AFFF, Analytical Concerns and Data Assessment

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Poly- or perfluorinated alkyl substances (PFAS) or Perfluorocarbons (PFC) – General term for all chemicals formed from carbon chains with fluorine substituting some/all of the hydrogens on the chain

- **C-F bond** very strong
- **Unique properties** – repel water and oil, surfactant, stable
- **Diverse and complex** chemistries based on product use
- **Precursors** FTS (Fluorotelomer Sulfonate), PAP (Polyfluorinated Alkyl Phosphate Esters), PFPA (Polyfluorinated phosphonic acid), FTOH (Fluorotelomer alcohol) can all degrade to Carboxylates and Sulfonates
What is Aqueous Film Forming Foam (AFFF)

- Only 3% of fluorochemical production is for AFFF
  - 75% of AFFF production used by military
  - 25% used by oil refineries, municipal airports & fire stations, tank farms

- Complex, proprietary mixtures
- PFAS a few % in mixture but still g/L levels

Brief history
- Mid 1960s – 1970: 3M sole source supplier of AFFF
- 1973: National Foam
- 1976: Ansul
- 1994 to present: Angus, Chemguard, Fire Service Plus

Bottom line = multiple AFFFs used at most sites

Types of Firefighting Foams

- **CLASS A Foams** - Developed in the 1980s for fighting wildfires. Also used for structure fires.

- **CLASS B Foams** - Used for flammable and combustible liquids and gases; petroleum greases, tars, oils and gasoline; and solvents and alcohols.

  Several Class B foams contain PFAS.

  AFFF are the primary Class B foam that contain fluorosurfactants.

Source: S. Thomas, Wood plc, used with permission from *Aqueous Film-forming Foam Fact sheet (ITRC, 2018)*
Types: Legacy PFOS AFFF

- **ECF chemistry**
  - Homologous series (C2-C13)\(^1\)
  - Branched & linear isomers (30:70)\(^2\)
    - If exclude branched isomers, concentrations underestimated (biased low)
  - Crude synthesis, many side products
  - **PFAS composition**
    - 89% PFSAs (e.g., PFOS) in 3M AFFF
    - 1.6% PFCAs (e.g., PFOA)
    - 9.4% other forms with multiple charged groups: zwitterionic (+/-) and cationic (+)

Types: Modern Fluorotelomer AFFFs

- In response to EPA 2010/2015 Voluntary PFOA Stewardship Program
- Contain almost exclusively short-chain PFAS (C6)
- Currently considered lower in toxicity and significantly reduced bioaccumulation potential compared to long-chain PFAS

1. May still contain trace quantities (ppb levels) of PFOA (or precursors) as by-products of the manufacturing process
- Some are less bioaccumulative, but are still as environmentally persistent as long-chain substances or have persistent transformation products


Alternatives to AFFF

- Current Mil-Spec 24385, used by both the DoD and FAA, requires the use of fluorosurfactants, i.e. AFFF

- However, Fluorine-free alternatives may be considered for other industry users. Key factors include:
  - The nature of the firefighting properties of the foam
  - The nature of the emergency
  - The risk to life, public safety, and property
  - Potential environmental, public health, and financial liabilities of using the foam

- Firefighting industry best practice for Class B foams calls for the use of fluorine-free foam (FFF) for testing and training

PFAS in an AFFF-impacted water supply

- PFAS analyzed by LC-QToF-MS
- 30 PFAS observed using HRMS library and/or authentic standards
  - 5 perfluorocarboxylates (C4-C8)
  - 6 perfluorosulfonates (C3-C8)
  - 2 fluorotelomer sulfonates (4:2 & 6:2)
  - 4 perfluoroalkyl sulfonamides (C3-C6)
  - 11 recently discovered polyfluorinated PFAS
  - 2 PFOS-like derivatives

Other PFAS are likely present in AFFF-impacted drinking water supplies

1Xiao et al., 2017. *ES&T* 51: 6342-6351

Figure courtesy of C. Higgins
Current US Regulations for AFFF

- FAA Reauthorization Act of 2018 (HR 302)- signed Oct.5, 2018 -allow use of F3 within 3 yrs

- New York-
  - 6 NYCRR Part 597 identifies PFOS/PFOA as hazardous substances.
  - Includes storage and registration for class B foams and reporting for spills (NYDEC 2017).

