Emerging Contaminants: Per- and Polyfluoroalkyl Substances (PFASs)

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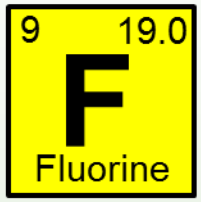
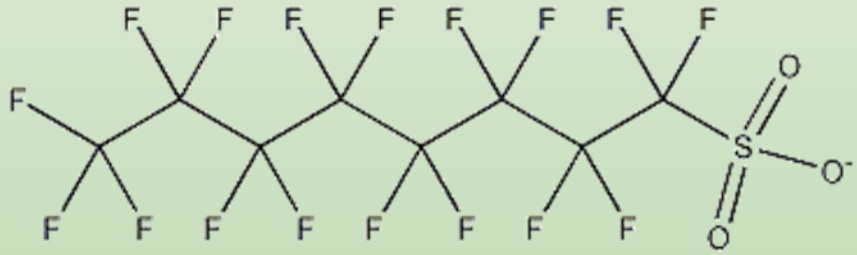
Topics in this Presentation

- Intro to PFASs
- Uses & Sources of PFASs
- Chemical/Physical Properties (incl. transformation)
- Environmental Fate
- Bioaccumulation of PFOA/PFOS
- Human and Ecological Exposure Pathways
- Toxicology
- 2016 Lifetime Health Advisory
- Treatment Technologies for PFASs
- Acknowledgments and Contact Info

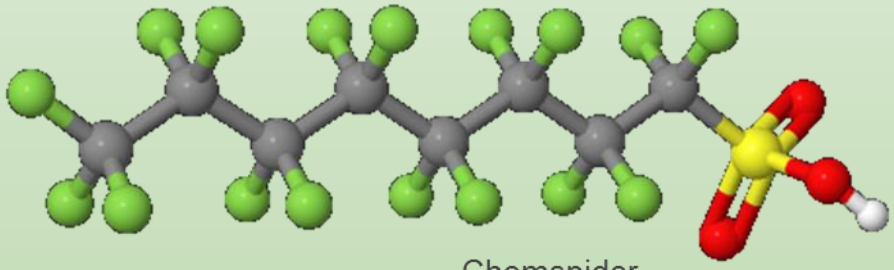
Introduction to PFASs

- A large family of synthetic organic compounds that contain multiple Fluorine (F) atoms.
- The 2 most studied PFASs are
  - Perfluorooctanoic Acid (PFOA)
  - Perfluorooctane Sulfonate (PFOS)
- PFAS family = thousands of diverse compounds





Conder et al. (2008)



Chemspider

Example molecular structures for perfluorooctane sulfonate (PFOS)

Introduction to PFASs

- A class of chemicals that are ubiquitous due to
  - Wide variety of uses
  - Persistence
  - High Mobility
- They are a concern due to:
  - Known or suspected toxicity, especially for PFOS and PFOA
  - Bioaccumulation
  - Some have very long half lives (several years), especially in humans
- Information on PFASs is rapidly evolving

Uses & Sources of PFASs

PFASs are used in a wide variety of industries and commercial products for their valuable properties, including fire resistance, dust suppression, and oil, stain, grease, and water repellence. (Some examples of uses are on the following slides)

- Fire fighting foams (AFFF) used in military and civilian airports as well as some other industrial facilities.

Uses & Sources of PFASs

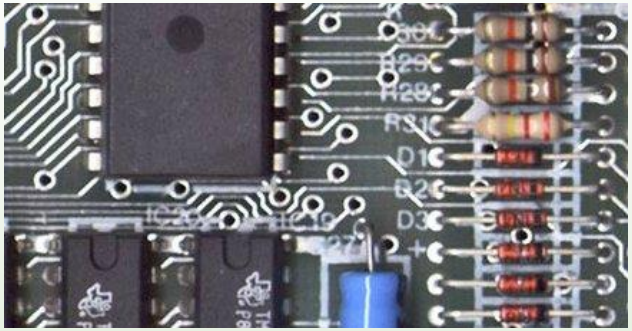
- Food surfaces (Teflon[1] pans, pizza boxes, popcorn bags)

[1] https://en.wikipedia.org/wiki/Polytetrafluoroethylene PFOA, which used to be a key ingredient in making Teflon, has been phased out, however there is little evidence that the chemicals that have replaced PFOA are much safer.

