

Per- and Polyfluoroalkyl substances (PFAS) in Agricultural Operations



NEBRA's PFAS page:

<https://www.nebiosolids.org/pfas-biosolids>

Includes "PFAS & Biosolids & Septage on NE Farms" and lit. reviews (click at bottom of page)

Ned Beecher, Special Projects Mgr., NEBRA
Linda S Lee, Purdue University

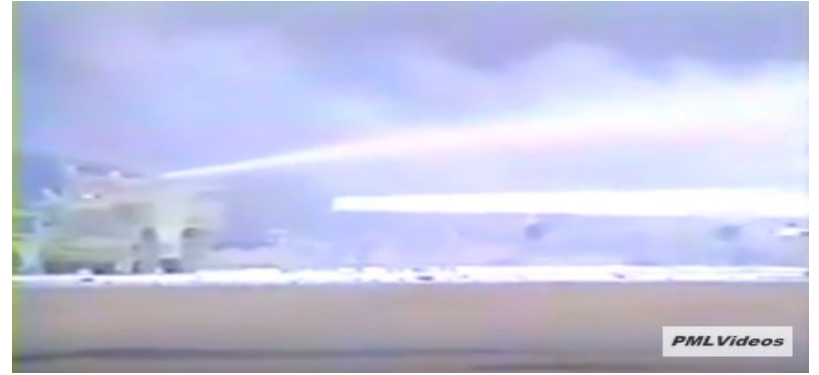
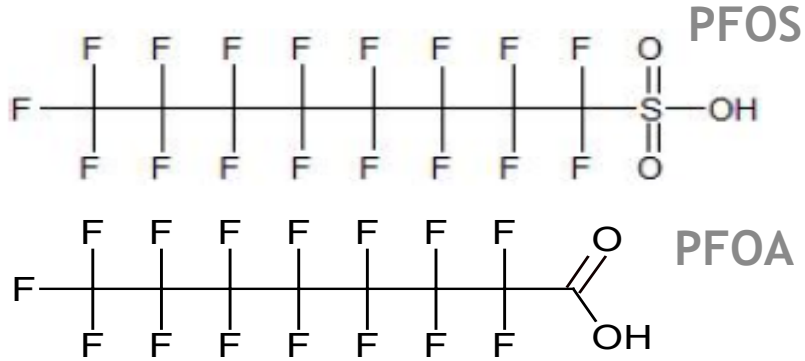
February 19, 2021

USDA • NRCS Conservation Webinars (<http://conservationwebinars.net/>)

Outline

- PFAS: Widely used! Much still unknown.
- Why concern about PFAS?
- Regulations near background levels
- Sources of PFAS in soils, on farms
- Why biosolids are applied to soils
- Data on PFAS in biosolids, manures, and farm soils
- PFAS fate in soils, plant uptake
- Industrially-impacted farm situations
- Ongoing PFAS research examples
- PFAS mitigation: most efficient is to phase out non-essential uses





PFAS* - especially PFOS

an extreme, worst-case contaminant of emerging concern

*the only *common* trace contaminant of drinking water regulated in low ppts*

Why the concern about PFAS?

Widespread contamination + potential health concerns...

- There are hundreds of U. S. drinking water & groundwater PFAS contamination sites from industry & fire-fighting.
- Scary: “forever chemicals,” research links PFAS to some negative health impacts
- Community groups, researchers calling for action; some states taking action. Voluntary phase-outs continue (e.g. ski wax).
- See varying perspectives:
 - <https://pfasproject.com/>
 - <https://www.ewg.org/key-issues/toxics/nonstick-chemicals>
 - <https://www.nebiosolids.org/pfas-biosolids>
 - <https://dec.vermont.gov/water/drinking-water/water-quality-monitoring/pfas>
 - <https://www1.health.gov.au/internet/main/publishing.nsf/Content/ohp-pfas-expert-panel.htm>

In the news...

NEWS CENTER
MAINE

News Weather 207 Connect Watch

VACCINE INFO PROJECT HEAT CLOSINGS AND DELAYS WCSH CLOSING REGISTRATIC

HEALTH

High PFOS levels detected on Maine farm, Maine milk supply deemed safe

DACF says Maine's retail milk supply continues to be safe for consumption, as 19 of the 20 samples tested were below the laboratory's reporting limit of 25 ppt.



