Perfluorinated Compounds (PFCs) in the Arctic Environment: Sources, Transport and Health Concerns for Fish, Wildlife and People

Alaska Community Action on Toxics
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Presentation Outline

1) Commercial sources of PFAS
   - What are they used for? What chemicals are used? **Importance of volatile precursors**
   - What products are they found in?
   - Changes in production of PFCs chemicals (3M production ban in year 2000)

2) Why do PFCs accumulate in the Arctic?
   - Transport pathways: atmospheric & oceanic
   - **Atmospheric degradation of volatile precursors**

3) PFC trends in arctic wildlife & humans
   - Which PFCs accumulate in wildlife & humans? **Chemicals that accumulate are NOT what is used in commercial products**
   - Temporal trends: changes since the 3M ban
   - Potential health risks
Early Scientific Interest

- In 2001, two *monitoring* studies drew attention to the global contamination of PFCs

**Wildlife (PFOS only)**

- Alaska (polar bear)
- Northwestern US (river otters)
- Canadian and Norwegian Arctic (seals)
- Great Lakes (bald eagles, fish and other birds)
- Coastal California (puffins)
- Southeastern US (birds and turtles)
- North Pacific (albatrosses)
- Baltic Sea (eagles, mammals)
- Mediterranean (fish, mammals, birds)
- Indian Ocean (dolphins)
- Korea and Japan (birds)
- Antartica (penguins, seals)

**Human Serum – United States**

- Concentration (ng/ml)

**Giesy & Kannan, ES&T, 2001, 35, 1339-1342**

**Hansen et al., ES&T, 2001, 35, 766-770**

- Perfluorooctane Sulfonate (PFOS)
- Perfluorooctanoate (PFOA)
Perfluorinated Alkyl Compounds

- Physical-chemical properties suggest that PFOS and PFCAs (carboxylates) should not undergo long-range transport in the atmosphere
- *How to explain contamination in remote environments, particularly top predators? How do they get into humans?*

- Perfluorinated Sulfonates (e.g. PFOS)
  - Primarily only the eight carbon molecule (PFOS)
  - Exclusively made by the 3M company
  - Production starting in the 1950s

- Perfluorinated Carboxylates (PFCAs)
  - Various chain-lengths
  - C8 molecule (PFOA) received considerable attention
  - Several companies, including Dupont
  - Production starting in the 1970s
  - *Fluorotelomer*-manufacturing process
Regulatory Interest

• Production of PFOS related chemicals was banned by 3M in 2000 due to presence in humans and the environment

• PFOS placed on the Stockholm Convention in May 2009 (Annex B)

• Canada banned the import of 4 fluorotelomer-based polymers that have the potential to degrade to bioaccumulative PFCAs (June 2006)

• US EPA initiated the 2010/2015 PFOA Stewardship Program, phase out of long-chain PFCAs by 2015
  – Commitments by the 8 major manufacturers (Arkema, Asahi, BASF, Clariant, Daikin, 3M, DuPont, Solvay Solexis)
  – Includes PFCAs and precursor chemicals
Commercial Sources of PFCs

- Poly- and Perfluorinated Compounds (PFCs) are widely used in commercial products
- Resists water (hydrophobic) and oil (oleophobic) and thus are used primarily for their unique stain repellency properties
- Specific uses include:
  1. surface treatment protection (carpets, textiles, leather) 80%
  2. paper protection (food paper packaging) 20%
  3. “performance chemicals” (firefighting foams, floor waxes, coatings, electroplating and etching baths, chemical intermediates) trace
PFC Uses

- Products containing poly- and perfluorinated compounds are widespread and *uses are growing*
Introduction: NOT Teflon!

- **Teflon** is a fluoropolymer made of polytetrafluoroethylene (PTFE)
- Manufactured by DuPont
- Main commercial application is non-stick pans
- Very low coefficient of friction, very non-reactive
- *PFOA is used a polymerization aid, but not detected in final products*
- **TEFLON PANS ARE NOT A SOURCE OF PFOA!**
PFAS Uses

• Fluorinated Polymers (80%)
  – Reduce the coefficient of friction for materials
  – High Molecular weight polymer, contains fluorinated monomer
  – Commercial Products: Stain repellents for carpets, textiles, leather (*Scotchgard, Teflon Advanced*)

