Characterization and Treatment of Perfluorinated Compounds: The Next Big Emerging Class of Contaminants

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Presentation Outline

• Background/Overview
• Regulatory Status/Considerations
• Site Characterization
• Risk Assessment
• Remedial Action Implications
• Summary
• Q&A and Discussion

PFOA

PFOS
**Background/Overview – Mfg. and Uses**

- Synthetic chemicals used in manufacturing fluoro-polymers
  - PFOA – perfluorooctanoic acid and its principle salts, manufactured from 1947-present. 8 manufacturers phased out production by 2010
  - PFOS – perfluorooctane sulfonate, manufactured from 1949-2002
- Typically only a fraction of final product/not an end product
- Used in making surface treatments
  - Non-stick cookware (Teflon®)
  - Breathable, all weather clothing (Gore-tex®)
  - Fluoro-elastomers (gaskets, O-rings, Hoses)
  - Paper and packaging protectors
- Used in making performance chemicals
  - Aqueous Film Forming Fire fighting foam (AFFF)
  - Mining and oil surfactants
  - Metal plating baths (chromium)
  - Insecticides

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**Aqueous Film Forming Foams (AFFF)**

- PFCs are used in AFFFs that were routinely used for fire fighter training at municipal and military fire training areas
- AFFF blankets fuel, cools the fuel surface, prevents re-ignition by suppressing release of flammable vapors
- Until 2000, AFFF effluent from fire-fighting activities were allowed to discharge to the environment
- C6 and Fluorine free AFFF developed as alternatives
- C8 AFFF still on DOD and other facilities
- At least 9 different formulations
Background/Overview – AFFF & Fire/Crash Sites

Estimated Quantity of AFFF in U.S.¹

<table>
<thead>
<tr>
<th>AFFF Use Sector</th>
<th>Estimated Quantity AFFF Concentrate (Gallons)</th>
<th>Possible Margin of Error ± %</th>
<th>Likely Range of Actual Quantity (Gallons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S. Military</td>
<td>2,838,500</td>
<td>± 5%</td>
<td>2,696,575 – 2,980,425</td>
</tr>
<tr>
<td>Other Federal</td>
<td>18,500</td>
<td>0 ± 25%</td>
<td>19,500 – 24,375</td>
</tr>
<tr>
<td>Aviation (ARFF)</td>
<td>729,016</td>
<td>-5 ± 20%</td>
<td>692,565 – 784,819</td>
</tr>
<tr>
<td>Aviation (Hangars)</td>
<td>850,000</td>
<td>± 25%</td>
<td>637,500 – 1,062,500</td>
</tr>
<tr>
<td>Merchant Ships/Offshore</td>
<td>80,000</td>
<td>± 25%</td>
<td>60,000 – 100,000</td>
</tr>
<tr>
<td>Fire Dept (non-aviation)</td>
<td>1,360,000</td>
<td>± 35%</td>
<td>884,000 – 1,836,000</td>
</tr>
<tr>
<td>Oil Refineries</td>
<td>1,900,000</td>
<td>± 25%</td>
<td>1,425,000 – 2,375,000</td>
</tr>
<tr>
<td>Other Petro-Chem</td>
<td>2,000,000</td>
<td>± 35%</td>
<td>1,300,000 – 2,700,000</td>
</tr>
<tr>
<td>Misc. Applications</td>
<td>150,000</td>
<td>± 35%</td>
<td>97,500 – 202,500</td>
</tr>
<tr>
<td>Total</td>
<td>9,927,016</td>
<td></td>
<td>7,812,640 – 12,155,619</td>
</tr>
</tbody>
</table>

¹Robert Darwin, Hughes & Assoc., Aug 2004

DoD Fire/Crash/Training Sites²

<table>
<thead>
<tr>
<th>Service</th>
<th>Total Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Force</td>
<td>353</td>
</tr>
<tr>
<td>Army</td>
<td>94</td>
</tr>
<tr>
<td>Navy</td>
<td>132</td>
</tr>
<tr>
<td>DLA</td>
<td>3</td>
</tr>
<tr>
<td>FUDS</td>
<td>12</td>
</tr>
<tr>
<td>Total</td>
<td>584</td>
</tr>
</tbody>
</table>