Uses & Sources of PFASs

- Polishes, waxes, paints
- Stain repellants (carpets, clothing and upholstered furniture)
- Cleaning products

Uses & Sources of PFASs



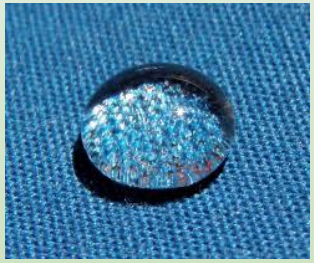
- Dust suppression for chrome plating
- Electronics manufacturing
- Oil and mining for enhanced recovery
- Performance chemicals (hydraulic fluid, fuel)

Uses & Sources of PFASs

- Landfills
- Land where biosolids from wastewater treatment plants treating PFAS-containing wastewater was applied
- Direct release of PFAS products into the environment – such as use of AFFF in training and at crash sites

Chemical and Physical Properties

- Properties of PFASs range and are not well understood
- PFASs are commercially useful because they repel both oil and water
- The fluorinated carbon tail is both lipophobic/oleophobic (repelled by fats and oils) and hydrophobic (repelled by water)
- The functional group head can vary but is often hydrophilic (attracted to water)
- Because of these properties, they are often used as surfactants and stain preventers

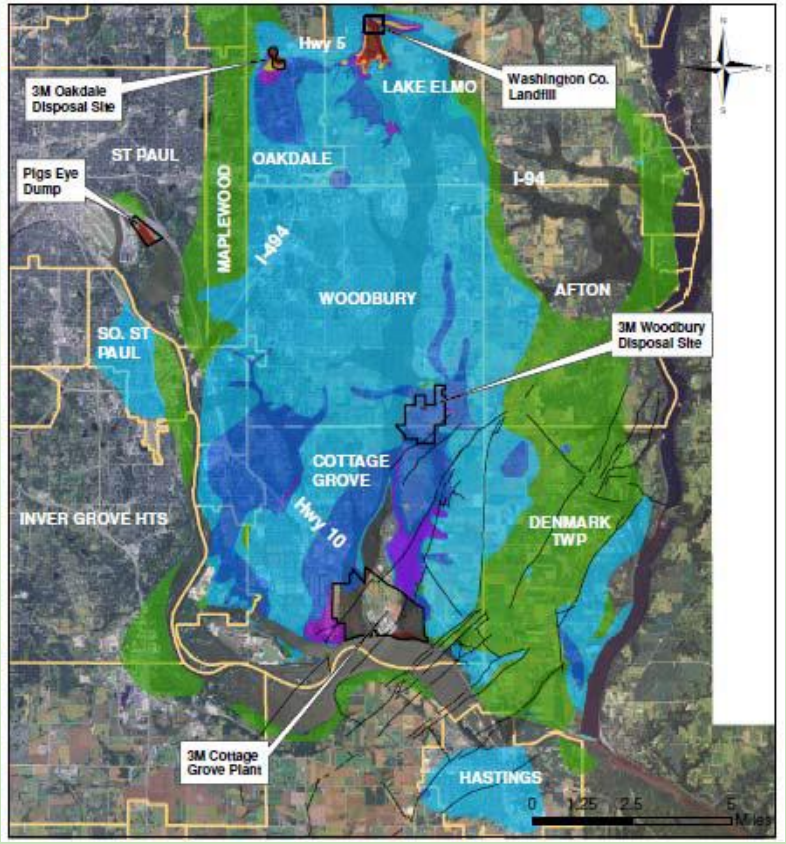


Chem and Phys Properties of PFOA/PFOS

- PFOA/PFOS (and many other PFASs) are extremely persistent in the environment
- PFOA/PFOS do not biodegrade, hydrolyze, oxidize, or photolyze
- PFOA/PFOS are non-volatile and not detected using traditional analytical instruments (GC/MS)

