PFAS, Wastewater, and Biosolids Management

Wednesday August 1, 2018

1:00 – 2:30 PM ET

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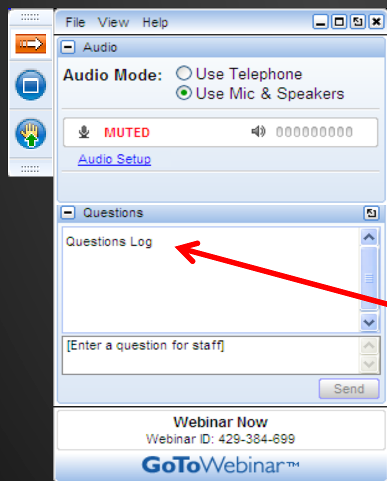
How to Participate Today



- Audio Modes
  - Listen using Mic & Speakers
  - Or, select “Use Telephone” and dial the conference (please remember long distance phone charges apply).
- Submit your questions using the Questions pane.
- A recording will be available for replay shortly after this webcast.

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Today’s Moderator

Ned Beecher
Executive Director

nebra
North East Biosolids & Residuals Association

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Today's Speakers

- Stephen Zemba
  - Introduction to PFAS
- Ned Beecher
  - How Did We Get Here?/Perspectives
- Linda Lee
  - PFAS Levels in Composts and Biosolids Products

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Our Next Speaker

Stephen Zemba
Project Director

SANBORN 25 HEAD 1993 - 2018

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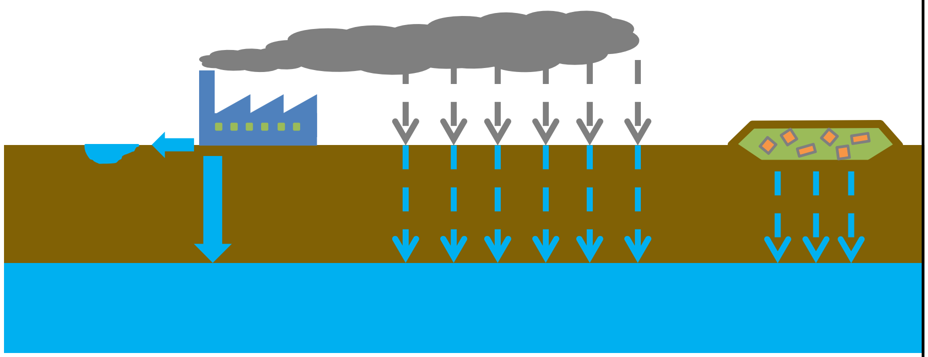
Introduction to Per- and Polyfluoroalkyl Substances (PFAS)

Introduction to Per- and Polyfluoroalkyl Substances (PFAS)

- Basics (Sources and Characteristics)
- Exposure (Environmental Presence)
- Health Effects



PFAS - THE BASICS

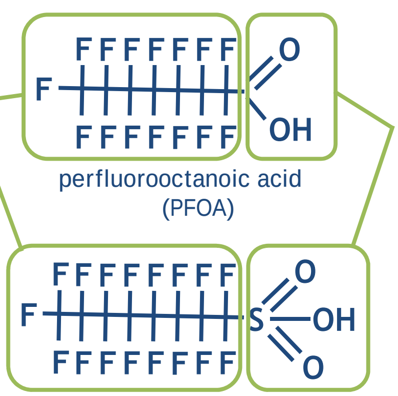
PFAS - The Basics

PFAS = Per- and Poly- Fluorinated Alkylated (Fluoroalkyl) Substances; also PFCs (subset) – Perfluorinated Compounds)

Fluorocarbon tail

- Strong bonds
- Hydrophobic
- Oleophobic
- Varying length

Also Note:
Precursors
Substitutes – Gen-X, Adona, et al.



perfluorooctanoic acid (PFOA)

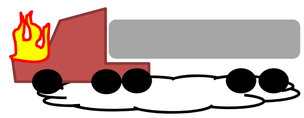
perfluorooctane sulfonic acid (PFOS)

Functional group

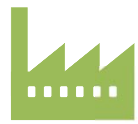
- Strong to weak acids
- Hydrophilic

More than 3,000 PFAS compounds identified

PFAS in the Environment



- Entered Commerce in 1940s
- AFFF use for firefighting
- Household products
- Stormwater runoff/street dust
- Industrial/commercial facilities
  - Textile coaters
  - Chromium platers
  - Car washes
- PFAS-containing wastes
  - Landfills
  - Wastewater treatment effluent/biosolids



PFAS Physicochemical Properties (PFOA and PFOS)

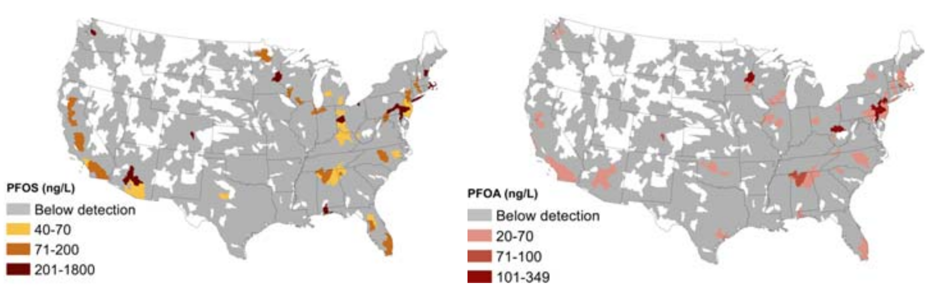
- Soluble in water
- Resistant to degradation
- Low volatility
- Primary transport pathways
  - Air Deposition
  - Groundwater migration
- Primary exposure pathway
  - Ingestion of drinking water

PFAS – EXPOSURE

PFAS in Public Drinking Water

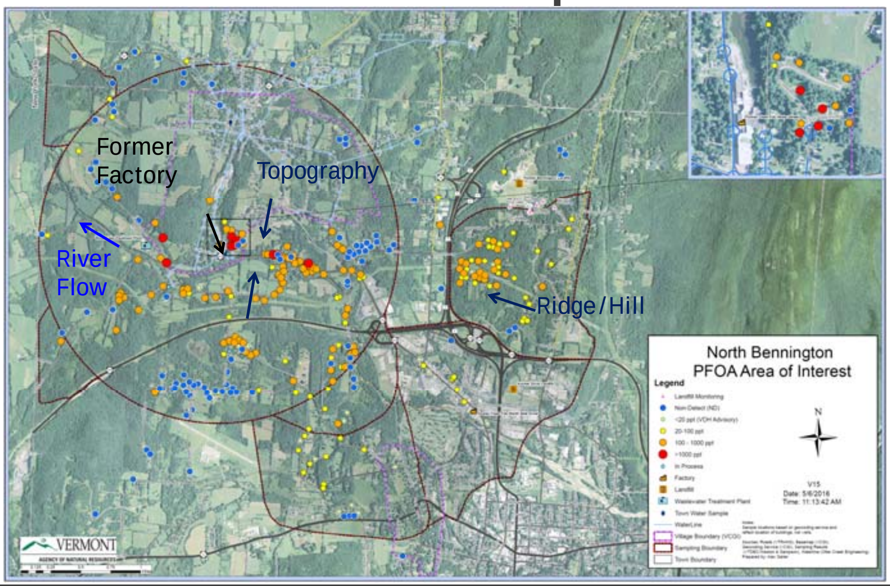
U.S. EPA 2013–2015 Unregulated Contaminant Monitoring Rule Sampling

Hu et al., ES&T Letters, August 2016, http://pubs.acs.org/doi/abs/10.1021/acs.estlett.6b00260



- Areas indicated watersheds
- Large water supplies (> 10,000 people)
- Estimated 6,000,000 people > EPA Health Advisory

PFAS – Airborne Transport in VT



VT Groundwater Standard = 20 ppt

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PFAS – Importance of Soil

- Direct exposure to PFAS in soil is not generally a significant pathway v. drinking water
  - 0.1 g/d (100 mg/d) v. 2,000 g/d (2 l/d)
- Soil can be an important reservoir and continuing source to groundwater
  - ppb levels in soils can sustain ppt levels in groundwater for many years

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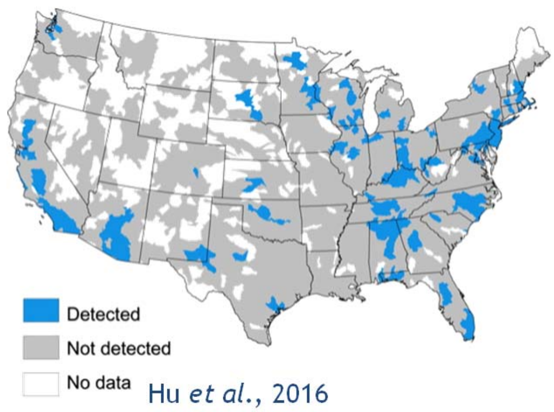


Hu *et al.*, 2016

PFAS HEALTH EFFECTS

PFAS – Health Concerns!?

