PFAS Sampling

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Background Levels
Where Do We Find PFASs?

FluoroTechnology makes important products for vital industries possible. FluoroCouncil member companies voluntarily committed to a global phase-out of long-chain fluorochemicals by the end of 2015, resulting in the transition to alternatives, such as short-chain fluorochemicals that offer the same high-performance benefits, but with improved environmental and health profiles.

**Where Do We Find PFASs?**

- **Aerospace/Defense**
  - Enables chemical-resistant tubes, hoses, and fluid seals; high and low temperature brake and hydraulic fluids used in aircraft control systems and brakes; and ultra-high frequency wire and cable insulation necessary for navigation, fly-by-wire control, and aircraft communications.

- **Building/Construction**
  - Enhances durability, UV resistance, and anti-corrosive properties to lengthen the lifetime of infrastructure, facades, and surfaces.

- **Electronics**
  - Improves in solvation, weatherability, transparency, and water-resistance. Provides smooth and smudge-resistant touch screens.

- **First Responders**
  - Offers life-saving protection in safety gear and firefighting foams used to fight flammable liquid fires.

- **Automotive**
  - Provides every automotive system with durability, heat and chemical resistance, and corrosion barriers. Increases reliability of engine compartment wiring and gauges and improves auto safety by reducing engine compartment fires. Protects carpets and seats against stains, soil, oil, and water.

- **Oil and Gas**
  - Provides reliable equipment to help improve the safety and affordability of oilfield and pipeline operations. Improves the reliability and safety of fuel system seals and hoses, O-rings, and downhole and field equipment gaskets.

- **Military**
  - Enables apparel and equipment to provide high-barrier skin protection in extreme environments and against chemical warfare agents.

- **Chemical/Pharmaceutical Manufacturing**
  - Provides sterile, corrosion-resistant coatings, linings, and equipment.

- **Healthcare**
  - Serves as high dielectric insulators in medical equipment that relies on high frequency signals, like defibrillators, pacemakers, and MRIs, PET, and MRI imaging devices. Used to treat medical garments, drapes, and surgical gowns to protect against the transmission of diseases and infections.

- **Semiconductors**
  - Creates ultra-pure manufacturing environments necessary for micro-electronics. Used for plasma machinery, etching materials, cleaning fluids, and wetting surfactants for chemical etchants.

- **Outdoor Apparel/Equipment**
  - Creates breathable membranes and long-lasting finishes that provide water repellency, oil repellency, stain resistance, and soil release with abrasion-resistant finishes for apparel and equipment.

FluoroTechnology is the use of fluorine chemistry to create any fluorinated product. When fluorine and carbon atoms join together, they create a powerful chemical bond. The use and manipulation of this bond gives FluoroTechnology its distinct properties of strength, durability, heat-resistance, and stability. These properties are critical to the reliable and safe function of myriad products that industry and consumer rely on every day.

www.FluoroCouncil.org
## Background Levels

### Perfluorocarboxylic Acid Content in 116 Articles of Commerce

Table 6-1. Comparison of source strengths for total amount of PFCA (TPFCA) in a hypothetical, “typical” American home

<table>
<thead>
<tr>
<th>Group ID</th>
<th>Article category</th>
<th>TPFCA in article</th>
<th>Article quantity</th>
<th>TPFCA in home (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pre-treated carpeting</td>
<td>48.4 ng/cm²</td>
<td>150 m²</td>
<td>72.6</td>
</tr>
<tr>
<td>B</td>
<td>Commercial carpet-care liquids</td>
<td>12000 ng/g</td>
<td>6 kg</td>
<td>71.8</td>
</tr>
<tr>
<td>C</td>
<td>Household carpet/fabric-care liquids and foams</td>
<td>953 ng/g</td>
<td>1 kg</td>
<td>0.95</td>
</tr>
<tr>
<td>D</td>
<td>Treated apparel</td>
<td>198 ng/g</td>
<td>2 kg</td>
<td>0.40</td>
</tr>
<tr>
<td>E</td>
<td>Treated home textile and upholstery</td>
<td>336 ng/g</td>
<td>5 kg</td>
<td>1.68</td>
</tr>
<tr>
<td>F</td>
<td>Treated non-woven medical garments</td>
<td>795 ng/g</td>
<td>0 kg</td>
<td>0</td>
</tr>
<tr>
<td>G</td>
<td>Treated floor waxes and stone/tile/wood sealants</td>
<td>2430 ng/g</td>
<td>1 kg</td>
<td>2.42</td>
</tr>
<tr>
<td>H</td>
<td>Treated food contact paper</td>
<td>3100 ng/g</td>
<td>0.01 kg</td>
<td>0.03</td>
</tr>
<tr>
<td>I</td>
<td>Membranes for apparel</td>
<td>124 ng/g</td>
<td>1 kg</td>
<td>0.12</td>
</tr>
<tr>
<td>J</td>
<td>Thread seal tapes and pastes</td>
<td>603 ng/g</td>
<td>0.02 kg</td>
<td>0.01</td>
</tr>
<tr>
<td>K</td>
<td>Non-stick cookware</td>
<td>0.028 ng/cm²</td>
<td>1 m²</td>
<td>0.0003</td>
</tr>
<tr>
<td>L</td>
<td>Dental floss and plaque removers</td>
<td>31.3 ng/g</td>
<td>0.005 kg</td>
<td>0.0002</td>
</tr>
<tr>
<td>M</td>
<td>Miscellaneous</td>
<td>69.5 ng/g</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*The average, single-family home size in the U.S. in 2004 was 2330 ft² (http://www.nahb.org/). The quantities of articles are rough estimates. Assuming 70% of floor area is carpet; conversion factors for total PFCA are given in supporting information. For one application; dilution factor is considered.

