Navigating the Symposium

Welcome! While we wait, please:
• Update your name to include your pronouns and organization
• Message Marielle with any access needs
• Introduce yourself in the chat. We’ve muted participants to minimize technical issues, so we encourage you to use the chat to say hello instead

Questions or Comments?
• Add them to the chat
• Raise your hand and we’ll unmute you

The slides and recording will be available on Puget Sound Institute’s website
PCB Symposiums
Cross Program Contaminant Working Group

BACKGROUND:
• Many estuaries (and river systems) are dealing with anthropogenic contaminants. Face similar challenges in this work.

• Share information on programs, projects, and best practices across regions to improve the effectiveness by which toxics contaminants are managed, controlled, and remediated.

• Initial focus on PCBs. Then poll those who are involved in contaminant management, and address the topics that are of interest.
Previous Symposia

- PCB Program Overviews
- Source Identification & Tracking
- PCBs in Building Materials & Schools

Learn More
www.pugetsoundinstitute.org/about/cross-program-contaminant-working-group/
From PCBs to PFAS
May 9, 2024

Dr. Steven Eisenreich

Dr. Scott Mabury
PCBs: what we know and lessons learned

Physical - Chemical Properties
Environmental Processing controls
PCBs fate in aquatic systems

Steven Eisenreich
Rene Schwarzenbach
Phillip Gschwend
Dieter Imboden
Why do we care?

Biomagnification of PCBs in the Aquatic Foodweb

Chen et al., Chemical Pollution of the Ocean,
What are PCBs and how used

209 possible PCB congeners
~130 congeners in commercial mixtures

- Co-planar PCBs
  12 PCB congeners in this pool
  (dioxin-like)
- Non-planar PCBs

Coolants and lubricants in transformers, capacitors, and other electrical equipment. Electrical, heat transfer and hydraulic equipment. Plasticizers in paints, plastics and rubber products. Hydraulic fluids, ...

- Last decade has shown aquatic and air presence of ‘non-Arochor PCB’ – PCB 11 (di-Cl) produced as incidental by-products in pain pigment, cabinet sealing, and silicone rubber production ...
- PCB congeners 47,51, 68 found in CA and Europe atmosphere related to silicone rubber and polyester production.
- Aroclor PCBs still dominate but unintentional by-products could be 10% of atmospheric burden in CA.
- ‘Legal’ production today in manufacturing as incidental could approach Aroclor production peak.
- Check out: K. Hornbuckle, F. Wania, K. Hombrecher, L. Rodenberg
Glass Capillary Gas Chromatography columns with coatings – 1960s-1970s
→ Congener-specific analysis (e.g., vs % Arochlor)

Electron Capture Detector (ECD) invented in 1958 by Lovelock
(sensitive to halogenated (here, Chlorinated) organics)

‘Inexpensive’ Desktop GC-Mass Spectrometers

High Resolution GC- High Resolution MS(-MS)

GC-MS-MS

Improved and sustainable sample extraction/cleanup techniques

Stable-isotope labelled internal and external standards

Passive sampling for Air and Water (spatial and temporal trends)
Temporal Trends of PCBs across Africa after a Decade of MONET Passive Air Sampling

White et al., ES&T, 2024
Passive-Sampler-Derived PCB and OCP Concentrations in the Waters of the World First Results from the AQUA-GAPS/MONET Network

Lohmann, et al., ES&T, 2023

Concentrations, Trends, and Air–Water Exchange of PCBs and Organochlorine Pesticides Derived from Passive Samplers in Lake Superior in 2011

Ruge et al., ES&T, 2023
# PCB Congeners analyzed in air, water, and sediment samples

<table>
<thead>
<tr>
<th>PCB Congeners</th>
<th>Number of Congeners</th>
<th>Log Kow</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 congeners</td>
<td>22 congeners</td>
<td></td>
</tr>
<tr>
<td>Σ190PCB</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17 151</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18 149</td>
<td></td>
</tr>
<tr>
<td>43 congeners</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Σ143PCB</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28 118</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31 153</td>
<td></td>
</tr>
<tr>
<td></td>
<td>33 132/105</td>
<td></td>
</tr>
<tr>
<td>30 congeners</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Σ130PCB</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>49 138</td>
<td></td>
</tr>
<tr>
<td></td>
<td>52 187</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49 183</td>
<td></td>
</tr>
<tr>
<td>12 congeners</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Σ112PCB</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>99/101 128</td>
<td></td>
</tr>
<tr>
<td></td>
<td>110 177</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82 171/156</td>
<td></td>
</tr>
<tr>
<td></td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Σ22PCB</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Σ18PCB</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Σ7PCB</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7 congeners</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ICES ‘Indicator’ PCBs)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>28 - tri</td>
<td></td>
</tr>
<tr>
<td></td>
<td>52 - tetra</td>
<td></td>
</tr>
<tr>
<td></td>
<td>101 - penta</td>
<td></td>
</tr>
<tr>
<td></td>
<td>118 - penta</td>
<td></td>
</tr>
<tr>
<td></td>
<td>138 - hexa</td>
<td></td>
</tr>
<tr>
<td></td>
<td>153 - hexa</td>
<td></td>
</tr>
<tr>
<td></td>
<td>180 - hepta</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Σ7PCB</td>
<td>180</td>
</tr>
</tbody>
</table>

We have a problem!
Polychlorinated biphenyls (PCBs)

Classified as PBTs, Hydrophobic, Moderate VP, Fate linked to C Cycle in aquatic systems, High Volume Production, Globally Distributed (LRAT & Oceanic), Banned for > 50 years


Partitions preferentially to living and dead OM

Partition behavior to Atmospheric particles and vegetation

Low MW PCBs preferentially transported over mid- and high MW PCBs.

