Introduction To PFAS

ASTSWMO
Milwaukee, WI
August 14, 2019

Topics for Plenary Session

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<td>Intro to ITRC</td>
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<tr>
<td>PFAS Background:</td>
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<tr>
<td>• PFAS Sources &amp; Naming Conventions</td>
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<tr>
<td>• Basic Chemical &amp; Physical Properties</td>
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<td>Toxicity, Risk Assessment, &amp; Regulations/Guidance Values</td>
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<td>Fate &amp; Transport</td>
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<td>Treatment Technologies</td>
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<td>Q&amp;A</td>
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What is ITRC?

- ITRC is a state-led coalition working to advance the use of innovative environmental technologies and approaches. ITRC’s work translates good science into better decision making.

ITRC PFAS Team

- 500+ PFAS experts from all sectors: academics, stakeholders; state and local; federal; industry and consulting
- Producing concise technical resources for project managers – regulators, consultants, responsible parties, and stakeholders
- Why: State and federal environmental regulators and others need easily accessible information to aid them in evaluating risks and selecting appropriate response actions at PFAS release sites
ITRC PFAS Team Products

- Factsheets
  - History and Use (Nov. 2017)
  - Naming Conventions & Physical and Chemical Properties (March 2018)
  - Regulations, Guidance, and Advisories (January 2018)
  - Fate & Transport (March 2018)
  - Site Characterization, Sampling Techniques, and Lab Analytical Methods (March 2018)
  - Remediation Technologies (March 2018)
  - AFFF (October 2018)
- Web-based, updated information tables

- Online training modules in early 2020
- Publication of the Risk Communication Toolkit in early 2020
- Publication of the web-based Technical and Regulatory Document in early 2020

https://pfas-1.itrcweb.org
What Are Per- and Polyfluoroalkyl Substances (PFAS)?

- Large class of surfactants (>4000) 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 & industrial applications

PFAS Major Sources

- Fire Training/Fire Response Sites
- Industrial Sites
- Landfills*
- WWTPs/Biosolids*

*PFAS concentrations vary widely depending on the waste stream – not all landfills or WWTPs are major sources
The General Classes of Per- and Polyfluoroalkyl Substances (PFAS)

PFAS

Non-polymer

Polymer

Perfluorinated

Polyfluorinated

Perfluoroalkyl acids:
• Carboxylates
• Sulfonates

Fluorotelomers:
• Sulfonates
• Carboxylates
• Alcohols

Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet

Basic PFAA Structure

- Perfluoroalkyl Acids (PFAAs)
  - Fully fluorinated chain (2 or more carbon or alkane “tail”)
  - Functional group (“head”)
    - PFCAs: Carboxylate group (COO⁻)
    - PFSAs: Sulfonate group (SO₃⁻)

Perfluorooctane sulfonate (PFOS)

Source: open access image from bing.com

Perfluorooctane carboxylate (PFOA)
PFAA Naming System

- **PFXY**
  - **PF** = perfluoro
  - **X** = number of carbons
    - Same convention as hydrocarbons
    - Includes C in the carboxylate group
  - **Y** = functional group
    - S = sulfonate
    - A = carboxylate

- **Example:**
  - **X**: 8 carbons = “octa”
  - **Y**: S = sulfonate

Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet
Polyfluoroalkyl Substances

- Partially fluorinated
- Non-fluorine atom (usually H or O) attached to at least one, but not all, of the carbons in the alkane chain

![Chemical Structure](image)

- Creates a “weak link” susceptible to biotic or abiotic degradation
- Often named using a “n:x” prefix
  - n = number of fully fluorinated carbons
  - x = number of non-fully fluorinated carbons

Replacement Chemistry

- Short chain PFAS chemistries do not degrade to longer PFAAs
- New applications, but not necessarily new chemicals
  - HFPO-DA (Hexafluoropropylene oxide dimer acid), a component of GenX processing aid technology (Shoemaker and Tettenhorst 2018)
  - used for decades in fluoropolymer production
- For most replacement chemistries, limited information on toxicities, properties, fate and transport, and treatment options
  - USEPA released a draft toxicity assessment for GenX chemicals in November 2018

Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet
PFAS Chemical & Physical Properties

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

<table>
<thead>
<tr>
<th>High C-F Bond Energy</th>
<th>kJ/mol of bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-F</td>
<td>485</td>
</tr>
<tr>
<td>C-H</td>
<td>438</td>
</tr>
<tr>
<td>C-C</td>
<td>346</td>
</tr>
<tr>
<td>C-Cl</td>
<td>339</td>
</tr>
<tr>
<td>C-N</td>
<td>305</td>
</tr>
<tr>
<td>C-Br</td>
<td>285</td>
</tr>
<tr>
<td>C-S</td>
<td>272</td>
</tr>
</tbody>
</table>

- The anion of the perfluoroalkyl acids (PFAAs) are negatively charged
  - Interact and sorb on positively charged minerals
  - Mediated by pH, chain length, and functional group
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.