- Washington-
  - Law restricts the sale and use of Class B foams that contain PFAS.
  - Exceptions for FAA airports, military, petroleum terminals, oil refineries, chemical plants

- Take-Back Programs
  - Several states (MA, NY, VT, MI [in planning stages]) have programs to assist fire departments in the proper disposal of legacy firefighting foams
  - It includes the identification and disposal of legacy foams


Washington Senate Bill 6413 (2018). Engrossed Substitute Senate Bill 6413. 65th Legislature 2018 Regular Session. March 5 2018
BMPs- AFFF Selection

- Evaluate (in advance) whether a Class B fluorine-free foam (FFF) can be used
- Use only with significant flammable liquid hazard with risk for public safety or significant property loss.
- Consider adopting a two-foam approach

HAZARD
Anything that has the potential to cause harm

RISK
How great are the chances someone or something will be harmed by the hazard

BMPs- AFFF Storage

- Develop inventory and tracking system
- Designate transfer and storage areas
- Design storage tanks to minimize evaporation of concentrate
- Properly maintain foam systems
- Ensure compatibility of foams before change-outs
BMPs- AFFF Use

- Consider the firefighter and public safety first
- Eliminate fluorinated Class B foams for training and testing
- Provide containment, treatment, and proper disposal
- Collect, treat and properly dispose of runoff/wastewater
- Use appropriate PPE
- Keep records of when/where foam is used
- Make note of any sensitive receptors
BMPs- AFFF Planning, Mitigation

- Develop plans and communicate
- Quickly and thoroughly clean up after an AFFF release
- Design new firefighting systems, when needed, to accommodate FFFs
- Prioritize proper education, training, preplanning
BMPs- AFFF Disposal

- Dispose of foam concentrate at an incinerator with appropriate environmental controls
- Monitor developments in new disposal technologies
- Discontinue AFFF donation programs

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

- Immediately cleanup foam and impacted materials
- Gather release information as soon as possible
- Do a visual surface delineation after new release
- Perform field screening after release

Source: open access images – bing.com
Transport in the Vadose Zone

- Chain-length dependent transport
- Sorption: $K_{oc}$ important, but not fully sufficient
- Low volatility
- Surfactant properties – PFAS **likely** adhere to air/water interfaces

Source: ITRC Environmental Fate and Transport fact sheet, Figure Adapted from figure by L. Trozzolo, TRC, used with permission
Atmospheric Transport

- Particularly important for industrial sites with stack emissions
- Atmospheric deposition around industrial sites = large impacted areas

Source: ITRC Environmental Fate and Transport fact sheet, Figure Adapted from figure by L. Trozzolo, TRC, used with permission
Transport in Groundwater

- Readily transported once in groundwater
- Composition may be impacted by remedial activities

Source: ITRC Environmental Fate and Transport fact sheet, Figure Adapted from figure by L. Trozzolo, TRC, used with permission
Key Takeaways for Planning Site Investigations

- **Perfluorinated PFAS:**
  - Extremely stable
  - Mobility is chain-length dependent, affected by OC, pH, inorganic cations, etc.

