EBC Rhode Island Program

Contaminants of Emerging Concern
Update on PFAS
General Overview of PFAS

Elizabeth Denly

Program Co-Chair

Quality Assurance & Chemistry Systems Manager

TRC
GENERAL OVERVIEW OF PFAS
PER- AND POLYFLUOROALKYL SUBSTANCES
Today’s Topics

- PFAS Naming Conventions
- Physical/Chemical Properties of PFAS
- Sources of PFAS and Potentially-affected Sites
- Sampling Issues and Quality Control
- EPA Update
PFAS Naming Conventions
Acronyms

- **PFC** = Per-fluorinated chemical
- **PFAS** = Per- and Poly-fluoroalkyl substances

Perfluoroalkyl Substances

- **PFAA** = Perfluoroalkyl acids
- **PFOA** = Perfluorooctanoic acid (perfluorooctanoate)
- **PFOS** = Perfluorooctane sulfonic acid (perfluorooctane sulfonate)
- **PFCA** = Perfluorocarboxylic acids
- **PFSA** = Perfluorosulfonic acids
Perfluorinated Compounds (PFCs)

**PFCs**: Do not use this acronym anymore!

- PFCs previously used to describe greenhouse gases
- PFCs do not include polyfluorinated compounds
Quick Chemistry Lesson #1

- Remember: PFAS are **Per** and **Poly**fluoroalkyl substances
  - **Per-fluoroalkyl substances**: fully fluorinated alkyl tail
  - **Perfluoroalkane carboxylates (or carboxylic acids):** PFCAs
  - **Perfluoroalkane sulfonates (or sulfonic acids):** PFSAs

(PFOS)

(PFOA)

COOH = Head

SO$_3$H = Head

Alkyl tail, fully fluorinated
Quick Chemistry Lesson #2

- **Remember:** PFAS are **Per** and **Poly**fluoroalkyl substances

- **Poly-fluoroalkyl substances:** non-fluorine atom (typically hydrogen or oxygen) attached to at least one carbon atom

Fluorotelomer Alcohol (8:2 FTOH)

Polyfluoroalkyl substances can also be precursors.
Nomenclature

- Remember: PFAS are Per and Polyfluoroalkyl substances

- **Per-fluoroalkyl substances**: fully fluorinated alkyl tail

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Compound Name</th>
<th>Carbon Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>Perfluorooctanoic acid</td>
<td>C8</td>
</tr>
<tr>
<td>PFOS</td>
<td>Perfluorooctanesulfonic acid</td>
<td>C8</td>
</tr>
<tr>
<td>PFBA</td>
<td>Perfluorobutanoic acid</td>
<td>C4</td>
</tr>
<tr>
<td>PFBS</td>
<td>Perfluorobutane sulfonic acid</td>
<td>C4</td>
</tr>
<tr>
<td>PFHxA</td>
<td>Perfluorohexanoic acid</td>
<td>C6</td>
</tr>
<tr>
<td>PFHxS</td>
<td>Perfluorohexane sulfonic acid</td>
<td>C6</td>
</tr>
</tbody>
</table>

- **Poly-fluoroalkyl substances**: partially fluorinated alkyl tail
  - Fluorotelomers

Polyfluoroalkyl substances can also be precursors.
Summary of PFAS Families

PFAS

Non-polymer

Perfluorinated
- PFAAs
- PFCAs
- PFSAs
- FASAs

Polyfluorinated Precursors

Polymer
Potential Precursors

Polyfluorinated
- FTSAs
- FTCAs
- FTOHs
- FASEs
- FASAs
What is a Precursor?

- Polyfluoroalkyl substances transformed to PFAAs
- Transformation
- Precursors are a concern
- 1000s of these

FTSAs:
- Stable under anoxic conditions
- Likely degrade to PFCAs in aerobic surface waters
PFAS Families

- PFCA
- PFSA
- PFAA

Fluorotelomer-based Substances:
- FTOH
- FTSA
- FTCA

- From telomerization process
- Can biotransform into PFCAs
  - FTOH far more volatile

ECF-based Substances:
- FOSE: raw material in ECF process
- FOSAA: degradation intermediate
- Can biotransform into PFCAs and PFSAs

- Directly released to environment
- Produced by precursor degradation
PFOS: Linear and Branched Isomers

**3M AFFF**: Branched and linear isomers (30:70)

If exclude branched isomers, concentrations underestimated and biased low.
### PFOS: Linear and Branched Isomers

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Abbreviation</th>
<th>PFOS Isomer Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-perfluoro-1-octanesulfonate</td>
<td>L-PFOS</td>
<td><img src="image1" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>perfluoro-1-methyl-heptanesulfonate</td>
<td>P1MhPS</td>
<td><img src="image2" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>perfluoro-2-methyl-heptanesulfonate</td>
<td>P2MhPS</td>
<td><img src="image3" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>perfluoro-3-methyl-heptanesulfonate</td>
<td>P3MhPS</td>
<td><img src="image4" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>perfluoro-4-methyl-heptanesulfonate</td>
<td>P4MhPS</td>
<td><img src="image5" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>perfluoro-5-methyl-heptanesulfonate</td>
<td>P5MhPS</td>
<td><img src="image6" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>perfluoro-6-methyl-heptanesulfonate</td>
<td>P6MhPS</td>
<td><img src="image7" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>perfluoro-3,5-dimethyl-hexanesulfonate</td>
<td>P35DMhXS</td>
<td><img src="image8" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>perfluoro-4,4-dimethyl-hexanesulfonate</td>
<td>P44DMhXS</td>
<td><img src="image9" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>
PFOA: Branched and Linear Isomers: Lab Quantitation

Correct integration of PFOA

Incorrect integration of PFOA
Long Chain Versus Short Chain

- **Why does it matter?**
  - Short chain:
    - PFCAs with seven or fewer carbons
    - PFSAs with five carbons or less

  *Perfluorohexanoic acid (PFHxA) is short chain PFCA.*

- Long chain:
  - PFCAs with 8 or more carbons
  - PFSAs with six or more carbons

  *Perfluorohexane sulfonic acid (PFHxS) is long chain PFSA.*
What Are PFAS?

- Poly- and per-fluoroalkyl substances
  - Generic family of chemicals
  - Manmade and do not occur naturally
  - Used since 1940 (Critical for the Manhattan Project)
  - Can be branched or unbranched
  - Used to make products that resist heat, oils, grease, stains, and water

- Most prevalent and researched: PFOA and PFOS

- PFAS: Acid or anion?

PFOS is present in the environment in the anionic form: perfluorooctane sulfonate.

