PFAS: Analytical Challenges and Best Practices

Karla Buechler – Corporate Technical Director
PFAS - Outline

Introduction:
What are PFAS?
Exposure, Toxicity and Risk
Formation, Chemistry
Sources, Exposure Routes
Regulatory Progress

Sampling & Analytical Challenges:
Which Method Do I Need?
What is Isotope Dilution?
Branched and Linear Isomers
What is the TOP Assay?
Replacement Chemicals
Field Screening
What’s Next?
Briefly - What are PFASs?

Class of synthetic compounds containing thousands of chemicals formed from carbon chains with fluorine attached to these chains.

The C-F bond is the shortest and the strongest bond in nature.

PFOS and PFOA are fully fluorinated and the most common perfluorinated chemicals (PFCs).

Persistent and resistant to degradation
Found in soil, air and groundwater.
Exposure, Toxicity and Risk

Human exposure is primarily from:
- food (fish) and air

Exposure continues beyond phase out:
- due to persistence

Half-lives in humans:
- 2 to 9 years

PFOA associated with:
- liver, pancreatic, testicular, mammary gland tumors in animals.

PFOS associated with:
- liver and thyroid cancer in rats.

PFOA and PFOS associated with:
- cancers in humans; toxicology still being studied
PFAS Formation

➢ **ECF Reaction**: Process yields a mixture of B/L isomers

\[
C_8H_{17}SO_2F + 34HF \rightarrow C_8F_{17}SO_2F + 17H_2 \text{ (POSF)}
\]

➢ **Telomer Reaction**: Process yields 100% linear isomers

(Synthesis of building blocks leading to fluorotelomer alcohols)

\[
\begin{align*}
F(CF_2)_2I & \rightarrow F(CF_2)_nI \\
\text{PFEI} & \quad \text{Telomer A} \quad \text{Telomer B} \quad \text{Telomer alcohols}
\end{align*}
\]

\[
+ CF_2=CF_2 \quad + CH_2=CH_2
\]
Chemical Structure
Why is it Important?

Perfluoroalkyl Carboxylate
Perfluoroalkyl Sulfonate
Perfluoroalkyl Sulfonamido Amines
Fluorotelomer Sulfonates
Perfluoroalkyl Sulfonamido acetic acid amine
3 Unique Chemical Properties

Hydrophobic and Lipophobic

Hydrophilic and Electrostatic

Interfacial Behaviors
Major Sources to the Environment

- Industrial Sites – Manufacturing and secondary industries
- Any locations where AFFF was stored or used
- Landfills – lined and unlined. Leachates
- WWTP and Biosolids used as agricultural amendments
- Many non-point sources
How are we exposed to them?
What have we done about it?

- **2002**: Voluntary phase out of PFOS
- **2006**: PFOA Stewardship Program
- **2015**: Lifetime Health Advisory Limits 70ppt for PFOA/PFOS
- **2016**: Stewardship Program Complete
- **2018**: USEPA National PFAS Summit
- **2018**: ATSDR Draft Toxicological Profile
Regulatory Challenges and New Developments

- Lack of regulatory guidance for most matrices and most PFAS compounds
- Wide variety of detection limits and analyte lists
- Lack of published method – expect multi-lab validated methods in 2019
- DoD QSM 5.2 published – changes are significant
## State Drinking Water Limits

<table>
<thead>
<tr>
<th>State</th>
<th>PFOA ppt</th>
<th>PFOS ppt</th>
<th>Ratified Y/N</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Carolina</td>
<td>NA</td>
<td>NA</td>
<td>N</td>
<td>&quot;GenX&quot; 140 ppt</td>
</tr>
<tr>
<td>Nevada</td>
<td>667</td>
<td>667</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>AZ, AL, CO, ME, MI, RI, WV</td>
<td>70</td>
<td>70</td>
<td>Varies</td>
<td>Adopted HAL from 2016</td>
</tr>
<tr>
<td>CT &amp; MA</td>
<td>70</td>
<td>70</td>
<td>N</td>
<td>PFNA, PFHxA, PFHpA</td>
</tr>
<tr>
<td>Alaska</td>
<td>70</td>
<td>70</td>
<td>N</td>
<td>PFBS, PFNA, PFHxA, PFHpA</td>
</tr>
<tr>
<td>Minnesota</td>
<td>35</td>
<td>27</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>New Hampshire</td>
<td>38</td>
<td>70</td>
<td>N</td>
<td>PFNA 23ppt</td>
</tr>
<tr>
<td>Vermont</td>
<td>20</td>
<td>20</td>
<td>Y</td>
<td>PFNA, PFHxA, PFHpA</td>
</tr>
<tr>
<td>California</td>
<td>14</td>
<td>13</td>
<td>N</td>
<td>Interim Notification Levels</td>
</tr>
<tr>
<td>New Jersey</td>
<td>14</td>
<td>13</td>
<td>N/Y</td>
<td>PFNA 13 ppt</td>
</tr>
<tr>
<td>New York</td>
<td>10</td>
<td>10</td>
<td>N</td>
<td></td>
</tr>
</tbody>
</table>

