Per- and Polyfluoroalkyl Substances (PFAS) Training

ASTSWMO Superfund and Brownfields Symposium
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What Are Per- and Polyfluoroalkyl Substances (PFAS)?

• Large (4,000+) class of surfactants with unique chemical & physical properties that make many of them extremely persistent and mobile in the environment

• Used since 1940s in wide range of consumer and industrial applications

Source: open access images – bing.com
Major PFAS Sources...so far

- **Fire Training/Fire Response Sites**
- **Industrial Sites**
  - Chemical plants
  - Plating and etching
  - Paper/textile/leather coating
  - Semiconductor
  - Photo- and lithographic
- **Landfills**
- **WWTPs/Biosolids**

LEACHATE
## “What’s So Special About PFAS?”

Table modified from Ducatman, 2018

<table>
<thead>
<tr>
<th>Property</th>
<th>PFAAs</th>
<th>Dioxins &amp; PCBs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly water soluble</td>
<td>Yes</td>
<td>No</td>
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<tr>
<td>Bind well to soil &amp; sediments</td>
<td>No</td>
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<tr>
<td>Degrades to some extent in the environment</td>
<td>No</td>
<td>Yes</td>
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<tr>
<td>Bioaccumulate in fish</td>
<td>Yes*</td>
<td>Yes</td>
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<tr>
<td>Bioaccumulate in lipids</td>
<td>No</td>
<td>Yes</td>
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<tr>
<td>“Proteinphilic”</td>
<td>Yes</td>
<td>No</td>
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<td>Drinking water is major exposure route</td>
<td>Yes</td>
<td>No</td>
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<tr>
<td>Removed by conventional wastewater treatment</td>
<td>No</td>
<td>Maybe (TSS)</td>
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</tbody>
</table>

* True for PFAAs with 8 or more fluorinated carbons (PFOS, PFNA, and longer-chain).

Drinking water is a major exposure route.

ppt in water → ppb in serum

Complicates our understanding of bioaccumulation and toxicity.
The General Classes of Per- and Polyfluoroalkyl Substances (PFAS)

Perfluoroalkyl acids
- Carboxylates
- Sulfonates

Fluorotelomers:
- Sulfonates
- Carboxylates
- Alcohols

Source: ITRC Naming Conventions and Physical Chemical Properties factsheet
Basic PFAA Structure

Perfluoroalkyl Acids (PFAAs)

- Fully (per-) fluorinated chain (2 to 40+ carbon “tail”)
- Functional group (“head”)
  - PFCAs: Carboxylate group (COO⁻)
  - PFSAs: Sulfonate group (SO₃⁻)

Source: ITRC Naming Conventions and Physical Chemical Properties factsheet
Highlights of PFAS Properties

- **C-F is the shortest and strongest bond in chemistry**
  - Small, highly electronegative fluorine atoms “shield” the carbon from chemical reactions
  - No biotic or abiotic degradation of PFAA under natural conditions
  - PFAAs thermally degrade only at high temperatures

- **Perfluoroalkyl acids (PFAAs) are negatively charged**
  - Present as anions in the environment
  - Interact and sorb on positively charged minerals
  - Mediated by pH, chain length, and functional group

**High C-F Bond Energy**

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<tr>
<th>Bond</th>
<th>kJ/mol of bonds</th>
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<td>C-F</td>
<td>485</td>
</tr>
<tr>
<td>C-H</td>
<td>436</td>
</tr>
<tr>
<td>C-C</td>
<td>346</td>
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<td>C-Cl</td>
<td>339</td>
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<td>C-N</td>
<td>305</td>
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<tr>
<td>C-Br</td>
<td>285</td>
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<tr>
<td>C-S</td>
<td>272</td>
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</tbody>
</table>

Source: open access image - bing.com
Polyfluorinated Substances

Partially (poly-) fluorinated

• Non-fluorine atom (usually H or O) attached to at least one, but not all, of the carbon atoms in the “tail”

• Creates a “weak link” susceptible to biotic or abiotic degradation

• May be anions (-), cations (+), or zwitterions (both + and -)

• Often named using a “n:x” prefix
  • n = number of fully fluorinated carbons
  • x = number of non-fully fluorinated carbons

Source: ITRC Naming Conventions and Physical Chemical Properties factsheet
PFAA Precursors

• Some PFAS can degrade to PFAAs
  • Referred to as “PFAA precursors” or “precursor compounds”
  • Resulting PFAAs sometimes referred to as “terminal PFAAs”

• Perfluoroalkane sulfonamides (FASAs) → PFSAs

• Polyfluoroalkyl Substances
  • Fluorotelomers → PFCAs
    • Fluorotelomer alcohols (FTOH)
    • Fluorotelomer sulfonates (FTSA)
    • Fluorotelomer carboxylates (FTCA)