VP $\propto 1/T$

KH is $\sim$ constant across PCB congeners

Physical-Chemical Properties of PCB congeners
**Vapor Pressure**

**Diurnal** PCB concentrations in an Ombrotrophic wetland

![Graph showing diurnal PCB concentrations](image1.png)

**Monthly** PCB concentrations at IADN, NA Great Lakes

![Graph showing monthly PCB concentrations](image2.png)

- **Chicago**
  - $R^2 = 0.83$
  - Black – Conc, Red – fit seasonal cycle, Blue - trends

- **Eagle Harbor**
  - $R^2 = 0.80$

**Great Lakes, IADN**

![Map of Great Lakes, IADN](image3.png)

- **Chicago only**
  - $\Sigma$-PCBs
  - PCB-11

---

Hornbuckle et al., 1996

Diurnal PCB concentrations in an Ombrotrophic wetland

Diurnal PCB concentrations in an Ombrotrophic wetland

Monetary PCB concentrations at IADN, NA Great Lakes

- Chicago
  - $R^2 = 0.83$
  - Black – Conc, Red – fit seasonal cycle, Blue - trends

- Eagle Harbor
  - $R^2 = 0.80$

Great Lakes, IADN

- Chicago only
  - $\Sigma$-PCBs
  - PCB-11
PCB Sorption/Partitioning of PCBs to Aquatic OM/OC

Sorption Coefficients of PCBs to Natural Organic Matter

\[ K_{OC} = \frac{K_d}{f_{OC}} \text{ or } K_d = K_{OC} f_{OC} \]

Bioaccumulation and Bioconcentration Factors for PCBs (measured and modeled)

\[ \log \text{BCF or BAF vs Kow} \]

\[ K_{ioc} = \frac{K_{id}}{f_{OC}} \]

\[ F_{\text{diss, part}} = \text{function (Kow, TSS, fOC)} \]

Schwarzenbach et al., 2013

The Global Distribution of PCBs

PCBs are emitted in the mid-latitudes where it is warm or seasonally warm and are transported and deposited in regions where it is cold or seasonally cold.

Global Production Polychlorinated biphenyls PCBs)

(a) Global production of PCBs (Breivik et al., 2002a,b) and
(b) Estimated Primary Emission of PCBs due to usage, disposal, and accidental release (Breivik et al., 2002b).

Global production and use = 1 312 Mt
96% in Northern Hemisphere
Onset in early 1930’s; Peak production in ~ 1970
Banned from open systems – 1974; general ban 1979
~ 1-3% of global PCB production in global environment (uncertain)
Lakes as Biogeochemical Reactors

Once PCBs enter the water column, partition/sorb to OC-rich particles and settle / deposit / accumulate in bottom sediments.

Environmental processes and P-C properties linked to the C Cycle Control the Fate of PCBs in aquatic systems

(Chattopadhyay et al., 2015)

Accumulation of PCBs in Lake Superior sediments: atmospheric deposition

Airborne organic contaminants in the Great Lakes ecosystem.
Eisenreich, et al., ES&T, 1981, 15:30-38

Atmospheric deposition accounted for 90, 58 and 63% of Direct PCB inputs to Lakes Superior, Michigan and Huron.
Strachan and Eisenreich, (1988)

US Clean Air Act Amendments (1990):
*GREAT Waters Program*

.."to identify and assess the extent of atmospheric deposition of air pollutants on the Great Lakes, the Chesapeake Bay, Lake Champlain, etc.

**ROLE OF THE ATMOSPHERE**

International Great Lakes Atmospheric Deposition Network (IADN) 1991 - present

AEOLOS – Atmospheric Exchange over Lakes and Oceans
LMMB – Lake Michigan Mass Balance (PCBs, ecosystem approach)
Major cities are large sources of PCBs to neighboring Great Waters

AEOLOS (Atmospheric Exchange over Lakes and Oceans)
LMMB (Lake Michigan Mass Balance)

Chicago Metropolis

- \([\text{PCB}]_{\text{air}}\) in Chicago > ~10 - > 100x regional \([\text{PCB}]_{\text{air}}\)
- ~25% of Annual PCB loading to Lake Michigan comes from Emissions from Chicago area.

Courtesy – K. Hornbuckle
PCB Concentration Decreases in Lake Superior Water

Where did the PCBs go?

Water and Settling Fluxes of [PCBs] in Lake Superior Decrease at \( \sim 0.2 \text{ yr}^{-1} \)

PCB loss \( \sim 10,000 \text{ kg} \)

\[ [\text{PCB}]_w \sim 50-100 \text{ pg/L}; [\text{PCB}]_a \sim 100 \text{ pg/m}^3 \rightarrow \text{Ratio} \sim 10^{-3} \rightarrow K_H 10^{-3} \]

Water in near equilibrium with atmosphere PCB concentration (TODAY)

Deplyment of sediment traps: Sedimentary Recycling of PCBs

Atmospheric Deposition
- Wet
- Dry
- Gas Absorption

Particle  →  Dissolved

→

Particle  →  Settling

→

Recycling

→

Accumulation

RR = \[
\frac{\text{Vertical Flux}}{\text{Accumulation Rate}}
\]
\[
\text{Surface Sediment}
\]

Apparent Settling Velocity (m/d)
- PCBs > 1 m/day
- 20 to <50% OM ‘lost’ on settling
- <10% PCBs ‘lost’ on settling

Of 100% PCB settling to sediment,
- <5% PCB reaching sediment accumulates
- >95% of total PCB is recycled

Lake Superior

1  2

3  4

5
Recycling Ratio of PCBs and PAHs in Lake Superior

\[ RR = \frac{F_{\text{settling}}}{\text{Accum}_{\text{sed}}} \]

