Massachusetts Chemistry & Technology Alliance
Per- and Polyfluoroalkyl Substances
May 10, 2018

Proactive By Design.
Our Company Commitment

Introduction to PFAS

Karen Kinsella
GZA GeoEnvironmental

Program Overview

(1) Background

What are PFAS? Why are they challenging?

(2) Stewardship

What are the alternative fluorochemistries?

(3) Hazards & Risks

What are the concerns? What are the Massachusetts regulations?

(4) Environmental

What are the PFAS impacts? How do we remediate?

(5) Sampling & Analytical Considerations

What are the sampling and analytical challenges?

(6) Regulations & Ramifications

What are the emerging areas of legal exposure?

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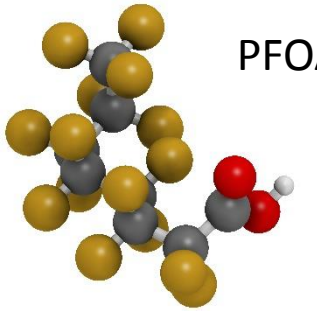
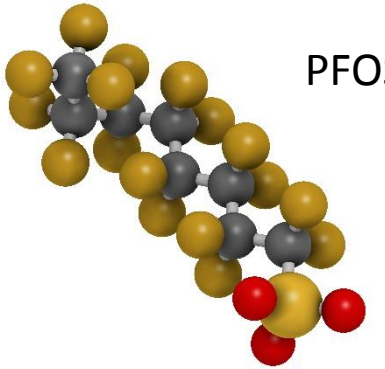
Per- and Polyfluoroalkyl Substances

Perfluoroalkyl: all available carbons have fluorines instead of hydrogens



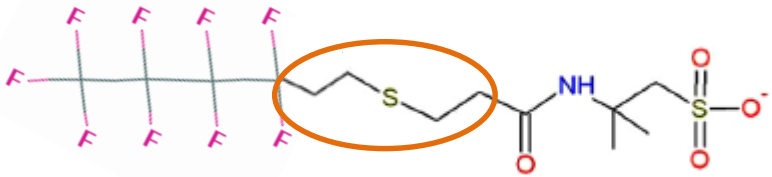
PFOA



PFOS

Polyfluoroalkyl: some carbons with fluorines, some with hydrogens

Fluorotelomer

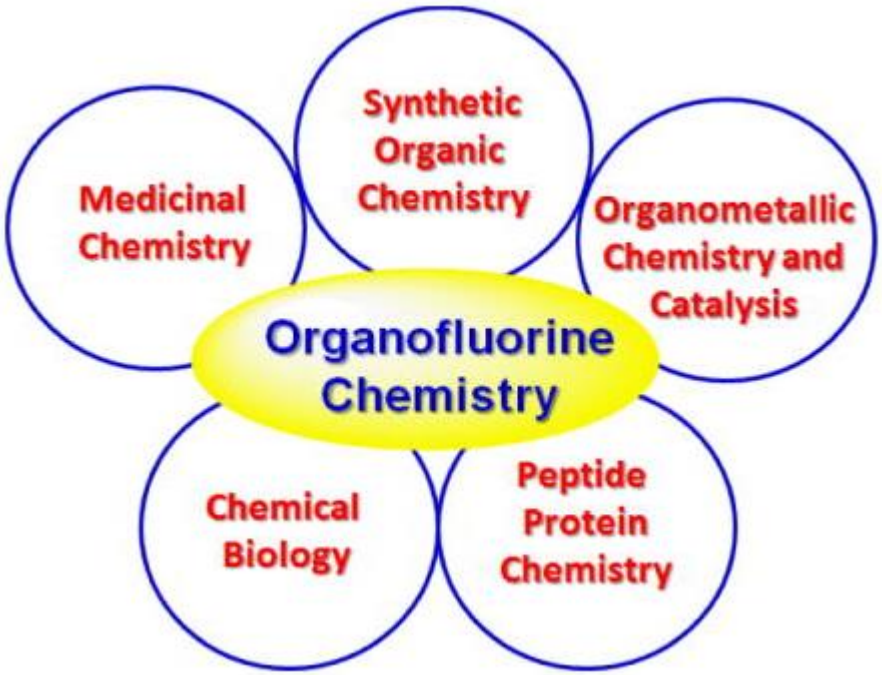


PTFE: fluoropolymer

Unique Chemistry of Fluorine

Fluorine special properties

Small atomic radius • High electronegativity
• Low polarizability of the C–F bond



Many biologically relevant molecules

Peptide/protein chemistry
Medicinal chemistry
Chemical biology
Pharmacology
Drug discovery
Diagnostic and therapeutic applications

