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PER & POLYFLUOROALKYL SUBSTANCES

(PFAS)

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October 9, 2019

2019 Indiana Environmental Conference – Indiana Chamber

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PFAS - What are They?

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- A large group (near 5,000) organic fluorinated chemicals; including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) - most researched & bioaccumulates in human blood & persists in humans for years.
- PFAS are anthropogenic chemicals and do not occur naturally in the environment.
- Are comprised of a carbon backbone containing many carbon-fluorine (C-F) bonds (the C-F bond is the shortest and strongest in nature). Due to their unique chemical structure, PFAS are very stable and are resistant to biodegradation.

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PFAS – Why the Concern

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Resistant to degradation, have low water solubilities, and love organic matter

Sorb easily to soil/sediment and partition into animal and human tissues

Persistent Bioaccumulative Toxic (PBT) Organic Pollutant (DDT, benzo(a)pyrene, PCBs, and dioxins/furans)

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PFAS – Why the Concern cont.

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- The International Agency for Research on Cancer (IARC) has classified PFOA as a '**possible carcinogenic to humans**' (group 2b)
- Persists in the human body and are eliminated slowly.
- Can be found in blood, urine, breast milk and in umbilical cord blood.

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PFAS - History

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PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production		Protective Coatings				
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /		Initial Chemical Synthesis / Production			Commercial Products Introduced and Used			

Notes:
1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

Sources: Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017

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History and Use of Per- and Polyfluoroalkyl Substances (PFAS), ITRC

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PFAS – History cont.

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- Started to get publicity in 2001 & 2002 due to water contamination from the Washington Works Plant located outside of Parkersburg, WV on the WV/OH border. The class-action lawsuit against DuPont due to water contamination at Little Hocking Water District.
- In 2006, DuPont and other manufacturers such as 3M, agreed to principally phase out US-based production of PFOA and PFOS.
  - PFAS production continued through 2016 in China, India, Russia
  - China only producer of PFOS thru early 2017s
- 2009 EPA advisory level established 0.07 ppb

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PFAS - Sources

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- Production & Manufacturing Facilities
  - Due to the solubility and persistence of many PFAS, environmental release mechanisms associated with these facilities include: • air dispersion • spills • disposal of manufacturing wastes and wastewaters
- Potential impacts to air, soil, surface water, stormwater, and groundwater are present not only at release areas but potentially over the surrounding area

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PFAS – Sources cont.

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- Textiles and Leather: factory and consumer applied coating to repel water, oil, and stains
- Paper Products: surface coatings to repel grease and moisture
- Metal Plating and Etching: corrosion prevention, wear reduction, surfactant, fume suppressant
- Wire Manufacturing: coating and insulation
- Pesticides, cleaning products, polishes, photo processing

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PFAS – Sources cont.

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- Aqueous Film Forming Foam (AFFF)
  - These foams have been stored and used for fire suppression, fire training, and flammable vapor suppression at hundreds of military installations and civilian airports (Hu et al. 2016), as well as at petroleum refineries and storage facilities, and chemical manufacturing plants throughout the United States.
- 594 DoD facilities have been categorized as Fire/Crash/Training Sites

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PFAS – Sources cont.

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- Waste Disposal
  - PFAS production facilities waste disposal
  - Secondary manufacturing sites waste disposal
  - Facilities that incorporate PFAS into the manufacturing process
- Municipal Solid Waste Facilities
  - Disposal of consumer goods coated with PFAS
  - Leachate

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PFAS - Sources cont.

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- Wastewater Treatment
  - Consumer and industrial use of PFAS-containing materials, including disposal of landfill leachate and firefighting foam, results in the discharge of PFAS to waste water treatment plants (WWTPs).
- WWTP Operations
  - Conventional sewage treatment methods do not efficiently remove PFAAs

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PFAS - Sources – WTTP cont.

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- WTTP Biosolids
  - More than half of the sludge produced in the United States is applied to agricultural land as biosolids
  - Application of biosolids as a soil amendment can result in a transfer of PFAS to soil
  - PFAS can enter the food chain through the use of biosolids amended soil
  - PFAS concentrations can be elevated in surface and groundwater in the vicinity of agricultural fields that received PFAS contaminated biosolids

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Consumer Products

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- Industrial surfactants, emulsifiers, wetting agents
- Class B fire-fighting foams, electrical wire casings, thread seal tapes

- Food contact paper and cardboard packaging
- Clothing and carpets
- Outdoor textiles and sporting equipment
- Ski and snowboard waxes
- Non-stick cookware
- Cleaning agents and fabric softeners
- Polishes and waxes, and latex paints
- Pesticides and herbicides
- Hydraulic fluids
- Windshield wipers
- Paints, varnishes, dyes, and inks
- Adhesives
- Medical products
- Personal care products {for example, shampoo, hair conditioners, sunscreen, cosmetics, toothpaste, dental floss)

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PFAS - Exposures

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- **Ingestion** of PFAS is considered the major human exposure pathway. The major types of human exposure sources for PFAS include:
  - Drinking contaminated water
  - Ingesting food contaminated with PFAS (fish, shellfish).
  - Eating food packaged in materials containing PFAS (e.g., popcorn bags, fast food containers, and pizza boxes).

