PFAS Analytical Methods – New Hampshire’s Experience

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PFAS Analytical Methods Application, Comparison, and Lab Accreditation

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Presentation Overview

1) PFAS Sampling In New Hampshire
   • Public water systems
   • Other sites and media

2) ASDWA’s Primer on Sampling for PFAS in Public Water Systems
   • Analytical options
   • Target analytes
   • Reporting limits
   • Identifying a qualified laboratory
   • Causes for variability in results
   • Interpreting data
   • Sample collection procedures
   • Development of new analytical methods
PFAS Regulation in NH

- Ambient Groundwater Quality Standard (clean-up and enforceable drinking water standard of 70 ppt for PFOA/PFOS combined (based on health criteria only)

- Per state law, must initiate rulemaking for MCLs by 1/1/19 for PFOA, PFOS, PFNA and PFHxS (considers health benefits, costs and technical feasibility)

- Per state law, must develop a plan and budget for developing surface water quality standards by 1/1/20

- Per state law, has clear authority to regulate air emissions to protect water quality
PFAS Sampling Timeline in NH

2013-2015 UCMR 3
(21 water systems / 80 sources)

2014 – DoD / Superfund Sampling
(3 major water supply wells)

2016 – Sampling of wells around two air emissions sites
(1000+ wells)

Present – Statewide sampling
(3000+ multi-media samples)
Sampling for PFAS in NH

- Potential PFAS Sources/Targeted Sampling
- State-wide Surface Water Sampling
- Waste Sites Sampling
- New Sources of Water for Public Water Systems
- Public Water Systems
- Wastewater/Biosolids
- Groundwater at Wastewater Discharge Sites
- Air Emissions

Potential PFAS Sources/Targeted Sampling

State-wide Surface Water Sampling

Waste Sites Sampling

New Sources of Water for Public Water Systems

Public Water Systems

Wastewater/Biosolids

Groundwater at Wastewater Discharge Sites

Air Emissions
PFAS INVESTIGATION
Updated: September 24, 2018

SAMPLES WITH PFAS DETECTS
TOTAL PFAS (ppt)
- 70+
- 45 - <70
- Detect - <45

★ Existing Remedial Site with PFAS Detections

Political Boundary

Major Waterbody

0 12.5 25 50 Miles

NEW HAMPSHIRE DEPARTMENT OF Environmental Services
~2,900 water samples
~2,300 sample locations

http://nhdes.maps.arcgis.com/apps/View/index.html?appid=68770bef141c13368a445c54a17720e2&extent=-73.5743,42.5413,-69.6852,45.4489
# Public Water System Sampling in New Hampshire

<table>
<thead>
<tr>
<th>Combined PFOA &amp; PFOS Result</th>
<th>Number of Public Water System Sources</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greater than 70 ppt</td>
<td>7</td>
<td>1.6%</td>
</tr>
<tr>
<td>Greater than 60 ppt</td>
<td>9</td>
<td>2.1%</td>
</tr>
<tr>
<td>Greater than 50 ppt</td>
<td>9</td>
<td>2.1%</td>
</tr>
<tr>
<td>Greater than 40 ppt</td>
<td>10</td>
<td>2.3%</td>
</tr>
<tr>
<td>Greater than 30 ppt</td>
<td>17</td>
<td>4.0%</td>
</tr>
<tr>
<td>Greater than 20 ppt</td>
<td>32</td>
<td>7.5%</td>
</tr>
<tr>
<td>Greater than 10 ppt</td>
<td>57</td>
<td>13.3%</td>
</tr>
<tr>
<td>Greater than 5 ppt</td>
<td>73</td>
<td>17.0%</td>
</tr>
</tbody>
</table>