USEPA Health Advisory Limit = 70 ppt

https://pfas-1.itrcweb.org/fact-sheets/
## State GW/SW Limits

<table>
<thead>
<tr>
<th>State</th>
<th>PFOA ppt</th>
<th>PFOS ppt</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oregon</td>
<td>24,000</td>
<td>300,000</td>
<td>SW; PFNA, PFHpA, PFOSA</td>
</tr>
<tr>
<td>North Carolina</td>
<td>2,000</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Texas</td>
<td>290</td>
<td>560</td>
<td>PCLs for 16 PFCs</td>
</tr>
<tr>
<td>Maine</td>
<td>130</td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>PA, RI, DE, IA, NH</td>
<td>70</td>
<td>70</td>
<td>PFNA, PFHxA, PFHpA</td>
</tr>
<tr>
<td>Connecticut</td>
<td>70</td>
<td>70</td>
<td>PFNA, PFHxA, PFHpA, PFBS</td>
</tr>
<tr>
<td>Alaska</td>
<td>70</td>
<td>70</td>
<td>PFNA, PFHxA, PFHpA, PFBS</td>
</tr>
<tr>
<td>Minnesota</td>
<td>35</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>New Hampshire</td>
<td>38</td>
<td>70</td>
<td>PFNA, PFHxS</td>
</tr>
<tr>
<td>Vermont</td>
<td>20</td>
<td>20</td>
<td>PFNA, PFHxA, PFHpA</td>
</tr>
<tr>
<td>Michigan</td>
<td>420</td>
<td>11</td>
<td>SW; 70ppt GW</td>
</tr>
<tr>
<td>New Jersey</td>
<td>10</td>
<td>10</td>
<td>13 ppt for PFNA</td>
</tr>
</tbody>
</table>

https://pfas-1.itrcweb.org/fact-sheets/
LOOKING BACK

2018

LOOKING AHEAD

2019

- Additional state limits
- Method 537.1
- QSM 5.2
- Published standardized methods
- Target analyte list
- ATSDR toxicology report finalized?
- EPA draft toxicology report finalized?
- Groundwater Cleanup Criteria?
- Hazardous Substance Designation?
- Formal Guidance?
Why are PFAS an Analytical Challenge?

- Globally distributed
- Present at low concentrations and high
- Contamination and analyte loss at all stages of collection and analysis
- Lack of authentic standards
- Unusual physical and chemical properties
- Lack of consensus “best” method for non-DW
Sampling – Manage Artifacts

- Collected in HDPE bottles fitted with unlined polyethylene screw caps.
- The field crew – personnel hygiene, clothing, food products, sunscreens and insect repellants.
- Sampling equipment – avoid fluoropolymer bailers, pump bladders, tubing, valves etc.
- Sample collection – wash hands, wear nitrile gloves, do not filter samples, add field QC samples routinely
- Avoid food or drink on-site
- Limit visitors during sample collection
Managing Loss/Adsorption

- Many PFAS are surface active, which cause them to stratify, adsorb to surfaces
- Extraction type – whole bottle or subsample play a more significant role than material type
- PFAS can adsorb to the filtration equipment. PFAS in the dissolved phase can also adsorb to the filter material
- Unless the samples are analyzed immediately adsorption to glass vials may occur
PFAS Analytical Methods

- Manufacturer’s methods were adopted by the environmental industry – SW-846 Method 8321
- EPA expanded manufacturer’s method for drinking water - Method 537 – Labs commercialized 537
- Labs had to modify Method 537 in order to meet client needs
- Then ASTM Methods published - not widely adopted by industry
- EPA Published Method 537.1
- DoD QSM 5.1 addresses PFAS – then 5.2
Step 1 - Separation chemistry occurs in the LC column
Step 2 – Excess solvent is removed and ions are formed.
Step 3 – Ions travel through the first quadrupole and ion selection occurs
Step 4- Selected ions travel through the second quadrupole where selection occurs again
Hence, tandem MS
Step 5 – A response is measured and reported
What is Isotope Dilution?