Ojima 2013. *Journal of Organic Chemistry 78:6358.*

Unique Chemistry of PFAS

Carbon-Fluorine

Fluorine has high electronegativity

Forms very strong, highly polar bonds

Resulting PFAS Properties

Hydrophobic, lipophobic, surfactant

Stable in acids, caustics, oxidants, heat

Resistant to biodegradation

Unique Chemistry = Usefulness

- Aqueous Film Forming Foams (AFFF) – firefighting
- Fluoropolymer polymerization aid
- Cutting-oil mist suppression – metal-working
- Water/stain/oil/grease/heat/chemical resistance – coatings on packaging, paper, carpeting, upholstery, clothing, and wire; chemical and heat-resistant seals
- Specialty chemicals – insecticides, lubricants
- Fuel cell membranes

Unique Chemistry = Usefulness

Historical *per*fluoroalkyl substance use as a polymerization aid could potentially lead to *trace* amounts of *per*fluoroalkyl impurities in *poly*fluoroalkyl substances

Important to note that the polymers and coatings themselves are non-toxic, because they are not bioavailable

Historical PFAS

1970s-present

Fluorotelomers – older long-chain, newer short-chain

Some are precursors

1980s-2000

Perfluorocarboxylic acids (PFCAs, *e.g.*, PFOA)

Perfluorosulfonic acids (PFSAs, *e.g.*, PFOS)

Few precursors

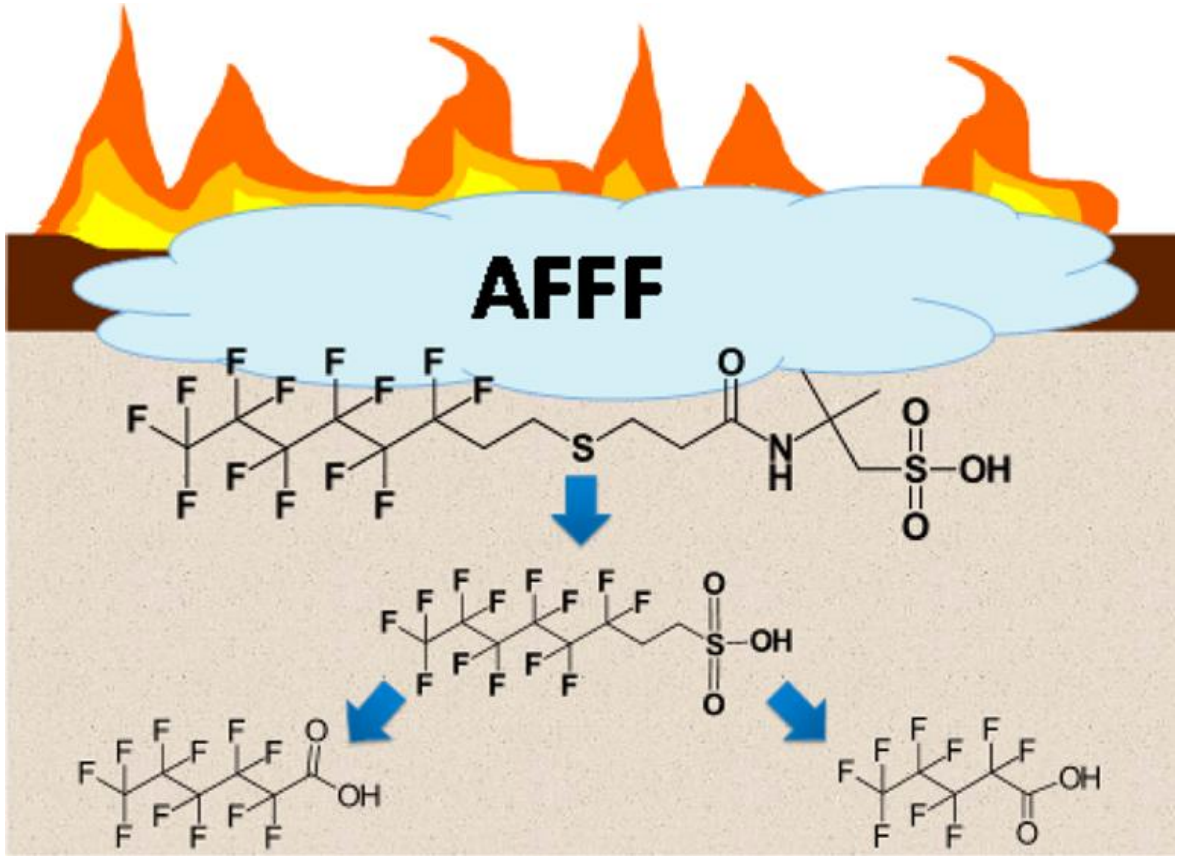
2000s-present

Fewer PFCAs & PFSAs

Shorter chains

What is a precursor?

Polyfluoroalkyl substances that can undergo degradation to form ***per***fluoroalkyl acids



Harding-Marjanovic et al. 2015. *Environmental Science & Technology 49:7666.*

What is a precursor?

