A Legal Perspective on PFOS/PFAS Contamination Issues

July 10, 2018
Noon-1:00 p.m.

Email questions to: parks.maryanne@gmail.com or use the question option on your screen
Participants

Moderator: Tammy Helminski
Barnes & Thornburg LLP

Panelists: Benjamn Fruchey, Foley Baron Metzger & Juip PLLC
Taryn McKnight, Product Manager at Test America
Ryan Thomas, Environmental Scientist at GHD
Per- and Polyfluoroalkyl Substances
Overview of physical properties, regulation and remediation.
INTRODUCTION TO PFAS
HISTORICAL USES

PFAS Sources

- Paint
- Pesticides
- Spray Can
- Photography
- Rain Resistance
HEAT RESISTANT
WATER REPELLENT
STAIN RESISTANT
## Long-Chain Perfluorinated Chemicals (PFCs) Action Plan

### Table 1. Comparative Rates of Elimination*

<table>
<thead>
<tr>
<th>Serum Half-life</th>
<th>PFHxS (C6)</th>
<th>PFOS (C8)</th>
<th>PFOA (C8)</th>
<th>PFNA (C9)</th>
<th>PFDA (C10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human</td>
<td>8.5 years</td>
<td>5.4 years</td>
<td>2.3-3.8 years</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
BIOACCUMULATION
INDUSTRIAL PRETREATMENT PROGRAM INITIATIVE
Gilkey Creek

sanitary sewer

Former Pretreatment System site

Industry sludge disposal

29 ng/l PFOS

Plater (effluent PFOS ND)

2006 Oil Fire, AFFF used

920 ng/l PFOS

Gilkey Creek
Chemistry & Analysis of PFAS

Taryn McKnight
TestAmerica Laboratories, Inc.
Briefly - What are PFASs?

Class of synthetic compounds containing thousands of chemicals formed from carbon chains with fluorine attached.

The C-F bond is one of the shortest and strongest in nature.

Properties:
- Persistent
- Bio-accumulative
- Toxic
Nomenclature

PFAS
Per- and Polyfluoroalkyl Substances

PFCs
Perfluorinated Compounds

PFAAs
Perfluorooalkyl Acids

PFSAs
Perfluorinated sulfonic acids

PFCAs
Perfluorooalkylcarboxylic acids

PFOS

PFOA

you say TOMATO
I say TOMATO

Not the greenhouse gas
Chemical Structure

- Chain Length
- Carbon Backbone
- Functional Group
# Carbon Chain Nomenclature

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Compound Name</th>
<th>Carbon Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFUnA</td>
<td>Perfluoro<strong>undeca</strong>noic acid</td>
<td>C11</td>
</tr>
<tr>
<td>PFDA</td>
<td>Perfluoro<strong>deca</strong>noic acid</td>
<td>C10</td>
</tr>
<tr>
<td>PFNA</td>
<td>Perfluoro<strong>nona</strong>noic acid</td>
<td>C9</td>
</tr>
<tr>
<td>PFOA</td>
<td>Perfluoro<strong>octa</strong>noic acid</td>
<td>C8</td>
</tr>
<tr>
<td>PFHpS</td>
<td>Perfluoro<strong>hepta</strong>nesulfonic acid</td>
<td>C7</td>
</tr>
<tr>
<td>PFHxS</td>
<td>Perfluoro<strong>hexa</strong>nesulfonic acid</td>
<td>C6</td>
</tr>
<tr>
<td>PFBS</td>
<td>Perfluoro<strong>buta</strong>nesulfonic acid</td>
<td>C4</td>
</tr>
</tbody>
</table>
Properties

Fluorocarbon “Tail” = Hydrophobic and Oleophobic

Functional Group “Head” = Hydrophilic
Branched & Linear Isomers

PFOS linear isomer

PFOS branched isomer
PFAS Formation

**ECF Reaction** = B&L & Unintended Byproducts

**Telomer Reaction:** Unintended Byproducts

\[
\begin{align*}
F(CF_2)_{2I} & \rightarrow F(CF_2)_nI \\
+ \text{CF}_2=\text{CF}_2 & \rightarrow F(CF_2)_n + \text{CH}_2=\text{CH}_2 \\
+ \text{CH}_2=\text{CH}_2 & \rightarrow F(CF_2)_n\text{CH}_2\text{CH}_2\text{I} \\
\rightarrow T & \rightarrow F(CH_2)_n\text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]
A lesson ...
... in jumping to CONCLUSIONS
Precursors

