PFAS: Assessing Laboratory Data Quality

NEWMOA Webinar
April 4, 2019

Nancy C. Rothman, Ph.D.
New Environmental Horizons, Inc.
34 Pheasant Run Drive, Skillman, NJ 08558
Phone: 908-874-5686
e-mail: nrothman_neh@comcast.net
web site: www.neh-inc.com

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
Environmental Fate of PFAS


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
Data Quality Using PARCCS

**Precision**
- Variability, reproducibility
- QC = replicates

**Accuracy**
- bias from “true”
- QC = blanks, spikes, calibration

**Representativeness**
- Data point vs. population
- QC = field duplicates, sample locations

**Comparability**
- Temporal and methodological consistency
- field vs. lab data

**Completeness**
- amount of data planned vs. usable data collected

**Sensitivity**
- Quantitation Limits
- Regulatory Standards
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**

### Method Reference

- Project ID: 6634
- Sample ID: Sample 1 DW
- Sampled: 2/10/2019
- Extracted: 2/23/2019
- Analyzed: 3/5/2019
- Dilution Factor: 1
- Sample Amount: 245 mL
- Matrix: DW
- % Solids: NA

### Units

**CONCENTRATION UNITS:** ng/L

### Analyte List and Results with Data Qualifiers

- **Compound**
- **Result**
- **Acceptance Criteria**
  - **Key:**
    - U - Analyzed but not found.

### Surrogate Recovery Data

<table>
<thead>
<tr>
<th>Surrogate</th>
<th>% Recovery</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>13C2-PFHxA</td>
<td>95%</td>
<td>70-130%</td>
</tr>
<tr>
<td>13C2-PFDoA</td>
<td>80%</td>
<td>70-130%</td>
</tr>
<tr>
<td>J5s-NFOSAA</td>
<td>85%</td>
<td>70-130%</td>
</tr>
<tr>
<td>13C2-HFPO-DA</td>
<td>92%</td>
<td>70-130%</td>
</tr>
</tbody>
</table>
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

Holding Time

• Check sample data sheet for HT acceptance

<table>
<thead>
<tr>
<th>Date</th>
<th>Date</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampled</td>
<td>Extracted</td>
<td>Analyzed</td>
</tr>
<tr>
<td>2/20/19</td>
<td>2/23/19</td>
<td>3/5/19</td>
</tr>
</tbody>
</table>

Date extracted - Date sampled ≤ Preparation Holding Time
Method 537.1 preparation HT = 14 days;
2/23/19 - 2/20/19 = 3 days:
HT OK

Date analyzed - Date extracted ≤ Analytical Holding Time
Method 537.1 analytical HT = 28 days;
3/5/19 - 2/23/19 = 11 days:
HT OK
### Preservation & Holding Time

- Method 537.1 requires addition of **Trizma**
  - Acts as a buffer and removes free-chlorine from Drinking Water samples
- Samples shipped cold (< 10 °C) to lab
- If Preservation not correct or Holding Time (HT) exceeded – potential for loss of PFAS content and false negative results

*If Preservation and/or HT a problem, all results are considered uncertain with possible low bias*

### Detection and Reporting Limits

- **Instrument Detection Limit** (IDL) is the “Best” the instrument can detect
- **Method Detection Limit** (MDL or LOD) is the “Best” the instrument can detect by the method - statistically
- **Quantitation Limit** (QL/RL/LOQ) is the “Practical” level of accurate quantitation – Must be supported by calibration curve and should be < Project Level of Concern
**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

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

\[
\text{Compounds} = \text{Target PFAS}
\]

\[
\text{Rec. Surrogate} = \text{Recovery Surrogate}
\]

Isotope Dilution Methods

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

\[
\text{Compounds} = \text{Target PFAS}
\]

\[
\text{ID Surrogate} = \text{Isotope Dilution}
\]

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
Expanded Analyte List with 4 Precursors at the end of the list

Surrogates (Isotopes) Data

Low 13C9PFNA only impacts PFNA result

Blank Samples

- Method Blank (MB) – lab-generated
  - Evaluates whether contamination may have been introduced by the laboratory
  - Associated with all samples in the Analytical Batch

- Field Blank (FB) / Equipment Blank (EB)
  - Evaluates whether contamination may have been introduced during sample collection and transport
  - Associated with specific field sample results

Compare Blank results to Sample results to evaluate potential lab/field contamination that may cause high bias or false positives in field sample data
Laboratory Control Sample (LCS)

- LCS = Method Blank that is spiked with all the PFAS compounds of interest
- LCS Recoveries = within acceptance criteria as specified in Method or project QAPP
- LCS recovery outside criteria = impact for affected compound for all samples in the Analytical Batch

*Compare LCS results to Method / QAPP acceptance criteria to evaluate potential accuracy / bias in associated Sample data; may qualify results*

