iodide \hspace{2cm} Ethylene \hspace{2cm} n:2 Fluorotelomer iodide

**Ex. 2**

\[F(CF_2)_nI \xrightarrow{\text{Oleum, heat, pressure}} CF_3(CF_2)_{n-1}CF_2OOH + \frac{1}{2}I_2\]

Perfluoroalkyl iodide \hspace{2cm} Perfluoroalkyl carboxylic acid
Fluorine Property: high electronegativity$^{4,5}$

**Description:**

\[
\text{C} \quad \text{F} \\
\delta^+ \quad \delta^-
\]

**Effects:**

- Strongest covalent bond in organic chemistry
- Polar bond

---

PFAS OVERVIEW: CHEMISTRY\textsuperscript{4,5}

Fluorine Property: high electronegativity\textsuperscript{4,5}

\[
\begin{align*}
\text{C} & \quad \text{F} \\
\delta^+ & \quad \delta^-
\end{align*}
\]

Description:

\[\text{C} - \text{F}\]

Effects:

- Strongest covalent bond in organic chemistry
- Polar bond

Resulting PFAS properties:

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{F} & \quad \text{F}
\end{align*}
\]

Description:

\[
\begin{align*}
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{C} & \quad \text{C}
\end{align*}
\]

Effects:

- Strong acidity (low pK\textsubscript{a})\textsuperscript{*}
- Thermal stability
- Chemical stability

\*When paired with an acidic functional group

PFAS OVERVIEW: CHEMISTRY

Fluorine Property: low polarizability

Description:

Polarizable
PFAS OVERVIEW: CHEMISTRY

Fluorine Property: low polarizability\textsuperscript{4,5}

\textbf{Description:}

\begin{itemize}
  \item Not polarizable
\end{itemize}

\textbf{Effects:}

\begin{itemize}
  \item Weak intermolecular interactions
  \item Ex: van der Waals
\end{itemize}
PFAS OVERVIEW: CHEMISTRY

Fluorine Property: low polarizability$^{4,5}$

Description:

![Not polarizable](image)

Effects:

- Weak intermolecular interactions
- Ex: van der Waals

Resulting PFAS properties:

- Hydrophobic & lipophobichc
PFAS OVERVIEW: CHEMISTRY

Fluorine Property: low polarizability\(^4,5\)

**Description:**
- Not polarizable

**Effects:**
- Weak intermolecular interactions
- Ex: van der Waals

**Resulting PFAS properties:**
- Hydrophobic & lipophobic
- Surfactant*  

*When paired with a hydrophilic functional group*
Fluorine Property: small size\textsuperscript{4,5}

**Description:**
- F
- Cl
- Br
- I
- At

**Effects:**
- Atomic radius = 0.72Å
- Shields carbon

**Resulting PFAS properties:**
- Chemical stability
PRESENTATION OUTLINE

PFAS Overview

• Summary of state regulations
• Typical sample precautions
• Target methods and PFASs, state by state
• Overview of standard methods & labs
• Other analytical tools

Regulation, Sampling & analysis

Uses & Sources
### PFAS REGULATION, SAMPLING & ANALYSIS

#### Drinking Water Health Advisories for PFOA, PFOS

70 ng/L: individually or in combination

<table>
<thead>
<tr>
<th>State</th>
<th>Drinking Water Standard</th>
<th>Other Matrices?</th>
<th>Which?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Connecticut</td>
<td>70 ng/L $\sum$ PFOA, PFOS, PFNA, PFHxS, PFHpA</td>
<td>Yes</td>
<td>Soil, groundwater</td>
</tr>
<tr>
<td>Maine</td>
<td>70 ng/L $\sum$ PFOA, PFOS$^1$</td>
<td>Yes$^1$</td>
<td>Soil, sediment, groundwater, surface water, fish</td>
</tr>
<tr>
<td>Massachusetts</td>
<td>70 ng/L $\sum$ PFOA, PFOS</td>
<td>No</td>
<td>NA</td>
</tr>
<tr>
<td>New Hampshire</td>
<td>70 ng/L $\sum$ PFOA, PFOS</td>
<td>Yes</td>
<td>Soil</td>
</tr>
<tr>
<td>New Jersey</td>
<td>40 ng/L PFOA$^2$ 10 ng/L PFNA$^2$</td>
<td>No</td>
<td>NA</td>
</tr>
<tr>
<td>New York</td>
<td>70 ng/L $\sum$ PFOA, PFOS$^3$</td>
<td>No</td>
<td>NA</td>
</tr>
<tr>
<td>Rhode Island</td>
<td>70 ng/L $\sum$ PFOA, PFOS</td>
<td>No</td>
<td>NA</td>
</tr>
<tr>
<td>Vermont</td>
<td>20 ng/L $\sum$ PFOA, PFOS</td>
<td>Yes</td>
<td>Soil</td>
</tr>
</tbody>
</table>

