Pefluorocarbons in the Environment: Fate, Persistence and Remediation Options

A. Eduardo Sáez, James Farrell, Kimberly Carter, Tristan Day and Eric A. Betterton

Departments of Chemical and Environmental Engineering and Atmospheric Sciences, The University of Arizona, Tucson, AZ

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Trace Chemical Contaminants in Water and Wastewater – Semiarid Perspectives
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Perfluorocarbons (PFCs)
- Heavily fluorinated polymers and telomers (short-chain polymers) are ubiquitous in domestic and industrial applications
- Commercial products: Gore-Tex™, Scotchgard™, Stainmaster™
  Teflon™: PTFE \((-CF_2-\underset{n}{\cdots}CF_2-\)\)

Surfactants: Coatings:
- Shampoos Cleaning products
- Fire-fighting foams Clothing
- Semiconductor industry Food wrapping
- Metal plating Nonstick cookware

Specific applications:
- Photolithography (semiconductors) – anti-reflective coatings
- Aviation hydraulic fluids

Fluorinated Alkyl Surfactants
- Have tails that are both hydrophobic and lipophobic: repel both water and organics.
- Reduce surface tension to lower levels than typical hydrocarbon surfactants.
- Form very thin and robust liquid films when dissolved in water: ideal for production of persistent foams used in fire-fighting applications and as detergents and cleaners.

PFOA and PFOS
Perfluorooctanoic acid (PFOA)
Perfluorooctanesulfonate (PFOS)
PFCs in the Environment

PFCs have been found in:
- Soils, groundwater, tap water, plants and animals.
- Human food chain: beans, bread, fruits, beef.
- Air; C-10 fluorinated alcohol: \( \text{CF}_2(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{OH} \)
- Human blood.
- Tissues of animals from low-population regions of the world with no industrial sources of PFCs.
- Only stored human blood samples analyzed that were free of PFOS were from military personnel in the Korean War (1950-1953), which predates industrial production of PFCs.

Sources of PFOA and PFOS

(1) Manufacturing
- Both chemicals are currently produced. PFOA and PFOS synthesis is achieved by three commercial processes:
  a. Electrochemical fluorination of organic compounds in the presence of HF.
  b. Telomerization: polymerization of TFE by fluororidation.
  c. Oxidation of perfluorooctyl iodide
- Numerous PFCs are produced as intermediates and by-products of synthesis processes, e.g., the main source of PFOS is believed to be the synthesis of PFOA.

(2) Products of degradation of other PFCs
N-EtFOSE, [2-(N-ethyl-perfluorooctane sulfonamide) ethyl alcohol], a monomer used in the manufacture of PFCs, biodegrades in the presence of sludge from municipal wastewater treatment facilities to PFOA and PFOS.

Other fluorotelomer alcohols biodegrade to PFOA; e.g.,

\[
\text{CF}_2\text{CF}_2\text{OH} \rightarrow \text{PFNA} \quad \text{PFOS}
\]

Fluorotelomer alcohols slowly degrade by hydrolysis: N-EtFOSE has a hydrolysis half-life between 7 and 27 years. Final degradation product is PFOS.

(2) Products of degradation of other PFCs (cont.)
Fluorinated alcohols are emitted by a wide variety of commercial products. They are left over from manufacturing (Dinglasan-Panlilio and Mabury, 2006). PFOA precursors?

(3) Direct release from manufactured products.
A recent study (Sinclair et al., 2007) measured detectable release of PFOA from some frying pans at normal cooking temperatures, and fluorinated alcohols from pre-packed microwave popcorn.
### PFOS and PFOA in Physical Matrices

#### Near production/storage facilities:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Surface water (µg/L)</th>
<th>Groundwater (µg/L)</th>
<th>Air (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>0.03&lt;sup&gt;1&lt;/sup&gt;, 0.11&lt;sup&gt;2&lt;/sup&gt;</td>
<td>3-130</td>
<td>NA</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.39&lt;sup&gt;2&lt;/sup&gt;</td>
<td>≤DL</td>
<td>186.720</td>
</tr>
</tbody>
</table>