Perfluorobutanoic acid \( \rightleftharpoons \) Perfluorobutanoate (+ dissociated proton)
# CAS Numbers and PFAS State

![PFAS State Diagram](image)

<table>
<thead>
<tr>
<th>PFAS State</th>
<th>Structure</th>
<th>CAS No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PFOA</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anion</td>
<td>Perfluoroctanoate</td>
<td>$\text{C}<em>7\text{F}</em>{15}\text{CO}_2^-$</td>
</tr>
<tr>
<td>Acid</td>
<td>Perfluoroctanoic acid</td>
<td>$\text{C}<em>7\text{F}</em>{15}\text{COOH}$</td>
</tr>
<tr>
<td><strong>PFOS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anion</td>
<td>Perfluorooctane sulfonate</td>
<td>$\text{C}<em>8\text{F}</em>{17}\text{SO}_3^-$</td>
</tr>
<tr>
<td>Acid</td>
<td>Perfluorooctane sulfonic acid</td>
<td>$\text{C}<em>8\text{F}</em>{17}\text{SO}_3\text{H}$</td>
</tr>
</tbody>
</table>

**Why is this important?**
Chemical Properties of Perfluoroalkyl Substances

- C-F: Strong bond
- Chemically and thermally stable
- Water soluble and mobile in groundwater
- Surfactant properties
- Recalcitrant in environment
# Properties: Acid vs Cation vs Anion Form

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>AVAILABILITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical description</td>
<td>White powder or waxy substance</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Known</td>
</tr>
<tr>
<td>Solubility in water</td>
<td><strong>Known for acid and cation</strong>; N/A for Anion</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td><strong>Known for acid</strong>; N/A for anion and cation (*)</td>
</tr>
<tr>
<td>Henry’s Law constant</td>
<td><strong>Estimated for acid</strong>; N/A for anion and cation (*)</td>
</tr>
<tr>
<td>Kow</td>
<td><strong>Typically see values for acid form</strong></td>
</tr>
<tr>
<td>pKa</td>
<td>Generally not available (some modeled values available)</td>
</tr>
<tr>
<td>Half-life</td>
<td>Known for anion; N/A for acid &amp; cation</td>
</tr>
<tr>
<td>BCF and/or BAF</td>
<td></td>
</tr>
</tbody>
</table>
Sources of PFAS and Potentially Affected Sites

ARE YOU DRINKING TEFLOM CONTAMINATED WATER?
Where Are PFAS Used?
What Types of Sites Can Be Sources of PFAS?

- Fire training facilities
- Fire stations
- Refineries
- DoD sites/Military bases
- Commercial and private airports
- Landfills (leaching from consumer products)
- Biosolids land application
- Rail yards
- Chemical facilities
- Plating facilities
- Textile/carpet manufacturers
- Residential areas with septic systems
Timeline of PFAS

1938
- PTFE discovered

1949
- PTFE used in products

1956
- Stain-resistant products (PFOS)

1968
- Navy developed AFFF

1978
- Detected in blood of manufacturing workers

2002
- PFOS manufacturing phased out

2006
- PFOA phased out
- EPA PFOA Stewardship Program

2009
- Stockholm Convention classifies PFOS as POP

2013-2015
- PFOA phase-out complete
- Sampling of public drinking water wells for PFAAs (UCMR3)

2016
- EPA Health Advisory announced for PFOA/PFOS (70 ppt)
Global Manufacture and Use of PFAS

PFAS Manufactured Globally

- PFOA & PFOS No Longer Produced
- EtFOSA Produced on Industrial Scale
- Prohibits Import, Manufacture, Use & Sale of PFOS/PFOA
- Banned Sale, Use and Import of PFOA
- Class B AFFF with PFAS Banned
- Restrict Manufacture, Import, Export, and Use of PFOS
- Increased Production of PFOA
Replacement Chemistry

- GenX replaces PFOA
- ADONA replaces PFOA
- 6:2 Fluorotelomers replace PFOS in metals plating
- Telomers replace PFOS and PFHxS in AFFF
- Shorter chain PFAAs replace PFOA: PFBA, PFPeA
Aqueous Film Forming Foam
What is AFFF?

- Highly effective fire-fighting foam
- Used for hydrocarbon fuel fires

- AFFF acts as follows
  - As an aqueous foam: primary fire extinguishing agent
  - As an aqueous film former: a fuel vapor suppressor
Where is AFFF Used?

- **Airports**
  - Emergency response
  - Fire Training Areas
  - Nozzle Testing Areas
  - Storage Areas

- **Municipal Fire Departments**
- **Industrial Fixed Systems**
- **Petrochemical**
- **Military / Government**
- **Marine – Off Shore Fire Protection**
Types of AFFF

Legacy PFOS AFFF
- “3M Lightwater”
- Sales ended in 2002
- Inventory remains in many locations
- Contain or breakdown to PFOS & PFHxS and possibly PFOA

Legacy Fluorotelomer AFFF
- Sold from 1970s - 2016
- All other brands of AFFF except “3M Lightwater”
- No PFOS and no breakdown to PFOS
- Long-chain fluorotelomers (6:2 FTS) can breakdown to PFOA

Modern Fluorotelomer AFFF
- Most foam mfrs transitioned to this
- No PFOS and no breakdown to PFOS
- Short-chain fluorotelomers (6:2 and 4:2 FTS)
- May contain trace amts of PFOA and PFOA precursors
- Considered lower in toxicity and reduced BAP
Fluorine-Free Foams

- Alternative to AFFF in some applications
- Being used at some airports and industrial facilities in Europe, Australia, and other countries
- Do not contain PFAS or other persistent chemicals
- Contain hydrocarbon surfactants, solvents, and stabilizers
PFAS Sampling Issues and Quality Control
How Do We Sample PFAS?

- Similar to conventional sampling (e.g., low-flow techniques, direct push, etc.)
- Special care required to prevent cross contamination
- Use of and exclusion of specific sampling equipment and materials
## PFAS Sampling Dos and Don’ts

<table>
<thead>
<tr>
<th>WHAT SHOULD I AVOID?</th>
<th>USE INSTEAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passive diffusion bags (PDBs)</td>
<td></td>
</tr>
<tr>
<td>LDPE Hydrasleeves</td>
<td>✔ HDPE Hydrasleeves</td>
</tr>
<tr>
<td>Post-It notes during sample handling</td>
<td></td>
</tr>
<tr>
<td><strong>Blue Ice® (chemical ice packs)</strong></td>
<td>✔ Regular ice in Ziploc® bags</td>
</tr>
<tr>
<td><strong>Waterproof field books, plastic clipboards and spiral bound</strong></td>
<td>✔ Field notes recorded on loose paper</td>
</tr>
<tr>
<td><strong>notebooks</strong></td>
<td>✔ Field forms maintained in aluminum or Masonite clipboards</td>
</tr>
<tr>
<td>Unnecessary handling of items with nitrile gloves</td>
<td>✔ Personnel collecting and handling samples should wear nitrile gloves at all times while collecting and handling samples or sampling equipment</td>
</tr>
</tbody>
</table>
# PFAS Sampling Dos and Don’ts