- EPA Lifetime Health Advisory of 70 ppt issued May 19, 2016
- EPA PFAS Summit held May 22-23, 2018
  - MCL process to be investigated
  - PFOA and PFOS to be made CERCLA hazardous substances
  - Toxicity values for GenX and PFBS by end of summer
- ATSDR draft Toxicological Profile for Perfluoroalkyls contains Minimum Risk Levels (MRLs) for PFOA, PFOS, PFHxS, and PFNA
- Australian Expert Health Panel (May 7, 2018)
  - "… there is mostly limited, or in some cases no evidence, that human exposure to PFAS is linked with human disease" and "there is no current evidence that suggests an increase in overall cancer risk"
  - "… even though the evidence for PFAS exposure and links to health effects is very weak and inconsistent, important health effects for individuals exposed to PFAS cannot be ruled out based on the current evidence"

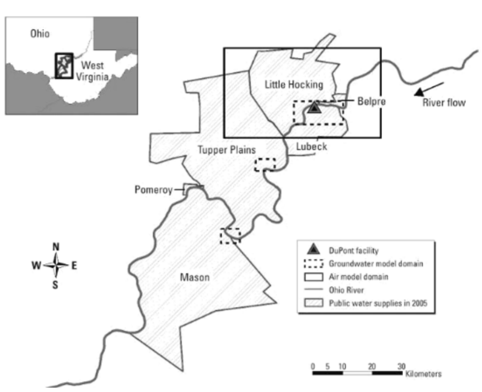
State Groundwater Standards/Guidelines

State	PFOA	PFOS	Notes
Al, CA, CO, DE, FL, ME, NH, NY, RI	70 ng/L		Adopted EPA HAL
Alaska and Illinois	400 ng/L	200 ng/L	
Maine	130 ng/l	560 ng/l	
Massachusetts & Connecticut	70 ng/l		Includes sum of 5 PFAS
Michigan	420 ng/L	11 ng/L	
Minnesota	35 ng/L	27 ng/L	
New Jersey	14 ng/L	13 ng/l	
North Carolina	1,000 ng/L	---	
Texas	290 ng/L	560 ng/L	
Vermont	20 ng/L		Includes sum of 5 PFAS
West Virginia	500 ng/L	---	

C8 Panel Studies

http://www.c8sciencepanel.org/prob_link.html

Dupont Washington Works Wood County, WV



- "Probable links" between PFOA exposure and:
  - Diagnosed high cholesterol
  - Ulcerative colitis
  - Thyroid disease
  - Testicular and kidney cancers
  - Pregnancy-induced hypertension
- No correlations with:
  - Birth defects
  - Miscarriages and stillbirths
  - Preterm birth and low birth weight
  - Liver disease
  - 19 other cancers and 11 other non-cancer effects

Does PFAS cause Cancer?

- Evidence of PFAS carcinogenicity from C8 Panel studies and animal studies is inconsistent and/or inconclusive
- Results of local health studies have been negative or inconsistent
  - Hoosick Falls, NY (2017) – only lung cancer statistically elevated (lung cancer not otherwise linked to PFAS)
  - Merrimack, NH (2018) – no significantly different cancer rates, including cancers associated with PFOA
  - Washington and Dakota Counties, MN (2018) – overall cancer rate same as statewide
- Issue is somewhat moot as non-cancer health effects are driving the 70 ppt Lifetime Health Advisory, and this level is protective of potential cancer risk

Risk-Based Standards

- Regulatory authorities are making different assumptions and interpretations in the face of uncertainty
- Results thus far: Substantial variability and in some cases adoption of very protective assumptions

Animal Lab Dose → Equivalent Human Dose → Reference Dose → Incremental Exposure → Drinking Water Level

LOAEL 1,000,000 ng/kg-d | 200×↓ Metabolism 5,000 ng/kg-d | 300 ×↓ Safety 20 ng/kg-d | 5×↓ Background 4 ng/kg-d | 4.3 L/day, 70 kg 70 ng/L

Regulatory Authority	Receptor	Chemical	Reference Dose (ng/kg-d)	Background Exemption	Exposure Rate (l/kg-d)	Risk-Based Concentration (ng/l = ppt)
U.S. EPA LHA	Nursing mother	PFOA + PFOS	20	80%	0.061	70
VT DOH	Nursing infant	PFOA + PFOS	20	80%	0.175	20
TX CEQ	Small child	PFOA	12	0%	0.041	290
		PFOS	23			560

PFAS Toxicity Values

Compound	U.S. EPA Reference Dose (ng/kg-d)	ATSDR (draft) Minimum Risk Levels (ng/kg-d)
PFBS	20,000 ?	–
PFHxS	–	20
PFOA	20	3
PFOS	20	2
PFNA	–	3
Gen-X	?	–

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Drinking Water Criteria Examples

Maximum Contaminant Level (MCL)

- Legally enforceable
- **2 liter/day water ingestion**
- 70 kg adult
- Background exposure 80%

$$\frac{0.2 \times 20 \text{ ng/kg-d} \times 70 \text{ kg}}{2 \text{ l/d}} = 140 \text{ ng/l}$$

Lifetime Health Advisory (LHA)

- Guidance
- **4.3 l/day water ingestion**
- 70 kg adult
- Background exposure 80%

$$\frac{0.2 \times 20 \text{ ng/kg-d} \times 70 \text{ kg}}{4.3 \text{ l/d}} = 65 \text{ ng/l}$$

- (Rounds to the 70 ng/l LHA)

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Background Exposure to PFAS

- Is it reasonable/appropriate/necessary to assume that 80% of PFAS exposure derives from non-drinking water sources?
- Can we derive a better background exposure estimate?
- What estimates are available in the literature?

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Background Exposure to PFAS

- NJ's *former* 40 ppt (ng/l) PFOA groundwater standard was based on doubling of exposure via drinking water
- Background estimate:
  - 40 ng/l × 2 l/d = 80 ng/day
- Reference Dose (RfD) exposure:
  - 20 ng/kg-day × 70 kg = 1,400 ng/day
- Background = 80/1,400 = 6% of RfD

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Background Exposure to PFAS

- PFOA+PFOS exposure estimates for a 70 kg adult Gebbink et al. , Environment International 74 (2015) 160–169

	Low	Intermediate	High
Exposure (ng/day)	9	48	343
% of RfD	0.7%	3%	25%

20 ng/kg-d Reference Dose (RfD) corresponds to 1400 ng/day exposure estimates for a 70 kg adult

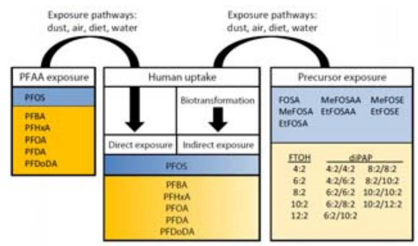


Fig. 1. Schematic of direct and indirect (precursor) exposure pathways for PFOS and PFCAs.

Empirical Background Exposure

$$\frac{d}{dt}(C_b V_d) = D_{back} - k_e C_b V_d$$

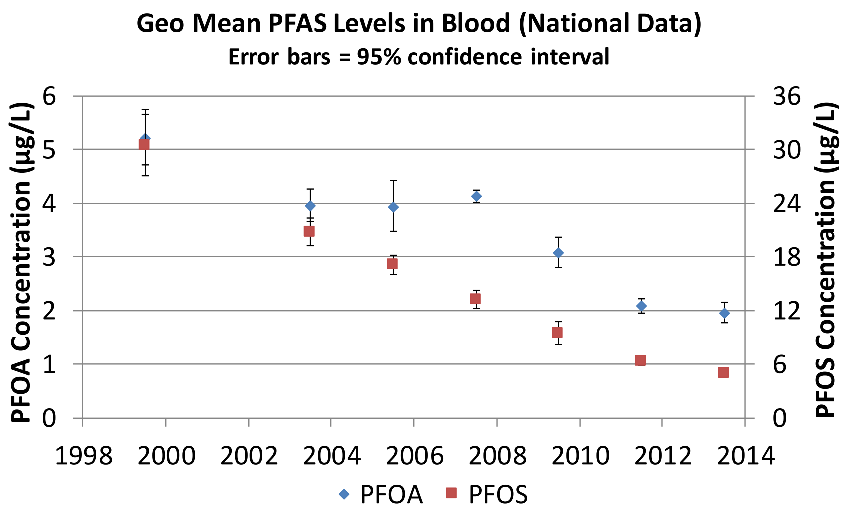
$$k_e = \frac{\ln(2)}{t_{1/2}}$$

where the terms are:

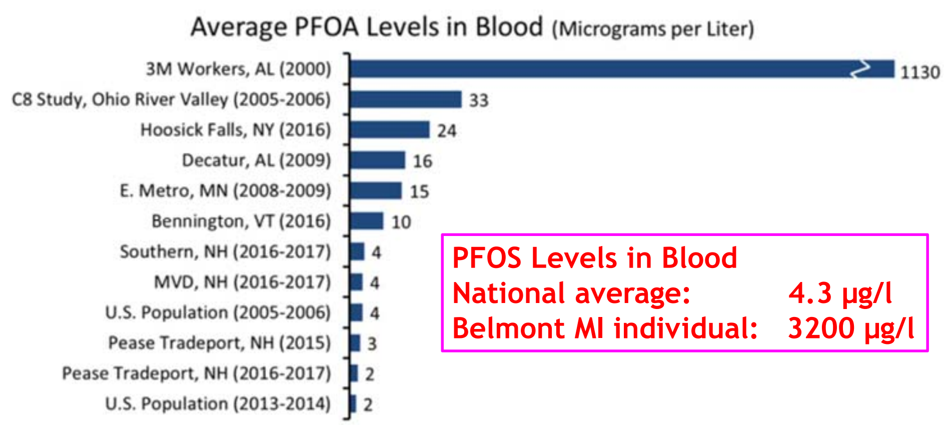
C_b	Concentration of PFAS in blood (ng/l);
V_d	Apparent volume of PFAS distribution (l/kg);
D_{back}	Background exposure to PFAS (ng/kg-d);
k_e	PFAS elimination constant (d^{-1}); and
$t_{1/2}$	PFAS half-life in the body (d).