1. Guidelines (not standards)
2. Standard under review
3. Other PFASs may be considered if $\sum$PFOA,PFOS is slightly less than 70 ng/L
# PFAS REGULATION, SAMPLING & ANALYSIS

<table>
<thead>
<tr>
<th>Prohibited Items</th>
<th>Acceptable Items</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Field Equipment</strong></td>
<td></td>
</tr>
<tr>
<td>Teflon® containing materials</td>
<td>High-density polyethylene (HDPE) materials</td>
</tr>
<tr>
<td>Low density polyethylene (LDPE) materials</td>
<td>Acetate liners</td>
</tr>
<tr>
<td>Paper towels containing recycled materials</td>
<td>Silicon tubing</td>
</tr>
<tr>
<td>Waterproof field books</td>
<td>Loose paper</td>
</tr>
<tr>
<td>Plastic clipboards, binders, or spiral hard cover notebooks</td>
<td>Masonite or aluminum clipboards</td>
</tr>
<tr>
<td>Sharpies or markers</td>
<td>Pens</td>
</tr>
<tr>
<td>Post-It Notes</td>
<td>Loose paper</td>
</tr>
<tr>
<td>Chemical (blue) ice packs</td>
<td>Regular ice</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Field Clothing and PPE</strong></td>
<td></td>
</tr>
<tr>
<td>New cotton clothing or synthetic water resistant, waterproof, or stain-treated</td>
<td>Well laundered clothing made of natural fibers (preferable cotton)</td>
</tr>
<tr>
<td>clothing containing Gore-Tex</td>
<td></td>
</tr>
<tr>
<td>Clothing laundered using fabric softener</td>
<td>No fabric softener</td>
</tr>
<tr>
<td>Boots containing Gore-Tex</td>
<td>Boots made with polyurethane and PVC</td>
</tr>
<tr>
<td>Tyvek</td>
<td>Cotton clothing</td>
</tr>
<tr>
<td>No cosmetics, moisturizers, hand cream, or other related products as part of</td>
<td>100% Natural sunscreen and insect repellent</td>
</tr>
<tr>
<td>personal cleaning/showering routine on the morning of sampling</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sample Containers</strong></td>
<td></td>
</tr>
<tr>
<td>LDPE or glass containers</td>
<td>HDPE or polypropylene</td>
</tr>
<tr>
<td>Teflon-lined caps</td>
<td>Unlined polypropylene caps</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Rain Events</strong></td>
<td></td>
</tr>
<tr>
<td>Waterproof or resistant rain gear</td>
<td>Gazebo tent that is only touched or moved prior to and following sampling</td>
</tr>
<tr>
<td></td>
<td>activities</td>
</tr>
<tr>
<td><strong>Equipment Decontamination</strong></td>
<td></td>
</tr>
<tr>
<td>Decon 90</td>
<td>Alconox or Liquinox</td>
</tr>
<tr>
<td>Water from an on-site well</td>
<td>Potable water from municipal drinking water supply</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Food Considerations</strong></td>
<td></td>
</tr>
<tr>
<td>All food and drink, with exceptions noted on the right</td>
<td>Bottled water and hydration drinks (i.e. Gatorade and Powerade) to be brought</td>
</tr>
<tr>
<td></td>
<td>and consumed only in the staging area</td>
</tr>
</tbody>
</table>
PFAS REGULATION, SAMPLING & ANALYSIS

Is it necessary?

• Some literature show PFAS occurrence in cosmetics, sunscreens\textsuperscript{6,7}
• Textbooks/literature support historical use in other relevant products (but w/no supporting analysis)\textsuperscript{4}

But...

• No literature data about transfer from prohibited items during sampling
• Unpublished data suggests no transfer from many field materials (e.g. personal products, field notebooks, etc.)