What happens to unreacted monomer?
PFAS Uses

- **Fluorinated Surfactants (20%)**
  - Reduce the surface tension of surfaces and liquid
  - Chemicals: *Polyfluorinated Phosphates (PAPs)* and *Perfluorinated Sulfonates (PFOS)*
  - Commercial Products: Fire Fighting Foams, Stain Repellents for Paper, Leveling Agents for Floor Waxes, Cosmetics

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\begin{align*}
\text{Mono-PAPs} & : CF_3(CF_2)_x \quad \text{OH} \\
\text{Di-PAPs} & : CF_3(CF_2)_x \quad \text{OH}
\end{align*}
\]

\[
\text{Perfluorooctane Sulfonate (PFOS)}
\]
Fluorotelomer Production

Volatile “precursors” observed in the atmosphere

Various Chain Lengths (e.g. 6:2, 8:2, 10:2)

Ethane “spacer”, susceptible to degradation

- Made by Dupont & others (Asahi, BASF, Clariant, Daikin, Solvay Solexis) from 1970s-present
- Telomer-based chemicals, many different sizes (8:2 was most common)
- Degrade to PFOA and other chain-length PFCAs
Perfluorooctane Sulfonyle Fluoride (POSF) Compounds (3M)

- Made by the 3M company from 1950-2002
- Sulfonamide chemicals, **only 8 carbons**
- Degrade to PFOS during metabolism; degrade to PFOA & PFOS in the atmosphere

**Observed in the Atmosphere**

**Sulfonamides and Sulfonamide alcohols**

**Intermediates for surfactants, phosphates and polymers**

- Made by the 3M company from 1950-2002
- Sulfonamide chemicals, **only 8 carbons**
- Degrade to PFOS during metabolism; degrade to PFOA & PFOS in the atmosphere
How do PFCs get into the environment?

- **Commercial products**
- **Direct release to air, water**
- **Volatile precursors**
  - FT phosphates
  - Food, dust ingestion
  - Atmospheric & biological degradation

**PFCAs (e.g. PFOA), PFSAs (PFOS)**

**PFCAs**

**River & ocean contamination**

**PFCAs (e.g. PFOA), PFSAs (PFOS)**
Atmospheric Degradation: Formation of PFCAs and PFOS

- Fluorotelomer Acrylate
- Fluorotelomer Alcohol
- Fluorotelomer Iodide
- Fluorotelomer Olefins
- Perfluorinated Aldehyde
- Perfluorinated Carboxylates
- Sulfonamide Alcohol
- Sulfonamide
- PFOS
- PFOA
Volatile precursors are found in the atmosphere

Source: Shoeib et al., Environ. Sci. Technol. 2006, 40, 7577-7583
Precursors & PFCAs in Waterproof Clothing

Source: Greenpeace, “Chemistry for any weather”, 2012
Transport Pathways to the Arctic

PFCAs & PFOS precursors are detected in the atmosphere

PFCAs & PFOS are detected in the ocean
Biological Transformation

- Perfluorinated carboxylates (PFCAs) and sulfonates (PFSAs) are **NOT** susceptible to biological transformation (metabolism)

- However, polyfluorinated compounds (e.g. alcohols, acrylates) can undergo oxidative metabolism to eventually yield PFCAs and PFSAs
Fluorinated Phosphate Surfactants

- Fluorinated phosphate (ester) surfactants are added to food packaging paper to resist oil and water.
- Most well-known application is microwave popcorn bags, but they are widely used and detected!
- The fluorinated “tail” may be either telomer- or sulfonamide-based (formally produced by the 3M company).
- Fluorotelomer PAPS have been shown to degrade to PFCAs in rat studies.
Human Blood: PFCs widely detected

- Detected in human blood from North America, South America, Europe, Asia, Africa and Australia
- Levels of PFOS are decreasing since early 2000s, coinciding with the 3M production ban

PFCs in Human Blood from Norway

Human Blood: Arctic regions

- Only two studies from arctic regions, both from Nunavik (Northern Quebec)

- PFOS in adults (19 ng/ml) was comparable to those in more southern regions (Dallaire, Environ. Sci. Technol., 2009, 43, 5130-5136)

- Children had lower PFOS levels (3.4 ng/ml) as compared to adults (O’Brien, Environ. Sci. Technol., 2012, 46, 4614-4623)