Example LCS Evaluation

<table>
<thead>
<tr>
<th>Compound</th>
<th>%Recovery</th>
<th>Acceptance Criteria</th>
<th>Issue?</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>75%</td>
<td>70-130%</td>
<td>No</td>
</tr>
<tr>
<td>PFOS</td>
<td>80%</td>
<td>70-130%</td>
<td>No</td>
</tr>
<tr>
<td>PFNA</td>
<td>60%</td>
<td>70-130%</td>
<td>PFNA in all associated samples may be biased low</td>
</tr>
<tr>
<td>FOSA</td>
<td>145%</td>
<td>70-130%</td>
<td>Non-detects acceptable but detected results may be biased high</td>
</tr>
</tbody>
</table>
Matrix Spike Samples (MS/MSD)

- MS/MSD = Sample aliquots spiked with all PFAS compounds of interest
- MS/MSD Recoveries = within acceptance criteria as specified in Method or project QAPP
- If MS/MSD recovery outside criteria = impact for affected compound in the **unspiked sample**
- If MS/MSD RPD outside criteria = results for **unspiked sample** uncertain

*Compare MS/MSD results to Unspiked Sample to evaluate potential accuracy / bias and precision issues in Unspiked Sample data; may qualify results*

---

### Example MS/MSD Evaluation

<table>
<thead>
<tr>
<th>Cpd</th>
<th>Unspiked Sample (ng/L)</th>
<th>MS %Rec</th>
<th>MSD %Rec</th>
<th>RPD</th>
<th>Acceptance Criteria Recovery/RPD</th>
<th>Issue?</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>5 U</td>
<td>75%</td>
<td>80%</td>
<td>6.4%</td>
<td>70-130% / 30%</td>
<td>No</td>
</tr>
<tr>
<td>PFOS</td>
<td>5 U</td>
<td>71%</td>
<td>128%</td>
<td>57.3%</td>
<td>70-130% / 30%</td>
<td>Imprecision may indicate result is non-representative and uncertain</td>
</tr>
<tr>
<td>PFNA</td>
<td>8</td>
<td>60%</td>
<td>57%</td>
<td>5.1%</td>
<td>70-130% / 30%</td>
<td>PFNA in unspiked sample may be biased low</td>
</tr>
<tr>
<td>FOSA</td>
<td>5 U</td>
<td>145%</td>
<td>145%</td>
<td>0%</td>
<td>70-130% / 30%</td>
<td>No Issue – Non-detect for Unspiked sample accurate as reported</td>
</tr>
</tbody>
</table>
**Data Comparability**

**Precision** = variability and reproducibility of results
- Assessed by evaluating the Relative Percent Difference (RPD) between duplicate results or Percent Relative Standard Deviation (RSD) between more than 2 results

\[
\text{RPD} = \frac{|\text{Result 1} - \text{Result 2}|}{\frac{2}{\text{Result 1} + \text{Result 2}}}
\]

*Compare RPD to Method / QAPP criteria and possibly qualify results due to imprecision*

**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)
LINEAR VS. BRANCHED ISOMERS

- Eleven known isomers of PFOS
- 499>80 and 499>99 transitions have different relative response factors for the linear and the branched isomers.
- Quantitative biases possible depending on standard type and MRM transitions used for quantitation
- Distribution/half lives in tissue are different between linear and branched
- Speciation is more important in research applications. Contaminant analysis issues centered around accuracy of quantitation


Sampling QA - Representativeness and Precision

- **Representativeness** of samples to site conditions acceptable?
  - Review MS/MSD and FD precision as quantitative measures of quality – Heterogeneity issues
  - Generally, results may be considered uncertain due to precision QC results but are not rejected
### Field Duplicate Comparison

<table>
<thead>
<tr>
<th>Compound</th>
<th>QL (ng/L)</th>
<th>Sample Result (ng/L)</th>
<th>FD result (ng/L)</th>
<th>RPD</th>
<th>Issue?</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>2</td>
<td>2 U</td>
<td>2 U</td>
<td>NC</td>
<td>No: Both results are non-detect</td>
</tr>
<tr>
<td>PFAS</td>
<td>2</td>
<td>11</td>
<td>8</td>
<td>32%</td>
<td>Yes: Both results &gt; 2 x QL and RPD &gt; 30%</td>
</tr>
<tr>
<td>PFNA</td>
<td>2</td>
<td>2.2</td>
<td>3.9</td>
<td>56%</td>
<td>Yes: Both results &lt; 2 x QL and RPD &gt; 50%</td>
</tr>
<tr>
<td>FOSA</td>
<td>2</td>
<td>9</td>
<td>10</td>
<td>11%</td>
<td>No: Both results &gt; 2 x QL and RPD &lt; 30%</td>
</tr>
</tbody>
</table>

Method 537.1 RPD acceptance: RPD ≤ 30% for values > 2x QL and RPD ≤ 50% for values < 2x QL

As a conservative approach, the highest of the two values should be associated with PFAS and PFNA for the sampling location.

### 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/