Surfactant properties are important
- Partitioning to interfaces (air-water, soil-water, NAPL-water) and micelles
- PFAAs can be both hydrophobic and hydrophilic

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

PFAAs generally have low volatility, however...
- Air transport may occur for PFAAs sorbed to particulates or dissolved in water droplets
- PFAAs may be formed from volatile precursors (e.g., FTOHs)

Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet
Toxicity, Risk Assessment, and Regulations

Health Effects of PFOA and PFOS

- **Animal**
  - Liver effects
  - Immunological effects
  - Developmental effects
  - Endocrine effects (thyroid)
  - Reproductive effects
  - Tumors (liver, testicular*, pancreatic*)

- **Human (possible links)**
  - Liver effects (serum enzymes/bilirubin, cholesterol)
  - Immunological effects (decreased vaccination response, asthma)
  - Developmental effects (birth weight)
  - Endocrine effects (thyroid disease)
  - Reproductive effects (decreased fertility)
  - Cardiovascular effects (pregnancy induced hypertension)
  - Cancer* (testicular, kidney)

* PFOA Only
Toxicology of PFOA and PFOS

- Most toxicology studies have focused on PFOA and PFOS
- Non-cancer effects in mammals are primarily focused on developmental effects
- Immunotoxicity potential
- Potential carcinogenic properties
  - “Suggestive” for both (USEPA) and “Possibly” for PFOA (International Agency for Research on Cancer)
  - Cancer Slope Factor (CSF) for PFOA: 0.07 (mg/kg*day)^-1
    - Risk-based drinking water threshold for cancer endpoint higher (less conservative) than non-cancer endpoint

Factors Impacting Numerical Value of PFAS Drinking Water Guidelines

<table>
<thead>
<tr>
<th>Factor</th>
<th>Explanation</th>
<th>Examples</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Dose (POD)</td>
<td>Dose (mg/kg/day) from animal study used as starting point</td>
<td>• LOAEL for ↓ offspring body weight in rats</td>
<td>↑ POD → ↑ Guideline</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• NOAEL for ↓ immune response in mice.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Benchmark Dose (BMDL)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Point of Departure (POD):</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• POD is divided by individual UFs of 1-10</td>
<td>• Interindividual</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Total UF generally 30-300</td>
<td>• Animal-to-human</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Uncertainty factors (UFs)</td>
<td>• Data gaps</td>
<td>↑ Total UF → ↓ Guideline</td>
</tr>
<tr>
<td></td>
<td>To account for higher internal levels in humans than lab animals from same dose</td>
<td>• Serum PFAS levels as dose metric</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Animal-to-human dose extrapolation</td>
<td>• Human-to-animal half-life ratio</td>
<td>Depends on specifics of approach.</td>
</tr>
<tr>
<td></td>
<td>Exposure</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Drinking water consumption rate</td>
<td>• L/kg/day.</td>
<td>↑ Ingestion rate → ↓ Guideline</td>
</tr>
<tr>
<td></td>
<td>• Based on daily ingestion (L/day) and body wt. (kg)</td>
<td>• Default &gt; Lactating Woman &gt; Default Adult</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Relative Source Contribution (RSC)</td>
<td>Accounts for non-drinking water exposure sources</td>
<td>↑ RSC → ↑ Guideline</td>
</tr>
<tr>
<td></td>
<td>(e.g. food, air.)</td>
<td>• Default - 20%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Up to 80% based on chemical-specific data.</td>
<td></td>
</tr>
</tbody>
</table>

Drinking Water Guideline = Reference Dose (mg/kg/day) x Relative Source Contribution (%)
Toxicology of Other PFAS

- Information for some PFAS in peer-reviewed literature and chemical registration information (REACH dossiers, TSCA submittals)
- Most focused on the PFCAs and PFSAs, the perfluoroalkyl acid “families” to which PFOA and PFOS belong
- Effects generally similar (developmental, liver, kidney, etc.)
  - Long-chain PFAAs appear to have effects generally similar in animal studies (developmental, immune, liver, etc.)
  - Animal data for short-chain PFAAs show liver and kidney effects at high concentrations
- USEPA IRIS announced in December 2018 five PFAS will be reviewed for toxicity assessment (PFNA, PFBA, PFHxA, PFHxS, PFDA), no timeline given