Polyfluoroalkyl substances that can undergo degradation to form ***per***fluoroalkyl substances
Examples of ***per***fluoroalkyl substance formation from biological degradation of a precursor:

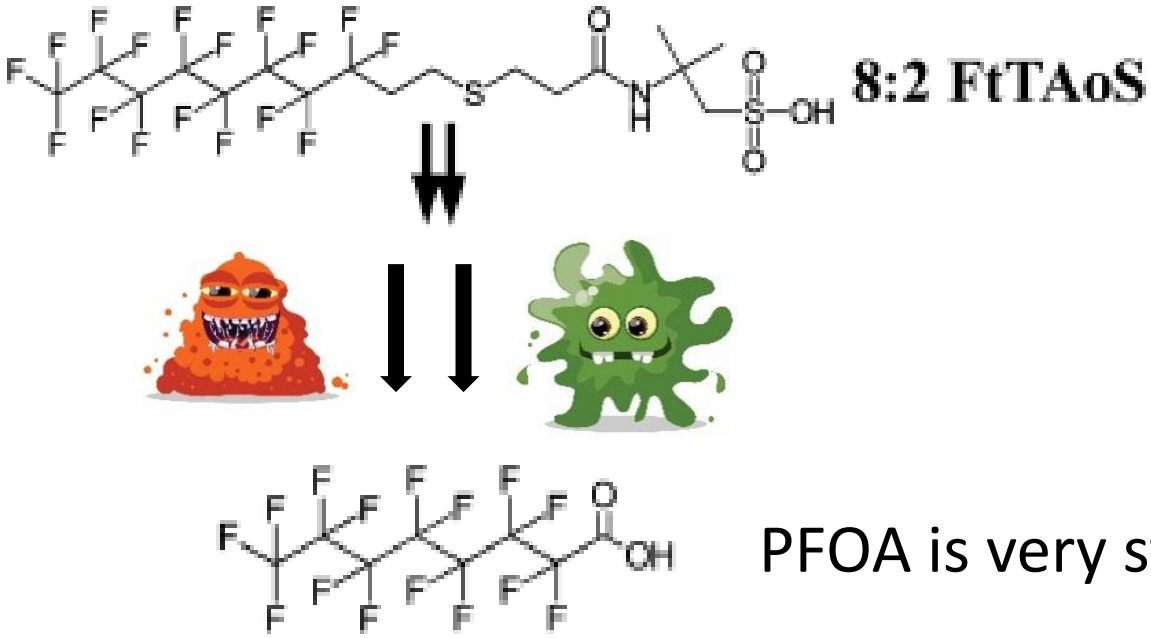
4:2, 6:2, and 8:2 fluorotelomer thioether amido sulfonate (FtTAoS)

Perfluorocarboxylic acids (PFCAs): PFBA, PFHxA, and PFOA

Precursor degradation

Biological degradation

- Perfluoroalkyl acids are resistant to biodegradation
- Some polyfluoroalkyl substances have the potential to aerobically biodegrade to perfluoroalkyl acids



Precursor degradation

Abiotic degradation – slower

Hydrolysis

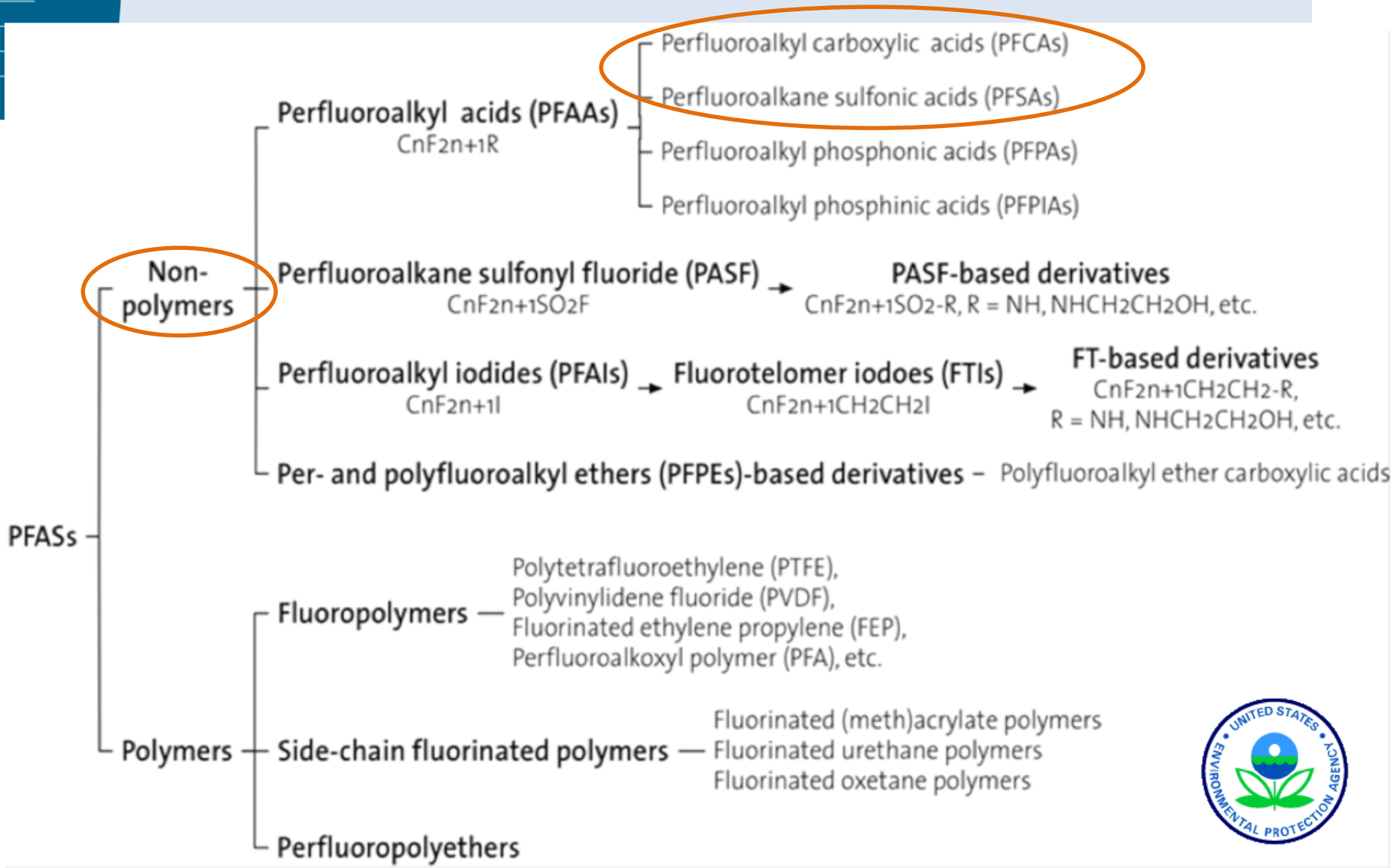
Fluorotelomer-derived precursors ⟶ PFOA, other PFCAs