²DoD Knowledge Based Corporate Reporting System, 2008

Background/Overview – Chemical Properties

<table>
<thead>
<tr>
<th>Chemical Properties</th>
<th>PCB (Arochlor 1260)</th>
<th>PFOA</th>
<th>PFOS</th>
<th>TCE</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>357.7</td>
<td>414.07</td>
<td>538</td>
<td>131.5</td>
<td>78.11</td>
</tr>
<tr>
<td>Solubility</td>
<td>0.0027 mg/L @24°C</td>
<td>3400 – 9500 mg/L @25°C</td>
<td>519 mg/L @20°C</td>
<td>1100 mg/L @20°C</td>
<td>1780 mg/L @20°C</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>4.05x10⁻⁶ mmHg</td>
<td>0.5-10 mmHg</td>
<td>2.48x10⁻⁸ mmHg</td>
<td>77.5 mmHg</td>
<td>97 mmHg</td>
</tr>
<tr>
<td>Henry’s Constant</td>
<td>4.6x10⁻³ atm-m³/mol</td>
<td>0.0908 atm-m³/mol</td>
<td>3.05 x10⁻⁶ atm-m³/mol</td>
<td>0.0103 atm-m³/mol</td>
<td>0.0056 atm-m³/mol</td>
</tr>
</tbody>
</table>
Regulatory Status – Increasing Concerns

- Concerns originated in 1999 - 3M submitted information to US EPA regarding potential risks, 3M phased out PFOS production in 2002
- 2002 market shift in focus to C4-C6 chain length sulfonates and fluoro-telemer sulfonates (Fts)
- Several EPA, OECD, and UK Environmental Hazard/Risk Assessments between 2002 and 2006
- 2005 Stockholm Convention on Persistent Organic Pollutants listing
- EPA included several PFCs on Contaminant Candidate List-3 in 2009
- EPA included 6 PFCs in Unregulated Contaminant Monitoring Rule-3
- 2014 – US EPA OSWER crafting PFC screening levels, established Health Advisory Levels
- At present, no ‘regulatory driver’ or minimum risk level (MRL) in US

Background/Overview - Other PFCs

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Acronym</th>
<th>Chemical Abstract Services Registry Number (CASRN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-ethyl perfluorooctanesulfonamidoacetic acid</td>
<td>NEtFOSAA</td>
<td>-</td>
</tr>
<tr>
<td>N-methyl perfluorooctanesulfonamidoacetic acid</td>
<td>NMeFOSAA</td>
<td>-</td>
</tr>
<tr>
<td>Perfluorobutanesulfonic acid</td>
<td>PFBS</td>
<td>375-73-5</td>
</tr>
<tr>
<td>Perfluorodecanoic acid</td>
<td>PFDA</td>
<td>335-76-2</td>
</tr>
<tr>
<td>Perfluorododecanoic acid</td>
<td>PFDoA</td>
<td>307-55-1</td>
</tr>
<tr>
<td>Perfluorooctanoic acid</td>
<td>PFHxA</td>
<td>307-24-4</td>
</tr>
<tr>
<td>Perfluorobutanoic acid</td>
<td>PFUnA</td>
<td>72629-94-8</td>
</tr>
<tr>
<td>Perfluorooctanesulfonic acid</td>
<td>PFOS</td>
<td>1763-23-1</td>
</tr>
<tr>
<td>Perfluorooctanoic acid</td>
<td>PFOA</td>
<td>335-67-1</td>
</tr>
<tr>
<td>Perfluorotetradecanoic acid</td>
<td>PFTA</td>
<td>376-06-7</td>
</tr>
<tr>
<td>Perfluorotridecanoic acid</td>
<td>PFTrDA</td>
<td>72629-94-8</td>
</tr>
<tr>
<td>Perfluorooctanoic acid</td>
<td>PFUnA</td>
<td>2058-94-8</td>
</tr>
</tbody>
</table>

**Bold** = on UCMR3 monitoring list plus PFOS/PFOA
Site Characterization - Recommended Sampling Procedures

- Sampling & QAPPs must address potential for cross contamination and/or false positives, sources include:
  - Water proof field notebooks
  - Teflon® Liner in bottles
  - Teflon® bailers or wells
  - Decon 90 decon solution, possibly others
  - Fast food wrappers
  - Tyvek® suits