<sup>1</sup> Firefighting facilities  
<sup>2</sup> Upstream of Decatur, AL fluorochemical manufacturing facility  
<sup>3</sup> Downstream of Decatur, AL fluorochemical manufacturing facility

Sources: Hansen et al. (2002), Moody and Field (1999), Moody et al. (2003)

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### PFOS and PFOA in Biological Matrices

#### Nonoccupationally exposed human sera (µg/L)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Range (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>14-52</td>
</tr>
<tr>
<td>PFOA</td>
<td>3.17</td>
</tr>
</tbody>
</table>

#### Occupationally exposed human sera (µg/L)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Range (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>250-12,800</td>
</tr>
<tr>
<td>PFOA</td>
<td>100-6,400</td>
</tr>
</tbody>
</table>

#### Animal livers from remote locations (ng/g)

- PFOS: 20-5,140<sup>2</sup>
- PFOA: 4.5-27<sup>2</sup>

#### Animal livers from populated locations (ng/g)

- PFOS: 10122<sup>1</sup>
- PFOA: 4,523<sup>1</sup>

<sup>1</sup> Northern fur seals (Alaska)  
<sup>2</sup> Minks from US


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### PFOS and PFOA in Physical Matrices

- Precipitation: PFOA found in urban and remote areas in rainwater (North America), with higher concentrations in “urban influenced sites” (Scott et al., 2006)
- National Environmental Research Institute of Denmark (associated with other Nordic institutes) found PFOA/PFOS in sewage sludge and landfill leachates

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### PFC’s in sewage sludge (ng/g)

#### PFOS

<table>
<thead>
<tr>
<th>Species (organ)</th>
<th>Range of PFOS levels (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Various fish</td>
<td>&lt; 7.5 - 46</td>
</tr>
<tr>
<td>Laysan albatross (liver)</td>
<td>&lt; 8.0 - 35.9</td>
</tr>
<tr>
<td>Common cormorant (liver)</td>
<td>&lt; 180 - 182</td>
</tr>
<tr>
<td>Common seal (liver)</td>
<td>&lt; 35.9 - 41</td>
</tr>
<tr>
<td>Ring-billed gull (yolk)</td>
<td>&lt; 7.5 - 20</td>
</tr>
<tr>
<td>Short-snouted spinner dolphin (liver)</td>
<td>&lt; 8.03 - 12.9</td>
</tr>
</tbody>
</table>

#### PFOA

<table>
<thead>
<tr>
<th>Species (organ)</th>
<th>Range of PFOA levels (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Western loggerhead turtle (skin)</td>
<td>&lt; 130</td>
</tr>
<tr>
<td>Common seal (liver)</td>
<td>&lt; 180 - 182</td>
</tr>
</tbody>
</table>

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### PFOS and PFOA in Physical Matrices

<table>
<thead>
<tr>
<th>Year samples were collected</th>
<th>Location</th>
<th>Number of animals with PFOA</th>
<th>Species (organ)</th>
<th>Range of PFOA levels (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1993-2000</td>
<td>US</td>
<td>1 of 1</td>
<td>Lapin abnormans (liver)</td>
<td>&lt;75 - 20</td>
</tr>
<tr>
<td>1999</td>
<td>US</td>
<td>2 of 3</td>
<td>Lapin abnormans (liver)</td>
<td>&lt;75 - 20</td>
</tr>
<tr>
<td>2005</td>
<td>US</td>
<td>1 of 1</td>
<td>Lapin abnormans (liver)</td>
<td>&lt;75 - 20</td>
</tr>
<tr>
<td>2005</td>
<td>Europe</td>
<td>12 of 12</td>
<td>Common seal (liver)</td>
<td>&lt;20 - 20 (average 98 ng/g)</td>
</tr>
<tr>
<td>2005</td>
<td>US</td>
<td>1 of 1</td>
<td>Common seal (liver)</td>
<td>&lt;20 - 20 (average 98 ng/g)</td>
</tr>
<tr>
<td>2005</td>
<td>Europe</td>
<td>1 of 1</td>
<td>Common seal (liver)</td>
<td>&lt;20 - 20 (average 98 ng/g)</td>
</tr>
<tr>
<td>2006</td>
<td>Europe</td>
<td>3 of 27</td>
<td>Common seal (liver)</td>
<td>&lt;20 - 20 (average 98 ng/g)</td>
</tr>
<tr>
<td>2000</td>
<td>US</td>
<td>1 of 1</td>
<td>Common seal (liver)</td>
<td>&lt;20 - 20 (average 98 ng/g)</td>
</tr>
</tbody>
</table>