Parameters/data from draft ATSDR Toxicological Profile indicate PFOA+PFOS background is 0.8% of the 20 ng/kg-d RfD

PFOA and PFOS in Blood: Trends



PFOA Levels in Blood (µg/L)



PFOS Levels in Blood
National average: 4.3 µg/l
Belmont MI individual: 3200 µg/l

https://www.dhhs.nh.gov/dphs/pfcs/documents/mvd-pfc-09252017.pdf

- Background levels decreased from 5 µg/l in late 1990s to present 2 µg/l
- Exposure to PFOA in water elevates levels in blood
- Bioconcentration over time ~100-fold

PFAS Health Risks - Summary

- Risk-based standards/guidelines for PFOA and PFOS are protective
- Toxicity of PFOA & PFOS not certain
  - Epidemiological studies and laboratory animal studies have not shown consistent and conclusive findings
  - Cancer incidence studies in NY, NH, and MN not indicative of PFAS effects
  - If PFAS is causing health effects, the effects appear to be subtle
- Reasons for concern
  - PFAS in drinking water elevates PFAS in blood
  - Little data for PFAS other than PFOA and PFOS

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Our Next Speaker

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Executive Director

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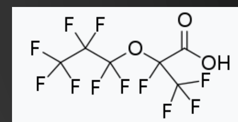

How did we get here?
PFAS* concerns affect wastewater & biosolids management…

* per- and poly-fluorinated alkyl substances, *aka* PFCs (perfluorinated compounds)

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How did we get here?

2000s → present:

Increasing focus on PFOA & PFOS in the environment worldwide.

PFOA & PFOS voluntary phase-out by 2015.

Industrially-impacted biosolids contamination at Decatur, AL.

http://www.fluoridealert.org/wp-content/pesticides/effect.pfos.class.timeline.htm

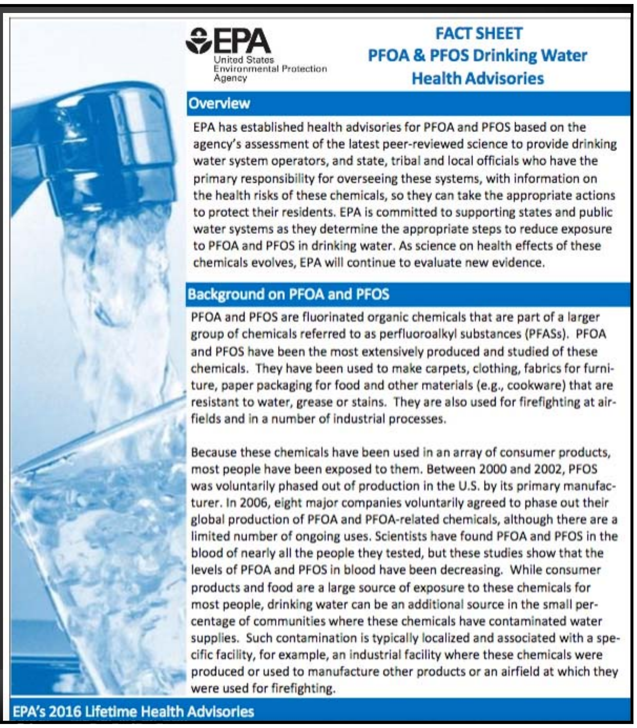
		rec
July 1999	The Tennant's sue DuPont alleging C8 disposal in landfill near their farm caused cattle to die.	Th hu ne co do cla Va
2000	DuPont releases 31,250 pounds of C8 into air	Du 20
May 2000	3 M announces phase out of C8	Un ou res
October 2000	DuPont reaches an out-of-court settled with the Tennants Note. other papers have reported the settlement was made in 2001.	Du Vir ca
August 2001	Attorneys file Class Action	Att res
October 2001	Consent Decreet between DuPont and West Virginia - Levels of C8 above 14 ppb in drinking water would trigger DuPont to provide alternative sources	An EF Du of ab rai Wo
November 2001	West Virgina and DuPont sign a Consent Order	We an
January 2002	Little Hocking Water Assoc. in Ohio find their water supply is contaminated with C8	Of the Th co ris he
March 2002	DuPont completes $50 million expansion of its Teflon business	Du bu
		C8

How did we get here?

May 2016 → EPA drinking water public health advisory (PHA) - 70 ng/L (ppt) for PFOA & PFOS combined.

- Rare ppt PHA.
- (A ppt is one second in 31,700 years.)

https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos



EPA United States Environmental Protection Agency

FACT SHEET
PFOA & PFOS Drinking Water Health Advisories

Overview

EPA has established health advisories for PFOA and PFOS based on the agency's assessment of the latest peer-reviewed science to provide drinking water system operators, and state, tribal and local officials who have the primary responsibility for overseeing these systems, with information on the health risks of these chemicals, so they can take the appropriate actions to protect their residents. EPA is committed to supporting states and public water systems as they determine the appropriate steps to reduce exposure to PFOA and PFOS in drinking water. As science on health effects of these chemicals evolves, EPA will continue to evaluate new evidence.

Background on PFOA and PFOS

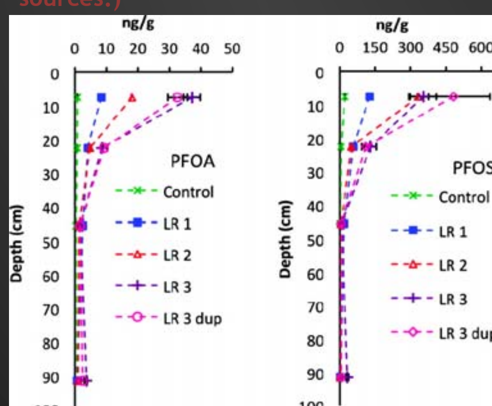
PFOA and PFOS are fluorinated organic chemicals that are part of a larger group of chemicals referred to as perfluoroalkyl substances (PFASs). PFOA and PFOS have been the most extensively produced and studied of these chemicals. They have been used to make carpets, clothing, fabrics for furniture, paper packaging for food and other materials (e.g., cookware) that are resistant to water, grease or stains. They are also used for firefighting at airfields and in a number of industrial processes.

Because these chemicals have been used in an array of consumer products, most people have been exposed to them. Between 2000 and 2002, PFOS was voluntarily phased out of production in the U.S. by its primary manufacturer. In 2006, eight major companies voluntarily agreed to phase out their global production of PFOA and PFOA-related chemicals, although there are a limited number of ongoing uses. Scientists have found PFOA and PFOS in the blood of nearly all the people they tested, but these studies show that the levels of PFOA and PFOS in blood have been decreasing. While consumer products and food are a large source of exposure to these chemicals for most people, drinking water can be an additional source in the small percentage of communities where these chemicals have contaminated water supplies. Such contamination is typically localized and associated with a specific facility, for example, an industrial facility where these chemicals were produced or used to manufacture other products or an airfield at which they were used for firefighting.

EPA's 2016 Lifetime Health Advisories

How did we get here?

State agencies look for sources → literature points to wastewater & residuals as some. (*Correction in thinking:* wastewater & biosolids *convey* PFAS; they are not sources.)



PFAS concentrations in soil with depth at long-term land application site.

Control = 0 Mg/ha

LR 1 = 553 Mg/ha

LR 2 = 1109 Mg/ha

LR 3 and LR 3 dup = 2218 Mg/ha

(dry weight basis)

Sepulvado et al; *Environ. Sci. Technol.* 2011, 45, 8106-8112

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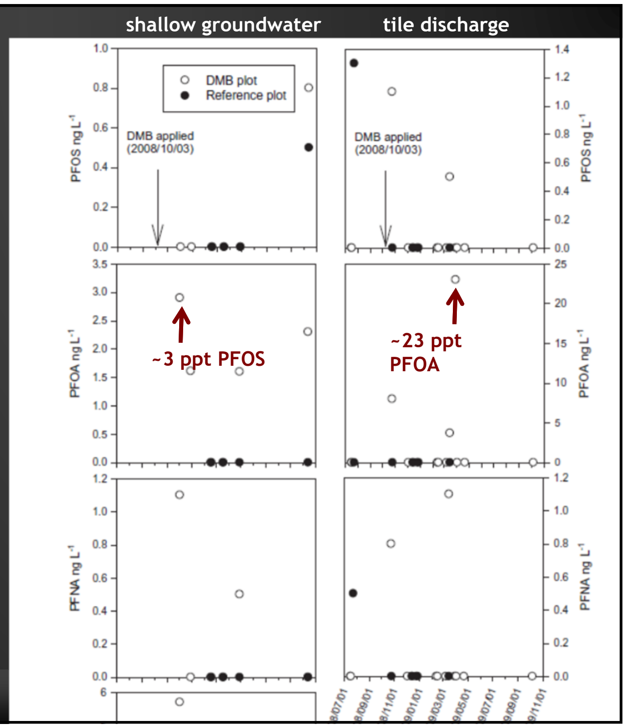
Application of typical biosolids finds:

- Perfluorinated chemicals detected in both groundwater and tile discharge after a single large biosolids application.
- Chemicals detected months after application.
- The contributions of leaching through the soil matrix and preferential flow through macropores are unknown.

Gottschall et. al. 2017. *Sci. Total Environ.* **574: 1345 - 1359**



How did we get here?

Because they reflect modern life, wastewater, biosolids, & other residuals (e.g. from recycle paper mills) contain low *u*/L (ppb) concentrations of PFAS.

	PFBA	PFHPA	PFHxS	PFHxA	PFNA	PFOA	PFOS	PFPeA
Small City Influent	13	<4	<4	7	<4	6	6	5
Small City Effluent	7	<4	<4	46	<4	6	7	21
Mid-size City Influent	<9.6	7	7	10	<4.8	15	22	29
Mid-size City Effluent	<9.6	5	8	20	<4.8	15	14	9
Municipality with industrial impacts Influent	56	8	<4	49	<4	50	4	36
Municipality with industrial impacts Effluent	73	19	<4	195	<4	49	<4	101

How did we get here?