Photolysis

Fluorotelomer alcohols can degrade in the atmosphere:

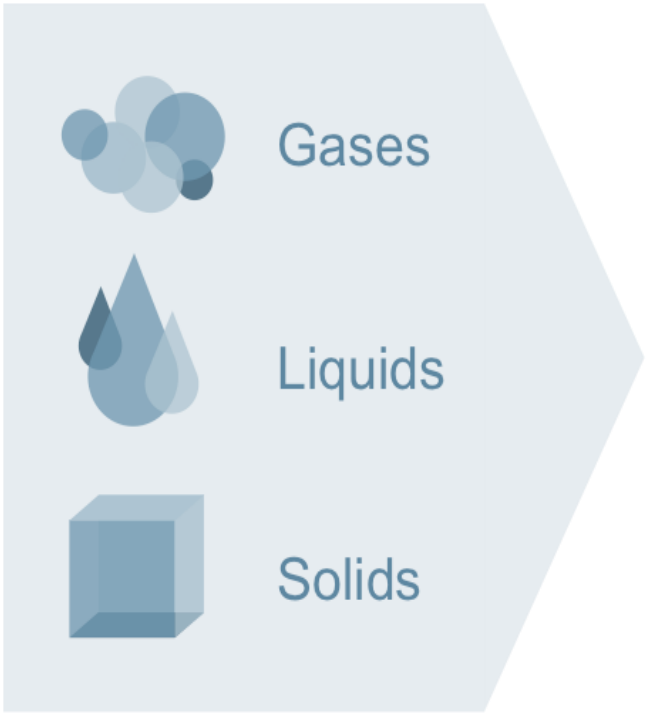
- 8:2 FTOH ⟶ PFOA
- 6:2 FTOH ⟶ PFHxA
- 4:2 FTOH ⟶ PFBA

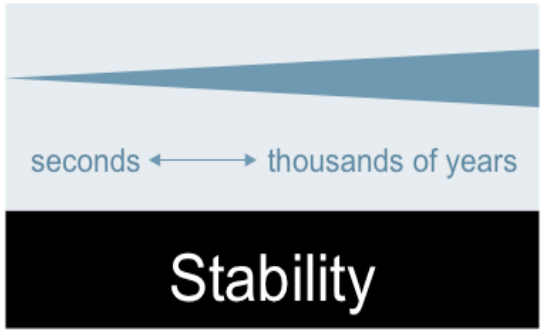
PFAS get complicated fast

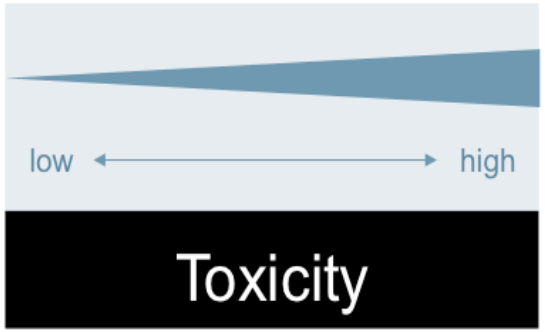


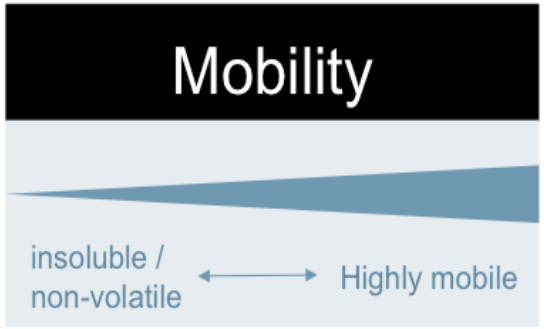
PFAS include thousands of possible substances with very different properties