<table>
<thead>
<tr>
<th>WHAT SHOULD I AVOID?</th>
<th>USE INSTEAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment with Teflon® (e.g., bailers, tubing, parts in pump) during sample handling or mobilization/demobilization</td>
<td>✓ High density polyethylene (HDPE) or silicone tubing/materials in lieu of Teflon®</td>
</tr>
<tr>
<td>Low-density polyethylene (LDPE) or glass sample containers or containers with Teflon-lined lids</td>
<td>✓ HDPE or polypropylene containers for sample storage</td>
</tr>
<tr>
<td></td>
<td>✓ HDPE or polypropylene caps</td>
</tr>
<tr>
<td>Tyvek® suits and waterproof boots</td>
<td>✓ Clothing made of cotton preferred</td>
</tr>
<tr>
<td></td>
<td>✓ Boots made with polyurethane and polyvinyl chloride (PVC)</td>
</tr>
<tr>
<td>Waterproof labels for sample bottles</td>
<td>✓ Paper labels with clear tape</td>
</tr>
<tr>
<td>Sunscreens, insect repellants</td>
<td>✓ Products that are 100% natural, DEET</td>
</tr>
<tr>
<td>Sharpies</td>
<td>✓ Ballpoint pens</td>
</tr>
<tr>
<td>Aluminum foil</td>
<td>✓ Thin HDPE sheeting</td>
</tr>
</tbody>
</table>
Other Special Considerations

- Field QC
- Decontamination of sampling equipment
- No pre-wrapped food or snacks
- Avoid cosmetics, moisturizers, hand creams on day of sampling.
- Do not filter aqueous samples.
- Visitors to site must remain at least 30 feet from sampling area.
- Wash hands with water after leaving vehicle before setting up on a well.
- Partitioning of PFAS to surface in wells and reservoirs
What Should I Wear?

- No clothing with fabric softeners
- No new clothing
- Avoid boots and other field clothing containing waterproof/resistant material
- Cotton is best
EPA National PFAS Summit

- “PFAS is a national priority”
- 4-Step Action Plan
  - MCLs for PFOS/PFOA
  - Groundwater Cleanup Standards
  - Liability under CERCLA; PFOA & PFOS hazardous substances
  - Developing toxicity values for PFBS and Gen-X
- National PFAS Management Plan
- EPA visiting states: NH, PA, CO, NC, KS
Plug for ITRC PFAS Team

- Includes >350 members: industry, academia, DOD, regulatory, consulting, analytical labs and vendors

- Seven PFAS Fact Sheets:
  - AFFF Introduction
  - History and Use
  - Naming Conventions and Chemical Properties
  - Regulations and Guidance
  - Fate and Transport
  - Site Characterization, Sampling, Lab Methods
  - Remediation Technologies and Methods

- 2018 – Technical Guidance Document
Summary

- PFAS = Per and poly-fluoroalkyl substances
- Poly-fluorinated substances can be precursors and can biotransform into PFAAs
- Unique chemical properties (C-F bond, surfactant, persistent)
- PFAS used in a wide variety of products
- Many different types of sites can be sources of PFAS
- PFAS has unique sampling requirements and need to avoid common sampling materials
Questions?

Elizabeth Denly, ASQ CMQ/OE
P: (978) 656-3577  |  E: EDenly@trcsolutions.com
www.trcsolutions.com
Analytical Laboratory Considerations for PFAS

Jim Occhialini

Vice President
Alpha Analytical
EBC Site Remediation & Redevelopment Program: Contaminants of Emerging Concern – Update on PFAS

PFAS Laboratory Considerations

Jim Occhialini
Alpha Analytical
MOVING TARGET

– Analytical methodologies
  – What methods, are they applicable?
  – Reference standard availability?

– Regulatory requirements
  – Requested target compound lists
  – Compliance guidelines, required reporting limits

– What’s next?
115TH CONGRESS 2d Session

H.R. ______

To encourage Federal agencies to enter into or amend cooperative agreements with States for removal and remedial actions to address PFAS contamination in drinking water, surface water, ground water, sediment, and soil, and for other purposes.

IN THE HOUSE OF REPRESENTATIVES

Mr. Utros introduced the following bill; which was referred to the Committee on ______

A BILL

To encourage Federal agencies to enter into or amend cooperative agreements with States for removal and remedial actions to address PFAS contamination in drinking water, surface water, ground water, sediment, and soil, and for other purposes.

Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled,

SECTION 1. SHORT TITLE.

This Act may be cited as the “PFAS Federal Facility Accountability Act of 2018”.
Unregulated Contaminant Monitoring Rule (UCMR)

1996 SDWA amendments

- UCMR 1  2001–2003  perchlorate, MTBE, explosives, pesticides
- UCMR 2  2008–2010  flame retardants, explosives, nitrosoamines
- UCMR 3  2013–2015  dioxane, PFAS, VOCs, metals, hormones
- UCMR 4  2018- 2020 (cyanotoxins, HAAs, pesticides)

- By law - needs to be updated every 5 years

- Some surprises…sources not considered…or sources not considered significant
PFAS Analysis

• **Primary methodology**
  – Method 537 rev1.1 Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) Sept, 2009

• **Sample preparation**
  – Solid phase extraction (SPE), *aqueous samples*

• **Analytical Instrumentation**
  – Liquid chromatography / tandem mass spectrometry (LC/MS/MS)
ANALYTICAL METHODOLOGIES
 PFAS can exist as linear & branched isomers
  – Method 537 addresses both for PFOS (2009)
• Standards not available at the time for PFOA
  – Discrepancies in PFOA reporting
    • Addressed in Tech Advisory
Method 537

- **SDWA drinking water method**
  - UCMR 3 method
    - Designed for chlorinated public water supplies
  - Amenable to a specific 14 cmpd PFAS target list

- **Specific method requirements**
  - Trizma® de-chlorinating agent/buffer
  - Field reagent blanks (FRB)
    - Section 3.8: aliquot of reagent water that is placed in a sample container in the laboratory
      - treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures.
• **Method 537**
  – “as specifically written”
  – Is not amenable to expanded list of compounds or other sample matrices without modification

• **Other methodologies**
  – “Laboratory proprietary method”
    • LC/MS/MS
    • May use different or multiple SPE cartridges
  – May use isotope dilution approach
  – Different sample preservation / handling potentially
Isotope Dilution Approach

- **Addition of known amount of isotopically-enriched, compound-specific internal standard**
  - PRIOR TO SAMPLE PREPARATION
  - Matrix recovery correction
    - Analysis-specific, analyte-specific concentration normalization

- **Provides additional qualitative certainty**
3 New EPA SW-846 Methods Proposed

- (1) Non-potable water: SW-846 Method 8327 draft, fall 2018
  - LC/MS/MS direct injection, external standard calibration
  - 24 analytes

- (2) Non-potable water: SW-846 Method 8328
  - LC/MS/MS SPE, isotope dilution
  - 24 analytes

- (3) Solids: SW-846 Method 8329 TBD
  - Will employ an extraction & potentially direct injection
Department of Defense (DoD)
Department of Energy (DOE)
Consolidated
Quality Systems Manual (QSM) for
Environmental Laboratories