- **Non-polymeric polyfluorinated PFAS (precursors) are varying in their stability**
  - Much more variable in terms of transport

- **Surfactant properties may lead to increased concentrations at air/water interface or at water/NAPL interface**

- **Source zones may be significant: long-term discharge potential**
  - Exceptionally low criteria + high transport potential: investigation areas may be larger than you’re used to
  - Oxidizing remedial techniques (ISCO, air sparge, aerobic bioremediation) can transform precursors to persistent PFAAs
Analysis of PFAS

**USEPA Method 537.1** (version 1.0, 2018)
- Only applicable to Drinking Water samples
- No Recovery Correction
- Analyte list limited - 18 PFAS (14 PFAS required by Method 537 + 4 added compounds)
- New DW method *(Summer 2019)* - 25 PFAS includes 11 “short chain” compounds

**ASTM D7979-17 & ASTM D7968 - 17a** (2017)
- Non-Drinking water Aqueous & Soils
- No Recovery Correction
- 25 PFAS
Analysis of PFAS

**SW-846 Method 8327 (Summer 2019)**
- Direct Injection
- Non-Drinking Water Aqueous
- 24 PFAS
- No Recovery Correction

**SW-846 Method 8328 (late 2019)**
- Solid Phase Extraction/Isotope Dilution (SPE-ID)
- Non-Drinking Water Aqueous & Solids
- 24+ PFAS
- Recovery Correction

**Lab-Specific Methods**
- Modifications to the above methods
- Vary lab-to-lab
Analysis of PFAS

Total Oxidizable Precursors (TOP)

- Comparison of LCS-MS/MS results for sample pre- and post-oxidation
- Useful for evaluating Precursor potential – may be biased low

Proton Induced Gamma-ray Emission (PIGE)

- Non-destructive technique for Total Fluorine

Adsorbable Organic Fluorine /Combustible Ion Chromatography (AOF/CIC)

- Destructive technique for Total Fluorine
Analytical Issues Begin With Collection of the Samples

DoD Requirements for Personnel Collecting Samples

- No Post-it Notes; No Notebooks; No Sharpies/Markers; No Gore-Tex or Tyvek material; No Cosmetics, insect repellants, sun block, lotions worn unless 100% natural; No Waterproof material; Nitrile Gloves MUST be worn at all times

All sources of possible cross-contamination need to be eliminated and/or Evaluated

- Use Disposable Equipment if Possible
- Decontaminate equipment, if necessary, with Alconox or Liquinox using Lab Certified “PFC-free” water
- Samples should be collected in High Density Polypropylene (HPDE) with Unlined HDPE screw Caps (Teflon-lined caps MUST NOT be used)
- Trip Blanks and Field Blanks should be collected

Field Sampling Protocols to Avoid Cross-Contamination During Water Sampling for Perfluorinated Compounds (PFCs); enclosure to Navy Drinking Water Sampling Policy for Perfluorochemicals Perfluorooctane Sulfonate and Perfluorooctanoic Acid, N45 Ser/15U132432, 14 SEP 15.
Types of Data Reports

1. Summary Data Package - *Recommended*
   - Narrative explaining Method of Analysis and any issues with sample receipt and analysis
   - Sample Results (including FB and FD) + Surrogate recoveries
   - QC results (MB, LCS, MS, & MSD or FD)
   - Executed Chain-of-Custody

2. Full Deliverable – all of above + raw data

3. Result Forms/Tables only – *Not Recommended*
Specific Laboratory QA/QC For PFAS

- Sample preservation
- Sample Holding Times / Analytical Batches (≤ 20 samples)
- QC Samples required for each Analytical Batch:
  - Laboratory Reagent Blank (LRB) / Method Blank (MB)
  - Laboratory Fortified Blank (LFB) / Laboratory Control Sample (LCS)
  - Laboratory Fortified Sample Matrix (LFSM) / Matrix Spike (MS)
  - Laboratory Fortified Matrix Sample Duplicate (LFSMD) or Field Duplicate (FD)
- Surrogates added to all samples & QC prior to extraction
- Internal Standards added to all extracts prior to analysis
Recovery Surrogates vs. Isotope Dilution Surrogates

Similarities:
Added directly to the sample prior to preparation and analysis

Differences:

Recovery Surrogates
• Surrogates used to infer accuracy of preparation and analysis
• Internal Standards spiked prior to analysis to quantitate surrogates and target compounds