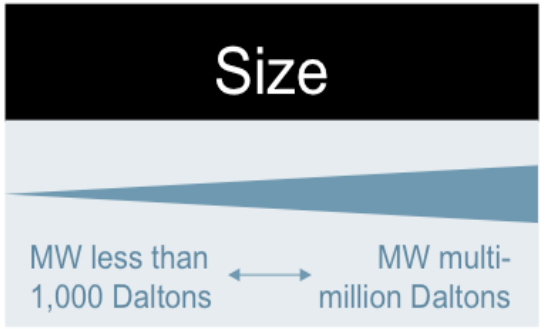
All have at least one carbon with fluorine instead of hydrogen – but otherwise thousands of different chemicals with different properties











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Global Industry Council for FluoroTechnology

Currently no single harmonized system for PFAS classification

What is Needed

A clearer understanding of PFAS in the environment and assessment of their properties to be able to determine which classes of PFAS require management action

Take into account differences in chemical, physical, thermal and biological properties

Distinguish classes of PFAS to assure that regulations are appropriate in scope and proportionality

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Global Industry Council for FluoroTechnology

Long Chains vs. Short Chains

Distinction based on science and policy

Long chains

Example: Fluorinated polymer with C8 side-chain

Example Degradation Products: PFOA, PFOS

Focus of regulatory action; no longer permitted for use in certain applications

Phase-out of long-chain PFAS under the EPA Stewardship Program has resulted in significant innovation and simplification in fluorotelomer manufacturing

Short chains

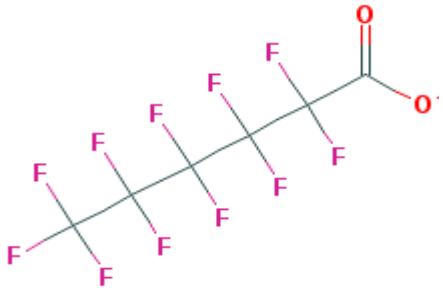
Example: Fluorinated polymer with C4 or C6 side-chain

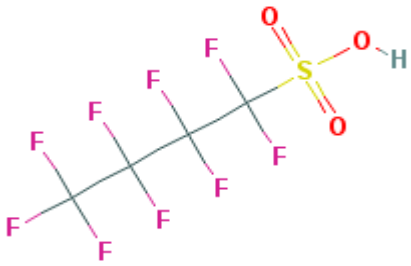
Example Degradation Products: PFBA, PFHxA

Modern Fluorosurfactants

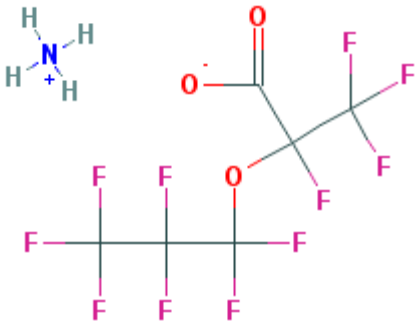
Short-chain PFAS

PFCA – like PFOA, but < 8 carbons,
PFSA – like PFOS, PFHpS, and PFHxS, but < 6 carbons

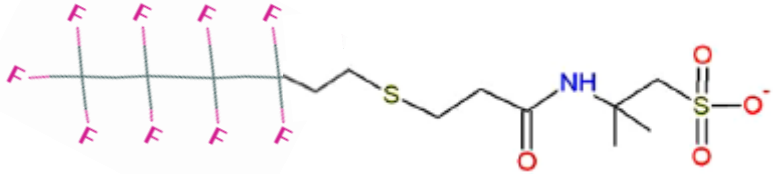




Fluoroethers



Fluorotelomers



https://pubchem.ncbi.nlm.nih.gov

Challenges

Perfluoroalkyl substances are 'Chemicals of Emerging Concern' –

Defined by EPA as chemicals which have previously not been considered a risk to humans and/or the environment.