Based on ISO/IEC 17025:2005(E)

and

The NELAC Institute (TNI) Standards, Volume 1, (September 2009)
<table>
<thead>
<tr>
<th>QC Check</th>
<th>Minimum Frequency</th>
<th>Acceptance Criteria</th>
<th>Corrective Action</th>
<th>Flagging Criteria</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Sample Preparation</td>
<td>Each sample and associated batch QC samples.</td>
<td>Solid Phase Extraction (SPE) must be used unless samples are known to contain high PFAS concentrations (e.g., AFFF formulations). Inline SPE is acceptable. Samples of known high PFAS concentrations can be prepared by serial dilution instead of SPE, with documented project approval.</td>
<td>NA.</td>
<td>NA.</td>
<td>NA.</td>
</tr>
<tr>
<td>Soil and Sediment Sample Preparation</td>
<td>Each sample and associated batch QC samples.</td>
<td>Entire sample received by the laboratory must be homogenized prior to subsampling.</td>
<td>NA.</td>
<td>NA.</td>
<td>NA.</td>
</tr>
<tr>
<td>Sample Cleanup Procedure using ENVI-Carb™ or equivalent</td>
<td>Each sample and associated batch QC samples. Not applicable to AFFF formulation samples.</td>
<td>Removal of interferences from matrix.</td>
<td>NA.</td>
<td>Flagging is not appropriate.</td>
<td>Cleanup should reduce bias from matrix background.</td>
</tr>
</tbody>
</table>
Acids or Anions?

Perfluorooctanesulfonic acid  Perfluorooctanesulfonate

Perfluoroalkylsulfonic Acids  Sulfonates

Perfluoroalkylcarboxylic Acids  Carboxylates
Acids or Salts – Laboratory Implications

• Terms used somewhat interchangeably in literature, regulatory guidance & media

• Dissolved in water, PFAS exists in anionic form
  – MS only detects/measures the anion

• Lab reporting acid or anion?
  – Different compounds, different CAS#’s

• EPA Method 537.1 specifies reporting the acid form
  – Form of lab calibration standard?
    • If prepared with salts, concentration must be adjusted to account for difference in mass
In NHDES’ experience, some analytical laboratories report slightly different forms of PFOS, PFHXS, and PFBS (i.e., perfluorooctanesulfonic acid vs. perfluorooctane sulfonate), which vary slightly from one another in molecular weight, resulting in slight differences in reported concentrations. Confirm with the analytical laboratory that the forms of PFOS, PFHXS, and PFBS being analyzed and reported correspond to the CAS No. presented in the table above.
So What Do You Analyze For?

- Industry

- AFFF
  Application dependent
  Source related, regulatory oversight
  Site characterization, remedial design?
  Residential wells, monitoring wells, soils...?

- Landfills
## UCMR 3 (Unregulated Contaminate Monitoring Rule)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>perfluorooctanesulfonic acid</td>
</tr>
<tr>
<td>PFOA</td>
<td>perfluorooctanoic acid</td>
</tr>
<tr>
<td>PFNA</td>
<td>perfluorononanoic acid</td>
</tr>
<tr>
<td>PFHxS</td>
<td>perfluorohexanesulfonic acid</td>
</tr>
<tr>
<td>PFHpA</td>
<td>perfluoroheptanoic acid</td>
</tr>
<tr>
<td>PFBS</td>
<td>perfluorobutanesulfonic acid</td>
</tr>
</tbody>
</table>
EPA Method 537 - List of 14 Compounds

<table>
<thead>
<tr>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorooctanoic acid (PFOA)</td>
</tr>
<tr>
<td>Perfluorooctane Sulfonate (PFOS)</td>
</tr>
<tr>
<td>Perfluorobutanesulfonic acid (PFBS)</td>
</tr>
<tr>
<td>Perfluoroheptanoic acid (PFHpA)</td>
</tr>
<tr>
<td>Perfluorohexane Sulfonate (PFHxS)</td>
</tr>
<tr>
<td>Perfluorononanoic acid (PFNA)</td>
</tr>
<tr>
<td>Perfluorohexanoic acid (PFHxA)</td>
</tr>
<tr>
<td>Perfluorodecanoic acid (PFDA)</td>
</tr>
<tr>
<td>Perfluoroundecanoic acid (PFUdA)</td>
</tr>
<tr>
<td>N-methyl perfluorooctanesulfonamidoacetic acid (MeFOSAA)</td>
</tr>
<tr>
<td>Perfluorododecanoic acid (PFDoA)</td>
</tr>
<tr>
<td>N-ethyl perfluorooctanesulfonamidoacetic acid (EtFOSAA)</td>
</tr>
<tr>
<td>Perfluorotridecanoic acid (PRTrDA)</td>
</tr>
<tr>
<td>Perfluorotetradecanoic acid (PFTeDA)</td>
</tr>
<tr>
<td>Analyte Name</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>Perfluorotetradecanoic acid*</td>
</tr>
<tr>
<td>Perfluorotridecanoic acid*</td>
</tr>
<tr>
<td>Perfluorododecanoic acid*</td>
</tr>
<tr>
<td>Perfluoroundecanoic acid*</td>
</tr>
<tr>
<td>Perfluorodecanoic acid*</td>
</tr>
<tr>
<td>Perfluorononanoic acid*</td>
</tr>
<tr>
<td>Perfluorooctanoic acid*</td>
</tr>
<tr>
<td>Perfluoroheptanoic acid*</td>
</tr>
<tr>
<td>Perfluorohexanoic acid*</td>
</tr>
<tr>
<td>Perfluoropentanoic acid</td>
</tr>
<tr>
<td>Perfluorobutanoic acid</td>
</tr>
<tr>
<td>Perfluorodecanesulfonate</td>
</tr>
<tr>
<td>Perfluorononanesulfonate</td>
</tr>
<tr>
<td>Perfluoroctanesulfonate*</td>
</tr>
<tr>
<td>Perfluoroheptanesulfonate</td>
</tr>
<tr>
<td>Perfluorohexanesulfonate*</td>
</tr>
<tr>
<td>Perfluoropentansulfonate</td>
</tr>
<tr>
<td>Perfluorobutanesulfonate*</td>
</tr>
<tr>
<td>Perfluoroctanesulfonamide</td>
</tr>
<tr>
<td>Fluorotelomer sulfonate 8:2</td>
</tr>
<tr>
<td>Fluorotelomer sulfonate 6:2</td>
</tr>
<tr>
<td>Fluorotelomer sulfonate 4:2</td>
</tr>
<tr>
<td>N-ethyl-N-((heptadecafluorooctyl)sulfonyl)glycine*</td>
</tr>
<tr>
<td>N-(Heptadecafluorooctylsulfonyl)-N-methylglycine*</td>
</tr>
</tbody>
</table>

*Method 537 proposed list, new EPA methods
Perfluoro-2-propoxypropanoic acid

- FRD-902 and FRD-903
  - 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid (FRD-903)
  - produces 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (FRD-902)

F53B trade name
chlorinated polyfluorinated ether sulfonate
PFOS alternative


US Navy Inquiry to Laboratories regarding GenX, ADONA & F53B

- Prompted by a US EPA review initiative of PFOA replacement products.
- EPA developing tox values for the two main components of Gen X
- Methodology options
Regulatory Guidelines & Criteria

• EPA Health Advisory Levels (HALs) adopted May 2016
  – PFOA 70 ng/L / PFOS 70 ng/L (total can not exceed 70 ng/L)
    • NY, MA, CT, RI, PA, MD recognize EPA HAL 70 ng/L for drinking water
      – RI DEM groundwater quality standard for GAA /GA groundwater
      – NHDES adopted 70 ng/L for AGQS