- Impact on thyroid hormones: Higher PFOS levels associated with lower TSH, total T3 and TBG but higher free T4 (Dallaire, EHP, 2009, 117, 1380-1386)

- Impact on plasma lipid levels: Higher PFOS levels associated with lower triglycerides and total cholesterol:HDL-C ratios, but higher levels of HDL-C (Chateau-Degat, Environ. Int., 2012, 110, 710-717)
PFCs in ringed seals from the Canadian Arctic

PFOS dominates, PFOA usually not detected in arctic wildlife but longer-chain PFCAs detected

Source: Butt et al., Environ. Toxicol. Chem. 2008, 27, 542-553
Wildlife: Biomagnification in Marine Food Webs

- Several studies on marine food webs from eastern & western Canada and Norway
- Increasing PFOS levels with trophic level, suggesting biomagnification

Polar bears have the highest PFC levels measured in wildlife

PFOS concentrations vs. tropic level for an eastern Canadian Arctic food web. BLKI = black-legged kittiwakes GLCU = glaucous gulls. Source: Tomy et al., 2004
Arctic Wildlife Levels Lower than Temperate/Sub-Tropical

PFOS concentrations (ng/g ww) in seals & sea otters from arctic and temperate/sub-tropical regions. Data represents mean, median or individual values in blood or liver.

Similar geographic trends for whales and birds

Source: Butt, unpublished
Health Concerns for Wildlife

- No known (observed) health effects of PFCs in arctic wildlife
- PFCs accumulate in the liver, potential for liver toxicity
- Recent study shows that PFCs can cross the blood-brain barrier in polar bears; potential for neurotoxicity (Greaves et al., 2013, Environ Toxicol. Chem. 2013, 32, 713-722)
- Laboratory studies show PFC exposure associated with immunosuppression, neurotoxicity and thyroid hormone alteration
- Recent fish study showed that embryos exposed to PFOS had liver damage and immune system suppression as larvae
PFCs in biological environment: Knowledge Gaps

- The marine food web is very well studied; many studies from the Canadian Arctic and Greenland
- Ringed seals and polar bears are the best studied
- Much less is known about terrestrial and freshwater food webs
- Very few reports on PFCs in fish
- Evidence for biomagnification in a lichen-wolf-caribou food web
* POSF-compounds degrade to PFOS via atmospheric oxidation and biotransformation

Source: Paul et al., 2009
• Levels of perfluorinated stain repellent (PFOS) are declining in ringed seals from the Canadian Arctic, in response to the voluntary ban in production by the major manufacturer (3M)

• Transport of volatile precursors in the major transport pathway to remote environments

Sea Otters from southern Alaska


Seabirds from Prince Leopold Island, Nunavut


$\Sigma$PFCAs increasing, PFOS steady from 1975-2010

![Graph showing PFCAs and PFOS levels in eggs from 1975 to 2010](image-url)
Ringed Seals from Greenland

Ittoqqortoormitt

PFOS

PFDA

PFUnA

Qeqertarsuaq

PFOS

PFDA

PFUnA

Source: Butt et al., Sci. Total Environ., 2010, 408, 2936-2965
Shifts in Production: Smaller Chemicals

- 3M shifted production to 4-carbon chemicals (PFBS)
- US EPA PFOA Stewardship Program: Fluorotelomer manufacturers shifted to 6:2-based chemistry (formation of PFHxA and smaller PFCAs)
- Smaller chemicals are less bioaccumulative, very few detections of PFBS in arctic wildlife
- Toxicity not well understood; likely similar effects but lower toxicity
PFCs in the Arctic - Recap

• Chemicals that accumulate in wildlife and humans are NOT what is commercially used

• Industrial synthesis of fluorinated polymers (80%) of commercial market produces several volatile, reactive chemicals that degrade (biologically or atmospherically) to PFCAs and PFOS

• Atmospheric half-life of these volatile precursors sufficient to allow for transport to remote environments

• Commercial market changed drastically in 2001

Perfluorooctane Sulfonate (PFOS)
PFCs in the Arctic - Recap

- PFCs are widely detected in the humans and wildlife
- The arctic environment is the most-studied region for PFCs
- PFCs biomagnify in the food web; polar bears have the highest concentrations of any wildlife or humans
- Temporal trends indicate PFOS levels declining, PFCA levels increasing; trends are variable in different regions
- Replacement chemicals?
- Unclear if PFCs are causing harmful effects in wildlife