- Most accurate and precise calibration method available
- Partial loss of analyte during preparation is compensated for since chemical interferences are not an issue
- Allows for matrix recovery correction – what affects the native analyte will equally affect the isotope
- Correction for signal drift
- Improved qualitative identification – RT shifts

Ideal MS Quantitative Method

Isotope Dilution Mass Spectrometry (IDMS) – use of a isotopically labeled internal standard.

1. Take aliquot
2. Add IS
3. Process Sample
4. Analyze by LC-MS/MS
5. Integrate and calculate areas of IS and analyte peaks – Quantitate using analyte/IS area ratio
1. Sample collection and shipment to the lab chilled in HDPE bottles with DW preservative if appropriate.

2. Measure 250 ml of sample and spike with isotopically labeled target analytes.

3. Prepare SPE, load sample and elute PFAS off the cartridge with an ammonium hydroxide/methanol solution. In line SPE is available.

1. Sample collection and shipment to the lab chilled in HDPE bottles.

2. Measure 5 g of sample and spike with isotopically labeled target analytes. Extract with KOH/MeOH. Shake for 3 hours and sonicate for 12 hours.

3. Prepare SPE, load sample and elute PFAS off the cartridge with an ammonium hydroxide/methanol solution.

Move on to the Analysis
Analysis by Method 537 Mod – Aqueous and Solid Matrices

4. Concentrate PFAS extract to dryness. Add methanol to each, soak and vortex to mix well. Then add water to final composition of 80:20 methanol:water

5. Analyze by LCMSMS using a C18 column with a gradient program using 20 mM ammonium acetate/water and methanol. Mass spec is operated in (ESI) negative ion mode.

Branched and Linear Error

PFOS

PFOA

0.99 vs 1.20 ng/ml
Secondary Ion Transition - PFOS

Standard

Sample
**SW-846 Methods**

- **EPA 8327**
  - Direct Injection, No SPE
  - External Standard
  - Non-potable Water

- **EPA 8328**
  - SPE
  - Isotope Dilution
  - Non-potable Water & Solids

**Guidance, Not Promulgated, It’s Your Choice**
## PFAS Method Comparison Table for Aqueous Matrix

<table>
<thead>
<tr>
<th>Features</th>
<th>Method 537</th>
<th>ASTM D7979-17</th>
<th>TestAmerica Sacramento Method 537M Manual SPE&lt;sup&gt;1&lt;/sup&gt;</th>
<th>TestAmerica Sacramento Method 537M In-line SPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample size</td>
<td>250 mls</td>
<td>Any are allowed (5 mls used in validation)</td>
<td>Same as 537</td>
<td>1 ml</td>
</tr>
<tr>
<td>Holding times</td>
<td>14 days for extraction</td>
<td>28 days for analysis</td>
<td>Same as 537</td>
<td>28 days for analysis</td>
</tr>
<tr>
<td>Matrices</td>
<td>Drinking Water</td>
<td>All aqueous matrices, no DW</td>
<td>All aqueous matrices</td>
<td>All aqueous matrices</td>
</tr>
<tr>
<td>Aqueous Extraction</td>
<td>SPE SDVB</td>
<td>DAI</td>
<td>SPE Waters WAX</td>
<td>DAI</td>
</tr>
<tr>
<td>Analysis</td>
<td>LCMSMS - no confirmation ion</td>
<td>LCMSMS with confirmation ion, if available</td>
<td>LCMSMS with confirmation ion, if available</td>
<td>LCMSMS with confirmation ion, if available</td>
</tr>
<tr>
<td>Mass Spec</td>
<td>ESI Negative ion mode</td>
<td>Same as 537</td>
<td>Same as 537</td>
<td>Same as 537</td>
</tr>
<tr>
<td>Result includes Branched and Linear isomers</td>
<td>Yes, for available standards</td>
<td>Same as 537</td>
<td>Same as 537</td>
<td>Same as 537</td>
</tr>
<tr>
<td>Quantitation</td>
<td>Internal standard</td>
<td>External standard</td>
<td>Isotope dilution</td>
<td>Isotope dilution</td>
</tr>
<tr>
<td>Reporting Limits</td>
<td>(2 ppt - 40 ppt)</td>
<td>(10ppt - 8000ppt)</td>
<td>(2ppt - 20ppt)</td>
<td>(2ppt - 20ppt)</td>
</tr>
<tr>
<td>Isotope Recovery Correction</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>LCS recovery limits</td>
<td>70-130</td>
<td>Default to 70-130 until a multi-lab validation study can be done or lab statistical limits are determined.</td>
<td>70 to 130 for DW, Statistical limits for others</td>
<td>70 to 130 for DW, Statistical limits for others</td>
</tr>
</tbody>
</table>