• CT
  – DPH DW Action Level 70 ppt for Σ PFOA, PFOS, PFHxS, PFNA, & PFHpA
  – Developing guidance for soils (proposed 1.4 ug/Kg)

• MA
  – DW Advisory Level 70 ppt for Σ PFOA, PFOS, PFHxS, PFNA, & PFHpA

• VT
  – Enforcement std PFOA/PFOS 20 ng/L (Dec 2016)
    • 20 ppt for Σ PFOA, PFOS, PFHxS, PFNA, & PFHpA (revised July 2018)
  – Preventive action level 10 ng/L
<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>perfluorooctanesulfonic acid</td>
</tr>
<tr>
<td>PFOA</td>
<td>perfluorooctanoic acid</td>
</tr>
<tr>
<td>PFNA</td>
<td>perfluorononanoic acid</td>
</tr>
<tr>
<td>PFHxS</td>
<td>perfluorohexanesulfonic acid</td>
</tr>
<tr>
<td>PFHpA</td>
<td>perfluoroheptanoic acid</td>
</tr>
<tr>
<td>PFBS</td>
<td>perfluorobutanesulfonic acid</td>
</tr>
</tbody>
</table>

**Summarized Data:**

- **70 PPT EPA HAL**
- **NJ GWQC 13 PPT MCL**
- **20 PPT VT DW HAL**
Recent State of NH Recommendations

PFAS Sampling Recommendations for Public Water Systems and Private Well Owners

1) Reporting Limits: Analytical methods with reporting limits of at least 5 nanograms per liter should be utilized.

2) Analytical Methods: 1) Analytical methods that use isotope dilution conducted by laboratories accredited by the Department of Defense or the National Environmental Laboratory Accreditation Program (NELAP); or 2) EPA Method 537 Rev 1.1 following the provisions of EPA Technical Advisory 815-B-16-021 issued in September 2016 for PFOA by laboratories with NELAP accreditation from NH or another state.

3) Analytes: The following PFAS were included on the United States Environmental Protection Agency’s Unregulated Contaminant Monitoring Rule (UCMR) Round 3 list and as a minimum, should be included in the requested analysis:

- Perfluorooctanesulfonic acid (PFOS)
- Perfluorooctanoic acid (PFOA)
- Perfluorononanoic acid (PFNA)
- Perfluorohexanesulfonic acid (PFHxS)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorobutanesulfonic acid (PFBS)
- Perfluorobutanoic acid (PFBA)
- Perfluoropentanoic acid (PFPeA)
- Perfluorohexanoic acid (PFHxA)

The following additional PFAS have been regularly detected in groundwater samples in New Hampshire Drinking Water PFOA Investigation and are also recommended target analytes to include in the PFAS analysis.

EPA Method 537
For GW, SW, soils, & sediments lab should be directed to report all calibrated PFAS cmpds.

Reported cmpds will include at a minimum (current Oct 2017)

ELAP offers DW cert for PFOA / PFOS. No certification for other matrices but lab should hold PFAS DW cert. "modified" method 537 or ISO 25101

Expected PFOA / PFOS RL 2 ng/L AQ, 3 ug/Kg soil

### Full PFAS Target Analyte List

<table>
<thead>
<tr>
<th>Perfluoroalkyl sulfonates</th>
<th>Perfluorobutanesulfonic acid</th>
<th>PFBS</th>
<th>375-75-5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Perfluorohexanesulfonic acid</td>
<td>PFHxS</td>
<td>355-46-4</td>
</tr>
<tr>
<td></td>
<td>Perfluoroheptanesulfonic acid</td>
<td>PFHpS</td>
<td>375-82-8</td>
</tr>
<tr>
<td></td>
<td>Perfluorooctanesulfonic acid</td>
<td>PFOS</td>
<td>1763-23-1</td>
</tr>
<tr>
<td></td>
<td>Perfluorodecanesulfonic acid</td>
<td>PFDS</td>
<td>335-77-3</td>
</tr>
<tr>
<td>Perfluoroalkyl carboxylates</td>
<td>Perfluorobutanoic acid</td>
<td>PFBA</td>
<td>375-22-4</td>
</tr>
<tr>
<td></td>
<td>Perfluoropentanoic acid</td>
<td>PFPoA</td>
<td>2706-90-3</td>
</tr>
<tr>
<td></td>
<td>Perfluorohexanoic acid</td>
<td>PFHxA</td>
<td>307-24-4</td>
</tr>
<tr>
<td></td>
<td>Perfluoroheptanoic acid</td>
<td>PFHpA</td>
<td>375-85-9</td>
</tr>
<tr>
<td></td>
<td>Perfluorooctanoic acid</td>
<td>PFOA</td>
<td>335-67-1</td>
</tr>
<tr>
<td></td>
<td>Perfluorononanoic acid</td>
<td>PFNA</td>
<td>375-95-1</td>
</tr>
<tr>
<td></td>
<td>Perfluorodecanoic acid</td>
<td>PFDA</td>
<td>335-76-2</td>
</tr>
<tr>
<td></td>
<td>Perfluoroundecanoic acid</td>
<td>PFUA/PFUdA</td>
<td>2058-94-8</td>
</tr>
<tr>
<td></td>
<td>Perfluorododecanoic acid</td>
<td>PFDoA</td>
<td>307-55-1</td>
</tr>
<tr>
<td></td>
<td>Perfluorotridecanoic acid</td>
<td>PFTrA/PFTrDA</td>
<td>72629-94-8</td>
</tr>
<tr>
<td></td>
<td>Perfluorotetradecanoic acid</td>
<td>PFTA/PFTeDA</td>
<td>376-06-7</td>
</tr>
<tr>
<td>Fluorinated Telomer Sulfonates</td>
<td>6:2 Fluorotelomer sulfonate</td>
<td>6:2 FTS</td>
<td>27619-97-2</td>
</tr>
<tr>
<td></td>
<td>8:2 Fluorotelomer sulfonate</td>
<td>8:2 FTS</td>
<td>39109-34-4</td>
</tr>
<tr>
<td>Perfluorooctanesulfonamides</td>
<td>Perfluorooctanesulfonamide</td>
<td>FOSA</td>
<td>754-91-6</td>
</tr>
<tr>
<td>Perfluorooctanesulfonamidoacetic acids</td>
<td>N-methyl perfluorooctanesulfonamidoacetic acid</td>
<td>N-MeFOSAA</td>
<td>2355-31-9</td>
</tr>
<tr>
<td></td>
<td>N-ethyl perfluorooctanesulfonamidoacetic acid</td>
<td>N-EtFOSAA</td>
<td>2981-50-6</td>
</tr>
</tbody>
</table>
Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs)

Environmental releases of perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and other perfluoroalkyl and polyfluoroalkyl substances (PFASs) have occurred at manufacturing facilities and in areas where aqueous film-forming foam (AFFF) was used to extinguish hydrocarbon fires. PFASs are suspected to cause adverse human health effects. They are highly stable in the environment and are typically removed from water supplies using granular activated carbon. There is a need for in situ treatment technologies and ex situ treatment methods that are more cost-effective.