Number of Sources Tested = 429
# Non Public Water System Samples

<table>
<thead>
<tr>
<th>Site Type</th>
<th># Sampled</th>
<th>Number of Detects</th>
<th>Combined PFOA &amp; PFOS &gt; 70 ppt</th>
<th>Percentage Exceeding 70 ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing Waste Sites (non-petroleum)</td>
<td>92</td>
<td>79</td>
<td>51</td>
<td>54%</td>
</tr>
<tr>
<td>Existing Petroleum Sites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Auto Salvage Yards</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>75%</td>
</tr>
<tr>
<td>Fuel Oil Bulk Storage</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>100%</td>
</tr>
<tr>
<td>Used Motor Oil Sites</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>100%</td>
</tr>
<tr>
<td>Residential Home Heating Oil Spills</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Gas Stations</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Landfills</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unlined</td>
<td>87</td>
<td>83</td>
<td>40</td>
<td>46%</td>
</tr>
<tr>
<td>Lined</td>
<td>10</td>
<td>9</td>
<td>2</td>
<td>17%</td>
</tr>
<tr>
<td>Wastewater Discharge to Groundwater Sites</td>
<td>47</td>
<td>39</td>
<td>8</td>
<td>17%</td>
</tr>
<tr>
<td>Fire Departments</td>
<td>17</td>
<td>12</td>
<td>7</td>
<td>41%</td>
</tr>
</tbody>
</table>
Wastewater Assessments
Topic 1: Selecting an Analytical Method

1) EPA Method 537 Rev 1.1
   
   **Pros**
   - Only standard method used by commercial labs
   - Method developed by USEPA
   - Cost less than other methods

   **Cons**
   - Includes only 14 analytes
   - Not intended for non-drinking water samples
   - Corrections are not made to account for matrix interference

2) Isotope Dilution
   
   **Pros**
   - Considered the best method by many chemists
   - Can be used for non-drinking water samples
   - Can include more analytes than Method 537
   - Makes corrections for matrix interference

   **Cons**
   - Cost more than Method 537
   - Labs use their own proprietary method/method different from lab to lab
Topic 2: Finding a Qualified Laboratory

Laboratory Accreditation Programs

• National Environmental Laboratory Accreditation Program
  http://lams.nelac-institute.org/Search) by selecting a common PFAS chemical
  such as perfluorooctanoic acid (PFOA) under the “Analyte” pulldown tool; and
  
  • The Department of Defense
  https://www.denix.osd.mil/edqw/accreditation/accreditedlabs/ by selecting
  EPA 537 or “EPA 537 Mod” under the “Method” pull down tool.

• Some states may have their own accreditation or certification
  programs
  Note: Isotope dilution is sometimes called “Method 537 Modified” even though it is
  completely different than Method 537

Other approaches to verify laboratory performance
  • Periodically split samples and send to multiple laboratories
  • Conduct double blind proficiency testing studies with labs you work with
  • Request that the lab provides the results of historical proficiency testing
Topic 3: Which PFAS Chemicals Should Be Analyzed?

- Methods 537 includes up to 14 PFAS analytes (labs performing Method 537 do not always include all 14 compounds however)

- Isotope dilution includes up to 30 compounds
  - Many labs offer more than one testing packages
  - Options vary from lab to lab

- Six PFAS (PFOS, PFOA, PFNA, PFHxS, PFHpA and PFBS) were included in USEPA’s UCMR3

- Three additional PFAS compounds are frequently detected (PFBA, PFPeA and PFHxA)
Topic 3: Which PFAS Chemicals Should Be Analyzed? (continued)

Benefits of using methods with an extended list of analytes
• Collect as much information as possible when sampling
• Assist with fingerprinting/segregating potential sources of contamination
• Future health studies may be completed and guidelines issued for additional PFAS compounds
• Some states are developing health guidelines using an additive approach/summing up the concentration of up to five PFAS compounds.

Challenges of using methods with an extended list of analytes
• The may be no health guidelines for some of the detected PFAS
• Cost per analysis may be higher
• More data processing and reporting
Discrepancies and Inconsistencies with Lab Reports

Lab reports and electronic data deliverables are problematic

- Different labs are reporting different forms of PFAS compounds – same acronym but different properties (do not assume they are the same)
- Form of compound can affect the concentration reported
- Lab reports/electronic data deliverables contain mismatching CAS #s and chemical names/forms
- Creates havoc in data management and maintaining database integrity

EPA’s health advisory & NHDES standards reference the acid form

Table 3-1. Basic naming structure and shorthand for perfluoroalkyl acids (PFAAs)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Acronym</th>
<th>Name</th>
<th>Formula</th>
<th>CAS No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O = octa (8 carbon)</td>
<td></td>
<td>PFOA</td>
<td>Perfluoroctanoate</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;F&lt;sub&gt;15&lt;/sub&gt;CO&lt;sub&gt;2&lt;/sub&gt;−</td>
<td>45285-51-6</td>
</tr>
<tr>
<td></td>
<td>A = Carboxylate or carboxylic acid</td>
<td></td>
<td>Perfluoroctanoic acid</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;F&lt;sub&gt;15&lt;/sub&gt;COOH</td>
<td>335-67-1</td>
</tr>
<tr>
<td></td>
<td>S = Sulfonate or sulfonic acid</td>
<td></td>
<td>Perfluoroctane sulfonate</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;F&lt;sub&gt;17&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;−</td>
<td>45298-90-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PFOS</td>
<td>Perfluoroctane sulfonic acid</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;F&lt;sub&gt;17&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;−</td>
<td>1763-23-1</td>
</tr>
</tbody>
</table>

Topic 4: What Reporting Limit Should Be Used?