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PFAS – Exposures Summary

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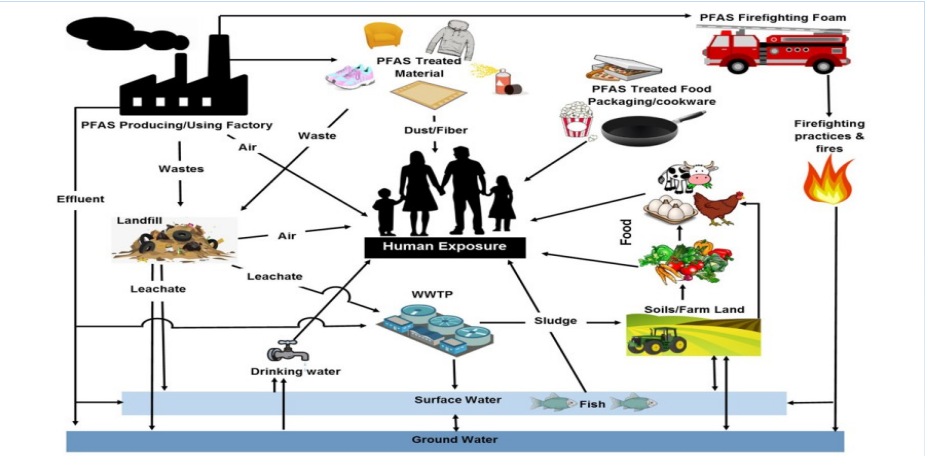

Human Exposure and sources of PFAS
Image: DWP, adapted from Oliaei et al. 2013.

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PFAS – Regulatory Perspective

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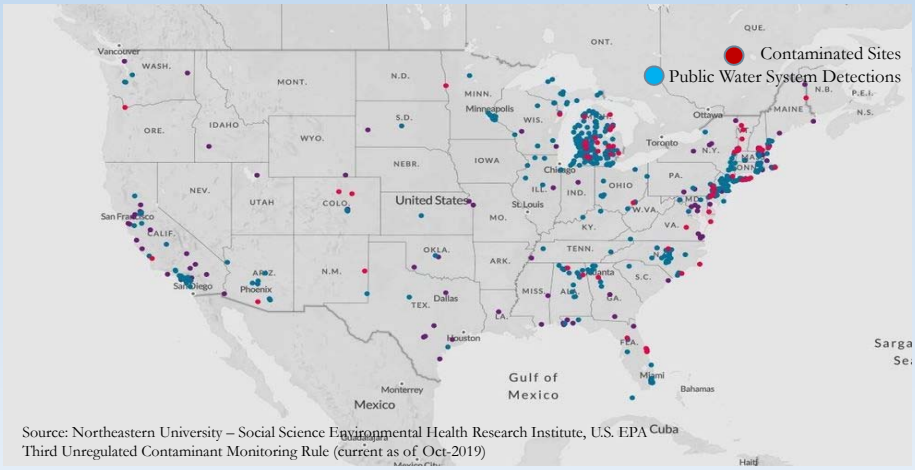

Source: Northeastern University – Social Science Environmental Health Research Institute, U.S. EPA Third Unregulated Contaminant Monitoring Rule (current as of Oct-2019)

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PFAS – Regulatory Perspective

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EPA's 2016 **health advisory limit** based on ingestion for combined concentration of PFOA and PFOS in drinking water is **70 parts per trillion** (0.07 ppb)

0.000001 ppm = 0.001 ppb = 1 ppt

EPA's health advisories are **non-enforceable** and **non-regulatory**. Provide technical information to states agencies and other public health officials on health effects, analytical methodologies, and treatment technologies associated with drinking water contamination.

