PFAS Monitoring in a Post Health Advisory World—What Should We Be Doing?
Poly- and Perfluoroalkyl Substances (PFASs)

• Large class (200+) of surfactants with unique chemical properties
  • Fluorinated carbon chain with various functional group(s)

• Used since 1940s in products that resist heat, stains, water, oil and grease; production increased rapidly in 1970s

• Many other specialized industrial and commercial uses (operative word: non-stick)

Courtesy of Virginia Yingling (MDH)
Perfluoro- means “fully” fluorinated
• All carbons in the chain bonded only to F
• “PFCs” actually is correct in this case
• Example: PFOA, PFOS, PFBA, PFBS, etc.
• Essentially non-degradable due to strength of C-F bond

Polyfluoro- means “partially fluorinated”
• Some carbons in the chain bonded to H
• Example: 6:2 FTSA (polyfluorotelomer sulfonate; 6 CF₂, 2 CH₂)
• Susceptible to degradation (biotic and abiotic) due to weakness of C-H bond
• Some polyfluorinated PFASs may degrade to PFCs
• May constitute the majority of PFASs at many sites, but typically not tested for

Courtesy of Virginia Yingling (MDH)
PFCs Behave in Unique Ways

- **Do not break down in the environment**
  - No hydrolysis, photolysis, or biodegradation

- **Do not adsorb readily to aquifer materials**
  - Infiltrate rapidly to the groundwater
  - Little or no retardation
  - Rates affected by PFC chain length and functional group partitioning
    - Carboxylates (PFBA, PFPeA, PFHxA, PFOA) - prefer water
    - Sulfonates (PFBS, PFHxS, PFOS) - prefer soil and sediment

- **Chemical structure of some are similar to fatty acids**
  - Readily adsorbed into blood serum of living organisms

Courtesy of Virginia Yingling (MDH)
Some “Rules of Thumb”

- **Adsorption:** Longer-chain PFCs > shorter-chain PFCs (Ex: PFOS > PFBS)

- **Solubility:** Perfluorinated carboxylates > perfluorinated sulfonates of similar chain length (Ex: PFOA > PFOS)

- **Environmental fate (generalized):**
  - PFCs with sulfonate group and/or longer chain:
    - less mobile
    - partition more into soil and more persistent in the body
  
  - PFCs with carboxylate group and/or short chain:
    - more mobile
    - partition more into water
Numerous studies have documented PFOS, PFOA, and other PFASs in wildlife worldwide, including deep sea and arctic species.

Human blood samples from US, Europe, and Asia also detected PFCs – especially PFOS, PFOA, PFHxS – concentrations higher in very young and the elderly.

Atmospheric and oceanic transport of PFC precursor chemicals are believed to be major mechanisms in the global distribution.
These Compounds Have Been Studied for a Long Time

Analytical PFC Publications in the Open Scientific Literature*

Most data not based on validated methods.

Data Accuracy? Data Comparable?

2008 – First EPA reference method (LC/MS) for PFCs in Water

2007 – Commercial Stable Isotope IS’s


How Do You Evaluate PFAS Occurrence (e.g. UCMR 3 Data)?

- You can focus on exceedances of Health Advisory Levels (HAs).

- You can focus on overall frequency of detection by count or PWS because you are dealing with a strictly anthropogenic contaminant and you don’t know when a detection is part of a plume.

- You can focus on either only PFOS and PFOA or a broader suite.

- And this is to help you make educated decisions about any non-UCMR monitoring and/or treatment.
Consider Some of The Monitoring Option Decisions

- How many PFAS compounds should you look for?
  - 2 (PFOS/PFOA)?
  - 6 UCMR compounds?
  - 14 that are in EPA 537?
  - 24 that DOD is now targeting?

Clearly there are options to consider
Consider Some of The Monitoring Option Decisions

- How low should you look?
  - UCMR 3 limits?
  - Levels that the method can reliably measure?

- EPA established a HA for PFOA & PFOS in drinking water at a combined concentration of 70 ppt
- NYDEP recommends labs that meet 2 ppt for PFOA
- VT has established a HA for PFOA in water at 20 ppt
- NH recommends at least a 5 ppt RL for PFAS
- NJ recommends at least a 10 ppt RL and a guidance level of 40 ppt for PFOA
UCMR 3 reporting limits were determined based on a simulation from data from multiple labs (see next slide).