Present in trace amounts – parts-per-trillion, analogous to:

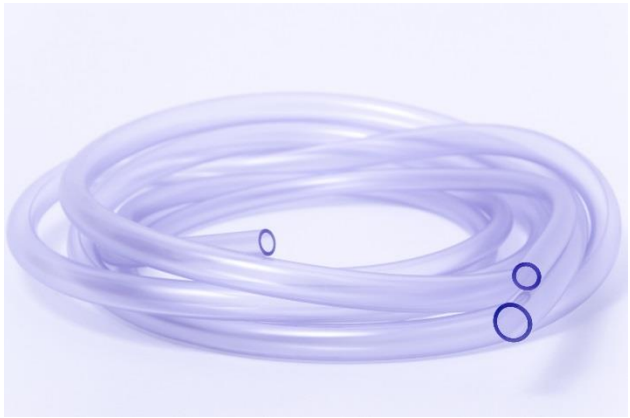
- one square inch in 250 square miles
- one second in 32,000 years
- one ounce in 7.5 billion gallons of water

Photo: https://www.atsdr.cdc.gov/

Analytical Challenges - Sampling

Cross-contamination possible during sample collection due to perfluoroalkyl impurities in fluoropolymers used in:

- Pumps, tubing, sample bottles
- Sampler's clothing, personal care products, fabric softeners
- Field notebooks, Sharpie® markers, Post-it ® notes
- Equipment decontamination detergents

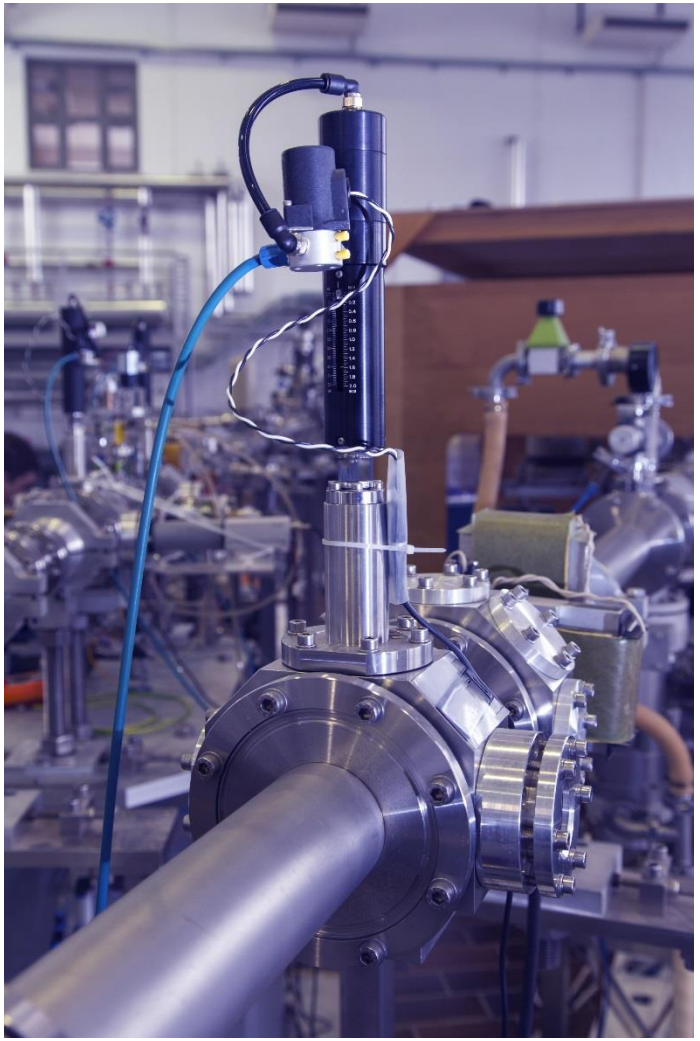


Analytical Challenges - Laboratory

Measuring nanograms per liter

Analytical instrumentation needs to be PFAS-free

Laboratories need to be PFAS-free – floor wax, workers



PFAS Health Effects

Some (not all) human studies have shown that higher concentrations of certain *per*fluoroalkyl substances (PFOS, PFOA, PFHxS, and PFNA) may:

- affect growth, learning, and behavior of children
- lower a woman's chance of getting pregnant
- interfere with the body's natural hormones
- increase cholesterol levels
- affect the immune system
- increase the risk of cancer

Human health effects from exposure to low environmental levels of PFCs [perfluorochemicals] are unknown.

Agency for Toxic Substances and Disease Registry https://www.atsdr.cdc.gov/

Challenges

Persistent – strong, stable C-F bond,

Resistant to heat, water, oil, biological degradation

Difficult to remediate

High profile chemicals in the national and local media – public fear, difficult to communicate risk

Public health advisory concentrations and State DOH regulations vary widely – this does not inspire public confidence!

Photo: Associated Press

Risk Perception Challenges

Risk Communication – according to the CDC:

Human health effects from exposure to low environmental levels of PFCs [perfluorochemicals] are unknown.

- How people can be exposed is as yet unclear.
- Some persist in the environment – people may be exposed via contaminated water or food.
- Exposure may also occur by using products that contain perfluoroalkyl substances.