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PFAS – Regulatory Perspective

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- Absence of Federal Standards
  - States (20 and counting) making decisions about whether or how to implement Health Advisory values and to address PFAS in drinking water.
  - Creates confusion about what levels of PFAS are safe in drinking water.
  - Companies have shifted to "short-chain" PFAS such as **GenX**, which are now a significant concern as well.
    - In production since 2010 as an alternative to PFOA

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State Initiatives / Studies

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- Michigan (michigan.gov/pfasresponse)
  - In 2017 the Michigan PFAS Action Response Team (MPART) was created as a temporary body by executive directive to investigate sources and locations of PFAS and protect drinking water and public health.
- Minnesota (health.state.mn.us)
  - Direct assistance in private well sampling (within designated study areas)
- New York (dec.ny.gov)
  - Statewide PFAS Survey (2016) + Suppression Foam Usage Survey (2019)
- US EPA Award $3.9 Million to Research PFAS (May-2019)

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PFAS Highlights & Treatment Challenges

Linda S. Lee

PURDUE UNIVERSITY

October 9, 2019
IN Environmental Conference
Indianapolis, IN

AGRONOMY grows here.

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Per- and Poly- Fluoroalkyl Substances (PFAS)

Examples

Perfluorooctane sulfonate (PFOS)

Tail F_3C-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2 — SO_3^- Head

Perfluorooctane carboxylate (PFOA)

Tail F_3C-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2 — CO_2^- Head

Polyfluorinated Substances

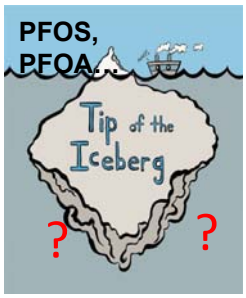
8 2

F_3C-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CF_2-CH_2CH_2-OH

8:2 FTOH (8:2 fluorotelomer alcohol)

$CF_3CF_2CF_2CF_2CF_2CF_2CH_2CH_2SO_3^-$

6:2 Fluorotelomer sulfonate (6:2 FtS)



'Head' also referred to as terminal functional group

Key piece in the current definition of 'PFAS' is the CF_3 group

IRTC PFAS Fact Sheet (Fig. 2.2); Buck et a

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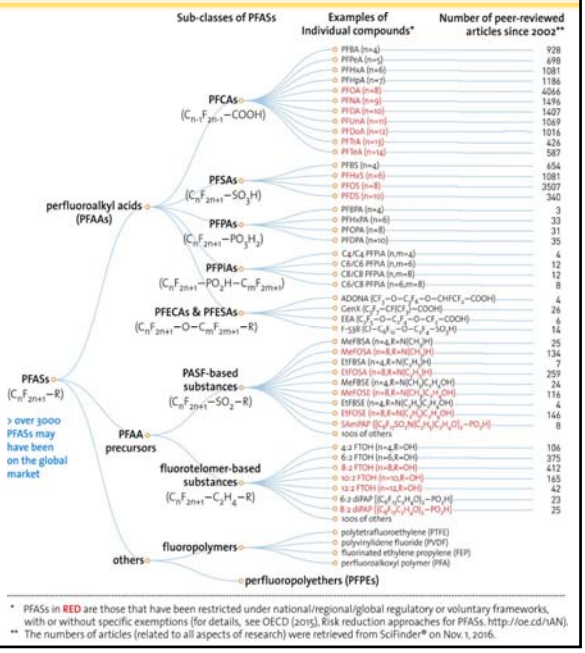
PFAS include Numerous Subclasses

- > 4000 *(growing)* individual PFAS (2018 OECD Global Database for PFAS)
- Numerous subclasses
- Each subclass has a differentiating characteristic
- Each subclass includes PFAS with several different perfluorinated chain lengths
- Each subclass either does not degrade or degrades to another subclass



Wang et al., 2017, ES&T,

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Why do we care? PFAS Health Concerns: Potential Adverse Effects

- Carcinogenicity (kidney & testicular)
- Cardiovascular tox (serum cholesterol)
- Endocrine tox (thyroid)
- Immunotoxicity (immume dysregulation)
- Reproductive toxicity (preg. hypertension)
- Bioaccumulative
- Maternal transfer
- Developmental toxicity (observed in zebrafish)
- Endocrine toxicity
- Hematoxicity
- Hepatotoxicity
- Neurodevelopmental toxicity
- Ocular toxicity (delayed pupil response in rodents)
- developmental toxicity

Jan 2019 - EPA announces plans to regulate cancer-causing chemicals found in America's drinking water

ulative BUT more mobile

- Epidemiological & lab animal studies have not shown consistent & conclusive findings
- ATSDR Tox. Profile contains Minimum Risk Levels for PFOA, PFOS, PFHxS, and PFNA
- Australian Expert Health Panel (May 2018): "… even though the evidence for PFAS exposure and links to health effects are very weak and inconsistent, important health effects for individuals exposed to PFAS cannot be ruled out