<sup>1</sup> - Please note that TestAmerica Sacramento's manual SPE method is DoD QSM 5.1 Table B-15 compliant.
Method 537M – In Line SPE (ASTM – Like)

- What is it?
  - Dilute a water sample with methanol and inject a large volume onto a modified UPLC

- What are the advantages?
  - Simplicity – reduced sample manipulation
  - Reduced sample volume (5 mls)
  - Speed, reduced TAT
  - Increased capacity
  - Reduced risk of laboratory background artifacts
Complex Matrices – Biphasic (Leachates, Biosolids, etc.)

Do you want results for the whole sample or the dissolved fraction?

- If whole sample then spike IDAs prior to sample manipulation
- Limited SPE capacity?
- If yes proceed with complex extraction option
- Complex option includes centrifuge and filter.
  Extraction of both fractions and recombine

- If only dissolved fraction
  - Then centrifuge to remove particulate fraction
  - Decant aqueous fraction
  - Spike with IDAs
  - Determine aqueous fraction by LCMSMS
What are Precursors and Why Do We Care?

- Thousands of precursors used in industrial and consumer products
- Some biotransform to make PFAAs
- Some are fluorotelomers
- Most are ionic, either positive, negative or both
- Fate and transport – complex process
What is the TOP Assay?

A new PFAS sample preparation technique

- Conceptually simple chemistry
- Used with 537M not 537
- Pre and Post results
- Indicates unidentified PFAS
How Does it Work in the Environment?

Low levels of discrete compounds are detected

High levels of discrete compounds are detected, which can include PFOA and PFOS

Give me an example:
TOP – How Does it Work in the Laboratory?

PFAA Precursors + OH• + OH• + OH• = PFOA + other PFCAs

85°C

[Image of laboratory equipment]
PFCA Pattern – Me-FOSA Precursor

- PFBA
- PFPeA
- PFHxA
- PFHpA
- PFOA
- PFNA
PFCA Pattern – 8:2 FTS

- PFBA
- PFPeA
- PFHxA
- PFHpA
- PFOA
- PFNA

ppt

PFHpA
Urban Runoff – San Jose, CA

Urban Runoff from SF Bay Area

Fluorinated Replacement Chemicals

- Since 2000, on-going industrial transition to replace LC PFCAs, PFSAs and precursors
- Many alternative chemicals are in use – below regulatory radar
- Unclear whether they are safe for humans or the environment
- DuPont developed patented GenX technology - enables them to make fluoropolymers without PFOA
- GenX is not a chemical it is a process
Emerging Field Screening Methods

- Methylene blue active substance (MBAS) anionic surfactant detection kit
- Fluorous membrane ion-selective electrode (ISE)
- Particle-induced gamma ray emissions (PIGE) spectroscopy
- Adsorbable organic fluorine (AOF)
Conclusions and Future Concerns

- PFAS include thousands of compounds, used in many industries
- Regulations developing in ppt
- Many secondary sources
- Sampling, analysis and data interpretation requires experience
- Remediation can be challenging and conventional approaches can make a site worse
- We need a consensus “best” method
- Analyte lists are growing for discrete methods and may lead to forensics
- Need effective field screening techniques
Experience
• 20 Years of Experience
• Significant Investment in Method Development

Capabilities
• Nations Largest LCMSMS Capacity
• Extensive Analyte List, TOP Assay & Replacement Chemicals

Ease of Use
• Consistent and Defensible Data
• Seamless Data Deliverable
• Nationwide Coverage

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