Environmental Fate

- **PFAS Plumes can be Huge!**
- **Minnesota PFAS plumes in groundwater**
  - **10+ miles long**
  - **cover over 100 mi²**

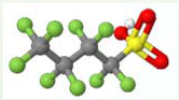


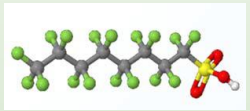
(MDH, 2012)

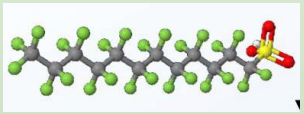
Bioaccumulation of PFOA/PFOS

- PFASs are detectable in nearly any biological tissue
- Many PFASs bioaccumulate, especially longer PFASs and sulfonated PFASs (e.g., PFOS)
- Partition to protein, not fat
  - Blood, liver, kidney, muscle are primary repositories
- Not metabolized, or metabolized to persistent PFASs

Less Bioaccumulative







More Bioaccumulative

Conder et al., 2008. Environ Sci Technol . 42:995-1003

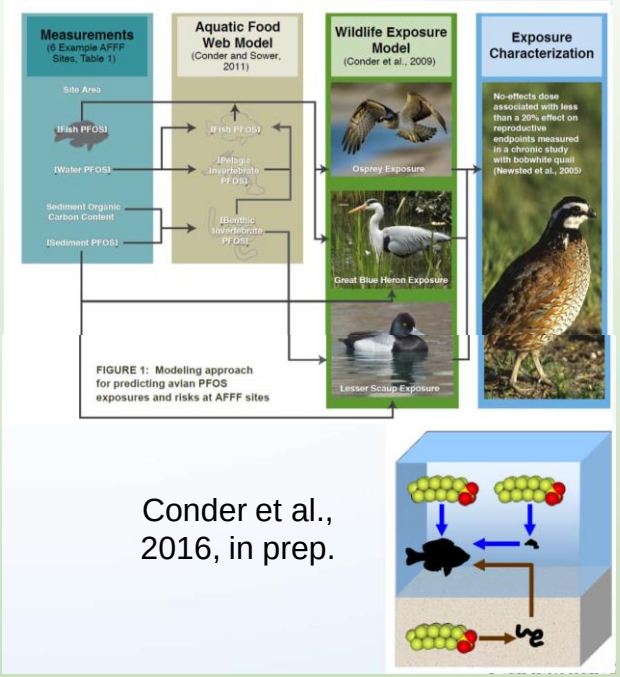
Human Exposure Pathway

- Major[1,2]
  - Diet (bioaccumulation)
    - Fish and seafood
    - Homegrown produce
  - Drinking water
  - Incidental soil/dust ingestion
- Usually insignificant or minor
  - Dermal absorption
  - Inhalation

1 Oliaei et al., 2013. Environ. Sci. Pollut. Res. Manag. 20:1977-1992
2 Domingo, 2012. Environment International 40:187-195

Ecological Exposure Pathway

- Major
  - Diet (bioaccumulation)
    - Aquatic food webs particularly susceptible[1]
    - Plants readily accumulate PFASs, but biosolids land app regs are protective[2]
  - Incidental soil/dust ingestion
- Usually insignificant or minor
  - Dermal absorption
  - Inhalation



Conder et al., 2016, in prep.

1 Giesey et al., 2010. Reviews of Environmental Contamination and Toxicology, 202
2 Blaine et al., 2014. Environ Sci Technol 48:7858-7865

Toxicology

- Non-cancer effects[1,2]
  - USEPA reference doses (RfD for PFOA and PFOS (non-cancer hazard only)
    - PFOS: 0.00002 mg/kg*day (reduced birth weight)
    - PFOA: 0.00002 mg/kg*day (developmental effects in bones, accelerated puberty)
- Immunotoxicity potential[3,4]
- Potential carcinogenic/mutagenic properties[5]
  - "Cancer Slope Factor (CSF) for PFOA: 0.07 (mg/kg*day)
    - Risk-based drinking water threshold for cancer endpoint higher (less conservative) than non-cancer endpoint