2017 PFAS screening data compiled by NHDES & NEBRA:
22 facilities from NH and Northeast (n = 27)

Chemical	% detection	Conc. Range (ug/kg)	Ave. Conc. (ug/kg)
PFBA	20	0.54 – 140	34.6
PFPeA	8	18 – 27	22.5
PFHeA	84	0.21 – 75	11.0
PFHpA	26	0.077 – 2.8	1.1
PFOA	**32**	**1.1 - 15**	**6.7**
PFNA	30	1 – 3.6	2.6
PFBS	7	5.2 – 6.2	5.7
PFHxS	22	0.24 – 73	13.3
PFOS	**62**	**0.59 - 390**	**34**

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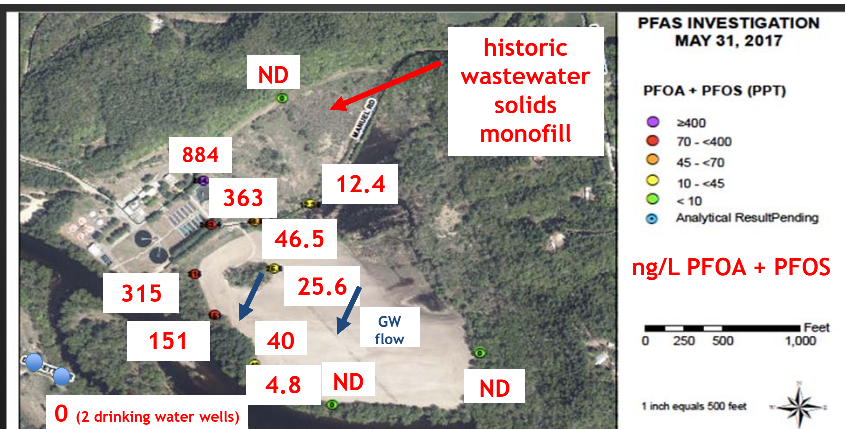
How did we get here?

PFOA & PFOS chemistry and persistence → Scant literature shows some leaching to groundwater possible at levels approaching the EPA PHA concentration → Regulators concerned. States' initial sampling & analysis don't assuage concerns.



Monofill used in 1980s. Since ~1996, all biosolids from WWTP (11.5 MGD) have been land applied, some on farm field shown. Kind of a worst-case scenario? But no drinking water impacts found.

Paper mill residuals & yard waste composting facility: water impacts…

Regulatory response in March 2017 drove recycle paper mill residuals to landfill. Composting business laid off workers. Due to non-drinking, surface water levels up to combined 240 ng/L (ppt).
(Not drinking water. Do we need to have all surface water meet drinking water screening levels?)

Facility continues to operate, but is challenged.

How did we get here?

State reactions are led by drinking water & clean-up divisions. Wastewater & biosolids programs are surprised. Examples:

- Michigan, 2014 Surface water human fish consumption PFOS limit: 12 ppt
  Clean, typical effluent *can't* meet that. ↑
- Alaska, 2016
  - Proposed migration-to-groundwater soil cleanup levels:
    PFOA: 1.7 ug/kg (ppb)
    PFOS: 3 ug/kg
- New York, 2017
  DEC interim preliminary screening level for one specific permit:
  PFOA + PFOS: 72 ug/kg ← Typical biosolids *can* meet this.
- Maine, 2018
  DEC Chapter 418 non-agronomic residuals screening level (developed using EPA RSL calculator):
  PFOA: 2.5 ug/kg ← Typical biosolids *can't* meet those.
  PFOS: 5.2 ug/kg What does this mean for effluent & biosolids?
- VT, 2017 Exemptions: Sewage and sludge. Septage? ↘
  DEC added PFOA & PFOS to Haz. Waste list for liquids: PFOA + PFOS >20 ppt

Reality check: **The science has not caught up. It's too early to set a defensible screening number for biosolids.**

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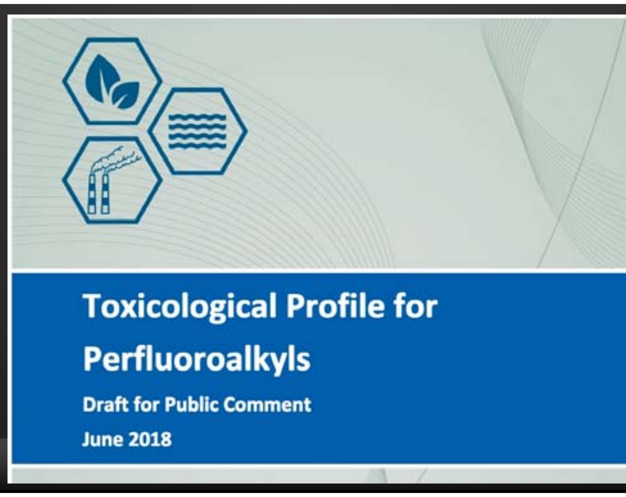
How did we get here?

2017 – 2018: Public & legislative pressure drives efforts to lower the benchmark below EPA's PHA of 70 ppt, which could impact biosolids & residuals management. Pressure mounts to set biosolids screening levels.
June 2018: ATSDR Tox Profile adds pressure.


Toxicological Profile for Perfluoroalkyls

Draft for Public Comment

June 2018

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Biosolids compost for my raspberries.

Thank you.

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Our Next Speaker

Linda S. Lee

Professor,
Environmental Chemistry
Department of Agronomy

PURDUE UNIVERSITY

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PFAS Levels in Composts and Biosolids Products

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Overview and Outline

- A few PFAS production points affecting environmental behavior
- Precursor PFAS biodegradation highlights
- PFAS Levels in biosolids and composts
- PFAS pore-water concentrations
- A few take-home messages

Two PFAS Production Approaches

Electro-Chemical Fluorination

$$C_nH_{2n+1} + SO_2Cl_2 + (2n+2)HF$$
$$\downarrow$$
$$C_nF_{2n+1}SO_2F + HCl + \text{byproducts}$$
$$\downarrow$$
$$C_8F_{17}SO_2F$$
$$\downarrow$$
$$C_8F_{17}SO_2H \text{ or } C_8F_{17}SO_2M$$

- 3M process (used until 2000)
- ~70/30 linear/branched F-alkyl chains

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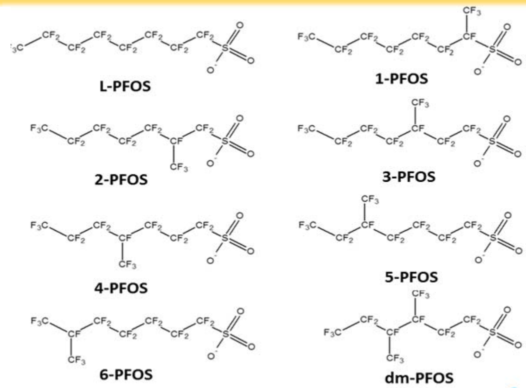
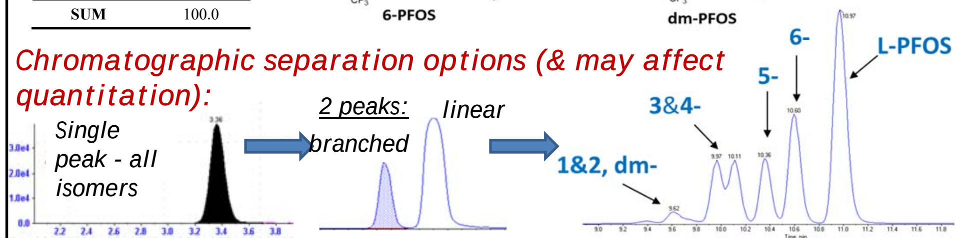
Electrochemical Process Leads to Multiple Isomers

L-PFOS 65-75%
Tends to be more bioaccumulative and more recalcitrant

	Sigma-Aldrich T-PFOS (%)
L-PFOS	68.1 ± 1.6
6-PFOS	10.0 ± 0.3
5-PFOS	5.6 ± 0.1
3 & 4-PFOS	8.2 ± 0.8
1 & dm-PFOS	8.1 ± 0.1
SUM	100.0



Chromatographic separation options (& may affect quantitation):



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Two PFAS Production Approaches

Electro-Chemical Fluorination

C_nH_{2n+1} + SO_2Cl_2 + (2n+2)HF
↓
$C_nF_{2n+1}SO_2F$ + HCl + byproducts
↓
$C_8F_{17}SO_2F$
↓
$C_8F_{17}SO_2H$ or $C_8F_{17}SO_2M$

- 3M process (used until 2000)
- ~70/30 linear/branched F-alkyl chains

Telomerization

$CF_3CF_2(CF_2CF_2)_nI$ + C_2H_2
↓
$CF_3(CF_2CF_2)_nC_2H_2I$
↓
(FT alcohols, FTOHs) $R_f CH_2CH_2OH$
↓
Acrylates, stearates, phosphates, urethanes

- DuPont, Asahi Glass, others
- Linear even numbered chains

Fluorotelomer (FT) surfactant schematic

Fluorinated "Tail"	Spacer	Hydrophilic Group

$CF_3CF_2CF_2CF_2CF_2CF_2CH_2CH_2SO_3$

Example: 6:2 Fluorotelomer sulfonate (6:2 FTS)

Buck et al., 2011

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Biodegradation of Precursor PFASs

- 'Precursor PFASs' biodegrade to multiple per/polyfluoroalkyl metabolites
- Some are known to be terminal metabolites and are usually per- & polyfluoroalkyl acids (PFAAs) such as, but not limited to, PFOA and PFOS
- Aerobic degradation tends to be much more significant than anaerobic degradation processes
- FT-based PFASs generally appear to yield much higher % of PFAAs
- There are numerous PFASs (> 4000) in the environment that are undergoing abiotic and biotic processes