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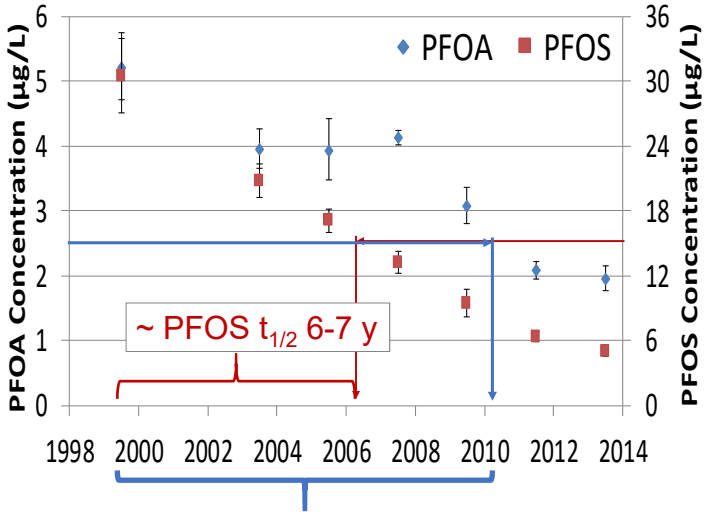
PFOA and PFOS in Blood: Decreasing Blood Levels

National Health & Nutrition Examination Survey (NHANES), Geo Means



- Decreasing trends with for PFOS and PFOA – direct response to phase-out
- Note - blood levels reported in ppb (g/L)
- Bioconcentration over time ~100-fold
- PFAS bind to proteins (blood, liver, kidney, muscle, brain)
- Effected by PFAS

NHANES data compiled by Stephen Zemba, Sanborn Head

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PFAS health concerns are impacting wastewater and biosolids management

PFAS input, multiple sources

Hard truth: Under current WWTP practices, PFAS coming in are leaving through effluent or sludge as the same or different PFAS!

Wastewater Influent

Varying process steps but some aerobic, **mostly anaerobic**

PFAS* Sorption to Sludge

Varying process steps; mostly aerobic

Effluent discharge*

Biosolids *

Land-application as a fertilizer amendment – *mostly aerobic*

* *Quantified PFAS levels (typically the PFAAs) often higher due to some PFAA precursor' degradation*

$t_{1/2}$: anaerobic << aerobic
(Not mineralization but PFAS to other PCAS)

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PFAS Subclass Perfluoroalkyl acids (PFAAs) vs Other PFAS

*OTHER PFAS: **PFAA Precursors***

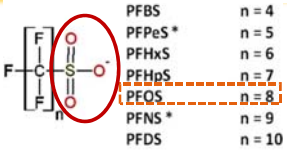
In soils, during composting, in WWTP processes, during other remedial activities, etc.

PFAS Intermediates (multiple steps)

PFAAs
Persistent (like PCBS)
But much more soluble & mobile

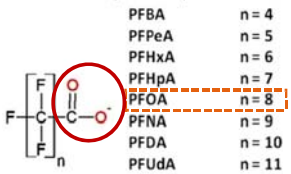
PFCAs + PFSAs = PFAAs
terminal microbial metabolites

Perfluoroalkylsulfonic acids



PFBS	n = 4
PFPeS *	n = 5
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFNS *	n = 9
PFDS	n = 10

Perfluoroalkylcarboxlic acids



PFBA	n = 4
PFPeA	n = 5
PFHxA	n = 6
PFHpA	n = 7
PFOA	n = 8
PFNA	n = 9
PFDA	n = 10
PFUdA	n = 11
PFDoA	n = 12
PFTrA	n = 13
PFTeA	n = 14

C1 Methane
C2 Ethane
C3 Propane
C4 Butane
C5 Pentane
Hexane
Heptane
C8 Octane
C9 Nonane
C10 Decane
C11 Unodecane
C12 Dodecane
C13 Tridecane
C14 Tetradecane

Buck et al., 2013

➢ **Short vs long** terminology (**perfluoroalkyl chain** not just carbon number)