Baker et al., 1991
Jeremiasen et al., 1998
Recycling Ratios of PCBs in Great Lakes Sediments

Net Volatilization is responsible for LOST PCBs since 1980!!! (LS)
OM Preservation in sediments
PCB Fate Linked to C Cycle
Critical Observation:
Field Observation of PCBs in atmosphere above water, in dissolved phase and in phytoplankton

Example: Evidence for Gas-Phase Driven Phytoplankton accumulation of PCBs

Critical Observation: Field Observation of PCBs in atmosphere above water, in dissolved phase and in phytoplankton

PCB congeners

Correlated:
- $R^2 = 0.90$
- $R^2 = 0.70$
- $R^2 = 0.96$

un-correlated
Biological Carbon and PCB Pump
Air – Water - Phytoplankon

[PCB]_{air}

[PCB]_{w}

[PCB]_{phytoplankton}

[PCB]_{settling particles}
Air-Water-Phytoplankton Exchange of POPs

\[ C_A \]

Air-water exchange

\[ F_{AW} = (C_A - C_W) \]

Implications:

- The biological PCB pump is responsible for entry of PCBs into aquatic food chain in world’s oceans and many freshwaters.

- The biological PCB pump is a main process for loading and transport atmospheric PCBs into the world’s oceans and many freshwater systems.

- The biological PCB pump (and subsequent ‘ particle settling’) controls the ecosystem Residence Time and delivery of PCBs to deep ocean waters and sediments

- Primary Emissions vs Secondary emissions – need to greater focus on bio-physical-geo-chemical transfer processes as we transition from primary source emissions (global production) to secondary emissions


\[ k_{\text{Sink}} = F_{OM} \frac{k_u}{k_d + k_G} \]

At steady state, \( F_{AW} = F_{WP} = F_{\text{sink}} \)
Locations of global aquatic sediment cores revealing temporal PCB profiles and comparison to production and emissions

Majunder & Eisenreich, 2024

Criteria for core selection

1. Were the collections and sectioning of sediment cores described appropriately?

2. Were PCBs in sediment cores extracted and analyzed by the most appropriate analytical methodology?

3. Were the sediment cores dated with $^{210}\text{Pb}$ and/or $^{137}\text{Cs}$?

4. Were PCB sediment profiles consistent with onset, peak and decrease in global PCB production/use/regulation?
(A) Production/Use of PCBs (Breivik et al., 2002 a,b) and (B, C) sediment box cores from Lake Ontario (Eisenreich et al., 1989; Wong et al., 1995).
Synchronous signals of global Production of PCBs and PCBs in aquatic sediment cores from North America.
Comparison of global production/use of PCBs and time-depended PCB signals in selected aquatic sediment cores from Europe and beyond

Sediment core profiles of PCBs reflect the temporal signal of global PCB production
Comparison between the production of PCBs and ‘deviating’ cores (a) Production of PCBs (Breivik et al., 2002a) (b) Lake 382, Canada (Derek C. G. Muir et al., 1996); (c) Pearl River Delta, China (Mai et al., 2005b); (d) Santos Estuary, Brazil ( de Souza et al., 2018); (e) The Msimbazi River, Tabata, East Africa (Nipen et al., 2022); (f) Lake Oberaar, Switzerland (Bogdal et al., 2009); (g) Lake Iseo, Italy (Roberta Bettinetti et al., 2011); (h) Lake Winnipeg, Canada (Rawn et al., 2000b); (i) Po River Pro-delta, Western Adriatic Sea (Combi et al., 2020).
Examples: Sediment Cores That Deviated From Production/Emission

What we really need is an atmospheric signal of PCB input

Some reasons for Deviation:

- Non depositional area
- Bioturbation/internal mobilization
- Glacial melting
- River Basin Floods
- Mismanagement of PCBs (leakage)
- Illegal discharges
- Different (later) ‘local’ use & emission pattern

Lake Oberaar, Switzerland
Oberaarsee, near Grimsel

(Bogdal et al., 2009; Huo et al., 2017)
PCB Global production and primary emissions have synchronous sediment and peat (atmospheric) profile

Global PCB Production – Lake Sediment cores – ombrotrophic (atmospheric) signals are synchronous!

Onset – acceleration in 1950’s – peak at ~ 1970 – decrease to low present-day
Global Cycling of Persistent Organic Pollutants

Production → Use → Emission → Transport → Deposition → Accumulation

is remarkably fast and efficient in distributing PCBs

10’s -100’s kms distance → primary emissions
100’s –1000 kms/elevations → secondary emissions (remobilization of PCBs from environmental reservoirs)
Key Messages on on PCBs - what we know


Knowledge of P-C Properties and Environmental Processes are critical to understanding PCB cycling in environment.

Time from PCB production $\rightarrow$ emission $\rightarrow$ transport $\rightarrow$ deposition $\rightarrow$ accumulation in environment is ‘fast’.

Aquatic Cycle of PCBs is intimately lined to the C Cycle (role of trophic interactions).

(OM preservation in sediments is a requirement of PCB retention in water bodies).

PCB concentrations are decreasing worldwide at ~ 10-20% per year in atmosphere and aquatic systems.

Air–water–phytoplankton exchange is a major or dominant global process. A-W Exchange is major transport process.

Atmospheric PCBs are near ‘equilibrium’ with marine systems and many inland water bodies.

Present-day PCB emissions are still dominated by primary emissions (use, disposal, accidents).

PCB emissions are largely linked to urban-industrial areas (primary emissions).

Global reservoirs: 75% in ocean sediments; 6% in ocean reservoirs; 3% in terrestrial reservoir; 13% - degradation (ocean, atm)

Transition of PCB emissions from primary to secondary sources requires focus on bio-physical-geo-chemical processes.