Method 537 is capable of reliably measuring:
- Levels that are 10-20X lower than UCMR 3
- A much longer list of PFAS compounds
**LCMRLs from Multiple Labs in Initial Method Validation (2008)**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Method 537 DL (ng/L)</th>
<th>Method 537 LCMRL (ng/L)</th>
<th>Lab A DL (ng/L)</th>
<th>Lab A LCMRL (ng/L)</th>
<th>Lab B DL (ng/L)</th>
<th>Lab B LCMRL (ng/L)</th>
<th>Overall range Multi lab DL range</th>
<th>Overall range Multi lab LCMRL range</th>
<th>Overall range UCMR 3 MRL</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBS</td>
<td>3.1</td>
<td>3.7</td>
<td>4.1</td>
<td>16</td>
<td>ND</td>
<td>72&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1 to 4.1</td>
<td>3.7 to 72</td>
<td>90</td>
</tr>
<tr>
<td>PFHpA</td>
<td>0.5</td>
<td>3.8</td>
<td>1.2</td>
<td>8.1</td>
<td>ND</td>
<td>0.82</td>
<td>&lt;1 to 1.2</td>
<td>3.8 to 8.1</td>
<td>10</td>
</tr>
<tr>
<td>PFHxS</td>
<td>2</td>
<td>8</td>
<td>3.9</td>
<td>3.3</td>
<td>ND</td>
<td>40&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1 to 3.9</td>
<td>3.3 to 40</td>
<td>30</td>
</tr>
<tr>
<td>PFOA</td>
<td>1.7</td>
<td>5.1</td>
<td>1.3</td>
<td>14</td>
<td>ND</td>
<td>0.33</td>
<td>&lt;1 to 1.7</td>
<td>0.33 to 14</td>
<td>20</td>
</tr>
<tr>
<td>PFNA</td>
<td>0.7</td>
<td>5.5</td>
<td>1.7</td>
<td>12</td>
<td>ND</td>
<td>0.68</td>
<td>&lt;1 to 1.7</td>
<td>0.68 to 12</td>
<td>20</td>
</tr>
<tr>
<td>PFOS</td>
<td>1.4</td>
<td>6.5</td>
<td>3.5</td>
<td>11</td>
<td>ND</td>
<td>45&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;1 to 3.5</td>
<td>6.5 to 45</td>
<td>40</td>
</tr>
</tbody>
</table>

Note the DL variation is not nearly as great as the LCMRL variation.

The large variation in LCMRLs among labs results in a high “national” MRL for UCMR 3 because these data are used for the simulation to determine the national UCMR MRL.

The combined PFOS-PFOA UCMR 3 MRL is 60, just below the HA level.
How Can We Determine If There Are Significant Underestimates?

- EEA accounts for nearly 40% of the UCMR 3 PFAS data.

- EEA’s in-house MRLs for the 6 PFAS compounds are significantly lower than the UCMR 3 limits.

- We re-examined all of our data, censoring at 5 ng/L for all 6 UCMR 3 PFAS compounds.

- We then compared detection frequencies, and states where there is significant detection.
How Representative Are Our Data of the Whole NCOD?

<table>
<thead>
<tr>
<th>Factor</th>
<th>Overall UCMR 3 NCOD*</th>
<th>EEA UCMR 3 Data (UCMR 3 MRLs)</th>
</tr>
</thead>
<tbody>
<tr>
<td># of Samples</td>
<td>~36,000</td>
<td>~10,500</td>
</tr>
<tr>
<td># of PWS</td>
<td>~4900</td>
<td>~1800</td>
</tr>
<tr>
<td>% of PWS with UCMR3 detection</td>
<td>3.9%</td>
<td>5.3%</td>
</tr>
<tr>
<td>% of PWS with HA Exceedances</td>
<td>1.3%</td>
<td>1.8%</td>
</tr>
<tr>
<td># of States/Territories with samples</td>
<td>All</td>
<td>All</td>
</tr>
<tr>
<td># of states/territories with detection</td>
<td>36</td>
<td>27</td>
</tr>
<tr>
<td># of states/territories with HA Exceedances</td>
<td>24</td>
<td>18</td>
</tr>
</tbody>
</table>

* April 2016 release
UCMR 3 NCOD PFOS-PFOA Hits
EEA Subset of UCMR 3 NCOD Data
PFOS-PFOA Hits
The Picture is Not that Different For Overall UCMR 3 PFAS Occurrence
What if we Start Looking at Frequency by State?