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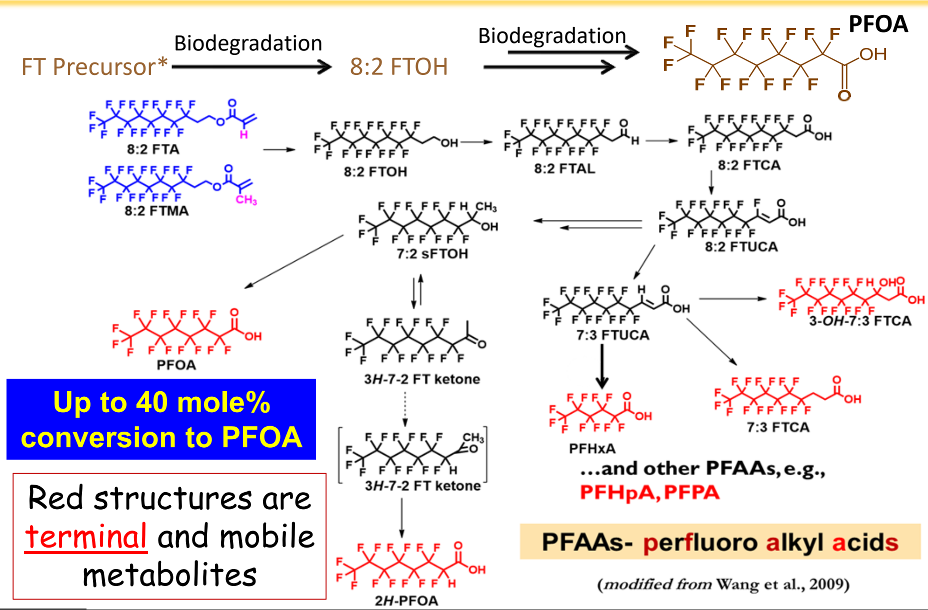
Fluorotelomer PFAS precursors to PFAAs: Biodegradation Example



(*modified from* Wang et al., 2009)

*Purdue biotransformation studies: Liu, Lee et al., 2007 etc.; Royer, Lee et al., 2015; Dasu, Lee et al., 2013, 2013, 2015

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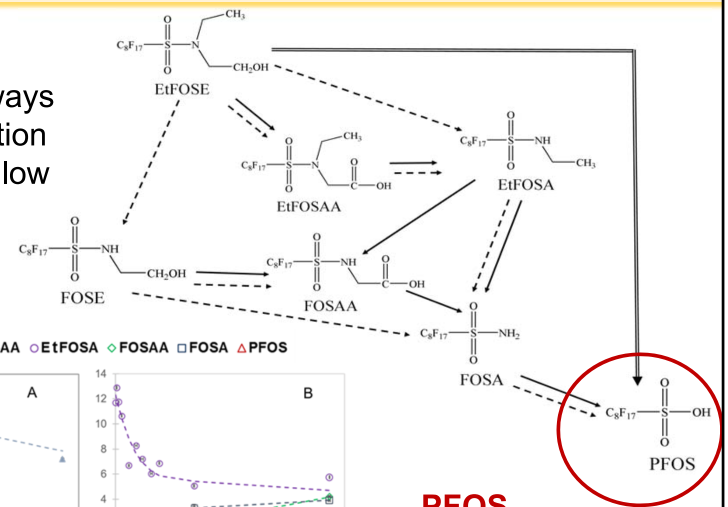
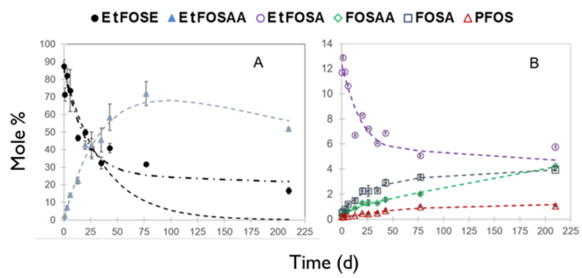
Precursor Electrochemical-PFAS to PFOS: Biodegradation Example

- Multiple pathways
- PFOS generation but 'relatively' low





Zhang, L; L.S. Lee; J. Niu: J. Liu. *Environ. Poll.*, 229:158-167

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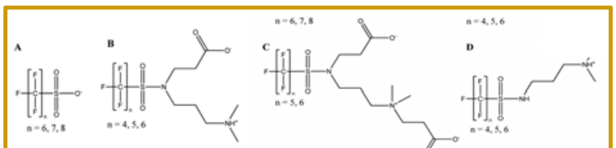
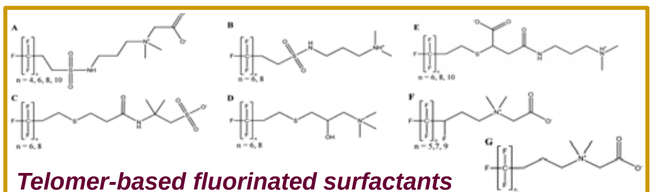
PFAS Suite in Aqueous Film Forming Foams (AFFFs)

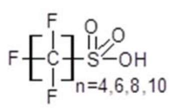


Electrofluorination-based fluorinated surfactants

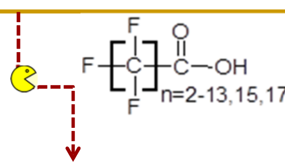
(Modified from Place & Field, EST, 2012)



Telomer-based fluorinated surfactants



Perfluorosulfonic acids
PFSAs (PFOS pK_a < 0)



Perfluorocarboxylic acids
PFCAs (PFOA pK_a < 4)

Terminal microbial end products

Σ = PFAAs = per/polyfluoro alkyl acids

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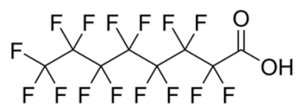
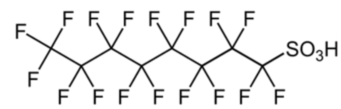
Today's *'elephant'* in the room? Yes, poly- & perfluoroalkyl substances (PFASs) but more specifically PFAAs

- PFASs including perfluoroalkyl acids (PFAAs) have chain lengths from ~4 to C16 – not just the infamous C8 PFOA and PFOS



PFOA C8: Perfluorooctanoic acid



PFOS C8: Perfluorooctane sulfonic acid

- They are everywhere
- Our challenge for the next few decades
- PFAAs are persistent like PCBs
- BUT PFAAs are much more mobile (mostly anionic)
- Level of concern are at the ppt level

PFAA Levels in Composts and Biosolids Products

- **Benefits of waste-derived fertilizers:** Recycling urban wastes for plant nutrients and improving soil health
- **Current challenge:** Primarily potential leaching to drinking water sources, but also uptake by plants and trophic transfer
- **Question being addressed in this talk:** What PFAAs are present in waste-derived fertilizers and what is released into pore-water (this leachable)?
- **Approach:** Quantify and compare the PFAA concentrations in different types of waste-derived fertilizers and in fertilizer pore-water

PFAA Levels in Composts and Biosolids Products

- **Analyzed for 17 PFAAs**
  - 13 PFCAs (C4 to C18): $CF_3(CF_2)_nCOOH$
  - 4 PFSAs (C4, C6, C8 and C10): : $CF_3(CF_2)_nSO_3^-$
- **18 Commercially Available Fertilizers**
  - 11 biosolids-based
  - 7 non-biosolids-based (< 2 mm fraction of fertilizers)
  - Obtained in 2014
  - Except for Milorganite (2014, 2016 & 2018)
- **10 Non-commercial Fertilizer Sources**
  - Municipal Wastes: Composted City Waste all obtained in 2017

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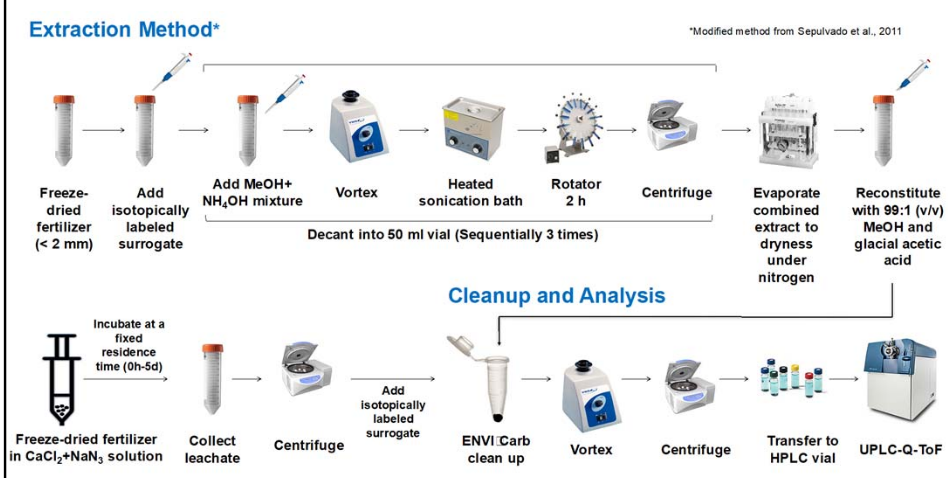
Biosolid and Non-biosolid Commercial Fertilizers



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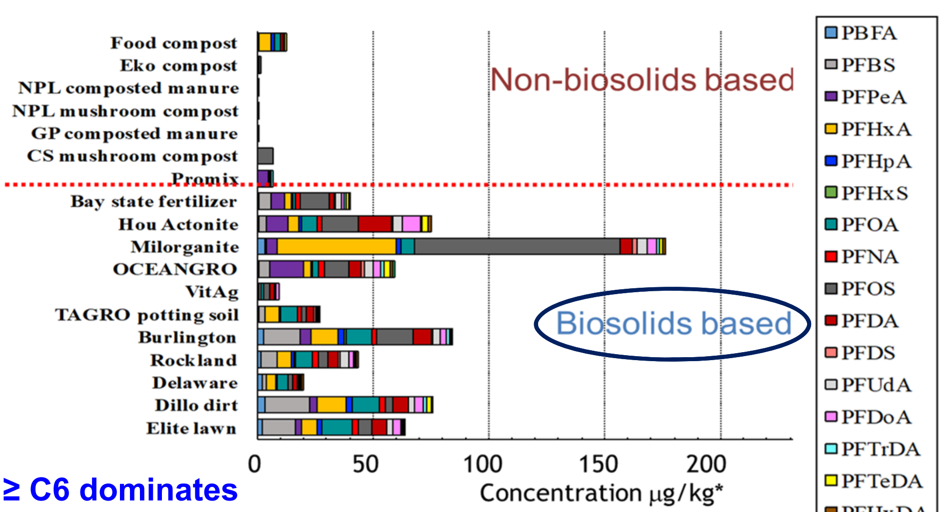
Biosolid and Non-biosolid Commercial Fertilizers