\textbf{Bottom line}: Many precautions may prove unnecessary but currently there is little data to support which can be eliminated


## PFAS REGULATION, SAMPLING & ANALYSIS

<table>
<thead>
<tr>
<th>State</th>
<th>Drinking Water</th>
<th>Soil</th>
<th>Ground- and Surface water</th>
<th>Target PFAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT</td>
<td>EPA 537</td>
<td>ASTM D-7968-14</td>
<td>ASTM D7979-15</td>
<td>No set list (more is better)</td>
</tr>
<tr>
<td>ME</td>
<td>EPA 537</td>
<td>EPA 537</td>
<td>EPA 537</td>
<td>26 PFAS (list not provided)</td>
</tr>
<tr>
<td>MA</td>
<td>EPA 537 or other approved method</td>
<td>NA</td>
<td>NA</td>
<td>UCMR 3</td>
</tr>
<tr>
<td>NH</td>
<td>DoD/NELAP certified lab or EPA 537</td>
<td>DoD/NELAP certified lab</td>
<td>DoD/NELAP certified lab</td>
<td>PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFBS, PFHxS, PFOS</td>
</tr>
<tr>
<td>NJ</td>
<td>EPA 537&lt;sup&gt;1&lt;/sup&gt;</td>
<td>NA</td>
<td>NA</td>
<td>PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTrDA, PFTA, PFBS, PFHxS, PFOS</td>
</tr>
<tr>
<td>NY</td>
<td>EPA 537 (past) ISO 25101 (now)</td>
<td>NA</td>
<td>NA</td>
<td>UCMR 3 + others depending on lab</td>
</tr>
<tr>
<td>RI</td>
<td>EPA 537</td>
<td>NA</td>
<td>NA</td>
<td>See New Hampshire</td>
</tr>
<tr>
<td>VT</td>
<td>EPA 537</td>
<td>EPA 537</td>
<td></td>
<td>UCMR 3 required, 12 usually reported</td>
</tr>
</tbody>
</table>

DoD = Department of Defense  
NELAP = National Environmental Laboratory Accreditation Program

<sup>1</sup>At NJDEP-certified lab with RL ≤ 6ng/L for PFOA and ≤ 10 ng/L for all other PFASs
# PFAS REGULATION, SAMPLING & ANALYSIS

## Standard methods for PFASs:

<table>
<thead>
<tr>
<th>Method Name</th>
<th>Method 537</th>
<th>ASTM D7979-16</th>
<th>ASTM D7968-14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Drinking water</td>
<td>Water, influent/effluent wastewater, sludge</td>
<td>Soil</td>
</tr>
<tr>
<td>Compound Classes</td>
<td>PFAA, FASAA</td>
<td>PFAA, n:3 acid, FTUCA, FTCA</td>
<td>PFAA, n:3 acid, FTUCA, FTCA</td>
</tr>
<tr>
<td>Sample container</td>
<td>Polypropylene</td>
<td>Polypropylene</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Sample volume</td>
<td>250 mL</td>
<td>5 mL</td>
<td>2g, adjust if needed</td>
</tr>
<tr>
<td>Extraction</td>
<td>SPE</td>
<td>None</td>
<td>50:50 H₂O: MeOH</td>
</tr>
<tr>
<td>Filtering</td>
<td>None</td>
<td>Polypropylene</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Reporting Limits</td>
<td>2.9-14 ng/L</td>
<td>10-300 ng/L</td>
<td>25-750 ng/kg</td>
</tr>
<tr>
<td>Holding Times</td>
<td>14 days</td>
<td>28 days</td>
<td>28 days</td>
</tr>
<tr>
<td>Preservation</td>
<td>5 g/L buffer, cooled &lt;10°C</td>
<td>Cooled, &lt;6°C</td>
<td>Cooled, &lt;6°C</td>
</tr>
<tr>
<td>Quantification</td>
<td>Internal std.</td>
<td>External cal.+ recovery of isotope labeled PFAS</td>
<td></td>
</tr>
</tbody>
</table>

- PFAA = perfluoroalkyl acids
- FASAA = perfluoroalkyl sulfonamidoacetic acid
- n:3 acid = n:3 saturated acid
- FTUCA = fluorotelomer unsaturated carboxylic acid
- FTCA = fluorotelomer carboxylic acid
### PFAS REGULATION, SAMPLING & ANALYSIS

#### Commercial lab availability:

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Method</th>
<th>Matrices</th>
<th>Compound Classes</th>
<th>Aqueous RL*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axys</td>
<td>Internal, TOP</td>
<td>Water, Solid, Air, Tissue, Serum, Urine</td>
<td>PFAA, FTS, FASA, FASAA, PAP, FTCA</td>
<td>1-80 ng/L</td>
</tr>
<tr>
<td>Eurofins</td>
<td>EPA 537 or direct injection</td>
<td>Water, Solid, Tissue, Products</td>
<td>PFAA, FTS, FASAA</td>
<td>2-10 ng/L</td>
</tr>
<tr>
<td>Test America</td>
<td>Mod EPA 537, TOP</td>
<td>Water, Solid</td>
<td>PFAA, FTS, FASA, FASAA, FASE, precursors</td>
<td>2-100 ng/L</td>
</tr>
<tr>
<td>Vista</td>
<td>Mod EPA 537</td>
<td>Water, Solid, Tissue</td>
<td>PFAA, FTS, FASA, FASE, FASAA</td>
<td>1-40 ng/L</td>
</tr>
</tbody>
</table>