PFAA Precursors → Biotransformation → PFAA → PFOA, PFOS

Oxidation via TOP Assay

Precursors → Oxidizer 5.1 → PFAAs
PFCA Pattern – MeFOSA Precursor

The graph shows the concentration of PFCA patterns in ppt. The bar for PFOA is significantly higher than the other PFCA patterns (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA).
PFAS – Regulatory Timeline

<table>
<thead>
<tr>
<th>When</th>
<th>Who</th>
<th>What Happened</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>US EPA</td>
<td>Initiated voluntary phase out of PFOS</td>
</tr>
<tr>
<td>2002</td>
<td>3M</td>
<td>Voluntarily discontinued making PFOS (7 other makers complied)</td>
</tr>
<tr>
<td>2006</td>
<td>US EPA</td>
<td>PFOA Stewardship Program initiated</td>
</tr>
<tr>
<td>2008</td>
<td>Canada</td>
<td>Regulated and prohibited PFOS imports to Canada</td>
</tr>
<tr>
<td>2009</td>
<td>UN</td>
<td>Stockholm Convention - adds PFOS to Annex B</td>
</tr>
<tr>
<td>2010</td>
<td>US EPA</td>
<td>PFOA Stewardship Program - PFOA reduced by 95%</td>
</tr>
<tr>
<td>2015</td>
<td>US EPA</td>
<td>Eliminate the use of PFOA by December 31, 2015</td>
</tr>
<tr>
<td>May 2016</td>
<td>US EPA</td>
<td>PFOS and PFOA lifetime health advisory limits reduced to 70 ppt combined</td>
</tr>
<tr>
<td>State</td>
<td>PFOA ppt</td>
<td>PFOS ppt</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>California</td>
<td>Prop 65</td>
<td>Prop 65</td>
</tr>
<tr>
<td>Washington</td>
<td>NA</td>
<td>TBD</td>
</tr>
<tr>
<td>Oregon</td>
<td>24000</td>
<td>300000</td>
</tr>
<tr>
<td>North Carolina</td>
<td>2000</td>
<td>NA</td>
</tr>
<tr>
<td>Alaska</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Texas</td>
<td>290</td>
<td>560</td>
</tr>
<tr>
<td>Illinois</td>
<td>400</td>
<td>200</td>
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<td>Kentucky</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>Ohio</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>Alabama</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Connecticut</td>
<td>70</td>
<td>70</td>
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<tr>
<td>Delaware</td>
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<td>70</td>
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<tr>
<td>Georgia</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Iowa</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Maine</td>
<td>70</td>
<td>70</td>
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<tr>
<td>Maryland</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td><strong>Michigan</strong></td>
<td><strong>70</strong></td>
<td><strong>70</strong></td>
</tr>
<tr>
<td>New Hampshire</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>New York</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Rhode Island</td>
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<td>Pennsylvania</td>
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<td>70</td>
</tr>
<tr>
<td>Minnesota</td>
<td>35</td>
<td>27</td>
</tr>
<tr>
<td>Vermont</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>New Jersey</td>
<td>14</td>
<td>TBD</td>
</tr>
</tbody>
</table>
Replacement Chemicals
Regulatory Challenges

- Formal Guidance
- Screening Levels
- Target Analytes
- Methods
EPA Method 537
“A Finished Drinking Water Method”

The Only Approved EPA Method for PFAS
Groundwater, Soil, Tissue?

What method do we use for non-potable water matrices?
537 “Modified”

The element of CONFUSION
Reducing Variability
Labeled Analogues

The Parr Family = Native PFOS

The Incredible Family = Labeled PFOS

\[ = ^{13}\text{C} \]
Branched and Linear Error

Standard

Sample

0.99 vs 1.20 ng/ml
Secondary Ion Transition - PFOS

Standard

Sample
Proficiency Testing
Why are PFAS a concern?

• Social drivers in response to:
  • Lowered USEPA drinking water advisory levels
  • Drinking water concentrations > advisory levels
  • Fish consumption advisories
  • Wide variety of sources
  • Lots of unknowns

Toxic chemicals pollute drinking water near old tannery dump

EPA data shows toxic PFCs in two large Michigan water systems

Anger, anxiety about PFAS expressed at landfill pollution meeting

Researchers find unsafe levels of industrial chemicals in drinking water of 6 million Americans

Michigan releases updated fish consumption guidelines relating to PFAS in Lake St. Clair, Flint River
**Potential Exposure Pathways – Drinking Water**

![Map showing hydrological units with detectable PFASs](image)