Brand name	Biosolid-based
Bay State Fertilizer	Tumble-dried granular biosolids
Hou-Actinite	Granular biosolids
Milorganite	Heat-dried granular biosolids
OceanGro	Granular biosolids
VitAg	Granular biosolids
Elite Lawn	Biosolids with plant material (composted)
Dillo Dirt	Biosolids with residential yard trimmings
Delaware biosolids	Composted
Rockland biosolids	Biosolids with woodchips
Burlington biosolids	Biosolids with wood, yard and food waste
TAGRO potting soil	Biosolids with maple sawdust and aged bark

Brand name	Non-biosolid based
Promix	Peat/compost based growing mix
Country soil	Mushroom compost
New plant life mushroom	Mushroom compost
New plant life manure	Manure and peat
Gardener's pride	Manure
EKO compost	Compost with untreated wood products
OCRRA, WeCare	Food compost

PFAAs in Biosolid & Non-biosolid Commercial Fertilizers



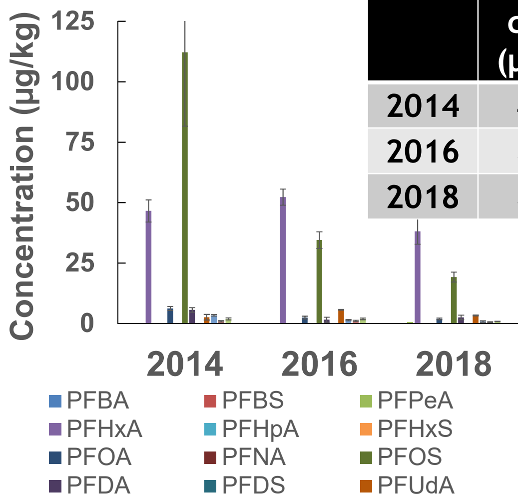
≥ C6 dominates

(collected in 2014)

Kim Lazcano et al., Manuscript in preparation

*Assumes PFAAs negligible in the > 2 mm fraction
PFAAs quantified in the < 2mm fraction (36-80%)

Milorganite: 2014, 2016, & 2018



Year	Short chain (µg/kg)	Long Chain (µg/kg)	Total PFAAs (µg/kg)
2014	46.6	132.8	179.4
2016	52.2	48.6	100.8
2018	38.6	29.2	67.8

- 2014 to 2016:
  ~44% PFAA reduction
- 2016 to 2018
  ~33% PFAA reduction
- Also substantial decrease in PFOS & total long chain PFAAs

Kim Lazcano et al., Manuscript in preparation

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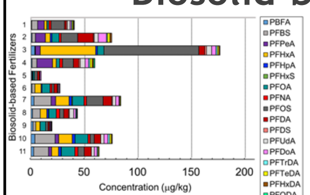
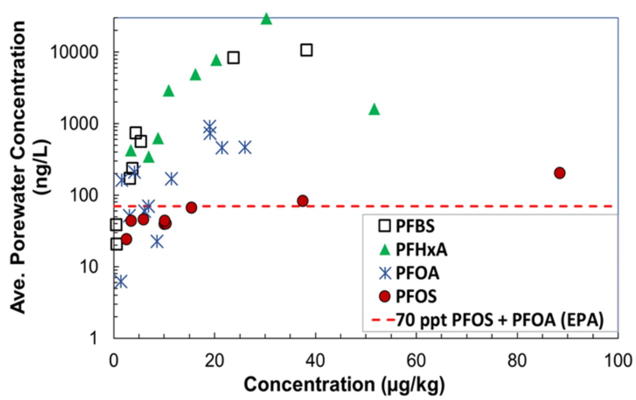
Selected PFAA Concentrations in Pore-water of Biosolid-based Commercial Fertilizers





Kinetic study (not shown) for residence times of a few hours to one week showed equilibrium reach in ≈1 day

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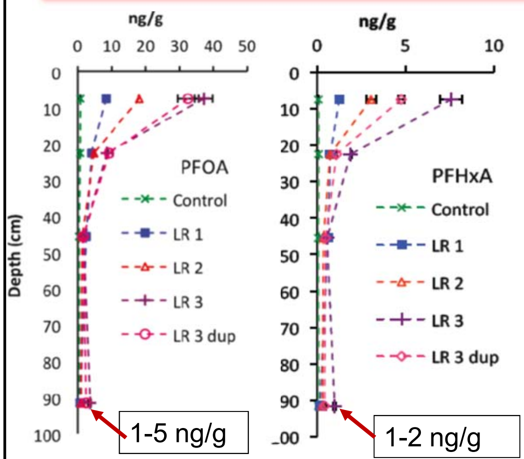
'Pore-water' Perspective

Once PFAAs leave the waste-derived fertilizer, they undergo leaching and sorption by soil



Example: IL, USA
PFOA & PFHxA with depth in long term (LT) plots at various cumulative loading rates of 2004-2007 Chicago MWWTP biosolids

- PFOA: 8-68 ng/g
- PFHxA: 25-50 ng/g
- PFOS: 80-219 ng/g

Control = 0 Mg/ha
LR 1 = 553 Mg/ha
LR 2 = 1109 Mg/ha
LR 3 = 2218 Mg/ha

(Sepulvado et al, 2011)

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Composted City Wastes

Park trimmings, food wastes, compostable service-ware, etc.

Study prompted by Zero Waste Washington (Heather Trim)

ID	Description
1	Municipal solid waste
2	Municipal solid waste and wood products
3	Residential and commercial food and yard waste (+compostable food service-ware products)
4	Residential and commercial food and year waste (+ compostable items)
5	Mixed food waste (residential, local grocers, restaurants, and commercial food handling facilities) and yard waste
6	Residential food and yard waste (+ compostable food service-ware)
7	Food waste, horse manure, wood shavings, coffee grounds and lobster shells, compostable food service-ware
8	Leaves and grass waste from municipalities
9	Residential yard waste
10	Leaves

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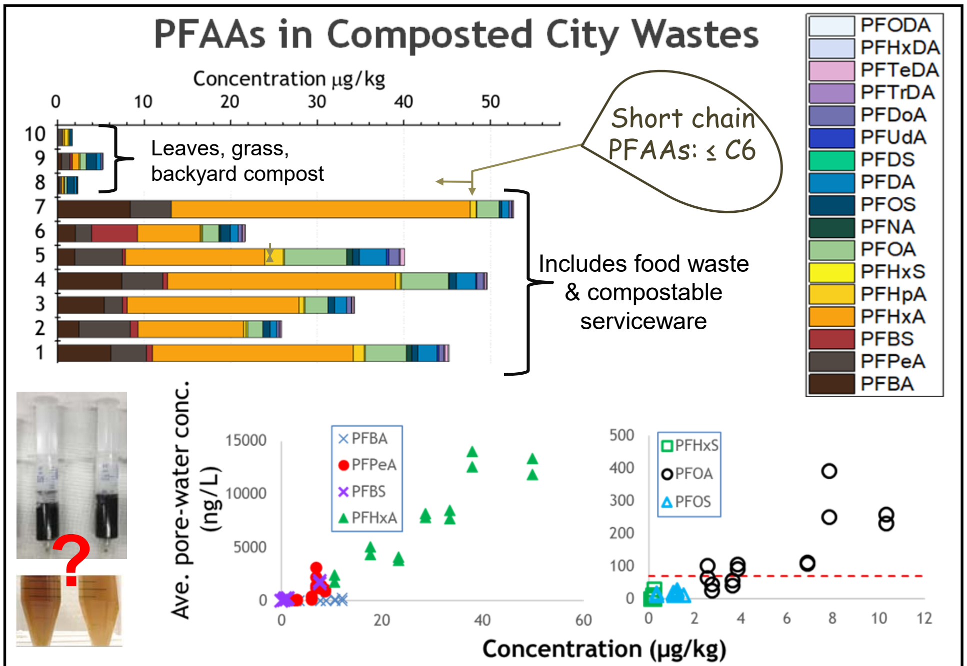
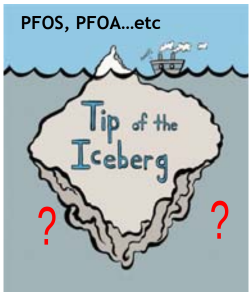


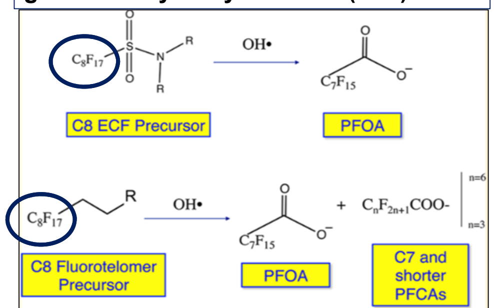
Our science with perspective can help

- ❑ 2 Bills past by the Washington State Legislative
  - ➢ HB 2658 - 2017-18: Concerning the use of perfluorinated chemicals in food packaging
  - ➢ SB 6413 - 2017-18: Reducing the use of certain toxic chemicals in firefighting activities



Total Oxidizable Precursor (TOP)
(Houtz and Sedlak, *EST*, 2012)

Heat-activated persulfate at pH > 11.5 generates hydroxyl radicals (OH•)



Waste-derived fertilizers: Maximum PFAA increase was 7-16%

Dried-Fertilizer Extract → Add 60 mM potassium sulfate + 150 mM sodium hydroxide mixture → Vortex → Heated water bath (85 °C for 6 h) → Ice water bath → Add HCl → Clean up & Analysis

A Few Take Home Messages

- Commercial Biosolids-based fertilizers contained higher total PFAA concentrations than nonbiosolid-based fertilizers.
- ≥ C6 (longer chains) dominated in the commercial fertilizers (2014)
- Milorgonite data suggests a decline in PFAAs, especially long chain PFAA (consistent with trends being observed for biosolids in general)
- For non-biosolids-based fertilizers, PFAA conc. were elevated for those with food wastes and compostable food packaging
- All fertilizers contained higher levels of PFCAs (carboxylates)
- ≤ C6 (shorter chain) dominated in composted city wastes (2017) TOP assay result did not show a significant increase in PFCAs concentrations.
- ‘Pore-water’ concentrations exceed regulatory or provisional guidance levels BUT PFAAs released will be diluted and attenuated considerably depending site characteristics, management, and PFAA chain length
- Strong correlation between pore water and waste-derived fertilizer concentrations for some PFAAs.