* Reporting limit (RL) range encompass all compound classes; RLs for all labs were below EPA HA levels for PFOS/PFOA

- PFAA = perfluoroalkyl acids
- FTS = fluorotelomer sulfonates
- PAP = polyfluoroalkyl phosphate esters
- FASA = perfluoroalkyl sulfonamides
- FTCA = fluorotelomer carboxylic acid
- FASE = perfluoroalkyl sulfonamidoesters
- FASAA = perfluoroalkyl sulfonamidoacetic acid
- FTUCA = fluorotelomer unsaturated carboxylic acid
- TOP = total oxidizable precursors
Other analytical tools: total oxidizable precursor (TOP) assay:

\[ \text{Total Precursors} = \text{PFAA}_{\text{final}} - \text{PFAA}_0 \]

- **Bulk** precursor quantification = total amt. precursors present
- Does **not** identify individual precursor compounds present
PFAS Mobile Lab:
- Cascade Environmental
- Mobile LC-MS/MS
- SPE & direct inject
- DoD QSM PFAS (24)
• PFAS manufacturing
• AFFF
• Other manufacturing
• Waste streams
PFAS USES & SOURCES

PFAS Manufacturing (NAICS 325)²⁸,⁹

PFAS manufacturers

- Arkema
- Asahi
- BASF/Ciba
- Clariant
- Daikin
- 3M/Dyneon
- DuPont/Chemours
- Solvay Solexis
- Dynax

Current manufacturing focus:

- 3M: no AFFF or food wrappers, current focus on ‘short chain’ (PFCA <8, PFSA <6), Ex: PFBS-based products, ADONA
- DuPont: GenX (a perfluropolyether)
- Daikin: 6:2 fluorotelomer products
- Solvay: perfluoropolyethers
- Asahi: perfluoropolyethers

PFAS USES & SOURCES

PFAS Manufacturing (NAICS 325)

Source zone examples:\textsuperscript{10,11}
\begin{itemize}
  \item 3M, MN
  \item 3M, AL
  \item Daikin, AL
\end{itemize}


Aqueous Film Forming Foams (AFFF, NAICS 325)

AFFF and PFAS: 13
- 3M, 1980’s-2000:
  - ~7-13 g/L PFCAs + PFSAs
  - 4.9-11.4 g/L PFOS
  - 0.5-1.4 g/L PFHxS
  - Negligible precursors

- 3M, National Foam, Buckeye, Chemguard, Ansul, 2000’s-present:
  - Negligible PFCAs + PFSAs
  - Primarily precursors

## PFAS USES & SOURCES

### AFFF manufacturers:
- 3M before 2002
- Chemguard
- Ansul
- National Foam
- Angus

### AFFF end users:
- Department of Defense
- Airports
- Fire stations
- Fire training areas
- Petroleum (NAICS 324)

### Source zone examples:
- Ellsworth AFB, SD
- Tyndall AFB, FL
- Wurtsmith AFB, SD

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PFAS USES & SOURCES

Other manufacturing: fluoropolymer (NAICS 325, 326)

Emulsion polymerization and PFASs

- PFOA historically for PTFE and others
- PFNA historically for polyvinylidene fluoride (PVDF)
- Used as ‘polymerization aids’ in emulsion polymerization
- Solubilize monomers
- Generates fine powder and dispersed fluoropolymers
- Used primarily in coatings (e.g. metals, plastics, fabrics)
Example replacement polymerization aids:\(^8\)

**ADONA (CAS No. 958445-44-8)**

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{F}_2 \\
\text{CF}_2 & \quad \text{O} \\
\text{COO}^- & \quad \\
\end{align*}
\]

**GenX (CAS No. 62037-80-3)**

\[
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F}_3\text{C} & \quad \text{C} \\
\text{COO}^- & \quad \text{CF}_3 \\
\end{align*}
\]

**Asahi's product (CAS No. 908020-52-0)**

\[
\begin{align*}
\text{F}_2 & \quad \text{F}_2 \\
\text{F}_3\text{C} & \quad \text{C} \\
\text{COO}^- & \quad \text{CF}_3 \\
\end{align*}
\]