Risk Assessment

\[
\text{RISK} = \text{EXPOSURE} \times \text{HAZARD}
\]

- How will receptors contact the chemical?
- What is the magnitude, frequency and duration of contact?
- What are the chemical’s health effects?
- What is the relationship between exposure and health effects?
Risk Assessment Challenges

- It’s not just PFOA and PFOS
  - 16 other PFAS by USEPA Method 537 (Nov. 2018)
  - Additional 10-15 more PFAS via other methods
  - Dozens to hundreds of other PFAS in AFFF

Risk Assessment Challenges

- Toxicity information
  - Room for improvement with existing PFOA and PFOS toxicity values and cancer assessments
  - Additivity of PFOA and PFOS
  - Other PFAS? Toxicity higher or lower?

Source: Geosyntec
Risk Assessment Challenges

- **Background/ambient issues**
  - How to manage non-site related PFAS from watershed or aquifer sources?
  - Background exposures for humans
  - Relative source contribution (0.2) in EPA Lifetime Health Advisory for Drinking Water
  - Assumes human receptor can receive only 20% of a reference dose from specific exposures (e.g., site-specific exposures must be 5X below reference dose)

- **No standard guidance or models for risk assessment** (conceptual site models, sampling approaches, uptake factors, toxicity values)
  - …yet

  - Health Canada has published a framework for Canadian federal sites (Human Health Risk Assessment Framework for Federal Sites Impacted with PFAS)

- **Where to focus assessment and management?**
  - Groundwater, surface water, sediment, soil, diet?
PFAS Regulatory Drivers

- EPA Drinking Water LHA for PFOA and PFOS not enforceable standards
- CERCLA and RCRA
  - PFAS not yet CERCLA hazardous substances, so no cost recovery for Superfund (although they are considered a pollutant or contaminant and can be investigated)
- Others
  - Site investigations and management driven by other forces, including: voluntary action (regulatory and public perception pressure), litigation, Clean Water Act (TMDL), variable approaches at state-level
- Available guidelines for PFOA and PFOS may be used as regulatory drivers, but that may not be sufficient to justify federal expenditures
- Consult legal counsel – PFAS regulatory landscape will continue to evolve
- Consult your local regulatory agency

Regulatory Approaches

- EPA 2009 Provisional Short-term Health Advisories have been replaced by 2016 Lifetime Health Advisories (LHAs)
- Many states with a variety of regulatory approaches, focusing primarily on PFOA and PFOS
  - 19 states have criteria in water
  - 6 states have drinking water values that are different from EPA's LHAs
- Variety of state approaches for other PFAS (6 have criteria for other PFAS)
  - Texas Commission on Environmental Quality (TCEQ) 14 PFAS besides PFOA and PFOS
  - California: PFOA and PFOS listed on Prop 65 (November 2017), PFAS-containing carpet and rugs proposed as “Priority Product” (evaluate use or ban in commerce, February 2018)
- Approaches and values are changing rapidly
- Visit ITRC for the latest compilation: https://pfas-1.itrcweb.org/
- Consult your local regulatory agency
Guidelines and Standards (µg/L) PFOA, PFOS

States with Values for Other PFAS
(and year implemented)

MN: “TEQ-like” additivity for 5 PFAS

VT: Sum of 5 PFAS < 0.02 µg/L (2018)

MA: Sum of 5 PFAS < 0.07 µg/L (June 2018)
Guidance and Screening Levels – Soil (mg/kg)

<table>
<thead>
<tr>
<th>Representative Residential Soil Screening Levels</th>
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<tbody>
<tr>
<td>Australia (2018)</td>
</tr>
<tr>
<td>Health Canada (2017)</td>
</tr>
<tr>
<td>EPA RSL (2018)</td>
</tr>
<tr>
<td>TX (2017) 30-acre source</td>
</tr>
<tr>
<td>NH (2017)</td>
</tr>
<tr>
<td>NV (2017)</td>
</tr>
<tr>
<td>MN (2016)</td>
</tr>
<tr>
<td>MI (2016)</td>
</tr>
<tr>
<td>ME (2018)</td>
</tr>
<tr>
<td>IA (2016)</td>
</tr>
<tr>
<td>DE (2016)</td>
</tr>
<tr>
<td>AK (2017)</td>
</tr>
</tbody>
</table>