- We can look at PFOS/PFOA alone.
- We can compare the frequency of occurrence in different states.
- We can drill down to see how the EEA database compares.
- Most significantly, we can see how the pattern changes when we reduce the reporting limit.
NCOD - 24 States/Territories with PWS with Health Advisory Exceedances

# of PWS Exceeding Health Advisory Levels

- **10+ PWS**
- **5 to 9 PWS**
- **2 to 4 PWS**
- **1 PWS**

Created with mapchart.net ©
NCOD - 36 States with PWS Detections of PFOS and/or PFOA at UCMR3 MRLs

And GU and MP
EEA Data - 27 States with PFOS/PFOA Detections based on UCMR 3 MRLs

States with stars are in NCOD, but not EEA at UCMR 3 MRLs

# of PWS with Detects
- 10 - 19 PWS
- 1-9 PWS

Created with mapchart.net ©
37 States/Territories have PWS with PFOS-PFOA Detects at 5 ng/L MRL
EEA Data - 511 PWS in 40 States/Territories Have at Least 1 Compound at 5 ng/L or More

This represents nearly 28% of PWS in our database.

Plus GU and MP

Plus 3 more states with NCOD detections but insufficient EEA data
## Frequency of Detection Comparison by # of Samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Official NCOD Database samples with detection (UCMR 3 MRLs)</th>
<th>EEA Subset of Samples with detection using UCMR 3 MRLs</th>
<th>EEA Subset of Samples with detection using 5 ng/L MRL</th>
<th>EEA Subset of Samples with detection using 2.5 ng/L MRL</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>~36,000</td>
<td>~10,500</td>
<td>~10,500</td>
<td>~10,500</td>
</tr>
<tr>
<td>PFOS</td>
<td>0.8%</td>
<td>1.3%</td>
<td>11.5%</td>
<td>20.5%</td>
</tr>
<tr>
<td>PFOA</td>
<td>1.0%</td>
<td>1.8%</td>
<td>12.5%</td>
<td>23.5%</td>
</tr>
<tr>
<td>PFNA</td>
<td>0.1%</td>
<td>0.1%</td>
<td>0.6%</td>
<td>1.9%</td>
</tr>
<tr>
<td>PFHxS</td>
<td>0.6%</td>
<td>1.0%</td>
<td>6.0%</td>
<td>12.3%</td>
</tr>
<tr>
<td>PFHpA</td>
<td>0.6%</td>
<td>1.5%</td>
<td>3.3%</td>
<td>8.8%</td>
</tr>
<tr>
<td>PFBS</td>
<td>&lt;0.1%</td>
<td>0.2%</td>
<td>5.3%</td>
<td>11.9%</td>
</tr>
</tbody>
</table>
Washington Co., MN: A PFC Megaplume Investigated Since 2003

- Over 100 mi² contaminated
  - 4 major aquifers
  - 8 municipal systems
  - 140,000+ residents
  - 4,000+ private wells
    - PFAS detected in 1,200+
  - Models under-predicted extent

- PFBA most widespread
  - Short-chain carboxylate
  - Also detect PFOA, PFOS, PFHxS in abundance
  - And.. PFPeA, PFHxA, PFBS

Courtesy of Virginia Yingling (MDH)
Biomonitoring – 3M Plume

- 196 initial participants (164 returned)
- PFCs decreased in blood of people drinking treated water (but ave. concentrations still > national ave.)

**Blood PFC levels in long-term East Metro residents**

Concentrations in micrograms PFC in liter blood (ppb)

- **PFOS**
  - 2008: 35
  - 2010: 25
  - 2014: 15
- **PFOA**
  - 2008: 10
  - 2010: 5
  - 2014: 5
- **PFHxS**
  - 2008: 5
  - 2010: 5
  - 2014: 5

- **U.S. population**
  - 2008: 5
  - 2010: 5
  - 2014: 5

Courtesy of Virginia Yingling (MDH)
Conclusions

- The UCMR3 database drastically underestimates the occurrence of PFAS compounds in municipal waters because of MRLs that were too high.

- The high frequency of 5 ng/L detection of any PFAS compound (28% of tested PWS) suggests that utilities should proactively consider monitoring to check for potential plumes, even if the UCMR3 database showed no detection.

- The megaplume in MN shows how complex the problem may be and if you restrict yourself to monitoring PFOS/PFOA you may be short sighted.
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