Long-chain PFCAs: ≥ C7 **Long-chain**

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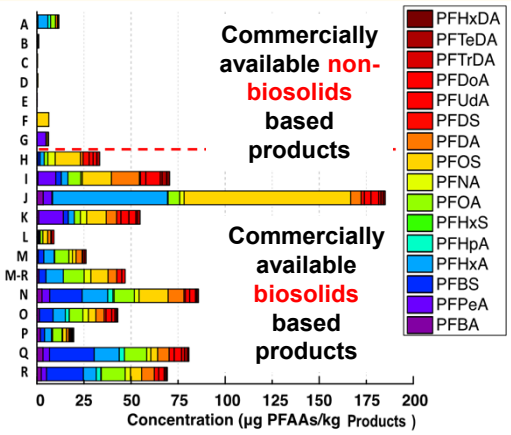
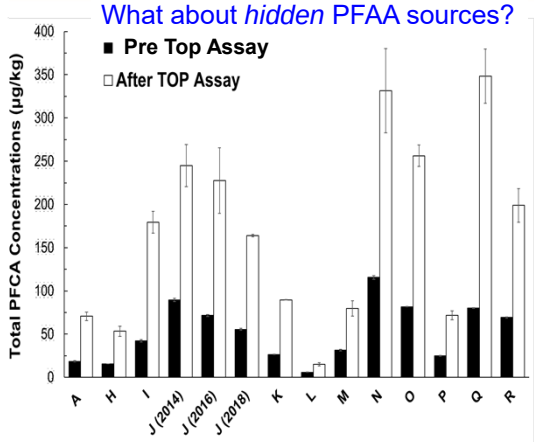
PFAS in **2014** Commercially Available Organic Products



What about *hidden* PFAA sources?



- Total PFAA load range in biosolid-based products: 30 - 80 g/kg *& 185 g/kg*
- TOP assay revealed presence of several precursors
- Current evidence indicates PFAA levels, particulary the long chains, are decreasing in biosolids

(Kim Lazcano et al., in preparation)

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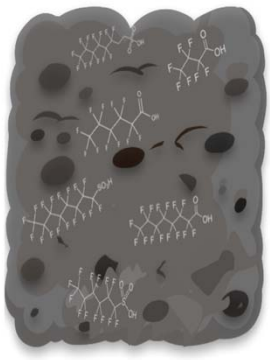
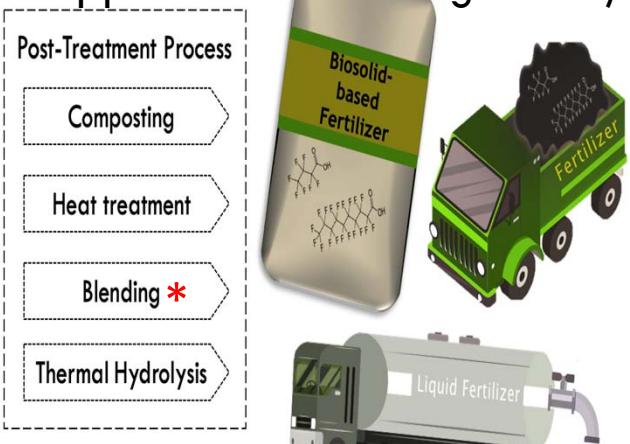
Effect of Common Biosolid Treatment Processes on PFAA levels

(prior to land application or use in gardens)





*Only blending decreased PFAS

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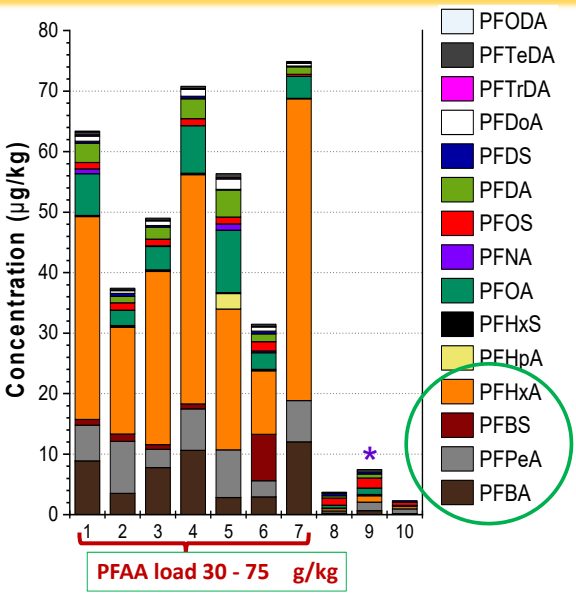
What about PFAAs in **2017 OFMSW** Composts?



Choi, Lee et al., ES&T Letters, https://doi.org/10.1021/acs.estlett.9b00280

- Higher PFAA loads in OFMSW #1-7 with compostable food packaging
- Shorter chains C ≤ 6 dominant
- #9* included food wastes, coffee grounds, unbleached coffee filters
- Background levels - atmospheric deposition, contaminated water and insecticides

Suite of PFAA precursors found similar to commercially available biosolid-based products

Data led to Washington's Healthy Food Packaging Act:
HB 2658 - 2017-18: Concerning the use of PFAS

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LLS1

State reactions to effluent and biosolids led by low ppt targets for drinking, surface and ground water

- Recent CA proposed drinking water notification limits of 6.5 PFOA and 5.1 PFOS
- Michigan Surface water for human fish consumption PFOS limit: 12 ppt
- Alaska, 2016
  - Proposed migration-to-groundwater soil cleanup levels:
    PFOA: 1.7 g/kg (ppb)
    PFOS: 3 g/kg
- New York - interim preliminary screening level for one specific permit:
  PFOA + PFOS: 72 g/kg
- Maine - sludge/biosolids program licensees and sludge/biosolids composting facilities
  PFOA: 2.5 g/kg
  PFOS: 5.2 g/kg
  PFBS: 1900 g/kg

Clean, typical effluent *can't* meet that.