USEPA Study, March 2009  
EPA/600/R-09/033
Class of PFAS Compounds in AFFF Formulations

Figure 1. Target analyte classes, structures, and acronyms. Fluorotelomer PFAS are listed to the left and perfluorinated PFAS are listed on the right.

1Legacy classes of PFAS. *Newly-identified classes of PFAS. Data quality levels include quantitative (Qn), semi-quantitative (Sq), and qualitative (Qi). *Indicates analytes analyzed for in AFFF only.

Sense of Scale

- PFOS/PFOA Health Advisories
  - 70 parts per trillion = 70/1,000,000,000,000

- World Population = 7.4 billion
  - 70 ppt ~ 1 person / 2 world populations

http://environment.org.uk/post/7837877866/7billion
PFASs Ongoing Evolution

Investigation/More Investigation

More Toxicology Data

Regulatory Decision Making

Communicate the Risk
Risk = Hazard + Outrage
(Sandman, 1987)

More PFAS Analytes

Changing Composition in Manufacturing

Treatment Technologies

Lower PFAS Detection Limits
Parts Per Trillion (ng/L)
PFAS Sampling for Water

- What are required and recommended when sampling for PFASs?
- Where to sample for PFASs?
- Which PFASs to analyze for?
- Can we trust the data (cross-contamination)?
Planning for PFAS Sampling

– Example PFAS sampling references
  • USEPA Method 537
  • Perfluorocarboxylic Acid Content in 116 Articles of Commerce, EPA/600/R-09/033
  • Navy Field Sampling Protocols for PFCs
  • Perfluorochemical (PFC) Field Sampling Protocol, Transport Canada, 2013
  • Interim Guideline on the Assessment and Management of Perfluoroalkyl and, Polyfluoroalkyl Substances (PFAS), Department of Environment Regulation, Western Australia, 2016
  • State guidance…

– Contact laboratory
– Develop quality assurance documents
– Conduct field crew training classes
– Site-specific work plan development on sampling strategy

<table>
<thead>
<tr>
<th>Category ID</th>
<th>Category name</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pre-treated carpeting</td>
<td>9</td>
</tr>
<tr>
<td>B</td>
<td>Commercial carpet-care liquids</td>
<td>9</td>
</tr>
<tr>
<td>C</td>
<td>Household carpet/fabric-care liquids and foams</td>
<td>12</td>
</tr>
<tr>
<td>D</td>
<td>Treated apparel</td>
<td>16</td>
</tr>
<tr>
<td>E</td>
<td>Treated home textile and upholstery</td>
<td>14</td>
</tr>
<tr>
<td>F</td>
<td>Treated non-woven medical garments</td>
<td>5</td>
</tr>
<tr>
<td>G</td>
<td>Treated floor waxes and stone/wood sealants</td>
<td>11</td>
</tr>
<tr>
<td>H</td>
<td>Treated food contact paper</td>
<td>5</td>
</tr>
<tr>
<td>I</td>
<td>Membranes for apparel</td>
<td>10</td>
</tr>
<tr>
<td>J</td>
<td>Thread sealant tapes and pastes</td>
<td>10</td>
</tr>
<tr>
<td>K</td>
<td>Non-stick cookware</td>
<td>14</td>
</tr>
<tr>
<td>L</td>
<td>Dental floss and plaque removers</td>
<td>8</td>
</tr>
<tr>
<td>M</td>
<td>Miscellaneous a</td>
<td>7</td>
</tr>
</tbody>
</table>

\[a\] Includes four car-care products, two boat-care products, one deck cleaner, and one dry sack for outdoor use.
Many Precautions for Sampling Procedures Don’t Have Scientific Data To Prove The Concerns