- Reporting limits of at least 2-4 ng/L should be utilized.
- Many labs performing isotope dilution achieve limits below 1 ng/L.
- Method 537 has reporting limits ranging from 2.9-14 ng/L.
- Benefits of low reporting limits:
  - Improve utility of the data in the event health advisories are lowered and use an additive approach.
  - Track concentration trends.
  - Fingerprint source of contamination.
Linear and Branched Isomers

- Prior to September 2016, Method 537 did not specify if branched isomers of PFOA should be measured and reported (some labs included it & others did not)
- PFOA was produced by Dupont & 3M
  - PFOA from Dupont contained only linear isomers of PFOA
  - PFOA from 3M contained 70% linear & 30% branched isomers
- Results from some samples analyzed prior to September 2016 may be underreported by 30% if contaminated with PFOA that was manufactured by 3M
Expected Accuracy of Testing Results and Common Biases Based on NHDES’ Experience

- Expected accuracy of analytical testing is +/-50% (higher than data from UCMR3 because high reporting limits were used)
- NHDES typically observed an accuracy of approximately -20% (biased low)
- NHDES split sample studies generally showed
  - Different labs reported similar results
  - Method 537 & isotope dilution reported similar results
- Occasional significant over reporting or under reporting occurred
Standards do not exist for many PFAS with branched isomers – labs estimate concentration using linear isomers.

Labs interpret branched isomers differently because the peaks on the chromatograph are less pronounced.

Certified standard from different vendors can cause results to vary by as much as 20%.

<table>
<thead>
<tr>
<th>ID</th>
<th>Analyte</th>
<th>Results Using Standard “A” Calibration Curve</th>
<th>Results Using Standard “B” Calibration Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PFOA</td>
<td>59 ppt</td>
<td>79 ppt</td>
</tr>
<tr>
<td>2</td>
<td>PFOA</td>
<td>104 ppt</td>
<td>132 ppt</td>
</tr>
<tr>
<td>3</td>
<td>PFOA</td>
<td>50 ppt</td>
<td>70 ppt</td>
</tr>
<tr>
<td>4</td>
<td>PFOA</td>
<td>49 ppt</td>
<td>63 ppt</td>
</tr>
<tr>
<td>5</td>
<td>PFOA</td>
<td>61 ppt</td>
<td>76 ppt</td>
</tr>
<tr>
<td>6</td>
<td>PFOA</td>
<td>54 ppt</td>
<td>73 ppt</td>
</tr>
<tr>
<td>7</td>
<td>PFOA</td>
<td>86 ppt</td>
<td>136 ppt</td>
</tr>
</tbody>
</table>
Topic 6: Sample Collection Procedures

• Low detection limits combined with the widespread use of items with PFAS increases the potential for sampling errors
• However, drinking water sampling agents and operators are qualified to complete the sampling
• Sampling taps and plumbing should be free of materials containing Teflon
• Samplers should wear well laundered cotton clothing without the use of softeners
• Samplers should not wear cosmetics, moisturizers, hand cream and related products
• Avoid the use of traditional weatherproof field books/paper
• Samplers should wash hands and wear nitrile gloves
• Field blanks and trip blanks should be periodically used – With each batch of samples or some other predetermined frequency
**Topic 7: Interpretation of Results**

- Compare results against USEPA’s health advisory or state guidance – ITRC maintains a table of standards and guidance values for other states and countries.

- The detection of low levels of PFAS do not mean there is a major source of PFAS Contamination at low levels could be associated with:
  - Teflon in components of the plumbing system??
  - Chemical feed tanks/tubing??
  - Regional septic systems or other numerous and dispersed uses and releases of PFAS.

- Lab blanks, trip blank, field blanks and duplicates are especially important when assessing low-level detections