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### PFOA in Wildlife

<table>
<thead>
<tr>
<th>Year samples were collected</th>
<th>Country</th>
<th>Location</th>
<th>Number of animals with PFOA</th>
<th>Species (organ)</th>
<th>Range of PFOA levels (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1993</td>
<td>US</td>
<td>Gulf of Mexico</td>
<td>1 of 1</td>
<td>Lapin abnormans (liver)</td>
<td>&lt;75 - 20</td>
</tr>
<tr>
<td>1993</td>
<td>US</td>
<td>Thailand</td>
<td>2 of 3</td>
<td>Lapin abnormans (liver)</td>
<td>&lt;75 - 20</td>
</tr>
<tr>
<td>2005</td>
<td>US</td>
<td>California Coast</td>
<td>1 of 1</td>
<td>Lapin abnormans (liver)</td>
<td>&lt;75 - 20</td>
</tr>
<tr>
<td>1997-1998</td>
<td>Japan</td>
<td>Hokkaido</td>
<td>1 of 1</td>
<td>Lapin abnormans (liver)</td>
<td>&lt;75 - 20</td>
</tr>
<tr>
<td>1998</td>
<td>US</td>
<td>Thunder Bay</td>
<td>1 of 1</td>
<td>Lapin abnormans (liver)</td>
<td>&lt;75 - 20</td>
</tr>
</tbody>
</table>

Sources: Giesy (2001), Kannan et al. (2002)
Persistence
- No mechanism has been found by which PFOA can be destroyed in the environment (hydrolysis, photolysis, biodegradation).
- Reported PFOA/PFOS half-life in human body (lost by excretion) varies from 4 to 10 years (3M studies).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Half-life in activated sewage sludge</th>
<th>Half-life in soil field plots</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA/PFOS</td>
<td>No degradation detected</td>
<td>NA</td>
</tr>
<tr>
<td>DDT</td>
<td>7 hours</td>
<td>15 years</td>
</tr>
<tr>
<td>Aerodol 1242</td>
<td>28 days</td>
<td>NA</td>
</tr>
</tbody>
</table>

- No degradation of PFOA/PFOS detected through wastewater treatment plants (Schultz et al., 2006)

Toxicity
- Rat embryos were exposed in utero to maternal blood levels of 40-1000 ppb PFOA. At 40 ppb, observations included:
  1. Low birth weight
  2. Decreased pituitary size
  3. Decreased liver size
  4. 10% excess mortality rate
  5. No effects observed in adult specimens

- US children typical blood levels of PFOA: 5.6-56 ppb
- Production workers at 3M (before 2001): 1,000-114,000 ppb
- Acute toxicity and death occurs when pet birds are exposed to fumes from teflon-covered pans exposed to high temperatures
PFOA Toxicity
- EPA classifies PFOA as a carcinogen in animals, linked to testicular, pancreatic, mammary and liver tumors in rats (EPA, 2002).
- PFOA alters reproductive hormones in the male (increased level of estrogen) (Biegel et al., 1995, 2001, Cook et al., 1992, Liu et al., 1996).
- PFOA or PFCs that degrade into PFOA damage thyroid gland of monkeys and other animals (Sibinski, 1987, Butenhoff et al., 2002, DuPont Haskell Laboratory, 2002).
- Nine types of cells that regulate immune functions are targets of PFOA (Yang et al., 2002).
- Birth defects confirmed in animals (rats, rabbits).