BE CAREFUL VS. OVER REACT

Because we believe….
• Extremely low reporting and regulatory limits magnify the importance of cross contamination
• Trace background PFAS levels can be detected
• Uncertainties on the patterns of PFAS released from the PFAS materials remain unknown
• Trace PFAS levels are detected in some drinking water systems

Because we believe…
• Stable chemistry, unlikely to be released under most conditions
• The PFAS levels from cross contamination cannot be quantified
• Manufacturing of PFOA and PFOS have been phased out between 2010-2015
PFAS Sampling
## The Field Crew

<table>
<thead>
<tr>
<th>Do Not Use</th>
<th>Acceptable Alternatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wearing/using personnel hygiene items (cosmetics, lotions, moisturizers)</td>
<td>Do not wear</td>
</tr>
<tr>
<td>Sunscreens, insect repellants</td>
<td>Long sleeve, light colored 100% cotton shirts, wide brimmed hats, products that are 100% natural ingredients, DEET, tuck pant legs into socks and/or boots and use duct tape</td>
</tr>
<tr>
<td>New or unwashed clothing</td>
<td>Well-washed clothing</td>
</tr>
<tr>
<td>Clothing washed in fabric softeners</td>
<td>Clothing not washed with fabric softeners</td>
</tr>
<tr>
<td>Treated clothing (waterproof, water resistant, stain-resistant)</td>
<td>Clothing made of synthetic or natural fibers</td>
</tr>
<tr>
<td>Treated boots (waterproof, water resistant, stain-resistant)</td>
<td>Steel-toed boots made with polyurethane and polyvinyl chloride (PVC).</td>
</tr>
<tr>
<td>Coated Tyvek® suits*</td>
<td>Tyvek® suits</td>
</tr>
<tr>
<td>Handing or prepackaged food products</td>
<td>Do not have at the sampling location, wash hands well after handling, wear powderless nitrile gloves</td>
</tr>
</tbody>
</table>
Sunscreens and Insect Repellants

- Many manufactured sunblock and insect repellants contain PFASs and should not be brought or used on-site.

- The following products are acceptable:
  - **Sunscreens** - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, and baby sunscreens that are “free” or “natural”
  - **Insect Repellents** - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellant, Herbal Armor, California Baby Natural Bug Spray, BabyGanics
  - **Sunscreen and insect repellant** - Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion

"..The highest concentrations of PFOS and PFOA were detected at 0.0671 ng/g and 21.0644 ng/g, respectively. Even though present concentrations are found at ng/g levels, the daily use of sunscreen products is normally several grams. Therefore, a risk assessment of PFOS and PFOA contamination in sunscreen products is an important concern, and more attention needs to be paid to the long-term effects on human health.” - 2015

“The concentrations of total PFCAs ranged from not detected to 5.9 μg g⁻¹ for cosmetics and from not detected to 19 μg g⁻¹ for sunscreens” – Chemosphere, 2013
## Sampling Equipment

<table>
<thead>
<tr>
<th>Do Not Use</th>
<th>Acceptable Alternatives</th>
</tr>
</thead>
</table>
| Fluoropolymer bailers or pump bladders | Disposable Equipment  
Dedicated Equipment (no PTFE parts) |
| Fluoropolymer tubing, valves and other parts in pumps | High-density polyethylene (HDPE) and silicon materials (i.e. tubing). |
| LDPE HydraSleeves | HDPE HydraSleeves |
| Decon 90 | Alconox® and Liquinox® soap for decontamination, if needed |
| Decontamination water from the site | Water used for the decontamination of sampling equipment will be laboratory certified "PFAS-free" water |
| Glass containers (due to potential loss of analyte through adsorption | Polypropylene or HDPE sample bottles fitted with an unlined (no PTFE), polypropylene or HDPE screw cap |
| Waterproof field books | Loose paper on aluminum clipboards |
| Sharpies (acceptable by EPA checklist) | Ball point pens |
| Post-it notes | |
| Blue (chemical) ice* | Ice contained in plastic (polyethylene) bags (double bagged), secured to avoid meltwater from contacting sample containers, overnight shipping |
| Aluminum foil | Thin HDPE sheeting can be used |
Sample Collection