Related Article(s):
- Soil & Groundwater Contaminants

CONTRIBUTOR(S): Dr. Rula Deeb, Dr. Jennifer Field, Elisabeth Hawley, and Dr. Christopher Higgins

Key Resource(s):
- U.S. EPA Emerging Contaminants - PFOS and PFOA Fact Sheet[1]
BACKGROUND CONTAMINATION?

PFAS False Positives ??

Ultra low detection limits **not new** to environmental data collection

Widespread “mainstream” sampling **is new** at this level of sensitivity

Ubiquitous nature of PFAS sources coupled with widespread sampling and ng/L RLs? **Unprecedented**

Single digit ng/L RLs
Sampling: need to address possible sources of contamination

**OK**

- **Field Equipment**
  - HDPE bottles, silicon tubing, loose paper, aluminum/Masonite clipboards, Alconox / Liquinox®, nitrile gloves
- **Clothing / PPE**
  - “Well laundered”, preferably cotton
- **Personal care products**
  - None, see “allowable” sun screens & insect repellants

**NOT OK**

- **Field Equipment**
  - LDPE bottles, Teflon® caps, Teflon® tubing, waterproof field books, plastic clipboards/binders, Post It® notes, chemical (blue ice)
- **Clothing / PPE**
  - No fabric softener, Gor-Tex®, “dri-fit”, Tyvek®
- **Personal care products**
  - No cosmetics, moisturizers, etc. as part of personal cleaning/showering routine on morning of sampling
  - Verify allowable sun screens / insect
  - Food packaging
Potential Contamination Study w/TRC
Waterproof Field Logbook

Cover of Field Logbook (ng/L)

- C4 PFSA
- C7 PFCA

Pages in Field Logbook (ng/L)

- No PFSAs
<table>
<thead>
<tr>
<th>Analyte</th>
<th>Acronym</th>
<th># Detections</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H,1H,2H,2H-perfluorohexane sulfonate (4:2)</td>
<td>4:2 FTS</td>
<td></td>
</tr>
<tr>
<td>1H,1H,2H,2H-perfluoroctane sulfonate (6:2)</td>
<td>6:2 FTS</td>
<td></td>
</tr>
<tr>
<td>1H,1H,2H,2H-perfluorodecane sulfonate (8:2)</td>
<td>8:2 FTS</td>
<td>2</td>
</tr>
<tr>
<td>N-methyl perfluoroctanesulfonamidoacetic acid</td>
<td>NEtFOSAA</td>
<td>0</td>
</tr>
<tr>
<td>N-ethyl perfluoroctanesulfonamidoacetic acid</td>
<td>NMeFOSAA</td>
<td>0</td>
</tr>
<tr>
<td>Perfluorobutanesulfonic acid</td>
<td>PFBS</td>
<td>3</td>
</tr>
<tr>
<td>Perfluorodecanoic acid</td>
<td>PFDA</td>
<td>7</td>
</tr>
<tr>
<td>Perfluorododecanoic acid</td>
<td>PFDoA</td>
<td>3</td>
</tr>
<tr>
<td>Perfluorodecansulfonic acid</td>
<td>PFDS</td>
<td>0</td>
</tr>
<tr>
<td>Perfluoroheptanoic acid</td>
<td>PFHpA</td>
<td>14</td>
</tr>
<tr>
<td>Perfluoroheptanesulfonic acid</td>
<td>PFHpS</td>
<td>0</td>
</tr>
<tr>
<td>Perfluorohexanoic acid</td>
<td>PFHxA</td>
<td>13</td>
</tr>
<tr>
<td>Perfluorohexanesulfonic acid</td>
<td>PFHxS</td>
<td>2</td>
</tr>
<tr>
<td>Perfluorononanoic acid</td>
<td>PFNA</td>
<td>8</td>
</tr>
<tr>
<td>Perfluorononanesulfonic acid</td>
<td>PFNS</td>
<td>0</td>
</tr>
<tr>
<td>Perfluoroctanoic acid</td>
<td>PFOA</td>
<td>14</td>
</tr>
<tr>
<td>Perfluoroctanesulfonic acid</td>
<td>PFOS</td>
<td>4</td>
</tr>
<tr>
<td>Perfluoropentanoic acid</td>
<td>PFPeA</td>
<td>9</td>
</tr>
<tr>
<td>Perfluoropentanesulfonic acid</td>
<td>PFPeS</td>
<td>0</td>
</tr>
<tr>
<td>Perfluorotetradecanoic acid</td>
<td>PFTA</td>
<td>2</td>
</tr>
<tr>
<td>Perfluorotridecanoic acid</td>
<td>PFTrDA</td>
<td>4</td>
</tr>
<tr>
<td>Perfluoroundecanoic acid</td>
<td>PFUnA</td>
<td>4</td>
</tr>
</tbody>
</table>
Wrap Up

MOVING TARGET
Understand regulatory landscape, have dialog with lab

Methods, blanks, TCLs, RLs

Jim Occhialini
jocchialini@alphalab.com
PFAS Case Studies (Characterization, Treatment, and Fingerprinting)

Steven LaRosa

Program Co-Chair

Technical Leader

Weston & Sampson
WESTON & SAMPSON ENGINEERS INC.

PFAS CASE STUDIES, FINGERPRINTING and TREATMENT

October 3, 2018
Release Sources

- “Traditional” Release Methods
  - Airborne Emissions from Manufacturing Facilities
  - Fire Training Facilities
  - Fire Responses
  - Spills
  - Landfill Disposal

- “Non-Traditional” Releases/Redistribution Methods
  - Land Application of WWTF Sludge
  - On-Site Septic Disposal Fields
  - Irrigation
Case Study: Bennington
Case Study: Bennington

- Industrial Plant operated in North Bennington from 1970 through 2002. During its operation the facility primarily applied PTFE (Teflon) coatings to fiberglass fabrics by dip coating the fabrics in a liquid bath of micron size PTFE particles and various additives (including PFOA) followed by ovens to dry and melt the Teflon onto the fabric.
Case Study: Bennington

- Airborne Release Dominates Initial Distribution of Contaminants
- Spills and Dumping
- Multiple Methods of Redistribution Exist
  - Domestic Septic System Discharges
  - WWTF Discharge
  - Waste Disposal in Landfill
  - Sludge Spreading
- Residual “Source” Remains in Shallow Soils Throughout Area
- “Recycling”/Redistribution is Major Confounding Factor in Impact
Case Study: Bennington

- Impacted Media
  - Shallow Water Supply Wells
  - Deep Water Supply Wells
  - Shallow Soils
  - Surface Waters
  - Sediment
  - Fish
  - WWTF and Domestic Sludges
  - Residents
Case Study: Bennington