Agency for Toxic Substances and Disease Registry – Centers for Disease Control and Prevention
https://www.atsdr.cdc.gov/

PFAS Categories and Classes

Potential health issues – subset of ***per***fluoroalkyl

1 Group — PFAS Per- and Polyfluoroalkyl substances

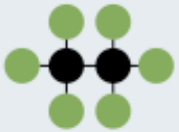
2 Categories

5 Classes

Non-Polymers

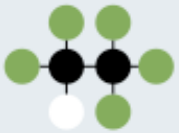
Perfluoroalkyl Substances

Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines



Polyfluoroalkyl Substances

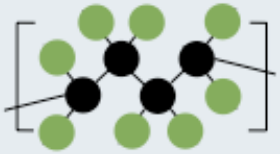
Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines



Polymers

Fluoropolymers

Carbon-only polymer backbone with fluorines directly attached

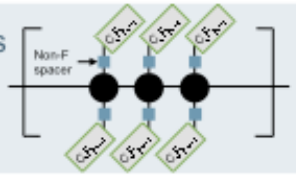


Polymeric Perfluoropolyethers

Carbon and oxygen polymer backbone with fluorines directly attached to carbon

Side-chain Fluorinated Polymers

Variable composition non-fluorinated polymer backbone with fluorinated side chains



- Fluorine
- Carbon
- Oxygen
- Hydrogen

Adapted from Buck et al. 2011.
Integrated Environmental Assessment and Management 7:513.

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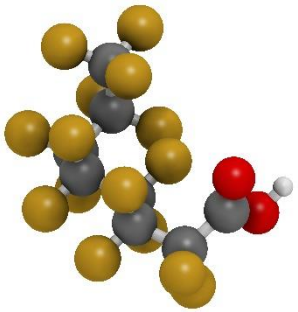
PFAS Categories and Classes

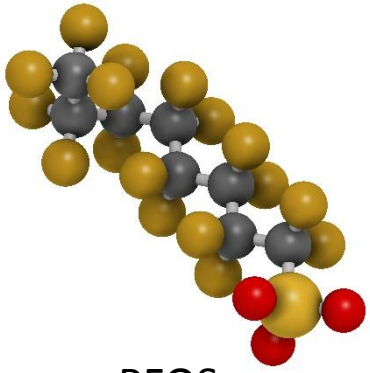
Potential health issues – subset of ***per***fluoroalkyl

PFOS, PFOA, PFHxS, and PFNA most studied



PFOA

Historical polymerization aid



PFOS

Historical use in fire-fighting foams

PFAS Categories and Classes

Fluoropolymers: nontoxic, stable, no known risks

1 Group — PFAS Per- and Polyfluoroalkyl substances

2 Categories

5 Classes

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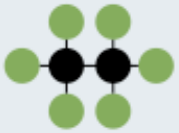
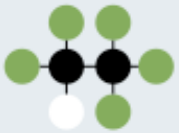
Perfluoroalkyl Substances
Compounds for which all hydrogens on all carbons (except for carbons associated with functional groups) have been replaced by fluorines

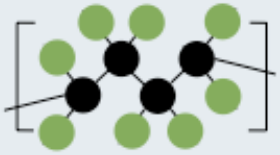


Polyfluoroalkyl Substances
Compounds for which all hydrogens on at least one (but not all) carbon have been replaced by fluorines



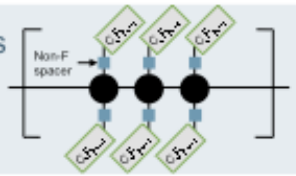
Polymers

Fluoropolymers
Carbon-only polymer backbone with fluorines directly attached



Polymeric Perfluoropolyethers
Carbon and oxygen polymer backbone with fluorines directly attached to carbon

Side-chain Fluorinated Polymers
Variable composition non-fluorinated polymer backbone with fluorinated side chains



- Fluorine
- Carbon
- Oxygen
- Hydrogen

Adapted from Buck et al. 2011.
Integrated Environmental Assessment and Management 7:513.

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Fluoropolymers and OECD Criteria

Fluoropolymers meet thirteen *Organization for Economic Co-operation and Development* Polymer of Low Concern Criteria

13 Criteria

Polymer composition

MW, M_n, MWD

wt% oligomer

Electrical charge

Reactive Functional Groups (RFG)

Functional Group Equivalent Weight (FGEW)