Anthropogenic climate change likely mobilizes PCB deposits from soils and water (e.g., Increased T, floods, melting glaciers)

‘Non-Aroclor’ PCB emissions today are high and implications not well known.
Thank you!
Σας ευχαριστώ!
“PFAS Today ...What Have We Learned So Far?”

Scott Mabury
Department of Chemistry
University of Toronto
“Small Polyfluorinated Organics”

Anthropogenic 'small organofluorines'

Aluminum Production: $\text{CF}_4\ (82)$, $\text{CF}_3\text{CF}_3\ (3)\ [0.75 \text{ and } 0.11 \text{ kg/ton of Al}]

Freons: $\text{CFCl}_3\ (267)$, $\text{CF}_2\text{Cl}_2\ (535)$, $\text{CF}_2\text{ClFCl}_2\ (85)$

HCFC: $\text{CF}_3\text{CFH}_2\ (12)$, $\text{CHF}_2\text{Cl}\ (145)$, $\text{CH}_3\text{CF}_2\text{Cl}\ (15)$

HFCs: $\text{CF}_3\text{CHFCF}_3$, $\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3$, $\text{CH}_2\text{FCF}_2\text{CHF}_2$

Note: numbers in (x) reflect atmospheric concentration pptv;

IPCC Climate Change 2001: The Scientific Basis

Natural Sources as well?

$\text{CF}_4$, $\text{CF}_2\text{Cl}_2$, $\text{CFCl}_3$, $\text{CF}_3\text{Cl}$, $\text{CHF}_3$, $\text{CF}_2=\text{CF}_2$ (fluorite)$^1$...

$\text{CFCl}_3$, $\text{CF}_2\text{Cl}_2$, $\text{CF}_2=\text{CF}_2$, $\text{CHF}_2\text{Cl}$, $\text{CHFCl}_2$, $\text{CCl}_2\text{FCClF}_2$ (volcanoes)$^2$...

$\text{CF}_3\text{COOH}$ ....estimate of 268 million tons in the world's oceans$^3$; (ocean vents$^4$)

3) Frank et al, 2002
4) Scott et al, 2005
Pesticides and Pharmaceuticals…
TFA
Do these “common” fluorinated polymers & surfactants contribute?

**Hydro & Lipo-Phobic**

**Polymer (Ester)**

**Surfactants (Phosphate)**
Fluoro alcohols ~ Fugitive Emissions from Residual Material
OR Does the Linkage Chemistry Break?

Potential Sources?

11 to 14 x10^6 kg/yr (2004)
40% in North America
80% are in polymers*

*Dupont Presentation to USEPA OPPT. Jan 31, 2005
US Public Docket AR226-1914
**Residuals could be important source of fluoroalcohols**
*...to the atmosphere*

<table>
<thead>
<tr>
<th>Fluorinated Material</th>
<th>Dry Weight % Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyfox-L-Diol</td>
<td>0.11 (0.03)</td>
</tr>
<tr>
<td>Teflon™ Advance</td>
<td>0.34 (0.20)</td>
</tr>
<tr>
<td>Zonyl™ FSO 100</td>
<td>1.03 (0.61)</td>
</tr>
<tr>
<td>Zonyl™ FSE</td>
<td>3.80 (1.09)</td>
</tr>
<tr>
<td>8:2 Methacrylate Monomer</td>
<td>0.04 (0.01)</td>
</tr>
<tr>
<td>Motomaster™ Windshield Washer Fluid w/ Teflon</td>
<td>0.36 (0.01)</td>
</tr>
<tr>
<td>Scotchgard™ Rug and Carpet Protector*</td>
<td>0.39 (0.06)</td>
</tr>
</tbody>
</table>

\[ n = 3 \text{ or } 6 \]


![FTOH](image)

Tentatively identified in a telomer phosphate mixture via GC/MS;

24:2 FTOH
"49 Fluorines"
Are Fluorinated Precursors in the Air?

Fluoroalcohol Trends in Toronto ~ long term monitoring

Published data, May-June/Nov 2001 air samples: FTOHs 100 to 350 pg/m$^3$; Sulfonamidoethanols: 30 to 500 pg/m$^3$.


Are PFCAs in Rain?

1 ng/L = 250 t across Northern Hemisphere
Equivalent to annual industrial production of PFOA

Background PFAS in soils

### Table 1
Continental PFAS concentration ranges in pg/g dry weight with the continental geometric mean in parentheses.

<table>
<thead>
<tr>
<th>Continent</th>
<th>ΣPFCA</th>
<th>ΣPFSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America (NA) (n = 33)*</td>
<td>145–6080 (1820)</td>
<td>35–1990 (410)</td>
</tr>
<tr>
<td>Europe (EU) (n = 10)</td>
<td>55–3640 (1000)</td>
<td>&lt;LOD–3270 (808)</td>
</tr>
<tr>
<td>Asia (AS) (n = 6)</td>
<td>129–14300 (4710)</td>
<td>79–421 (183)</td>
</tr>
<tr>
<td>Africa (AF) (n = 5)</td>
<td>124–1490 (548)</td>
<td>&lt;LOD–144 (67)</td>
</tr>
<tr>
<td>Australia (AU) (n = 4)</td>
<td>79–1260 (673)</td>
<td>44–297 (154)</td>
</tr>
<tr>
<td>South America (SA) (n = 3)</td>
<td>29–319 (138)</td>
<td>26–48 (36)</td>
</tr>
<tr>
<td>Antarctica (AN) (n = 1)</td>
<td>191</td>
<td>7</td>
</tr>
</tbody>
</table>

* Includes a sample from Waimea, Hawaii (NA19).