• 590 Wells Sampled
• 270 Wells > 20ppt,
• 80 Wells < 20ppt.
• 203 Wells ND.
  – 1st Resampling of 175 initially <20 ppt water
    • Approx. 10% reported as >20 ppt during.
  – 2nd Resampling of 115 <20 ppt water supplies
    • Another 10% reporting as >20 ppt
  – 3rd Resampling of 115 <20 ppt water supplies
    • Another 10% reporting as >20 ppt
• Currently >300 POET systems installed
• Expansion of 2 public water systems occurring
• More sampling being performed to define area of impact
Case Study: Burrillville
Case Study: Burrillville

Groundwater Quality Standard
PFOA & PFOS = 70ng/L (ppt)

RIDPH and Brown sampled 38 small public water systems
- Several between ND and 70 ppt
- Oakland Association public well impacted at >100 ppt

Immediate RIDEM Response
- All Oakland Association users given spring water deliveries
- All private water supply wells in a ¼ mile radius of Oakland Association Well
- Public meeting to inform impacted customers and nearby private well users
- Feasibility for extension of neighboring public water system to affected residences evaluated
Case Study: Burrillville

Potential PFAS Source Identification
– Similar to Phase I Environmental Site Assessment Research
– Multiple Potential Sources Identified

Initial Private Drinking Water Well Data Plotted via GIS
– Developed a Conceptual Site Model for PFAS makeup and distribution.
– Identified area for field data collection based on CSM to isolate source(s).

Targeted Site Investigation
– Single Mobilization
– Collection of discrete interval soil and groundwater samples
  • (shallow, intermediate, atop bedrock)
– Installed permanent monitoring wells
– Data evaluation and reporting
Case Study: Burrillville

- PFAS identified characteristic of AFFF
- Multiple PFAS quantified on soils at very low concentrations
- Shallow and Bedrock aquifer plumes are centered around Fire Department Building
  - AFFF stored on site
  - Fire Department officials report no AFFF training on site
- Review of Fire Department construction plans indicate storm water infiltration gallery collects floor drains and parking lot waters
  - Contaminated equipment washdown water and inadvertent spills enter the infiltration gallery
  - The stormwater infiltration gallery has intermittent shallow groundwater table beneath it. Infiltration waters directly enter bedrock when shallow groundwater is not present.
- More site characterization is needed to fully delineate impacts and determine remediation actions.
Source Characterization
“Fingerprinting”
Release Sources

- **“Traditional” Release Methods**
  - Airborne Emissions from Manufacturing Facilities
  - Fire Training Facilities
  - Fire Responses
  - Spills
  - Landfill Disposal

- **“Non-Traditional” Releases/Redistribution Methods**
  - Land Application of WWTF Sludge
  - On-Site Septic Disposal Fields
  - Irrigation
Composition of Releases

Thousands of compounds and compound mixtures are precursors to PFAS
The Precursor Problem
The Precursor Problem – TOP Assay

MW-9

Pre-Treatment
Post-Treatment

MW-9

PFBA  PFPeA  PFHxA  PFHpA  PFOA  PFBS  PFHxS  PFHpS  PFOS
The Precursor Problem – TOP Assay

MW-9

PFBA

PFPeA

PFHxA

PFHpA

PFOS

PFHpS

PFHxS

PFBS

PFOA

Pre-Treatment

Post-Treatment
Treatment Alternatives
Treatment Methods

- Lets Go Back To The 1980s!!

  - Groundwater Pumping for Containment
  - “Muck and Truck”
  - Granular Activated Carbon Treatment
Treatment Methods

- **Granular Activated Carbon** (long chains)
  - Calgon Filtersorb 400
- **Resin based system showing promise** (long and short chains)
- **No real in-situ destructive processes proven in field scale testing**
- **EPA has only approved high temp thermal destruction for waste**
- **Thermal treatment and recycling of GAC is being performed**
Treatment Methods

• **Granular Activated Carbon**
  – Arsenic levels higher than MCL for first few bed volumes
  – Must have disinfection after GAC
  – Other non target compounds can reduce GAC efficiency (Fe, Mn)
  – Flow and concentration variability confounds determining capacity/life span of GAC without frequent sampling

• **Proprietary Resins**
  – Good for short and long chain
  – Other non target compounds do not impact
  – Backwash likely a waste
Treatment Methods

GAC - PFOS

IX - PFOS
Questions?
RIDEM Regulatory Perspective on PFAS

Nicholas Noons

Sanitary Engineer
RIDEM
Regulatory Update on PFAS

Nicholas Noons, PE

Rhode Island Department of Environmental Management
Previously Identified Impacts

- Sampling for PFAS conducted at Naval Station (NAVSTA) Newport in advance of property transfer at Former Melville Defense Fuel Support Point (DFSP) in December 2015
  - PFAS detected in groundwater in ug/L (ppb) range associated with AFFF Fire Suppression Infrastructure (>20 ppb in some locations)
  - Base-Wide Preliminary Assessment and Site Inspection ongoing.
    - PFAS detected at nearly all sites sampled to date.

- Third Unregulated Contaminant Monitoring Rule (UCMR3)
  - Limited to six compounds and large public water systems (>10,000)
  - Two detections in supply wells in RI
Rhode Island Department of Health (RIDOH) initiated a state-wide sampling effort of small public water systems, license bottlers, and licensed childcare facilities.

Collaborative effort with RIDEM and Brown University Superfund Research Program (Dr. Jennifer Guelfo)

Focused on sampling those systems within one mile of a potential PFAS source.
2017 Surveillance Monitoring Study

- Potential Sources Considered
  - Airports
  - Fire Training Areas
  - EPCRA Tier II
  - Industrial Facilities with certain NAICS Codes
  - DOD Facilities and NPL Sites
  - Electroplating Operations
  - Oil Terminals (Tank Farms)
  - Wastewater Lagoons
  - Emergency Response Incidents (Limited information)

- Team from Brown University conducted separate geospatial analysis of potential impacts across the State
Brown University Geospatial Risk Evaluation
Study Results

- < MRL: 26 water systems
- Detected < 35 ng/L (ppt): 8 water systems
  - 4 - 24 ppt (Average and Median = 13 ppt)
- 35 – 70 ppt: 1 water system
  - Raw 43.2 ppt, Treated (GAC) 11.0 ppt
  - Has since connected to municipal water
- > 70 ppt: Oakland Water Association, Inc.

*Duplicate samples taken from all PWS and all private wells in Oakland were sent to Colorado School of Mines for high-resolution analysis.
Oakland-Mapleville Fire Dept.
Follow-up Investigations

- RIDEM conducted follow-up sampling of private wells in the vicinity of public water systems that tested positive for PFAS
  - Funding authorized through Pre-Remedial Program.
  - Two investigations ongoing… those locations with highest density of private wells in ¼ mile radius.

- RIDOH is currently planning second round of public well sampling
  - Approximately 30% of PWS sampled thus far.
  - Include additional potential sources (i.e. fire stations)
Other Initiatives

- Waste Facilities Management Program will require all landfills to sample for PFAS.
  - RCRA and Solid Waste Stakeholder Meeting in June, 2018
  - Specific requirements (i.e. Site Remediation and Brownfields Program is requiring sampling where warranted on new and active sites.