Typical biosolids *can* meet this.

Typical biosolids or commercial OFMSW composts *can't* meet these levels.

Modified and update from Ted Beecher, NEBRA

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Slide 30

LLS1 Lee, Linda S, 9/16/2019

PFAA Plant Uptake

- Shorter-chain PFAAs (C4-C6) accumulate in plants.
- Longer chains tend to remain in the growing media or sorbed to roots and root vegetables (mostly the peel).
- Higher application rate led to a more accumulation in the growing media than plant parts.

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And what about 'PFAS' Replacements – Just more PFAS

Shorter chain 'PFAS'

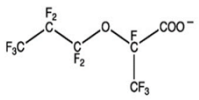
C8

C4 PFBS

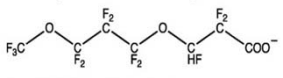
C6 PFHxA

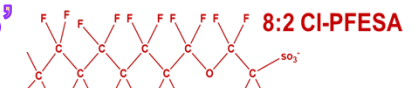
Perfluoroethers (e.g., GenX, ADONA)

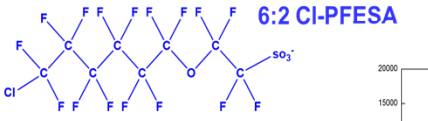
GenX (CAS No. 62037-80-3)

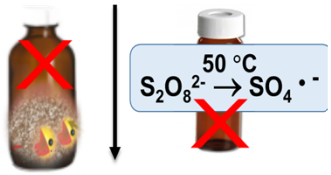


ADONA (CAS No. 958445-44-8)



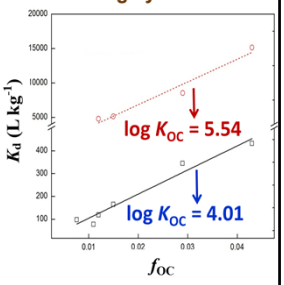






No biodegradation
No persulfate oxidation

Highly sorbed



Equally persistent
Data are indicating similar toxicity

Purdue: Chen, Lee et al., 2017, ES&T

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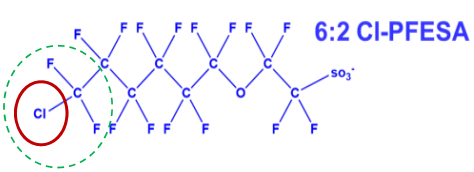
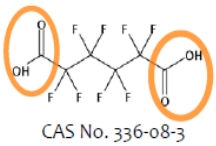
Alert! Latest Headlines

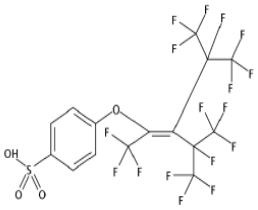
- Definition of a PFAS is being revisited, e.g., has a 'CF_3' group



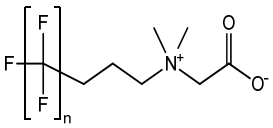


CAS No. 336-08-3

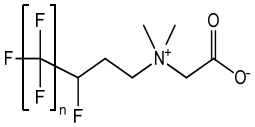
- Nomenclature is being expanded to accommodate additional PFAS structures not previously known.



CAS No. 70829-87-7



n:3 fluorotelomer betaines



n:1:2 fluorotelomer betaine

Zhanyun Wang, SETAC PFAS FTM, Aug. 12, 2019; Munoz et al. *Analytica Chimica Acta*, 2018, 1304,

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Analytical Challenges

- Requires advanced analytical instrumentation
- Cost is high
- PFAS during sampling and handling can cause contamination (equipment, apparel, lab procedures), which is a big challenge when we are talking low ppt
- Therefore, quality assurance and quality control (QAQC) documentation is a must for any lab you choose
- '*Approved*' contract labs are still limited
- Growing demand for high resolution mass spectrometry and not just typical mass spectrometry
- The list of PFAS that may be regulated is a moving target – EPA methods include 24 PFAS now
- Potential targets for regulation are likely to grow including PFAS substitutes that are replacing the phase-put PFAS (short chains, and other subclasses, e.g., GenX, ADONA, etc.)