- Preference for a 250 mL HDPE bottle, no preservatives

- 7-14 day holding time, Preserve on ice

- No commercially demonstrated screening kit/tools, several under development
  - Ziltek Remscan Infrared scanner (AUS)
  - CRC Care (AUS)
  - Methylene Blue Active Substance – Colorimetric test for Anionic Surfactants

Site Characterization - Laboratory Analysis

- Liquid Chromatography – Mass Spectrometry – EPA Method 537
  - LC / MS /MS

- International Standard ISO 25101
  - PFOS and PFOA in water

- Extraction / Holding Time
  - Water 7 days / 40 days
  - Soils 14 days / 40 days

- Method Detection Limits
  - Water
    - PFOS – 0.015 to 0.001 ug/L
    - PFOA – 0.010 to 0.004 ug/L
  - Soil
    - PFOS – 0.4 to 0.01 ug/kg
    - PFOA – 1.0 to 0.5 ug/kg

- Limited Certified Laboratories
  - USA Laboratories
    - Test America – Denver, CO
    - MPI Research Inc. – State College, PA
    - Pace Analytical
    - UL Laboratories – South Bend, IN
  - German Laboratories
    - Fresenius
    - Analytis
  - Canada Laboratories
    - Axys Analytical Services
    - Maxxam
    - Intertek – United Kingdom

- Data comparability between laboratories is difficult

- Costs
  - $250 to $500 per sample (US $)
Risk Assessment – What we know/don’t know

- Important to note that there are 2 distinct focuses on PFC risks
  - General exposures via non-environmental media (e.g. Teflon cooking products and food packaging materials)
  - Site-specific exposures by way of contaminated environmental media

- What we do know
  - Toxicity to animals
  - Bioaccumulates
  - Environmentally persistent
  - Widespread in human population around globe

- What we don’t know
  - Widespread Exposure at unacceptable concentrations?
  - Toxicity to humans?
  - Issue of potential for prostate cancer is contentious
  - Potential link to Autism is contentious
  - 2012 C8 Panel conclusions (Kidney Cancer) – 1st carcinogenic evidence?

Remedial Action Implications – Standards/SL’s

<table>
<thead>
<tr>
<th>Regulatory Agency</th>
<th>PFOS</th>
<th>PFOA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPCA – Residential SRV</td>
<td>2100 µg/kg</td>
<td>2100 µg/kg</td>
</tr>
<tr>
<td>MPCA – Recreational SRV</td>
<td>2500 µg/kg</td>
<td>2600 µg/kg</td>
</tr>
<tr>
<td>MPCA – Industrial SRV</td>
<td>14000 µg/kg</td>
<td>13000 µg/kg</td>
</tr>
<tr>
<td>US EPA Region 4 – Residential</td>
<td>6000 µg/kg</td>
<td>16000 µg/kg</td>
</tr>
</tbody>
</table>

| **Groundwater**                    |           |           |
| US EPA – drinking water HAL        | 0.2 µg/L  | 0.4 µg/L  |
| MDH – groundwater                  | 0.3 µg/L  | 0.3 µg/L  |
| New Jersey – drinking water        | ---       | 0.04 µg/L |
| North Carolina – groundwater       | ----      | 2 µg/L    |
| Canada DW Guidance Value           | 0.7 µg/L  | 0.7 µg/L  |
| UK DEFRA – drinking water          | 0.3 µg/L  | 10 µg/L   |
| Germany – drinking water           | 0.1 – 0.3 µg/L | 0.1 – 0.3 µg/L |
## Remedial Action Implications - Challenges

- Emerging concern with significant Site characterization challenges
  - large dilute plumes will likely form and a “source area” may not exist
  - co-mingled plumes (e.g. BTEX, TPH, Fuels)
  - Many sources, opportunities for cross contamination
- Limited remediation experience and almost no previous commercial focus on developing remediation technologies
- Chemical property challenges
  - resistant to most conventional treatment technologies
  - high solubility and low Henry’s law constant
- Existing aerobic bio or ISCO treatment may partially oxidize other AFFF compounds (e.g. precursors) and produce additional PFOS/PFOA