## Biosolid Results – Detected

<table>
<thead>
<tr>
<th>Chemical</th>
<th>LOD (ng/g biosolid)</th>
<th>LOQ (ng/g biosolid)</th>
<th>Biosolid Amended Soil (ng/g)</th>
<th>Not-Biosolid Amended Soil (ng/g)</th>
<th>NA Background Soils (Range) (ng/g)</th>
<th>Canadian Great Lakes Precipitation, (Median) (ng/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>0.067</td>
<td>0.224</td>
<td>&lt;LOD - 2.76</td>
<td>&lt;LOD - 1.79</td>
<td>N/A</td>
<td>0.00093</td>
</tr>
<tr>
<td>PFPeA</td>
<td>0.131</td>
<td>0.438</td>
<td>&lt;LOD - LOQ</td>
<td>&lt;LOD</td>
<td>N/A</td>
<td>&lt;RL</td>
</tr>
<tr>
<td>PFHxA</td>
<td>0.124</td>
<td>0.414</td>
<td>&lt;LOD - &lt;LOQ</td>
<td>&lt;LOD - &lt;LOQ</td>
<td>0.0323 - 1.986</td>
<td>0.00023</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.056</td>
<td>0.186</td>
<td>0.37 - 0.94</td>
<td>0.26 - 0.62</td>
<td>0.0217 - 1.838</td>
<td>0.00046</td>
</tr>
<tr>
<td>PFNA</td>
<td>0.091</td>
<td>0.304</td>
<td>&lt;LOD - 0.32</td>
<td>&lt;LOD - &lt;LOQ</td>
<td>0.0148 - 1.000</td>
<td>0.00030</td>
</tr>
<tr>
<td>PFDA</td>
<td>0.158</td>
<td>0.528</td>
<td>&lt;LOD - &lt;LOQ</td>
<td>&lt;LOD</td>
<td>0.0047 - 0.8804</td>
<td>0.00015</td>
</tr>
<tr>
<td>PFOS</td>
<td>0.096</td>
<td>0.323</td>
<td>&lt;LOD - 1.41</td>
<td>&lt;LOD - &lt;LOQ</td>
<td>0.0181 - 1.956</td>
<td>0.00039</td>
</tr>
<tr>
<td>6:2FTS</td>
<td>0.022</td>
<td>0.075</td>
<td>&lt;LOD - 0.17</td>
<td>&lt;LOD - 0.268</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* <RL is reported for non-detectable concentrations.

The LOD represents the lowest concentration of the chemical that can be detected by the method. The LOQ represents the lowest concentration that can be quantified with confidence by the method.
PFA Flux to Arctic (Devon Ice Cap)


PFSAs/PFCAs and FTUCAs IN ARCTIC SEDIMENT

BCF/BAF in Carcass, Liver, and Blood of Rainbows

BCF = k_u / k_d

Additional CF_2 results in a ~7x increase in the BCF.


Bioaccumulative
**Discovery of Long Chain PFCAs**

![Diagram of PFCAs](image)

**FIGURE 2.** Tandem mass spectrometry chromatogram of polar bear extract showing the homologous series of PFCAs detected and later confirmed.

**FIGURE 1.** Full scan high resolution mass spectrum for a polar bear extract showing the accurate mass associated with the negative molecular ion of PFtBu (m/z 562.9657) and of its characteristic fragment or daughter ion (m/z 518.9688).

**Confirm**

- Perfluoropentadecanoate (PPPA) \( CF_3(CF_2)_4CO_3 \) 763–719
- Perfluorotetradecanoate (PFtBu) \( CF_3(CF_2)_3CO_3 \) 713–669
- Perfluorotridecanoate (PFTrA) \( CF_3(CF_2)_2CO_3 \) 663–619
- Perfluorododecanoate (PFDoA) \( CF_3(CF_2)_1CO_3 \) 613–560
- Perfluoroundecanoate (PFUnA) \( CF_3(CF_2)_1CO_3 \) 563–519
- Perfluorodecanoate (PFDoA) \( CF_3(CF_2)_1CO_3 \) 513–469
- Perfluorononanoate (PFNA) \( CF_3(CF_2)_1CO_3 \) 463–419

**Table 1**

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Mass Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPPA</td>
<td>763–719</td>
</tr>
<tr>
<td>PFtBu</td>
<td>713–669</td>
</tr>
<tr>
<td>PFTrA</td>
<td>663–619</td>
</tr>
<tr>
<td>PFDoA</td>
<td>613–560</td>
</tr>
<tr>
<td>PFUnA</td>
<td>563–519</td>
</tr>
<tr>
<td>PFDoA</td>
<td>513–469</td>
</tr>
<tr>
<td>PFNA</td>
<td>463–419</td>
</tr>
</tbody>
</table>

**Retention Time (min) →**

Bruce E. Smart of DuPont in C&EN Feb 14, 2005 p 36 “It’s possible, with the right design, that some of these materials can be lightly fluorinated and still express the surface activity of the long-chain surfactants.”
C-F bond breakage & the "F" word....
Can you break a C-F bond?

Only in special cases or conditions
FIGURE 7. Proposed mechanism for the production of TFA from TFM (I). The alternate pathways for the degradation of TFM are also indicated.
Fluoride is a terrible leaving group:
Except in special cases...where $F^-$ is pushed!

\[
\begin{align*}
\text{F}\text{C}=\text{C}\text{F} \quad &\xrightarrow{\text{H}_2\text{O}}\quad \text{F}\text{C}=\text{O} + \text{F}^- \\
\text{F}\text{C}=\text{C}\text{F} \quad &\xrightarrow{\text{H}_2\text{O}}\quad \text{F}\text{C}=\text{O} + \text{F}^-
\end{align*}
\]
If the right ‘architecture’ then ELIMINATE?