Low MW leachables

Water / lipid solubility, octanol water partition

Particle size

Polymer stability

Thermal stability

Abiotic stability

Biotic stability

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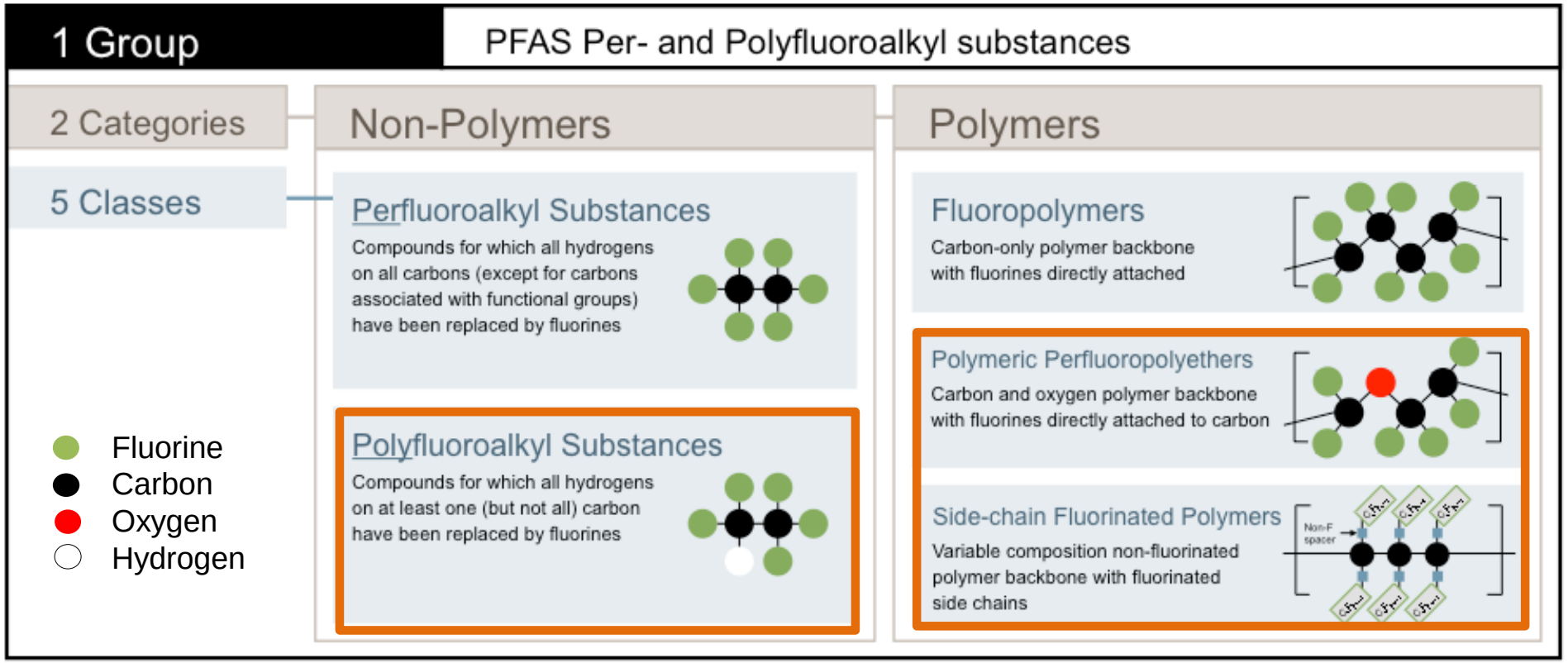
PFAS Categories and Classes

Fluorotelomer-based substances, fluoroethers: these are not known to be bioavailable – but a few can degrade to *per*fluoroalkyl substances



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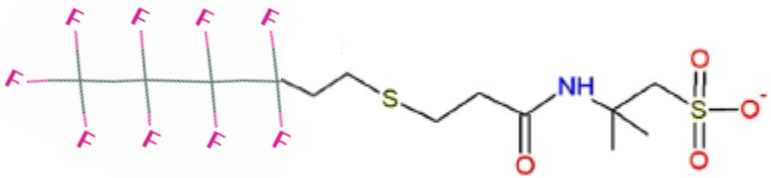
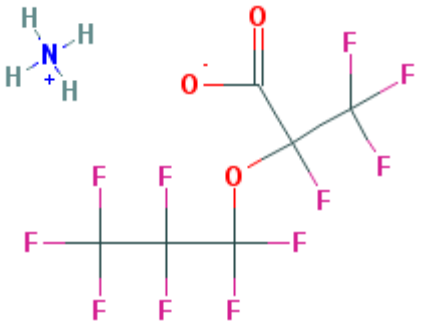
PFAS Categories and Classes

Fluorotelomer-based substances – some replace PFOS in fire-fighting foams (AFFF)



Fluoroethers – some replace PFOA in emulsion polymerization of fluoropolymers



Summary

What are PFAS? Why are they challenging?

- Thousands of different chemicals with diverse, useful properties
- A few degrade to 'dead-end daughter products' (1)
- Public perception influenced by variations in health advisories and regulations, unknown health risks
- Different categories and classes represent different risks
- Many alternatives – risks of a few have been studied

(1) Suthersan et al. 2016. *Groundwater Monitoring & Remediation 36:22.*

Thank you! Questions?

Resources

- Massachusetts Department of Environmental Protection
- Agency for Toxic Substances and Disease Registry – atsdr.cdc.gov
- U.S. Environmental Protection Agency (EPA) – clu-in.org
- U.S. Department of Defense, with EPA & DoE – www.serdp-estcp.org
- Air Force Center for Engineering and the Environment –
- www.usaf.com/orgs/environmental.htm
- Naval Facilities Engineering Command – www.navfac.navy.mil
- National Ground Water Association – www.ngwa.org
- Interstate Technology and Regulatory Council – www.itrcweb.org
- Karen.Kinsella@gza.com – 860-573-9787