Isotope Dilution Surrogates
• Labeled Isotopes of most target compound (e.g., 13C4-PFOA, 13C4-PFOS) used for quantitation
• Loss in Isotope mirrors loss of Unlabeled compound = data are Recovery-Corrected
Recovery Surrogates vs. Isotope Dilution Surrogates

**Non-Isotope Dilution Methods**

\[
\text{Compound Concentration} \equiv \frac{\text{Compound Response}}{\text{Internal Standard Response}}
\]

Compound = Target PFAS
Rec. Surrogate = Recovery Surrogate

**Isotope Dilution Methods**

\[
\text{Compound Concentration} \equiv \frac{\text{Compound Response}}{\text{ID Surrogate Response}}
\]

\[
\text{ID Surrogate Concentration} \equiv \frac{\text{ID Surrogate Response}}{\text{Internal Standard Response}}
\]

Compound = Target PFAS
ID Surrogate = Isotope Dilution
Surrogate Recovery Problems

- Surrogate recovery below criteria: potential low bias in data
  - Due to lab error or matrix effects
- Surrogate recovery above criteria: potential high bias
  - Due to interferences or instrument issues

• Non-Isotope Dilution Analysis = Detected and non-detected results may be uncertain

• Isotope Dilution Analysis = Only compound(s) associated with Isotope affected. Uncertain whether data are biased at all since results are recovery corrected
Data Comparability - PFAS

Factors Affecting Comparability

• Changes in Field Collection Techniques
  Elimination or introduction of PFAS during Sampling
• Not using Isotope Dilution for Recovery Correction of data
  Sample data may vary by ±30% based on Surrogate recovery acceptance limits of 70-130%
• Degradation of Precursors
  Formation of compounds of concern over time
• Not including Branched Isomers in reporting of data
  Historic data may not have included branched isomers
• Sensitivity differences in data sets (QLs not the same)
• Compound names being reported differently
## Usability Evaluation Example

<table>
<thead>
<tr>
<th>Sample</th>
<th>Advisory Level (ng/L)</th>
<th>Result (ng/L)</th>
<th>Surrogate %R</th>
<th>LCS %R</th>
<th>MS/MSD %R/RPD</th>
<th>Issue?</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>70</td>
<td>5 U</td>
<td>High</td>
<td>High</td>
<td>OK</td>
<td>No: Non-detect accurate as reported</td>
</tr>
<tr>
<td>B</td>
<td>70</td>
<td>66</td>
<td>OK</td>
<td>OK</td>
<td>%R low</td>
<td>Yes: result may be biased low and really &gt;70 ng/L</td>
</tr>
<tr>
<td>C</td>
<td>70</td>
<td>63</td>
<td>Low</td>
<td>High</td>
<td>OK</td>
<td>Maybe: conflicting bias</td>
</tr>
<tr>
<td>D</td>
<td>70</td>
<td>110</td>
<td>Low</td>
<td>OK</td>
<td>High</td>
<td>No: conflicting bias but 110 &gt;70 ng/L</td>
</tr>
</tbody>
</table>

Must evaluate the cumulative effect of **all** Quality Control to determine Usability and whether an Action Level has been exceeded.
Conclusion

- Overall Quality depends on cumulative Quality from sampling through analysis

- Specifically for PFAS – Field Collection & Analytical Method differences can introduce uncertainty

- Guidelines for Evaluating Quality
  - Data Review and Validation Guidelines for Perfluoroalkyl Substances (PFASs) Analyzed by Method 537, EPA 910-R-18-001 (November 2018)
  - Table B-15 of QSM 5.2 Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version 5.2 (DOD/DOE, 2018)
ITRC PFAS Resource

- Seven Fact Sheets (available now) and Technical Guidance Document (late 2019)
  - History and Use
  - Nomenclature Overview and Physicochemical Properties
  - Regulations, Guidance, and Advisories
  - Environmental Fate and Transport
  - Site Characterization Considerations, Sampling Techniques and Laboratory Analytical Methods
  - Remediation Technologies and Methods
  - Aqueous Film Forming Foam

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