Elimination

**b-Elimination**

Acidic "H"  

Telomer Acids

Acidic "F"  

Telomer Aldehyde

- **abiotic;** $x=6$, pH 7, T=23°C  
  ~35 days
- **biotic (bacteria);** $x=6$, pH 7, T=23°C  
  ~14 days
- **biotic (rats);** $x=6$, pH 7.2, T=23°C  
  ~very fast

Biotic & Abiotic are **much Faster**
Perfluorinated Acids... “extremely persistent”...?
Human Contamination of Fluorinated Chemicals

![Graph showing concentrations of various fluorinated chemicals](image)

**LEGEND**
- 6:2 diPAP
- N-MeFOSAA
- C6/C6 PFPiA
- PFHxA
- PFDA
- PFOS
- 6:2/8:2 diPAP
- N-EtFOSAA
- C6/C8 PFPiA
- PFHpA
- PFUnA
- PFDS
- 8:2 diPAP
- 6:2 FTS
- PFBA
- PFOA
- PFBS
- FOSAA
- 8:2 FTS
- PFPeA
- PFNA
- PFHxS

*Single donor (n = 40)*
*Pooled (n = 10)*

Yes detection of the perfluorophosphinates as well

NIST WWTP sludge standard reference material at 2 ng/g

C6/C6-PFPiA

Overall...


Ozone Depletion...Global Warming

CFC-11  HFC-134a  HFC-1234yf  HFC-152a
Atmo Fate
Reaction Products from OH Rxn w/ FTOHs

>90% Attack on \( \alpha \) hydrogens; H-Bond deactivates OH abstraction

8:2 FTOH

David Ellis
Jon Martin
Jessica D’eon
Cora Young
Tim Wallington
Mike Hurley
Mads Sulbaek Andersen
Scott Mabury
Confirmed via LC/MS/MS of Smog Chamber Air Sample
Fate of Perfluorocarbon Radicals

Atmospheric Reagents

NO/NO₂

R-CH-O-O⁻

-O₂

Reactive?

-F₄C⁻

Major

low %
**Overall Atmospheric Chemistry of FTOHs**

**OH Lifetime = 20 d**

1. **FTOH**
   - $\xrightarrow{+\text{OH}/-\text{H}_2\text{O}}$
   - $\xrightarrow{+\text{O}_2/-\text{HO}_2}$

2. **FT-Aldehyde**
   - $\xrightarrow{+\text{OH}/-\text{H}_2\text{O}}$

3. **PerfluoroAldehyde**
   - $\xrightarrow{+\text{OH}/-\text{H}_2\text{O}}$

**OH Lifetime = 30 d**

4. **Acyl Radical**
   - $\xrightarrow{+\text{O}_2}$
   - $\xrightarrow{-\text{CO}}$

5. **Hydrate**
   - $\xrightarrow{\text{H}_2\text{O}}$
   - $\xrightarrow{\text{OH}}$

**PFCAs ~ [1 to 10%]**

6. **PFNA (x=6)**
   - $\xrightarrow{+\text{HO}_2/-\text{O}_3}$

7. **PFOA (x=6)**
   - $\xrightarrow{+\text{H}_2\text{O}/-\text{HF}}$
   - $\xrightarrow{-\text{HF}}$

8. **"Unzipping"**
   - $\xrightarrow{+\text{NO}/-\text{NO}_2}$
   - $\xrightarrow{+\text{NO}/-\text{NO}_2}$

where $n=x-1, x-2, \text{etc.}$
Overall Big Picture of Atmospheric Pathways of Precursors

- FTOH
- FTAc
- FTI

- FTAL
- PFAL
- FTO
- CF₃(CF₂)ₓH

- Perfluoroacyl Peroxy Radical
- Perfluorinated Radical
- Perfluoroacyl Chloride
- Perfluoroacyl Fluoride

- CF₃(CF₂)ₓCHClBr
- CF₃(CF₂)ₓCHCl₂
- CF₃(CF₂)ₓCHClOCHF₂
- CF₃(CF₂)ₓCHFCF₃
- CF₃(CF₂)ₓCHFCl

- HFO
- NAFSA
- NAFSE
- PFSA
- PFAL Hydrate

Evolution....?

HFPO-DA (GenX)

F53B; 6:2 Cl-PFESA

ADONA

MeFESOH*

Next-generation replacement*
Folkerson, AP and SA Mabury. 2024. A Comparative Biodegradation Study to Assess the Ultimate Fate of Novel Highly Functionalized Hydrofluoroether Alcohols in Wastewater Treatment Plant Microcosms and Surface Waters. Env Tox Chem. DOI: 10.1003/etc.5815

Trends
Fig. 1. Median serum concentrations with 95% confidence intervals for PFOA and PFOS among the general US population.
Are humans exposed to lower amounts of PFAS?