• Perfluoroalkyl sulfonamidoethanols (FASE) & acetic acids (FASAA) → PFCAs or PFSAs
Biotransformation of Precursors

Can be analyzed using USEPA 537 Mod

Figure 4 from Harding-Marjanovic et al., 2015
• Use PFAS that will degrade to shorter-chain, less toxic (?) compounds:

• New applications, but not necessarily new chemicals
  • GenX used for decades in fluoropolymer production

• Only limited knowledge on their toxicities, properties, fate and transport, and treatment options
Highlights of PFAS Properties

• **Surfactant properties are important**
  - Partitioning to interfaces (air-water, soil-water, NAPL-water) & micelles
    - Implications for environmental sampling and sample handling
  - PFCAs can be both hydrophobic & hydrophilic

• **Chain length and functional group generally determine bioaccumulation**
  - Longer chain and sulfonates tend to accumulate more than shorter chain and carboxylates
  - PFHxS breaks this “rule” – longer half-life in humans than PFOS
  - Some PFAS are “proteinphiles”, so bioaccumulation process may be more complicated than for other environmental contaminants.
Highlights of PFAS Properties

- **PFAAs generally have low volatility**
  - Air transport may occur for PFAAs sorbed to particulates or dissolved in water droplets
  - Many precursors are volatile and some (e.g. FTOHs) may degrade to PFAAs

- **PFAAs may be linear or branched in form**
  - May affect partitioning and/or bioaccumulation - not well understood yet

\[ \text{Linear Perfluorooctane sulfonate (PFOS)} \]
\[ \text{Branched Perfluorooctane sulfonate (PFOS)} \]
### General “Rules of Thumb” for PFAS in the Environment

<table>
<thead>
<tr>
<th>Environment</th>
<th>PFCA</th>
<th>PFSAs</th>
<th>PFAAs</th>
<th>Precursors</th>
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<tbody>
<tr>
<td>Water</td>
<td>PFCAs</td>
<td>Shorter-chain &gt; Longer chain</td>
<td>Precursors</td>
<td>Shorter-chain</td>
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<tr>
<td>Soil &amp; Sediment</td>
<td>PFSAs</td>
<td>Longer-chain &gt; Shorter-chain</td>
<td>Precursors</td>
<td>Longer-chain</td>
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<tr>
<td>Biota</td>
<td>PFSAs</td>
<td>Longer-chain &gt; Shorter-chain</td>
<td>Precursors</td>
<td>Complicated</td>
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</tbody>
</table>

- **Solubility:**
  - PFCAs > PFSAs
  - Shorter-chain > Longer chain
  - PFAAs > Precursors

- **Sorption:**
  - PFSAs > PFCAs
  - Longer-chain > Shorter-chain
  - Precursors > PFAAs

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*Partitioning*
Case Study: Partitioning of PFAAs at AFFF Site

Values in ppb
You should expect:

• Very large plumes

• PFAAs may be much further downgradient than co-contaminants, including precursors

• Typically, shorter-chain and PFCAs travel further than longer-chain and PFSAs

• PFBA will act as a nearly perfect groundwater tracer
Case Study: Precursors and PFAAs at AFFF Site

**PFAS in Soil**

**PFAS in Groundwater**

PFCAs in green; PFSAs in black; precursors in red

Source: Casson and Chiang, 2018, Exhibit 4
PFAS in groundwater – Washington County, MN

- PFAAs highly soluble, mobile, persistent = very large plumes
  - Much larger than predicted by models
  - Co-mingled plumes

- PFBA most widespread
  - Extremely soluble and mobile = groundwater tracer
  - Distal plume difficult to distinguish from “ambient” levels

- Distribution controlled by:
  - Bedrock features (buried valleys and faults)
  - Groundwater divide (Mississippi R. and St. Croix R.)
  - Groundwater - surface water interactions
  - PFAS chemical properties (partitioning)
  - Source area PFAS “signature”
  - Groundwater pumping
PFOS - All Aquifers

- PFOS greater than 1.35ppb (>50x HBV)
- PFOS 0.271-1.35ppb (10-50x HBV)
- PFOS 0.136-0.27ppb (5-10x HBV)
- PFOS 0.028-0.135ppb (1-5x HBV)
- PFOS 0.021-0.027ppb (75-100% HBV)
- PFOS 0.0136-0.02ppb (50-75% HBV)
- PFOS 0.004-0.0135ppb (<50% HBV)
- PFOS not detected

MDH Health Based Value (HBV) for PFOS is 0.027 parts per billion (ppb; or 27 parts per trillion)