- Site Remediation and Brownfields Program is requiring sampling where warranted on new and active sites.
Current Regulations in RI

- RIDEM adopted EPA Health Advisory of 70 ng/L (ppt) combined PFOA/PFOS for groundwater classified as GAA or GA (presumed safe for drinking without treatment)
  - *Groundwater Quality Rules, Rule 11.2.2*
    - “…For a substance not listed in Table 1, the groundwater quality standard for class GAA and GA groundwater shall be determined by the Director on a case-by-case basis using United States Environmental Protection Agency health advisories and other public health information.”
EPA announced a series of PFAS Community Engagement Events in affected communities throughout the US

First event held in Portsmouth, NH on June 25th and 26th.

- Calls from States and Community groups to:
  - Treat PFAS as a class of compounds (similar to PCBs)
  - Classifying PFAS as a Hazardous Substance
  - Federal Maximum Contaminant Level (MCL)
The PFAS Treatment Lifecycle: From Analytical Evaluation to Media Destruction

AnnieLu DeWitt

Business Development Manager
Remediation Technologies
Clean Harbors
The Lifecycle of a PFAS Project

RI EBC Presentation
October 3rd, 2018
PFAS are per and poly-fluorinated chained carbon compounds

They are used to make fabrics water-proof
Non-stick cookware
AFFF (Aqueous Film Forming Foams)
Popcorn Bags
Post-It Notes
Countless Manufacturing Processes
PFAS Is a broad term used to encompass per-fluoroalkyl substances and poly-fluoroalkyl substances. There are many synonyms for the same compounds. Nomenclature of organic chemistry is similar to dialects of the same language. Therefore, if possible you use CAS numbers to simplify the possible confusion of having different methods of nomenclature to reference the same analyte.

• Per-fluoroalkyl substances- subset of PFAS that describes fully substituted alkyl chains where fluorine replaces the hydrogen.

• Poly-fluoroalkyl substances- subset of PFASs that describes compounds where not all of the hydrogens have been substituted with fluorine.

• There are over 2000 known PFAS compounds. PFOA and PFOS are just two of the PFAS. The others until identified can be considered as “dark matter” possibly present but not qualified or quantified.
History of PFAS Production

• In 1938 at Dupont in Deepwater, NJ Teflon was created by accident in a failed refrigerant experiment. The waxy material produced proved to be the most slippery material in existence.

• 1951 Dupont makes C8 to make Teflon and related polymers at the Washington Works plant near Parkersburg, W. VA and by Minnesota Mining (3M)

• 1956 3M begins selling Scotchgard protector

• 1962 FDA approval for Teflon cookware

• 1967 FDA approval of Zonyl for use in food packaging
Commercial and Consumer Products containing PFAS

- paper and packaging
- clothing and carpets
- outdoor textiles and sporting equipment
- ski and snowboard waxes
- non-stick cookware
- cleaning agents and fabric softeners
- polishes and waxes, and latex paints
- pesticides and herbicides
- windshield wipers
- paints, varnishes, dyes, and inks
- adhesives
- medical products
- personal care products (for example, shampoo)
Where Are They Found

- DoD sites
- Municipalities Drinking Water and Wastewater
- Landfills
- Airports
- Superfund Sites
- End-user Industrial Clients
- Plating Facilities
- Biosolids
- Fire Department Training Centers
Project LifeCycle Stages

- Identify- Characterize water with applicable test methods
- Pilot Study
- Define Project Objectives
- Select Best Fit Approach
- Choose Equipment
- O&M /Service System
- Final Deposition (landfill, reactivation, incineration)
Identification

- Analytical Lab Choice- experience is important. For example, multiple runs may be required to meet low detection levels if there are high concentrations for other PFAS compounds. 6:2 FTS dwarfing PFOS

- Choosing Appropriate Compound List- DoD list, not all labs have GenX standards

- Currently modified 537 is not standardized across laboratories. A new method is being developed by EPA that will create standardization between laboratories

- Test for other analytes that might interfere with adsorption and ion exchange. TOC, Fe, PO4

- TOP Assay- Total Oxidisable Precursor Assay analytical method helps to identify “dark matter”
Examples of C8

Generic PFC structures. The 8-carbon (8C) structures are shown. The 8C, or "long-chain" structures are generally the most persistent.
Unidentified PFAS Compounds

• Unidentified PFAS compounds can be considered “dark matter” they consume media and shorten life expectancy of media

• Double-edged sword low detection limits means very selective identification

• Top Assay offers ability to gently oxidize and break compound down to base structures that can be measured. Not qualitative but helps with quantitation of unknown competing analytes for removal
Pilot Study

Once analytical is evaluated a pilot study demonstrates a scaled down version of a proposed full scale system. It also allows for evaluation of systems that have variability in influent over time. Especially useful in production facilities where influent varies between batches and processes. Pilot studies also allow for competitive adsorption to be identified and more accurate exchange rate estimations for media.
Define Project Objectives

• Most important stage
• Requires communication of limits to be achieved 2ppt, 70ppt for PFOA, PFOS combined, GenX, PFNA, combined list of compounds to not exceed 70 ppt
• Media requirements, Is GAC the only acceptable technology for a municipality
• Discharge permits, pH spikes from treatment
• Space Constraints sizing for 10-12 minute EBCT per vessel means big vessels
Select Best Fit Approach

• Balancing cost and performance
• Depending upon concentration and flow there will be a best fit solution
• For example, very low flow and high concentration may be best for straight incineration
• Very high concentration and high flow may be best for a resin application. Smaller vessels and higher capacity for media.
• Moderate concentrations and medium flow is where other considerations will sway which approach makes the best sense for a project. For example, remote location may dictate remote monitoring and high capacity media in a conex box.
Current Options for Treatment

- **GAC** - Widely accepted treatment option for PFOA and PFOS
- **Resin** - Different resins are good options for longer chained compounds, PFOA, PFOS and for shorter chained PFAS that are poorly adsorbed by GAC. Shorter EBCT
- **Oxidation** - has shown effectiveness of breaking down longer chained compounds
- **Incineration of water**
- **Additives** - Effective for reducing PFAS in highly concentrated waste streams
Choose Equipment

When choosing equipment for a project it is important to make the most of the available resources. Weighing rental and purchase decisions. Many times we have customers choose to rent equipment in the beginning for PFAS projects. There is hesitation to invest in a solution that may evolve with changing regulations. Guidance from states is increasingly lower reporting levels. VT, MI, NJ, CT, MA, RI, NH, NC, NY
O&M/ Service

- With PFAS projects analytical is an important part of the operation and maintenance program. Proper sampling, monitoring for breakthrough and performance confirmation.
- Vessel swapping or on-site service. Remote locations can benefit from a vessel exchange program for lower flow applications.
- Documentation of variables in system, flow, pH, pressure drop assist with optimizing treatment.
Final Deposition of Media

• There are currently three options for media at the end of it’s lifecycle

• Landfill- many landfills are not accepting PFAS material. However, the Sarnia landfill which incinerates its leachate is an option

• Reactivation- Investigate to make sure temperature is adequate to destroy the C-F bond

• Incineration- Complete destruction of media is increasingly the choice for customers