Protective of Human Direct Contact

Protection of Drinking water

Risk Communication Principles for PFAS

1. Establish trust by supporting dialogues between the decision-makers and the affected stakeholders early and continue them through to resolution.
2. Include the community in the decision-making process.
3. Present information clearly and make it accessible to stakeholders.
4. Address uncertainties head on, be clear and transparent about knowns and unknowns.
5. Listen, acknowledge, and follow up with specific concerns.
6. Develop a context for the risk that will help audiences evaluate how to respond to risk.
Human Exposure Pathways

- Major
  - Diet (bioaccumulation)
    - Fish and seafood
    - Produce
  - Drinking water
  - Incidental soil/dust ingestion

- Usually insignificant or minor
  - Dermal absorption
  - Inhalation


Source: Open source, Pixabay

ITRC PFAS Risk Communication Toolkit

- Agenda for First Internal Communication Team Planning Meeting
- PFAS-specific SMART Goals
- Fact Sheets & FAQs Compilation
- Guidance for Writing Analytical Results Summary Letters
- Guidance for Writing Press Releases
- Social Factors Vision Board
- Message Mapping Guide
- PFAS-specific Key Messages

ITRC Draft material
## PFAA Sorption and Transport

<table>
<thead>
<tr>
<th>Analyte</th>
<th># Carbons</th>
<th>$K_{oc}^{1}$</th>
<th>$R_f$</th>
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<tbody>
<tr>
<td>PFBA</td>
<td>4</td>
<td>76</td>
<td>5</td>
</tr>
<tr>
<td>PFPeA</td>
<td>5</td>
<td>23</td>
<td>1.4</td>
</tr>
<tr>
<td>PFHxA</td>
<td>6</td>
<td>20</td>
<td>1.1</td>
</tr>
<tr>
<td>PFHpA</td>
<td>7</td>
<td>43</td>
<td>3</td>
</tr>
<tr>
<td>PFOA</td>
<td>8</td>
<td>78</td>
<td>5</td>
</tr>
<tr>
<td>PFNA</td>
<td>9</td>
<td>229</td>
<td>14</td>
</tr>
<tr>
<td>PFDA</td>
<td>10</td>
<td>912</td>
<td>57</td>
</tr>
<tr>
<td>PFUnA</td>
<td>11</td>
<td>3,600</td>
<td>225</td>
</tr>
<tr>
<td>PFBS</td>
<td>4</td>
<td>62</td>
<td>4</td>
</tr>
<tr>
<td>PFHxS</td>
<td>6</td>
<td>112</td>
<td>7</td>
</tr>
<tr>
<td>PFOS</td>
<td>8</td>
<td>631</td>
<td>39</td>
</tr>
</tbody>
</table>


- Sorption ($K_{oc}$ and $K_d$) (generally) increases with # of carbons
- Short-chain PFCAs have greater $K_{oc}$ than expected
- GENERALLY:
  - Solubility
    - PFCAs > PFSAs
    - Short chain > long chain
  - Sorption
    - PFSAs > PFCAs
    - Long chain > short chain
  - Relative partitioning
    - Soil, sediment, animals: PFSAs
    - Water, plants: PFCAs

## Other factors impacting PFAA Transport

- Increased retardation (sorption)
  - Lower pH (more acidic)$^{1,2}$
  - Greater polyvalent cations$^{1,2}$ (Ca$^{2+}$, Fe$^{3+}$, etc.)
  - Presence of non-aqueous phase liquids$^{3,4}$
- Retardation impacted by remedial approaches that change pH or introduces polyvalent cations (i.e., ISCO)$^{2,4}$

Transformation of PFAA Precursors

[Diagram showing the transformation of PFAS precursors]

Figure courtesy of C. Higgins

Complexity Varies with Time, Space, and History

[Diagram showing the complexity of PFAS sources and products]

Source: Adapted from figure by L. Trozzolo, TRC, used with permission
Water Treatment

- Effective conventional approaches, with limitations:
  - Carbon adsorption
  - Resin adsorption
  - Reverse osmosis

- Typically ineffective conventional technologies:
  - Air stripping, air sparging

- Technologies in development:
  - Examples include - bioremediation, chemical oxidation, chemical reduction, thermal desorption, electrochemical, others

- Be aware of precursor transformations via treatment processes, particularly with oxidation and biodegradation
Soil Remediation Technologies

- Conventional
  - Excavation and landfill
  - Excavation and offsite incineration
  - Stabilization
- Developing/Limited demonstrations
  - Soil Washing
  - Thermal

Photo courtesy of CH2M/Jacobs

Questions?

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