- Prior to collection of samples, field personnel must wash their hands and wear a new set of nitrile gloves
- Do not filter samples
- **Shaker Test:** A small portion of the sample (~10-25 mL) should be shaken by the sample collector on site. If foaming is noted within the sample, this should be documented when samples are submitted for analysis
- Field QA/QC Samples !!
  - Field blanks (bottle to bottle)
  - Equipment blanks (rinsate)
  - Trip or travel blank

<table>
<thead>
<tr>
<th>PFOA Site</th>
<th>FS/DUP</th>
<th>EB/FB</th>
<th>EB hits &gt;RL</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (landfill)</td>
<td>209</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>B (landfill)</td>
<td>77</td>
<td>21</td>
<td>2</td>
</tr>
<tr>
<td>C (landfill)</td>
<td>99</td>
<td>21</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>637</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>823</td>
<td>34</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AFFF Site Sample Type</th>
<th>Samples Analyzed</th>
<th>PFAS detected</th>
<th># detections</th>
<th>PFAS Analytes detected</th>
<th>Result (min-max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field Blank</td>
<td>11</td>
<td>No</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Equipment Blank</td>
<td>115</td>
<td>Yes</td>
<td>3</td>
<td>PFOS, 6:2 FTS</td>
<td>0.011-0.02 µg/L</td>
</tr>
</tbody>
</table>
Don’t use detergent to decon drilling equipment, scrub with a plastic brush and rinse thoroughly in tap water, then triple-rinse in distilled or deionized water

Use PFAS-free drilling fluids

Don’t re-use PVC well material which has been used previously at sites where PFAS is known or suspected to be present

Collect representative water sample used during drilling activities

Purged groundwater must be drummed, transported and managed properly

Surface water must be collected by inserting a capped sampling container (polypropylene or HDPE) with the opening pointing down to avoid the collection of surface films

Soil and sediment core samples must be collected directly from single-use PVC liners that must not be decontaminated or reused at different locations
Additional Considerations

– No food or drink shall be brought on-site, with the exception of bottled water and hydration drinks (i.e., Gatorade® and Powerade®) and available for consumption only in the staging area.

– When field personnel require a break to eat or drink, they should remove their gloves and coveralls and move to an appropriate location (preferably downwind). When finished, field personnel should then tidy up and put their coveralls and gloves back on prior to returning to the work area.

– Visitors to the site are asked to remain at least 30 feet from sampling areas.
Recommended PFAS Sampling Strategy

1. Drinking water
2. Surface water
3. Groundwater
   1) upgradient well(s).
   2) furthest downgradient of the interpreted or known source.
   3) downgradient to source
   4) the wells closest to the interpreted or known source are sampled last.

Large dilute plume intercepting multiple sensitive receptors
Multiple Transport Mechanisms
PFOA Releases From a Fluoropolymer Manufacturing Facility
Environmental Conditions
PFASs at AFFF Release Sites

Groundwater Flow
Fire Training Area

-300mV
-200mV
-100mV
0 mV
100 mV
200 mV

REDOX ZONATION

Precursors Oxidize & Dead End at PFOS/PFOA
High BOD PFASs extend anaerobic zone
Hydrocarbons biodegrade rapidly
Shorter chain PFASs become more mobile

Fuels
PFASs

Shorter chain PFASs become more mobile
Precursors Biotransformation
6:2 Fluorotelomer Biotransformation Pathways Converge

Raw materials:
6:2 FTOH and 6:2 FTSCI

Commercial products:
FT-based Surfactants
FT-based Polymers

Transient Intermediates

Terminal products:
PFBA, PFPa, PFHxA, PFHpA, 5:3 Acid
How PFAS Data Can Change with Time

– Contaminated Sites with Potential PFAS Impact
  • Active AFFF uses and unprotected storage
  • Remediation induced conditions can alter biotransformation of PFAS precursors (McGuire et al, ES&T, 2014), such as:
    o Air/oxygen sparging
    o Pump and treat
    o In-situ chemical oxidation
  • Surface and groundwater investigation program (uses of PTFE materials for VOC sampling)

– Off-Site Sampling
  • Private well installation
  • Cross contamination from household and personal use items which may contain PFASs
PFAS Sampling—Summary

- Identify sources of cross contamination in the field and lab environments
- Evaluate sampling protocols including field equipment and clothing in the field and collect banks
- At PFAS impacted sites, practice consistently to avoid cross contamination early for site-wide investigation program
- Use a lab with proven PFAS experience and understanding of potential PFAS contamination sources and PFAS analytical issues
- Document field practice changes to account for potential data variations between PFAS sampling events
- Need scientific data to document the PFAS impact from the personal protection and field equipment, remove or add precautions when more science evolves
Thank You!

“The significant problems we face cannot be solved at the same level of thinking we were at when we created them.”

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Q & A

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