NOTES: Map combines data from all aquifers, actual concentrations in any area may vary. Blank spaces indicate no sample data.
PFOS in Surface Water and Groundwater

Note: map combines groundwater data from all aquifers, actual concentrations in a given well may vary; blank spaces indicate no sample data

4/2/2018

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PFOS greater than 1.35ppb (>50x HBV)
PFOS 0.271-1.35ppb (10-50x HBV)
PFOS 0.136-0.27ppb (5-10x HBV)
PFOS 0.028-0.135ppb (1-5x HBV)
PFOS 0.021-0.027ppb (75-100% HBV)
PFOS 0.0136-0.02ppb (50-75% HBV)
PFOS not detected
Project1007

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mn.gov/websiteurl

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Groundwater flow

Surface water or stormwater flow

- Surface water transport may move PFAS many miles away from source areas (See also: Awad et al., 2011 and Kwadijk et al., 2014).
- Infiltration along a surface water pathway may create discrete groundwater plumes isolated from the source.
- Groundwater discharge to surface water may contaminate water bodies distant from source areas.
UCMR3 – Inviting everybody to the PFAS party

- 2013-2015 list included 6 PFAAs (PFOS, PFOA, PFNA, PFHxS, PFHpA, PFBS)
- Municipal systems >10,000 and selected smaller systems
- Detected in ~4%, exceeded EPA LHAs in ~1.3%
- High RLs and sampled only at entry points, not wellheads

Did NOT test for PFBA or PFPeA

Figure adapted from Andy Eaton, Eurofins Eaton Analytical
PFAS in the United States

Figure 3-1. Emerging awareness and emphasis on PFAS occurrence in the environment

*Common regulatory criteria or health advisories
^Sum of informal poll (NJ, NH, MN)

Source: ITRC (2017); image reprinted with permission of Jeff Hale, Kleinfelder.
### Target analyte lists still evolving

<table>
<thead>
<tr>
<th>Analyte Name</th>
<th>Acronym</th>
<th>CAS Number</th>
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<td>Perfluorotetradecanoic acid*</td>
<td>PFTreA**</td>
<td>376-06-7</td>
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<tr>
<td>Perfluorotridecanoic acid*</td>
<td>PFTriA***</td>
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<td>Fluorotelomer sulfonate 8:2</td>
<td>FtS 8:2</td>
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<td>Fluorotelomer sulfonate 6:2</td>
<td>FtS 6:2</td>
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<td>Fluorotelomer sulfonate 4:2</td>
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<td>N-(Heptadecafluoroocetyl)sulfonil-N-methylglycine*</td>
<td>NMeFOSAA</td>
<td>2355-31-9</td>
</tr>
</tbody>
</table>
Classic Emerging Contaminant Challenges

• Widely present in the environment
  • Detected in drinking water and biota

• Evolving understanding of fate & transport
  • ID’ing new pathways and affected areas create sense the problem is “getting worse”

• Evolving analytical capabilities
  • Expanding analyte lists and lowered detection limits = “more detections” and sense the problem is “getting worse”

• Evolving risk assessment
  • Changing guidance values = public confusion and sense the problem is “getting worse”

• Limited remedial technologies
State standards and guidance

States are setting their own standards or guidance within available regulatory frameworks:

• Most have adopted EPA LHAs
• Others have set lower values (MN, NJ, VT)
• Driven by the PFAAs being found...and the target analyte list
• Mixtures:
  • Most states adopted EPA additivity of PFOS and PFOA
  • Minnesota has a TEQ-like process for PFOA, PFOS, PFBA, PFBS, and PFHxS
  • Vermont recently announced $\Sigma$ PFOA+PFOS+PFHxS+PFHpA+PFNA must be <20 ng/L
• North Carolina has a non-promulgated value for GenX in drinking water
• Creates public confusion and makes risk communication even more difficult!
<table>
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<tr>
<th>Standard / Guidance</th>
<th>Type</th>
<th>Promulgated Rule (Y/N/O)</th>
<th>PFOSA</th>
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<th>PFBA</th>
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<th>PFDS, PFUnA, PFDoA, PFTrDA, PFTeDA</th>
<th>Gen-X</th>
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</table>

Table modified from ITRC (June 2018) Table 4-1: https://pfas-1.itrcweb.org/factsheets/
Why are some states setting such low values?

• Longer chain PFAAs are highly bioaccumulative
  • Parts per trillion in drinking water = parts per billion in blood serum
  • Ongoing exposures = lifetime steady state concentrations

• Relative source contribution (RSC) > default 20%
  • RSC = 50% - based on recent biomonitoring data of drinking water exposed pops.