Potential Exposure Pathways – Drinking Water

US EPA’s Health Advisory is 70 ng/L

### Potential Exposure Pathways – Consumption Fish and PFOS

<table>
<thead>
<tr>
<th>Region</th>
<th>County</th>
<th>Waterbody</th>
<th>Type of Fish</th>
<th>Size of Fish</th>
<th>Michigan (MI) Servings Per Month*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northeast</td>
<td>Kisco</td>
<td>Au Sable River (downstream of Foots Dam; Includes van Etten creek)</td>
<td>All Other Species (other than Bluegill, Largemouth, Smallmouth Bass, and Sunfish)</td>
<td>Any</td>
<td>Do not eat**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Largemouth Bass</td>
<td>Any</td>
<td>Do not eat**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rock Bass</td>
<td>Any</td>
<td>Do not eat**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Smallmouth Bass</td>
<td>Any</td>
<td>Do not eat**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sunfish</td>
<td>Any</td>
<td>Do not eat**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>All Other Species (other than Brown Trout, Chinook Salmon, Coho Salmon, Rainbow Trout, Steelhead, or Walleye)</td>
<td>Any</td>
<td>Do not eat**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bluegill</td>
<td>Any</td>
<td>Do not eat**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sunfish</td>
<td>Any</td>
<td>Do not eat**</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>All Other Species (other than Bluegill and Sunfish)</td>
<td>Any</td>
<td>Do not eat**</td>
</tr>
<tr>
<td>Southwest</td>
<td>Benzie</td>
<td>ST. Joseph River (downstream of the Benzie Springs Dam)</td>
<td>Rock Bass</td>
<td>Any</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Kent</td>
<td>Rogue River (upstream of Rockford Dam)</td>
<td>Suckers^</td>
<td>Any</td>
<td>4</td>
</tr>
<tr>
<td>Bay</td>
<td></td>
<td>Saginaw River</td>
<td>Bluegill</td>
<td>Any</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Largemouth Bass</td>
<td>Under 18^</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Smallmouth Bass</td>
<td>Under 18^</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sunfish</td>
<td>Any</td>
<td>4</td>
</tr>
<tr>
<td>Southeast</td>
<td>Genesee</td>
<td>Flint River (downstream of Mott Dam)</td>
<td>Largemouth Bass</td>
<td>Any</td>
<td>6 per year</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Smallmouth Bass</td>
<td>Any</td>
<td>6 per year</td>
</tr>
<tr>
<td></td>
<td>Saginaw</td>
<td></td>
<td>Bluegill</td>
<td>Any</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Largemouth Bass</td>
<td>Under 18^</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Smallmouth Bass</td>
<td>Under 18^</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sunfish</td>
<td>Any</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Largemouth Bass</td>
<td>Any</td>
<td>6 per year</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Smallmouth Bass</td>
<td>Any</td>
<td>6 per year</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rock Bass</td>
<td>Any</td>
<td>1</td>
</tr>
</tbody>
</table>

*Note: PFOS can’t be reduced by trimming and cooking.

**Weight of Person | MI Serving Size
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>45 pounds</td>
<td>2 ounces</td>
</tr>
<tr>
<td>90 pounds</td>
<td>4 ounces</td>
</tr>
<tr>
<td>180 pounds</td>
<td>8 ounces</td>
</tr>
</tbody>
</table>

* No one should eat fish listed as do not eat, regardless of age or health. When these fish were tested, MDHHS found very high levels of chemicals. Eating even one meal of these fish could possibly lead to health problems in the future, regardless of age or health.

^ In addition to PFOS, the guideline also includes mercury.

^ In addition to PFOS, the guideline also includes mercury and PCBs.

Source: [http://www.michigan.gov/mdhs/0,5886,7-330-71548_54734_54735_58671-296074--,00.html](http://www.michigan.gov/mdhs/0,5886,7-330-71548_54734_54735_58671-296074--,00.html)

**SOURCE:** US EPA. 2016. Fish and Shellfish Program Newsletter
Potential Exposure Pathways – Commercial and Consumer Products

Commercial and Consumer Products Containing PFAS:
- paper and packaging
- clothing and carpets
- outdoor textiles and sporting equipment
- ski and snowboard waxes
- non-stick cookware
- cleaning agents and fabric softeners
- polishes and waxes, and latex paints
- pesticides and herbicides
- hydraulic fluids
- windshield wipers
- paints, varnishes, dyes, and inks
- adhesives
- medical products
- personal care products (for example, shampoo, hair conditioners, sunscreen, cosmetics, toothpaste, dental floss)

SOURCE: www.atdsr.cdc.gov/pfas

SOURCE: ITRC – History and Use of PFAS Fact Sheet 2017
Status of PFAS Investigations in Michigan

Michigan Department of Environmental Quality
News Release

May 18, 2018

For More Information:
DEQ Media Office, deq-assist@michigan.gov, 517-284-9278

Michigan embarks on statewide study of PFAS in water supplies
**Sampling** Challenges – PFAS