PFOS

PFOA

EOF

Environmental Science & Technology 2013, 47, 8, 3865-3874
Environmental Science & Technology 2013, 47, 8, 3875-3882
Are humans exposed to lower amounts of PFAS?
PFAS Trends in Lake Ontario sediment core

- Similar to trends in trout, PFOS has declined since the 2000s
- In sediment, PFOS has the highest concentration of the other PFAAs
Human exposure etc
**Motivation: Polar Bears & Human Contamination**

<table>
<thead>
<tr>
<th>Location</th>
<th>PFOA</th>
<th>PFNA</th>
<th>PFDA</th>
<th>PFUnA</th>
<th>PFDa</th>
<th>PFOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Falandysz, 2006 Poland</td>
<td>3.0</td>
<td>0.56</td>
<td>0.18</td>
<td>0.09</td>
<td>0.018</td>
<td>13</td>
</tr>
<tr>
<td>Karrman, 2006 Sweden</td>
<td>4.8</td>
<td>0.6</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>Calafat, 2006 USA</td>
<td>3.7</td>
<td>0.56</td>
<td></td>
<td></td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>Kuklenyik, 2004 GA</td>
<td>4.9</td>
<td>2.6</td>
<td>0.51</td>
<td>0.68</td>
<td>0.14</td>
<td>56</td>
</tr>
<tr>
<td>Guruge, 2004 Sri Lanka</td>
<td>6.4</td>
<td>0.39</td>
<td>0.19</td>
<td>0.25</td>
<td>0.022</td>
<td>36</td>
</tr>
<tr>
<td>De Silva, 2006 USA</td>
<td>4.4</td>
<td>0.77</td>
<td>0.17</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


What is the Question and Why are we interested?

Interest: Significant [PFOS] & [PFCAs]

Question: How did they get there?

...two main ideas: Direct & Indirect
PFOA
0, 0.3, 1, 30, 70 mg/L

PFOS
0, 0.3, 3, 10, 30 mg/L

Aquatic invertebrates... e.g. *Daphnia Magna* – the Canary

<table>
<thead>
<tr>
<th>Design</th>
<th>PFOS LOEC&lt;sub&gt;community&lt;/sub&gt; (mg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Mean Δ</th>
<th>PFOA LOEC&lt;sub&gt;community&lt;/sub&gt; (mg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Mean Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laboratory</td>
<td>13–50 (D. pulex)</td>
<td>0.01</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>30-L indoor</td>
<td>1–10</td>
<td>0.21 and 0.39</td>
<td>30–70</td>
<td>0.15 and 0.83</td>
</tr>
<tr>
<td>12,000-L outdoor</td>
<td>10–30</td>
<td>0.63 and 0.99</td>
<td>30–70</td>
<td>0.57 and 0.99</td>
</tr>
</tbody>
</table>

Sanderson *et al*, 2004. Ecotox & Env Saf; **58**:68-76

"PFCs are extremely toxic chemicals..."
Keen Shoe ad
Globe & Mail
April 22, 2021

US EPA Health Advisory in Drinking Water: 0.00004 mg/L (4 ng/L)
or 750,000 x below the LOEC for PFOA
Do these “common” fluorinated polymers & surfactants contribute?

Hydro & Lipo-Phobic

Polymer (Ester)

Surfactants (Phosphate)
Two hypotheses:

Direct: Release of PFOS and PFOA/PFNA from industrial, commercial, or consumer uses has been significant and has resulted in global contamination, including the Arctic and humans.¹,²

- Thousands of tons of PFOA alone emitted from fluoropolymer manufacture
- Major releases to surface waters (58,000 lbs of PFOA in ’99/W.Va);
- Major fate is to the oceans;
- PPM 'residual' in products;

Indirect: Fluorinated precursors (FPs) are degraded atmospherically and metabolically to yield PFCAs. FPs are released from industrial sources and from ‘in use’ consumer products.³⁴⁵⁶

FTCAs and FTUCAs Toxicity

MacDonald et al. found:

- 8:2 and 10:2 FTCAs and FTUCAs are up to **10,000 times** more toxic than PFCAs in freshwater species
- *Daphnia magna* particularly sensitive to telomer acids with a carbon chain length 8 and greater
  - Longer chain length → greater hydrophobicity
  → greater bioaccumulation
- Compared with 8:2 telomer acids
  - 10:2 FTUCA 10x more toxic (EC50=0.28ppm)
  - 10:2 FTCA 100x more toxic (EC50=0.03ppm)
- FTCAs particularly toxic; idea why?

Human Contamination of Fluorinated Chemicals

![Graph showing concentrations of various fluorinated chemicals](graph.png)

**Legend**
- 6:2 diPAP
- N-MeFOSAA
- N-EtFOSAA
- C6/C6, C6/C8 PFPiA
- PFBA
- PFOA
- PFBS
- 8:2 diPAP
- 6:2, 8:2 FTS
- PFCAs
- PFSAs

**Log_{10}(Concentration of Analytes), (µg/L)**
- 0.001
- 0.01
- 0.1
- 1
- 10

**Human Contamination of Fluorinated Chemicals**

Metabolism of PAPs

PAPS and PFCA whole blood concentrations

8:2 monoPAPS concentration (ppb)

PFOA concentration (ppb)

D’eon & Mabury 2007 ES&T 41:4799-4805
It matters because of mammalian metabolism (rat)

Glutathione reactivity with fluorinated aldehydes

1,4 – Michael Addition

Protein binding?

Nabb et al, 2007; Martin et al, 2005; Martin et al, 2009; Fasano et al, 2006; Fasano et al 2006
Fluorinated aldehyde adduct formation with ApoMg

ApoMg:fl. aldehyde (molar ratio)

1:1

1:0.5

Control

m/z

940 960 980 1000 1020 1040 1060 1080

Rand and Mabury, EST, 2012
Cell survival and toxicity

50% Effect Concentration (μM)

Increasing Toxicity

Rand & Mabury, Toxicology 2017. 375:28-36
Human Serum Albumin (HSA) + \[
\begin{array}{c}
F \quad F \\
F \quad F \\
F \quad F \\
F \quad F \\
F \quad F
\end{array}
\]
\[\rightarrow\]
HSA adducts

HSA nucleophilic amino acids:
- 23 Arg
- 58 Lys
- 15 His
- 1 Cys

Rand A.A., Mabury S.A. Protein binding associated with exposure to fluorotelomer alcohols (FTOHs) and polyfluoroalkyl phosphate esters (PAPs) in rats. *Environmental Science and Technology*, 2014, 48, 2421-2429
polymers
Do these “common” fluorinated polymers & surfactants contribute?