Why are PFOS and PFOA so persistent?
C-F bond strength

<table>
<thead>
<tr>
<th>Bond dissociation energy (kJ/mol)</th>
<th>C-F</th>
<th>C-Cl</th>
<th>C-O</th>
<th>H-H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>485</td>
<td>340</td>
<td>361</td>
<td>436</td>
</tr>
</tbody>
</table>

- Few reactions are known to produce cleavage of the C-F bond and cause defluorination of PFCs. They usually involve extreme conditions or uncommon reactants.

Society of Toxicology Workshop
Perfluoroalkylacids and Related Chemistries (February 2007)
- Observed effects:
  - 400 mg/kg PFOA, 200 mg/kg PFOS cause liver damage in rats
  - 3-10 mg/kg PFOA leads to increase in liver weight in monkeys.
  - Blood: 1,562 serum samples (US general population) show detectable levels of PFOA and PFOS in all samples (male>female).
  - Newborn babies exposed to PFOA have been found to have decreased birth weight and head circumference.
  - Effect of phase-out of PFC production in Minneapolis-St. Paul

<table>
<thead>
<tr>
<th>(ppb)</th>
<th>2000</th>
<th>2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS</td>
<td>33.1</td>
<td>15.1</td>
</tr>
<tr>
<td>PFOA</td>
<td>4.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Red Cross blood donor sera
(study conducted by 3M)

Remediation options being pursued at the U of A
(1) Use of boron-doped diamond film (BDD) electrodes
- Diamond film grown on p-silicon substrate using CVD
- Boron doping provides electrical conductivity
- Highly stable under anodic polarization
- No catalyst to foul or leach from electrode

Proposed process:
1. Online adsorption concentration
2. off-line thermal desorption
3. electrolysis with recirculation
   - anode chamber
   - cathode chamber
Fluorinated products: mostly F\textsuperscript{-}, trace quantities of PFOA, perfluoroheptanoic acid, and perfluorohexanoic acid.

(2) Gamma irradiation
- Gamma radiolysis of water gives rise to three short-lived products: the aquated electron, e\textsuperscript{−}(aq), H\textbullet\textsuperscript{•} and OH\textbullet\textsuperscript{•}.
- Hypothesis: e\textsuperscript{−}(aq) will add to PFC (high F electronegativity), forming a chemically reactive radical anion intermediate that rapidly decomposes by F\textsuperscript{-} elimination.

Precautions:
- Use hydroxyl radical scavenger
- Increase pH
- Strip oxygen

Experimental
Seven reaction vials filled with PFC solutions were irradiated for periods of up to 70 hr.

Vial 4 was setup for Fricke dosimetry to measure absorbed dose.

Vial contents:
1 ppm (2.2 μM) PFOA and/or 1 ppm (1.9 μM) PFOS
0.2 M MeOH + 8 mM NaOH, bubbled with argon for 15 min (total vial volume: 5 mL)

Preliminary results: fluoride yield

<table>
<thead>
<tr>
<th>Vial #</th>
<th>PFOA</th>
<th>Total dose 4 kGy</th>
<th>PFOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

FDA recommended doses for frozen meat: 0.3 to 44 kGy
Recent Developments

- EPA fines DuPont $16.5 million for “two decades’ worth of covering up company studies that showed it was polluting drinking water” with PFCs (12/05).
- Office of Pollution Prevention and Toxics-EPA (01/06): voluntary reduction of emissions of PFOA of 95% by 2010 and complete elimination by 2015.
- EPA: PFOS is banned without new chemical approval. Limited exemption: use by the semiconductor industry.
- EU directive (12/06) regulates uses of PFOS.
- DuPont announced new technologies to eliminate 97% of 2000-level PFOA emissions (02/07).
- Department of Environmental Protection New Jersey (02/07): established a preliminary drinking water guidance for PFOA of 0.04 ppb (EPA standard set in 2006: 0.5 ppb)

Recommendations

- Monitor natural waterways for PFOA, PFOS
- Assess possible sources of PFCs in wastewater and survey local wastewater treatment plans (PFC balance)
- PFCs in local landfills
- PFOS in wastewater from semiconductor industry
- Identify transport mechanisms (global atmospheric transport?)