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- Research Scholars
  - Rooney Kim Lazcano (PhD Student)
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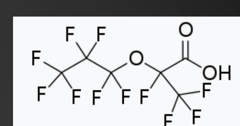
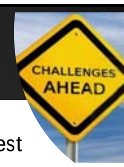
  - Dr. Chloe de Perre (Chemist)
  - Peyman Yousefi (PhD student)
- Funding:
  - Purdue Lynn Fellowship
  - USDA – Agriculture and Food Research Initiative Competitive Grant
  - DuPont



Perspective

It’s challenging to balance the response.

Reality check



- **PFAS are ubiquitous.** Wastewater & biosolids with no industrial inputs can have 1's to 10's parts per billion (ppb*). Source control & phase-outs are the best option for reductions. But we will not get to zero PFAS anytime soon.
- **Presence does not necessarily mean risk**. For wastewater & biosolids, there is no dermal, inhalation, or ingestion risk. Leaching is the only possible concern.
- **Limited data for a few biosolids sites** show groundwater impacts directly under several worst-case-scenario legacy biosolids sites, but no significant impacts on neighboring drinking water wells. Biosolids & soils bind longer-chain PFAS (e.g. PFOA and PFOS).
- **PFOA & PFOS are at lower levels in modern wastewater & biosolids than in the past**, due to phase-outs. Wastewater & biosolids today are conveying ~1/10th as much PFOA & PFOS.
- **Data are inadequate for robust modeling of leaching potential from biosolids applied to soils**. Most states recognize this. There are no approved EPA analytical methods.
- **Environmental impacts**: Wastewater & biosolids have contained PFAS for 50+ years – including PFOA & PFOS at higher levels than today. Bioassays of biosolids use have not found significant negative impacts, only benefits.
- **How much should society spend chasing trace PFAS**? What will the costs be to your utility?

*1 ppb = 1 sec. in 31.7 years / 1 ppt = 1 sec. in 31,700 years

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This is a major source of PFAS:

AFFF, Pease AFB, NH

https://www.youtube.com/watch?v=8W_zJfJGhSI&feature=youtu.be

All the white is AFFF
(PFAS-containing foam)

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These are major sources of PFAS:

Cottage Grove, MN

Parkersburg, WV

EPA reaches new C8 deal with DuPont

on January 16, 2017 at 4:54 pm

The Washington Works DuPont plant in Parkersburg, West Virginia, on Wednesday, August 5, 2015. Photo: Maddie McGarvey for The Intercept/Investigative Fund

PARKERSBURG, WV — "Less than two weeks before the Obama administration leaves office, the U.S. Environmental Protection Agency on Monday said it had reached a new agreement with DuPont Co. regarding pollution of drinking water in the Mid-Ohio Valley with the toxic chemical C8 from the company's manufacturing plant near Parkersburg.

EPA said in a news release that it had amended its 2009 agreement with DuPont to reflect a lower level of C8 exposure recommended in an EPA health advisory issued last year. While more

LAWSUITS CHARGE THAT 3M KN ABOUT THE DANGERS OF ITS CHI

Sharon Lerner

April 11 2016, 9:42 a.m.

FOR DECADES, 3M was the primary producer of C8, or PFOA, and was the sole producer of a related chemical known as PFOS. But while DuPont was caught up in a massive class-action suit over C8, 3M has largely avoided public scrutiny and serious legal or financial consequences for its role in developing and selling these industrial pollutants.

In February, however, a state court in Minnesota, where the company is headquartered, allowed a lawsuit against 3M to move forward. And late last year, lawyers filed a class-action suit in Decatur, Alabama, home to one of 3M's biggest plants. Both lawsuits charge that 3M knew about the health hazards posed by the perfluorinated chemicals it was manufacturing and using to make carpet coating, Scotchgard, firefighting foam, and other products — and that the company knew the chemicals were spreading beyond its sites. With PFCs cropping up in drinking water around the country and all over the world, the two lawsuits raise the possibility that 3M may finally be held accountable in a court of law.

State Attorney General Lori Swanson first filed the lawsuit against 3M on behalf of the people of Minnesota in 2010, claiming that the company polluted more than 100 square miles of groundwater near its plant in Cottage Grove, Minnesota, as well as four aquifers serving as drinking water for some 125,000 people in the Twin Cities. The suit charges that the company piped PFC-polluted wastewater into a stream that flows into the Mississippi River and disposed of it on land near the river, which allowed it to leach into the river.

Based on the company's own research, the complaint argues, 3M "knew or should have known" that PFCs harm human health and the environme[nt] that the chemicals would leach from their disposal sit

Flip Pl

Priori-tizing PFAS sources

(State of Nebraska)

and
ter

tics Products
ied Industries
Training Sites)
on Equipment
ion Equipment
g, & Gumming
ent, & Supplies
brics & Similar
Manufacturing
ather Products
Vatches, Clocks
lated Industries
le Mill Products
turing & Coating
turing & Coating

ustry Codes

Prioritized Potential PFC Sites Based on Products and Manufacturing Processes

High Priority

- AFFF
- Fire training areas
- Metal plating, chrome plating
- Paperboard mills, coating, laminating, and treating
- Paraffin waxes, floor waxes, and various cleaners
- Fabric and leather treatments
- Leather tanning and finishing
- Various surfactants
- Plastic food containers and products, waxed paper
- Waterproof fabric and coatings
- Photographic processes
- Non-stick cookware
- Dental wax manufacturing
- Various cosmetics
- Rubber and plastic products manufacturing (High or Low priority depends on treatment or coating)
- Pesticides

Low Priority

- Rubber and plastic products manufacturing (High or Low priority depends on treatment)
- Paints and special coatings
- Airplane hydraulic fluid
- Paper and textile products with unknown treatments or coating
- Semiconductor manufacturing
- Fire training schools, services, and departments

Conveyors of PFAS:

Wastewater & biosolids management do not create PFAS



effluent: 1 – 40 ug/kg (ppb) PFOA or PFOS

biosolids: 1 – 40 ug/kg (ppb) PFOA or PFOS

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But, the numbers set for PFAS in waters will dictate WRRF effluent & biosolids requirements.

- Drinking water:
  - 72 ppt PFOA + PFOS – U. S. EPA public health advisory (screening level)
  - 20 ppt PFOA, PFOS, +3 – Vermont standard
- Soil:
  - 300 ppb PFOA – the lowest state (VT) residential clean-up standard *based on dermal contact & ingestion – not leaching.*
  - Typical modern biosolids & paper mill residuals: 1's to low 10's ppb – no issue, *except maybe for leaching.*

Remember:

1 ppb = 1 second in 31.7 years

1 ppt = 1 second in 31,700 years

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What about risk to environmental organisms?

Possibly minimal:

Puddephat / McCarthy research (Puddephat, 2013)

Figure 17: Avoidance chamber setup for *Folsomia candida*

Brassica rapa

Zea mays

Figure 30: Feeding of Earthworms in Ryerson Long-Term Bioassay Chambers. Image shows the mating chambers atop the Evan's Boxes

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Conclusions of Puddephat / McCarthy:

Puddephat, 2013:

"…biosolids had little negative impact on the terrestrial biota examined and as a general rule, there was no impact observed. Where effects were observed, the majority of instances were positive. In the few instances where there was negative impact observed, for example in the initial growth stages of the plant bioassays, with further development of the organism, there was no longer a significant difference between the reference and treatment plants."

PFOA & PFOS were most likely in those biosolids at levels higher than today's biosolids.

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Perspective: **Wastewater & biosolids mirror modern life.**

- Wastewater solids management is not optional.
- Wastewater solids can be landfilled; incinerated; or treated, tested, & applied to soil as biosolids. The latter usually is best environmentally, overall.

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Health Department Updates Health Advisory for PFAS, State Expands Testing Plan to include 10 Schools in Pilot Project

Vermont

July 10, 2018

MONTPELIER – The Vermont Department of Health has updated its health advisory for drinking water of 20 parts per trillion (ppt) to cover five per- and polyfluoroalkyl substances (PFAS). PFAS are a large group of human-made chemicals that have been used in industry and consumer products worldwide since the 1950s. Exposure to certain PFAS may affect different systems in the human body.

The previous health advisory of 20 ppt for PFOA and PFOS combined was issued in 2016 following the discovery of PFOA in private drinking water wells in Bennington and a public drinking water supply well in Pownal, Vermont.