Hydro & Lipo-Phobic

Polymer (Ester)

Surfactants (Phosphate)
Fluorinated Polymers

Fluoropolymers (eg. PTFE)  Perfluoropolyethers (PFPEs)

\[ \ast \left[ \text{CF}_2\text{-CF}_2 \right]_x \ast \]
\[ \ast \text{-CF}_2\text{-O} \left[ \text{CF}_2\text{-CF}_2\text{-O} \right]_x \text{CF}_2\text{-O} \text{CF}_2\text{-} \ast \]

Side-Chain Fluorinated Polymers

\[ \text{C}_n\text{F}_{2n+1} \]
\[ \text{X} \]
\[ \text{O} \]
\[ \text{C}=\text{O} \]
\[ \text{NH} \]

Backbone

Urethane

Acrylate and Methacrylate

Oxetane
FTACPs

• Fluorotelomer-based acrylate polymers (FTACPs) are copolymers prepared fluorinated and non-fluorinated monomers
• Extremely effective surface protectants in carpet, textile and upholstery industries¹
• Largest fraction of commercial fluorotelomer products constituting >80% of all fluorotelomer-based raw material produced²,³

Do FTACPs biodegrade?

How labile is the ester moiety?

What analytical techniques are suitable to study FTACP biodegradation?

\[ \begin{align*}
&\text{CF}_3 \quad \text{(CF}_2\text{)}_m \\
&(\text{CH}_2\text{)}_2 \quad \text{O} \\
&\text{C=O}
\end{align*} \quad \begin{align*}
&\text{CH}_3 \quad \text{(CH}_2\text{)}_n \\
&(\text{CH}_2\text{)}_y \quad \text{O} \\
&\text{C=O} \\
&\text{X}
\end{align*} \]

\[ C\text{--CH}_2 \quad x \quad C\text{--CH}_2 \quad y \quad C\text{--CH}_2 \quad z \]

\[
(H \text{ or CH}_3) \quad (H \text{ or CH}_3) \quad (\text{Cl, H or CH}_3)
\]

\[ m = 5-13 \quad \text{and} \quad n=1-17 \]

\[ x = \text{variety of non-fluorinated monomers} \]

Our “New Model Polymer”

\[
A = 1
\]

\(M_w = 4186\)

\(M_n = 3351\)

Hydrolysis Study

FTAcP Soil Extracts

5.5 Months

3.5 Months

1.5 Months

Decreasing S/N
Fate of that Polymer in an Agrocosm?

- Sandy loam soil
- *Medicago truncatula*
- *Sinorhizobium meliloti* (innoculum)
- Sewage Sludge (16g/1000g soil)

Production of PFOA in Polymer-Spiked Pots

Concentration in soil (ng/g)

<table>
<thead>
<tr>
<th>Time</th>
<th>Soil Only</th>
<th>Soil/SS/Plant</th>
<th>Soil/Polymer</th>
<th>Soil/Plant/Polymer</th>
<th>Soil/SS/Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 Month</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.5 Month</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.5 Month</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5.5 Month</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Model Fluorotelomer-based Acrylate Polymer
FTACP Biodegradation

Direct Analysis (MALDI-TOF)

Indirect Analysis (LC-MS/MS)

Analytes measured in soil (A) and plant (B) for FTACP/Plant pots.

$^{19}$F NMR
Detailed analysis of Lake Niapenco

- **NMR** can identify additional fluorinated compounds in this sample compared with MS/MS measurements.

<table>
<thead>
<tr>
<th></th>
<th>$^{19}$F NMR</th>
<th>MS/MS</th>
<th>CIC-TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Fluorine</strong></td>
<td>65.7 µM</td>
<td>20.1 µM</td>
<td>66.9 µM</td>
</tr>
<tr>
<td>TFA</td>
<td>0.437 µM</td>
<td>0.433 µM</td>
<td>?</td>
</tr>
<tr>
<td>PFCAs</td>
<td>19 µM</td>
<td>18.5 µM</td>
<td>?</td>
</tr>
<tr>
<td>PFSAs</td>
<td>1.87 µM</td>
<td>0.321 µM</td>
<td>?</td>
</tr>
<tr>
<td>Aromatic CF$_3$</td>
<td>12.8 µM</td>
<td>0.178 µM</td>
<td>?</td>
</tr>
<tr>
<td>Fluoride</td>
<td>22.8 µM</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Others</td>
<td>8.79 µM</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>
Towards the future of 19F NMR

- New pulse sequences push the capability of NMR. Revealing more detail than ever before

**Sample Preparation**
- 100 mg Polar Bear Liver
- Homogenize in d4 MeOH, centrifuge

**New Pulse Sequence**
19F NMR
12 h, (ns = 3.9 million)
Summary thoughts

• we’ve learned a lot;
• Chain length matters;
• Not all C-F bonds are recalcitrant/persistent…but some ‘chemical architecture’ does define persistence;
• Many of the original longer chain PFAS (PFOS/PFOA etc) seem to be declining in humans….;
• Shorter chain PFAS appear to be more widely used;
• Quite a few areas of inquiry have relatively paltry activity in the scientific community – polymers, reactive intermediates, atmospheric;
• Analyte list often is quite traditional and unimpressive;
• 19F NMR is very complementary to mass spec etc;
• Some progress towards ‘greener use of F in chemical architecture’….need more creativity applied to the problem

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• All the talented students who produced this work
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Joel Baker  jebaker@uw.edu

www.pugetsoundinstitute.org/collaboration/cross-program-contaminant-working-group/