## Treatment of Solids

- **Landfill**
  - Commercially available vs. special construction
  - Leachate management & treatment considerations
- **Isolate in place**
  - Site specific considerations
  - Capping
  - Landfill reconstruction
- **Incineration**
  - Proven technology
  - Generally for lower Volume, higher Concentration materials
**Treatment of Water**

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Technology</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separation</td>
<td>Filtration</td>
<td>Lab</td>
</tr>
<tr>
<td></td>
<td>Adsorption</td>
<td>Full</td>
</tr>
<tr>
<td></td>
<td>Reduction</td>
<td>Lab</td>
</tr>
<tr>
<td>Destruction</td>
<td>Oxidation</td>
<td>Lab</td>
</tr>
<tr>
<td></td>
<td>Pyrolysis</td>
<td>Lab</td>
</tr>
<tr>
<td></td>
<td>Photochemical</td>
<td>Lab</td>
</tr>
<tr>
<td></td>
<td>Thermal Oxidation</td>
<td>Full</td>
</tr>
</tbody>
</table>

Optimal treatment technology would be highly dependent on the initial PFC concentration (i.e., high for manufacturing waste or low for environmental distributed) and the matrix in question.

**Remedial Action Implications – Scenarios**

- No current remediation with potential or confirmed presence of PFOA/PFOS
  - Potential - when to look and why?
  - Confirmed – Pump and treat likely best current option
- Existing pump and treat remedy with treatment via industrial WWTP
  - May or may not address PFOS/PFOA
  - Potential for PFC concentrations to increase
- Existing pump and treat remedy with independent GW treatment system
  - May or may not address PFOS/PFOA
- Existing in situ or approved Monitored Natural Attenuation remedy
  - Not likely to address PFOS/PFOA
### Possible In-Situ Treatment Technologies

- **FMC (now PeroxyChem)** - testing activated persulfate and Fenton's reagent to treat PFOS/PFOA
- **Washington State University** – testing degradation of PFOA through catalyzed hydrogen peroxide propagation reaction
- **ES&T** - Reductive Defluorination: Vitamin B12 as electron transfer mediator for PFOS reduction, Ti(III)-citrate as the bulk electron source
- **Removals of PFOA/PFOS in pilot-scale constructed wetland**
- **University of Arizona** - Boron-Doped Diamond Film Electrodes for oxidation of PFOS and TCE

### Enzyme Catalyzed Oxidative Coupling

- **UGA/AECOM** has been funded by AFCEC to evaluate “Enzyme Catalyzed Oxidative Coupling (ECOC) Reactions” to treat PFCs. This technology was originally developed for treatment of other persistent organics (PCBs, PAHs)
- **ECOC** is a process that is inspired by how natural organic matters are broken down naturally through enzyme catalyzed oxidation process
- In this process PFC is oxidized by organic radicals catalyzed by extracellular enzymes.

![Phanerochaete chrysosporium](Genus of White Rot Fungi)
Summary

• Primary sources of potential PFOS/PFOA includes AFFF releases, plating facilities, and landfills.

• AFFFs represent the likely most significant source, were produced in at least 9 different formulations, and contain many different PFCs

• Significant potential for background contamination/other sources

• Compounds are very soluble, recalcitrant and persistent

• Large dilute plumes will form and can represent potential financial and receptor risks, especially for surface water/ecological receptors

• No current ‘regulatory driver’ or MRL in US but EPA crafting screening levels and requesting sampling/analysis

Summary

• More cleanup standards will likely be established and trend downward

• Existing remediation systems are not likely addressing PFCs, could exacerbate problems (e.g. PFOS as metabolite of precursors)

• Landfill, isolation or incineration are likely best current soil treatment options

• P&T with GAC may be best current GW treatment option; Biological and Enzymatic treatment promising

• PFCs will likely increasingly become problematic for PRPs with a focus beyond PFOS/PFOA

• PFCs appear to be unlike anything we’ve dealt with before and represent a significant challenge.
Questions and Discussion

Key PFC Resources

- **Dave Woodward** – Vice President, Director of Remediation Technology
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