**Solvay's product (CAS No. 329238-24-6)**

\[
\begin{align*}
\text{C} & \quad \text{CF}_3 \\
\text{ClF}_6\text{C}_3 & \quad \text{C} \\
\text{COO}^- & \quad \\
\end{align*}
\]

**Source zone examples:**\(^{17,18}\)
- DuPont, Parkersburg, WV
- St. Gobain, NY, VT

PFAS USES & SOURCES

Other manufacturing: Miscellaneous

Electroplating (NAICS 332)
• PFOS used as mist suppressant

Paper
• PFAS used as grease/water repellant

Textiles (NAICS 313), carpets (NAICS 314, 561), furnishings (NAICS 423)
• Stain-resistant coatings
• Textiles source zone: Amherst, NH (NHDES)

Plus other uses too numerous to list
PFAS USES & SOURCES

Other sources: WWTPs, biosolids, landfills

Considerations
• PFAS occur in industrially- and municipally- sourced waste streams
• Target PFAS will vary based on waste received
PFAS USES & SOURCES

Other sources: WWTPs, biosolids, landfills


PFAS USES & SOURCES

Potential PFAS sources, RI

Future work and resources:
• Framework for geospatial ID of potential PFAS source zones (Brown)
  • NIEHS webinar (6/17):
    https://www.niehs.nih.gov/research/supported/centers/srp/events/riskelearning/analytical/index.cfm
• PFAS Fact Sheets (ITRC)
  • History & Use (8/17)
  • Nomenclature (8/17)
  • Regulatory Summary (8/17)
  • Fate & Transport (12/17)
  • Site Characterization (12/17)
  • Remediation (12/17)
• Reviewed by: EPA, DOD, DOE, industry, stakeholder, academic
Some people have said these compounds redefine persistence.

Jessica C. D’eon, chemistry professor, University of Toronto, on the stability of perfluorocarbons in the environment

Credit: Steve Johnson/Flickr

Questions?
Connecticut

For now, PFASs should be treated as an Additional Polluting Substance (APS) under CT’s Remediation Standard Regulations (RSRs), using EPA’s RfD of 0.00002 mg/kg/day for calculations. Recommended criteria to be applied at remediation sites:

<table>
<thead>
<tr>
<th>Applies to ( \Sigma ) PFOA, PFOS, PFNA, PFHxS, and PFHpA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residential Direct Exposure Criteria (DEC, soil)</td>
</tr>
<tr>
<td>Industrial/Commercial DEC</td>
</tr>
<tr>
<td>GA Pollutant Mobility Criteria (PMC, soil leaching to GW)</td>
</tr>
<tr>
<td>GB Pollutant Mobility Criteria</td>
</tr>
<tr>
<td>Groundwater Protection Criteria</td>
</tr>
<tr>
<td>Surface Water Protection Criteria (GW discharge to SW)</td>
</tr>
</tbody>
</table>

Note that site specific criteria can also be requested under the RSRs.

New Hampshire

- Does your state have standards or guidelines for soil or other media? If so, please answer the same set of Qs, as applicable.

Direct contact soil screening levels – 500 ppb for PFOA, 500 ppb for PFOS. Similar recommended analyte list and lab method.
**New York**

Part 597 - Hazardous Substances Identification, Release Prohibition, and Release Reporting - effective March 3, 2017. The amendments under this rule making finalized the (1) addition of perfluorooctanoic acid (PFOA-acid), ammonium perfluorooctanoate (PFOA-salt), perfluorooctane sulfonic acid (PFOS-acid), and perfluorooctane sulfonate (PFOS-salt) to the list of hazardous substances at 6 NYCRR Section 597.3; (2) allowance for continued use of firefighting foam that may contain PFOA-acid, PFOA-salt, PFOS-acid or PFOS-salt to fight fires (but not for training or any other purposes) on or before April 25, 2017 even if such use may result in the release of a reportable quantity (RQ), which is otherwise prohibited; and (3) correction to the list of hazardous substances by providing units for RQs.

**More info:** [http://www.dec.ny.gov/regulations/104968.html](http://www.dec.ny.gov/regulations/104968.html)

**Vermont**

For soil, the Vermont direct contact standard is 300 ug/kg combined PFOA/PFOS. Since EPA has no standard protocol for this analysis, labs have been using an Modified form of 537 (EPA doesn’t like this nomenclature). Number of compounds analyzed for varies from 12 to 22 compounds, but Vermont only has a standard for combined PFOA/PFOS.
Maine:
Information on screening levels in various media:
https://www1.maine.gov/dep/ftp/RAGS-Background-Documents/PFC_ScreeningLevels_060514.pdf