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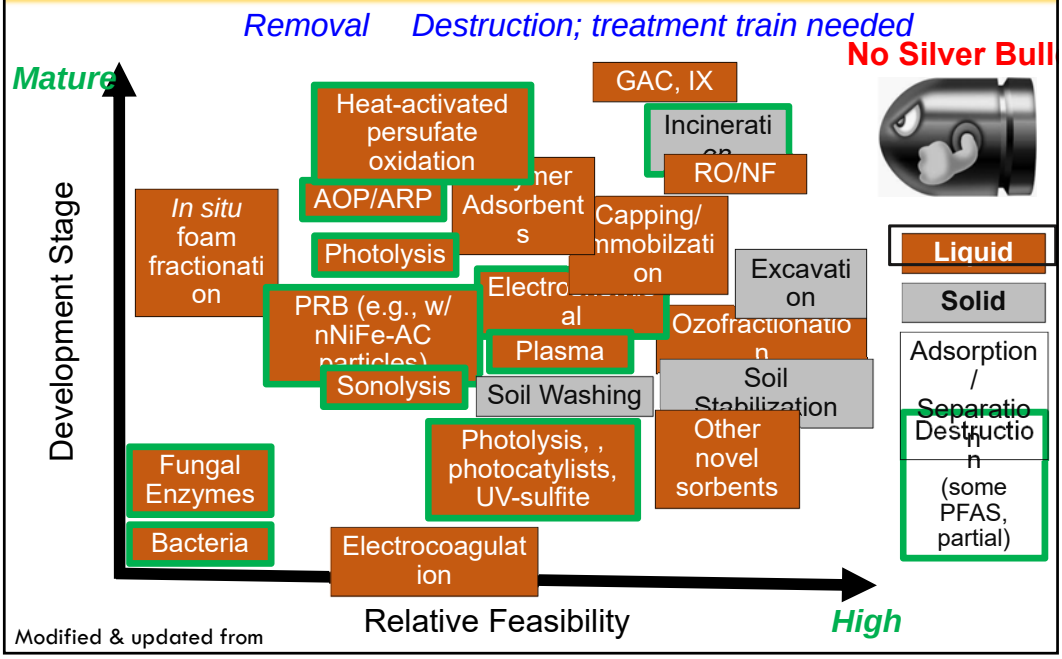
Synopsis of PFAS Treatment Strategies



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PFAS:

Federal and State Regulatory Efforts

Indiana Chamber of Commerce
2019 Environmental Law Conference
Donald M. Snemis
Ice Miller LLP
October 9, 2019

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U.S. EPA and PFAS

- Late 1990s: EPA identifies potential health issues presented by PFAS
- Early 2000s: EPA worked with companies to voluntarily phase out and eliminate PFAS
- 2006: 8 major chemical manufacturers join EPA's Stewardship Program to reduce or phase out long-chain PFAS

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U.S. EPA and PFAS

- 2009: Provisional health advisories for PFOA (400 PPT) and PFOS (200 PPT) in drinking water
- 2012: EPA adds 6 PFAS to its Third Unregulated Contaminants List for assessment monitoring under the SDWA
- 2015: Significant New Use Rule (SNUR) under TSCA regulating new uses of some long-chain PFAS
- 2016: PFOA and PFOS included in Contaminant Candidate List 4 under the SDWA

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U.S. EPA's 2016 Health Advisory

- Drinking water systems with combined PFOA/PFOS compounds above 70 PPT should assess contamination, inform consumers and limit exposure
  - 1.3% of the systems monitored from 2013-2015 had concentrations exceeding the advisory
  - Note: health advisories are not enforceable

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May 2018 National Leadership Summit

- U.S. EPA announced actions on PFAS
  - Evaluate the need for a Maximum Contaminant Level (MCL) for PFOA and PFOS in drinking water
  - Begin steps to propose designating PFOA and PFOS as CERCLA "hazardous substances"
  - Develop groundwater cleanup standards for PFOA and PFOS at contaminated sites
  - Develop toxicity values or oral reference doses for GenX chemicals and perfluorobutane sulfonic acid (PFBS)

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ATSDR's Draft Report on PFAS

- June 2018: the Agency for Toxic Substances and Disease Registry released draft toxicological profiles for multiple PFAS
  - Human "minimum risk levels" as low as 12 PPT for some PFAS
  - These findings contrast (conflict?) with EPA's 70 PPT health advisory in 2016

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U.S. EPA Draft Interim Recommendations

- 2019: U.S. EPA's Draft Interim Recommendations to address PFOA and PFOS in groundwater
  - Screening level of 40 PPT
  - Preliminary Remediation Goal of 70 PPT for groundwater that is a current or potential source of drinking water where no state or tribal MCL or other relevant and appropriate requirements (ARARs) exist
  - If groundwater is being used for drinking water, responsible parties must address levels of PFOA and/or PFOS over 70 PPT