• Variable, age-based intake rates (IR) – much higher for infants

• Biological activity at very low exposures = lower “allowed” serum levels

• Significant potential exposure for babies born to exposed mothers
  • Placental transfer: PFOA ~60-200% of drinking water concentrations
  • Breastmilk: PFOA ~2.6-12% of maternal serum concentrations
Accounting for breastfed infant exposures in PFOA value

PFOA Serum Concentration, Breast-Fed Scenario (95th% IR), Water Concentration = 0.035 μg/L

Breast-fed

Formula-fed

(Serum ~ 65 μg/L)

RSC 50%
## Sources of Variability in State Standards

<table>
<thead>
<tr>
<th>State</th>
<th>Receptor</th>
<th>Relative Source Contribution</th>
<th>Total Uncertainty</th>
<th>Species</th>
<th>Method for Administered Dose conversion to Internal Serum Level</th>
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<td>Alaska</td>
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<td>Maine</td>
<td>Adult</td>
<td>0.6</td>
<td>300</td>
<td>Mice, Rats and Monkeys</td>
<td>NA - used administered dose</td>
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<td>Minnesota</td>
<td>Infant exposure via breastmilk for 1 year, from mother chronically exposed via water, followed by lifetime of exposure via drinking water</td>
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<td>Cynomolgus monkeys</td>
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<td>Child (0-6 years) residential, non-cancer</td>
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</table>

Table used with permission from Shalene Thomas, Wood Group
Other state regulatory approaches

States are also using whatever regulatory or other tools are available to them to try to reduce PFAS releases and exposures:

- Product labeling and consumer product laws (ex: CA, WA)
- Chemical action plans (ex: WA)
- Designation as hazardous waste or substance (ex: CO, NY, VT)
- Effluent and surface water standards (ex: CA, MI, MN, OR)
- Risk-based soil and groundwater cleanup values (ex: TX)
- Prioritized source inventories (ex: MN)
- Testing all public water supplies for PFAS (ex: MI)
Remediation – “Back To The Future”

- Soil & Sediment
  - Excavation / dredging
  - Containment vaults / capping
  - Incineration
  - Stabilization / Binding

- Groundwater
  - Pump & treat
    - GAC
    - Ion Exchange
  - Injection / barrier walls
    - Colloidal carbon
ITRC PFAS Fact Sheets

- Available online [https://pfas-1.itrcweb.org/fact-sheets]
  - History and Use
  - Naming Conventions & Physical and Chemical Properties
  - Regulations, Guidance and Advisories
    - Guidance values tables updated monthly (US – federal & states, international)
  - Environmental Fate & Transport
  - Site Characterization Tools, Sampling Techniques, & Laboratory Analytical Methods
  - Remediation Technologies & Methods
  - AFFF (to be published August 2018)
  - Tailored to the needs of state regulatory program staff – concise, current, web-based
Other ITRC PFAS Products – in the works

• Technical-Regulatory Document (Oct.-Nov. 2019)
  • More in-depth exploration of current state of knowledge of PFAS
  • Includes stakeholder perspectives and case studies

• Training Workshops (Oct. 2018 – June 2019)
  • 8-9 regional trainings (4-hr or 8-hr)
  • Aimed at state regulatory program staff

• Risk Communication Toolkit (June 2019)

• Internet Based Training (Oct.-Nov. 2019)
Acknowledgements

• MDH – Environmental Health Division
• MPCA – Closed Landfill & Superfund
• Minnesota Public Health Laboratory
• Minnesota Geological Survey
• Valley Branch Watershed District
• West Central Environmental Consultants
• Washington County
• Interpoll Laboratories
• Barr Engineering
• 3M Company
• Wood Group (Amec Foster Wheeler)

• Weston Solutions
• Antea Group
• Agency for Toxic Substances and Disease Registry (ATSDR)
• U.S. Geological Survey
• Cities of Oakdale, Lake Elmo, Woodbury, Cottage Grove, Afton, Maplewood, Newport, Saint Paul Park
• Grey Cloud Island, West Lakeland, and Denmark Townships
This work was partially funded through a cooperative agreement grant from the Agency for Toxic Substances and Disease Registry (ATSDR) and the Center for Disease Control (CDC).

The opinions expressed are those of the author and do not necessarily reflect the official views of ATSDR, the CDC, the Department of Health and Human Services, or the Minnesota Department of Health.
Questions?
More Information and References

ITRC PFAS documents:
https://pfas-1.itrcweb.org/

MDH general PFAS Information and guidance values:
http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html
http://www.health.state.mn.us/divs/eh/risk/guidance/gw/table.html

MPCA PFAS Investigations:
http://www.pca.state.mn.us/index.php/waste/waste-and-clean up/cleanup-programs-and-topics/topics/perfluorochemicals-pfc/perfluorochemicals-pfcs.html?m enuid=&redirect=1