- PFAS are ubiquitous
- Can be on samplers clothing, gloves, sampling equipment
- Waterproof field note books
- Glass bottles can cause loss of analyte
- Water for blanks (must be certified-PFAS free)
- Clean hands / Dirty hands
## Sampling Challenges – PFAS

<table>
<thead>
<tr>
<th>Prohibited Items</th>
<th>Acceptable Items</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Field Equipment</strong></td>
<td></td>
</tr>
<tr>
<td>Teflon® containing materials (tubing, bladders, o-rings, caps)</td>
<td>High-density polyethylene (HDPE) materials</td>
</tr>
<tr>
<td>Low density polyethylene (LDPE) materials</td>
<td>Acetate Liners</td>
</tr>
<tr>
<td>Waterproof field books</td>
<td>Silicon Tubing</td>
</tr>
<tr>
<td>Plastic clipboards, binders, or spiral hard cover notebooks</td>
<td>Metal field clipboards or with Masonite</td>
</tr>
<tr>
<td>Post-it Notes®, Sharpies®</td>
<td>Ball point pens</td>
</tr>
<tr>
<td>Chemical (blue) ice packs</td>
<td>Regular ice</td>
</tr>
<tr>
<td><strong>Field Clothing and PPE</strong></td>
<td></td>
</tr>
<tr>
<td>New cotton clothing or synthetic water resistant, waterproof, or stain treated clothing, clothing containing Gore-Tex™</td>
<td>Well laundered clothing made of natural fibers (preferable cotton) washed at least 6 times since purchase</td>
</tr>
<tr>
<td>Clothing laundered using fabric softener</td>
<td>No fabric softener</td>
</tr>
<tr>
<td>Boots containing Gore-Tex™</td>
<td>Boots made with polyurethane and PVC (PVC over boots over leather steel toe safety boots are acceptable*)</td>
</tr>
<tr>
<td>Tyvek®</td>
<td>Powder-free nitrile gloves</td>
</tr>
<tr>
<td>No cosmetics, moisturizers, hand cream, or other related products as part of personal cleaning/showering routine on the morning of sampling</td>
<td><strong>Sunscreens</strong> - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are “free” or “natural”</td>
</tr>
<tr>
<td></td>
<td><strong>Insect Repellents</strong> - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellent, Herbal Armor, California Baby Natural Bug Spray, BabyGanics</td>
</tr>
<tr>
<td></td>
<td><strong>Sunscreen and insect repellent</strong> - Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion</td>
</tr>
</tbody>
</table>
Remediation Challenges – PFAS

Field Demonstrated Treatment Technologies for Liquids
- Extraction and sorption with granular activated carbon or anion exchange resin
- Extraction and membrane filtration/reverse osmosis
- Extraction and precipitation/flocculation

Field-Demonstrated Treatment Technologies for PFAS in Solids
- Excavation and off-site landfilling or incineration
- Sorption/stabilization through ex situ soil mixing
- Ex situ thermal desorption and off-gas destruction

SOURCE: ITRC’s Remediation Technologies and Methods for PFAS – Fact Sheet
Remediation Challenges – PFAS

Biodegradation

- Very limited research to date showing biodegradation of Per-PFAS
- Evidence of transformations of Poly-PFAS
- Ability to treat to the proposed standards?

Oxidative / Reductive Technologies

- Requires high energy and/or diverse reactive species – complex chemistry
- Several bench studies and few pilots performed showing destruction of PFAS
- Research is ongoing to treat precursors
Remediation Challenges – PFAS

Extremely recalcitrant to degradation or destruction

Technologies under investigation:
- Biodegradation
- Flocculation
- Sorption
Remediation Challenges – PFAS

**Biodegradation**

- Biodegradation of PFOS under aerobic conditions in wastewater treatment sludge has been observed
- Organism identified as Pseudomonas aeruginosa strain HJ4
- 67% of PFOS was biologically decomposed
- Research is ongoing

**SOURCE:** Chemosphere 109 (2014) 221 – 225
**Remediation** Challenges – PFAS

**Flocculation**
- PerfluorAd®
- Surface active liquid reagent
- Non-toxic and biodegradable
- Causes flocculation and precipitation of PFAS from water
- Approximately 95% removal of PFAS
- Mobile treatment system is available

SOURCE: tersusenv.com
**Remediation Challenges – PFAS**

**Sorption**

- Activated Carbon or RemBind®
- RemBind recently used in Australia to treat 1,000 tonnes of soil impacted with PFAS
- Mixing soil with 5% RemBind® decreased leaching of PFAS from soil to below the analytical detection limit

SOURCE: tersusenv.com
QUESTIONS?