[1]Lau, 2012. Clinical and Environmental Toxicology, Experientia Supplementum 101; [2]ATSDR, 2015. Draft Toxicological Profile for Perfluoroalkyls; [3]Grandjean et al., 2012. JAMA; [4]Granum et al., 2013. J Immunotox.; [5]USEPA, 2016. Drinking Water Health Advisories for PFOA and PFOS

Toxicology

- Many epidemiology studies (used qualitatively in support of RfDs and CSF)[1,2]
- PFASs other than PFOA and PFOS
  - Very limited information available in peer-reviewed literature and chemical registration information (REACH dossiers, TSCA submittals)

[1] C8 Science Panel (http://www.c8sciencepanel.org);
[2] Olsen et al., 2009. Reproductive Toxicology 27:212-230

Lifetime Health Advisory (HA) replaces Provisional Health Advisory (PHA)

- New Lifetime Drinking Water HA[1,2] was released May 2016 and replaces the PHA
  - Much lower value of 0.07 ug/L (70 ppt)
  - Provides peer reviewed reference dose and cancer slope factor
- Until May 2016, EPA's Office of Water's 2009 provisional health advisory (PHA) levels were in effect with much higher values:
  - PFOA 0.4 ug/L
  - PFOS 0.2 ug/L

[1] EPA. 2016a. "Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS)." EPA 822-R-16-004. www.epa.gov/ground-water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-and-pfos

[2] EPA. 2016b. "Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA)." EPA 822-R-16-005. www.epa.gov/ground-water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-and-pfos

Lifetime Health Advisory (HA) replaces Provisional Health Advisory (PHA) (cont.)

- The health advisories are not regulations and EPA does not have national drinking water regulations for PFOA and PFOS
- Risk-based screening levels can be calculated based on OW RfDs

Why should we care about PFASs other than PFOS/PFOA?

- Many PFASs are used in AFFF and other products and identified in groundwater, sediments and soil, but won't be on 'lists' anytime soon.
  - Toxicity data and analytical standards exist for some but not all PFASs. Analytical methods (ideally, multilab validated methods) are also needed.
- Treating drinking water sources require knowledge of target contaminants (consider all PFASs as well as other chemicals present onsite) when identifying appropriate treatment technology
  - EPA 2016 Health Advisories for PFOS[1] and PFOA[2] have good info on treatment
  - Short-chain PFASs exhibit early breakthrough on GAC, limited removal by conventional ion exchange[3,4]

[1] EPA. 2016a. "Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS)." EPA 822-R-16-004. www.epa.gov/ground-water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-and-pfos

[2] EPA. 2016b. "Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA)." EPA 822-R-16-005. www.epa.gov/ground-water-and-drinking-water/supporting-documents-drinking-water-health-advisories-pfoa-and-pfos

[3] Rahman, et al., 2014, Water Res

[4] Appleman et al., 2014, Water Res

Treatment Technologies for PFASs[1,2]

Ineffective:

- Coagulation
- Sedimentation
- Aeration
- Microfiltration
- Ultrafiltration
- Ozone
- Chlorine
- Ultraviolet Photolysis
- Advanced Oxidation Process

Partially Effective:

- Anion Exchange
- Granular Activated Carbon (GAC)

Effective:

- Reverse Osmosis

[1] As presented to RITS 2016 (Remediation Innovative Technology Seminar) by John Kornuc, Ph.D., NAVFAC EXWC
[2] Research on remediation of PFASs is only starting, so information is evolving

Treatment Technologies for PFASs by Media[1,2]

- Groundwater: GAC
- Drinking Water: GAC, RO, Nanofiltration, Anion Exchange
- Concentrates, Solids, etc.:
  - High Temperature Thermal Oxidation (>1100°F)
  - Excavation and offsite disposal
    - Select disposal site carefully as leachate could be an issue

[1] As presented to RITS 2016 (Remediation Innovative Technology Seminar) by John Kornuc, Ph.D., NAVFAC EXWC
[2] Research on treatment of PFASs is only starting, so information is evolving

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