Vermont Health Advisory for Drinking Water = 20 parts per trillion

The health advisory for PFAS in drinking water now includes three more PFAS in addition to PFOA and PFOS. Added together, the levels of these PFAS may not exceed 20 parts per trillion (ppt):

- PFOA - perfluorooctanoic acid
- PFOS - perfluorooctane sulfonic acid
- PFHxS - perfluorohexane sulfonic acid
- PFHpA - perfluoroheptanoic acid
- PFNA - perfluorononanoic acid

Vermont	Units	RANDOLPH WWTF SLUDGE	BARRE WWTF SLUDGE	SB AIRPORT PKWY WWTF SLUDGE	SB AIRPORT PKWY WWTF DUPLICATE-SLUDGE
Perfluorobutanoic acid (PFBA)	ug/kg	5.78	ND/< 1.420	ND/< 1.460	1.55
Perfluoropentanoic acid (PFPeA)	ug/kg	2.32	2.09	ND/< 0.729	ND/< 0.740
Perfluorohexanoic acid (PFHxA)	ug/kg	10.7	1.86 J	2.19 J	2.63
Perfluoroheptanoic acid (PFHxA)	ug/kg	1.03	ND/< 0.345	ND/< 0.356	ND/< 0.361
Perfluorooctanoic acid (PFOA)	ug/kg	13.1	2.99	0.811	[illegible]
Perfluorononanoic acid (PFNA)	ug/kg	2.92	1.91	1.31	[illegible]
Perfluorodecanoic acid (PFDA)	ug/kg	4.01	8.94	[illegible]	[illegible]
Perfluoroundecanoic acid (PFUnA)	ug/kg	1.01	[illegible]	[illegible]	1.67
Perfluorododecanoic acid (PFDoA)	ug/kg	0.792	[illegible]	2.53	2.36
Perfluorotridecanoic acid (PFTrDA)	ug/kg	[illegible]	[illegible]	0.629	0.617
Perfluorotetradecanoic acid (FTeDA)	[illegible]	[illegible]	0.693	1.43	1.38
Perfluorobutanesulfonic acid (PFBS)	[illegible]	[illegible]	ND/< 0.384	ND/< 0.356	ND/< 0.361
Perfluoropentanesulfonic acid (PFPeS)	[illegible]	ND/< 0.55	ND/< 0.488	1.18	1.99
Perfluorohexanesulfonic acid (PFHx[illegible]	ug/kg	0.744	ND/< 0.396	ND/< 0.782	ND/< 1.72
Perfluoroheptanesulfon[illegible]	ug/kg	ND/< 0.34	ND/< 0.635	ND/< 0.517	ND/< 0.902
Perfluorooctanesu[illegible]	ug/kg	5.56	8.5	13.9	17.7
Perfluorononanesulf[illegible]id (PFNS)	ug/kg	ND/< 0.44	0.328	ND/< 0.499	ND/< 0.409
Perfluorodecanesulfonic acid (PFDS)	ug/kg	2.06	5.3	14.1	15.8
Perfluorododecanesulfonic acid (PFDoS)	ug/kg	ND/< 0.33	13	17.6	19.7
Perfluorooctanesulfonamide (PFOSA)	ug/kg	1.68	3.5	4.78	5.06
N-Methylperfluorooctanesulfonamide (N-MeFOSA)	ug/kg	ND/< 0.41	ND/< 0.672	ND/< 0.647	ND/< 1.63
N-Ethylperfluorooctanesulfonamide (N-EtFOSA)	ug/kg	ND/< 2.77	ND/< 1.000	ND/< 1.030	ND/< 1.05
N-Methylperfluorooctanesulfonamidoacetic acid (N-MeFOSAA)	ug/kg	12.5	13.3	20.1	22.3
N-Ethylperfluorooctanesulfonamidoacetic acid (N-EtFOSAA)	ug/kg	19.8	10.8	4.98	4.87

Collecting data. But what are their significance?

NEWS

Washington Governor signs nation's 1st law banning PFAS in food packaging

New Jersey

Perfluorooctanoic Acid (PFOA):

In 2007, the New Jersey Department of Environmental Protection (NJDEP) issued a preliminary drinking water guidance level for perfluorooctanoic acid (PFOA) of 40 nanograms per liter (ng/L), or 0.04 parts per billion (ppb). In October of 2017, NJDEP issued an updated drinking-water guidance value for PFOA and announced that the NJDEP would accept the Drinking Water Quality Institute (DWQI) recommended health-based maximum contaminant level (MCL) of 14 parts per trillion (ppt), which is equivalent to 14 ng/L or 0.014 µg/L. DWQI is an advisory body to NJDEP responsible for recommending MCLs in drinking water.

For more information, visit: Perfluorooctanoic Acid (PFOA) in Drinking Water.

Perfluorononanoic Acid (PFNA):

In July 2015, DWQI recommended a health-based MCL for PFNA of 13 ng/L (0.013 µg/L), which served as the basis for an interim specific ground water quality standard for PFNA of 0.01 µg/L, which is equivalent to 10 ng/L or 0.01 ppb, established by NJDEP November 25, 2015. The interim specific ground water quality standard was replaced by a permanent, specific ground water quality standard of the same value (0.01 µg/L) under amendments to the Ground Water Quality Standards rules promulgated on January 16, 2018. Concurrent adoption of amendments to the Discharge of Petroleum and Other Hazardous Substances rules added PFNA to the List of Hazardous Substances. For more information, visit: Ground Water Quality Standards (GWQS).

On August 7, 2017, NJDEP proposed amendments to the Safe Drinking Water Act Rules that include establishing a new MCL for PFNA of 0.013 µg/L (13 ng/L).

Perfluorooctanesulfonic Acid (PFOS):

In May 2016, the United States Environmental Protection Agency (USEPA) issued a Drinking Water Health Advisory for PFOA and PFOS at 70 ng/L (0.070 ppb) individually or a total of the two compounds when both compounds are found.

In November 2017, DWQI published draft recommendations for a health-based MCL for PFOS of 13 ng/L. Details of the status of the DWQI evaluations can be found at: New Jersey Drinking Water Quality Institute.

still draft

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EPA

May 22 – 23: Summit in DC

June 25 – 26:
Region 1 Listening Session, Exeter, NH

July 25:
Region 3 Community Engagement, Horsham, PA

August 7 →

4 actions promised:

- MCL for PFOA & PFOS
- Define PFOS & PFOS as hazardous substances
- Groundwater cleanup recommendations for PFOA & PFOS (fall)
- Toxicity values for PFBS & GenX (summer)

An official website of the United States government.

We've made some changes to EPA.gov. If the information you are looking for is not here, you may be able to find it on the EPA Web Archive or the January 19, 2017 Web Snapshot. Close

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EPA To Hold PFAS Community Engagement in Colorado Springs

07/20/2018

Contact Information:
(press@epa.gov)

WASHINGTON — Starting on Tuesday, August 7, 2018, the U.S. Environmental Protection Agency (EPA) will hold the third PFAS community engagement event in Colorado Springs, Colorado. This two-day public event allows EPA to hear directly from Colorado communities, Mountain West states, and local and tribal partners about their experiences with PFAS.

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Thank you.

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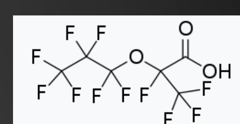

Status of analytical methods

update from Chris Impelliteri, U. S. EPA

Method for non-drinking-water
groundwater, surface water, wastewater

- Direct injection method for 24 analytes - 10-lab external in progress. This method is based on an EPA Region 5 standard operating procedure (SOP).
- Isotope dilution method (same 24 analytes). A draft SW846 Method is currently circulating w/in EPA for internal review. This method had a lot of input from DoD/Navy.
  - The basis of the method is an EPA-ORD SOP out of Dr. Mark Strynar's lab in NC.
  - After internal review of the current draft, one EPA lab will test/validate the method, address any issues, redraft, and go straight to an external validation.

Method for solids
soils, sediments, biosolids/sludge

- Beginning drafting SW846 Method now. Based on an EPA-ORD SOP (with DoD input as well).

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GenX, ADONA, other PFECAs in water

- Drinking Water: EPA-ORD and the Office of Water are currently developing a method for perfluoroalkyl ether carboxylic acids (PFECAs) in DW (emphasis right now on GenX, ADONA).
  - The chromatography and MS conditions are such that we probably will not be able to add an addendum or update Method 537; it will likely be a separate method.
  - The testing and validation requirements for DW methods are much more rigorous (relative to SW846) and there will probably not be a draft for public review until early 2019. However, an interim draft may be issued prior to that depending on the method efficacy based on preliminary data.
- Non-DW: EPA Regions 3 and 4 have been applying the direct injection method to the analysis of GenX.

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Be a Savvy Lab Consumer: Review Data Generated by Other Methods

- Previously Published methods on PFCs
  - EPA Method 537, ASTM D7979 or D7968, Journal?
  - Are they really following the methods they cite?
    - Using the entire sample?
    - Many sample manipulations involved?
    - Pre-filter?
    - Complicated Sample Preparation?
    - Batch QC-Surrogates, duplicates, matrix spikes, reporting limit checks?
    - Ongoing Method Performance in Real Matrices?
    - Quantitation?
  - SRM or MRM, Ion Ratios?
  - Are they getting poor recoveries of their isotopes and correcting the data using isotope dilution?
  - Isotope dilution- are they diluting samples- diluting out isotope, adding more isotopes after dilution? Not isotope dilution anymore.
  - Equilibration time of the isotopes in the sample?
  - Are the isotopes at a similar concentration as their reporting range?

Source: Lawrence B. Zintek, Danielle Kleinmaier, Dennis J. Wesolowski, Solidea Bonina[#] and Carolyn Acheson

89

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nebra North East Biosolids & Residuals Association

Thank you.

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Acknowledgements & Sources

Inclusion on this list does not imply endorsement.
Views expressed are those of the authors only.

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Questions?

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