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PFAS and CERCLA

- PFAS are not currently designated as hazardous substances under CERCLA
  - But federal authority under CERCLA can still be triggered if there is a finding of an "imminent and substantial" danger to public health and welfare
  - EPA is requiring sampling for PFAS before and after the implementation of a remedy

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State Actions

- Some states are not waiting for EPA/Congressional action on PFAS, and many have already taken action
- Proposals are pending in numerous states on the issue of regulating PFAS
- The following are examples of state-level actions and proposals

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State Actions - Drinking Water

State	PFOA	PFOS	Other
Michigan (recommended)	8 PPT	16 PPT	PFNA – 6 PPT
New Hampshire (proposed)	12 PPT	15 PPT	PFNA – 11 PPT PFHxS – 18 PPT
New Jersey	14 PPT	13 PPT	PFNA – 13 PPT
New York	10 PPT	10 PPT	
California	5.1 PPT (notification)	6.5 PPT (notification)	

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State Actions – Groundwater Standards

State	PFAS (combined)
Michigan	70 PPT
Massachusetts	70 PPT
New Hampshire	70 PPT
New Jersey	10 PPT
Alaska	400 PPT (PFOA) 400 PPT (PFOS)
Vermont	20 PPT

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State Action - Food Packaging

- California, Washington, Kentucky, New York, Connecticut, Rhode Island, Massachusetts, and Vermont have all taken steps to prohibit PFAS in food packaging.

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California Prop 65

- November 2017: PFOA and PFOS listed under Prop 65 as chemicals "known to the state to cause reproductive toxicity"
  - Will require a warning
  - Allows private enforcement mechanisms

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Michigan's Contaminated Deer

- In October of 2018, Michigan issued a "Do Not Eat" advisory for deer taken within 5 miles of a former U.S Air Force base
- The muscle fibers of 1 out of 20 deer were found to have high levels of PFOS (547 PPB)

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Indiana

- IDEM has a working group to monitor PFAS regulation by EPA and other states
- Still in the monitoring and investigating stages
- No regulations currently contemplated

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The Future?

- Continued research and sampling
- Federal MCLs for PFAS in drinking water
  - Monitoring and reporting requirements
- Addition of PFOA and PFOS to CERCLA's "hazardous substances" list
  - New Superfund sites based on the presence of PFAS

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The Future?

- Addition of PFAS to the list of chemicals required to report to the Toxic Release Inventory (TRI)
- Incorporation of PFAS assessments in Phase I ESAs
- More state-level groundwater remediation and screening levels

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The Future?

- More lawsuits based on federal statutes, state statutes or common law
  - Cost recovery
  - Toxic torts

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Questions?

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COMING SOON TO A COURT ROOM NEAR YOU!

PFAS LITIGATION

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Parkersburg, West Virginia, Litigation: The C8 Science Panel

- Class action for PFAS from DuPont's Parkersburg WV facility involving PFOA or C8
- 2004 settlement established and funded C8 Science Panel, while reserving personal injury claims. Concluded PFOA linked to cancer and other diseases.
- After several personal injury trials, class action settled for $670 million

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Aqueous Film-forming Fire Fighting Foams

- Over 80 AFFF cases consolidated in MDL pending in federal court in South Carolina involving scores of cases by states, water providers, and individuals arising from PFAS contamination attributable to Aqueous film-forming fire fighting foams.
- City of Newburgh, New York, brought claims for injunctive relief alleging that PFAS and other hazardous substances from Stewart International Airport and Stewart Air National Guard Base have contaminated the city's water supply.

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PFAS Class Action– 98% of US Population

- Nationwide class of people with PFAS in their blood to pay for nationwide independent health studies of PFAS in litigation pending in federal court in Ohio. *Hardwick v. 3M Co.*, No. 2:18-cv-01185 (S.D. Ohio 2018).

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Government Lawsuits

- Minnesota (settled for $850 Million)
- New Jersey
- New Hampshire
- Guam
- Ohio
- Michigan
- New York

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Private Party Litigation

- CERCLA, RCRA, trespass, nuisance negligence
- Consider CERCLA consequences: owner/operator liability; former owner liability; generator and transporter liability
- If PFAS becomes a hazardous substance and you bleed, you're a PFP!

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PFAS and Due Diligence

Figure 3: Current Fire Training Area at Peterson Air Force Base, Colorado

Source: GAO. | GAO-18-78

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Due Diligence—What should be done?

- Phase I's?
- Phase II's?

  But PFAS aren't regulated!!

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Due Diligence---Where?

- Airports
- Chrome plating facilities
- Firefighting training facilities
- Landfill leachate
- WWTP effluent

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QUESTIONS?

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