//www.newscentermaine.com

<https://www.newscentermaine.com/article/news/health/high-pfos-levels-detected-on-maine-farm-maine-milk-supply-deemed-safe/>

PFAS

February 19, 2019

Groundwater contamination devastates a New Mexico dairy – and threatens public health

By Amy Linn, Searchlight New Mexico



<https://nmpoliticalreport.com/2019/02/19/groundwater-contamination-devastates-a-new-mexico-dairy-and-threatens-public-health/>

PFAS: Widely used!

PAPER

[View Article Online](#)
[View Journal](#)



Cite this: DOI: 10.1039/d0em00291g

An overview of the uses of per- and polyfluoroalkyl substances (PFAS)[†]

Juliane Glüge,^{ib*} Martin Scheringer,^{ib^a} Ian T. Cousins,^{ib^b} Jamie C. DeWitt,^c Greta Goldenman,^d Dorte Herzke,^{ib^{ef}} Rainer Lohmann,^{ib^g} Carla A. Ng,^{ib^h} Xenia Trierⁱ and Zhanyun Wang^j

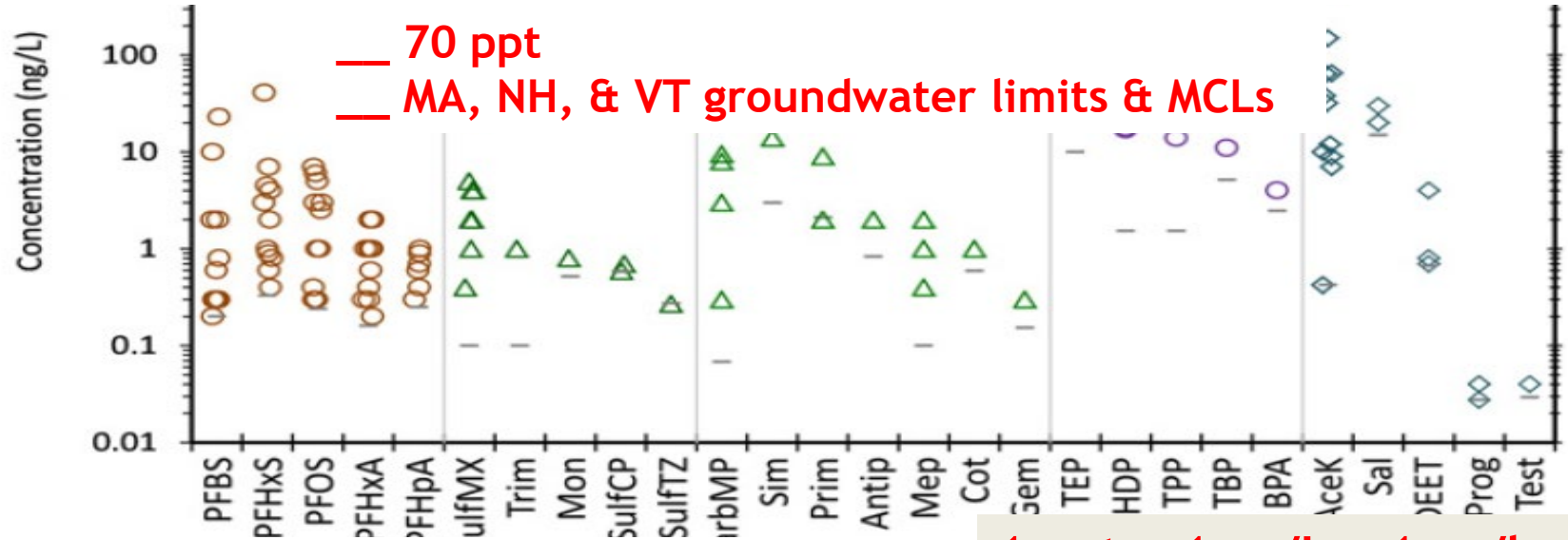
Per- and polyfluoroalkyl substances (PFAS) are of concern because of their high persistence (or that of their degradation products) and their impacts on human and environmental health that are known or can be deduced from some well-studied PFAS. Currently, many different PFAS (on the order of several

<https://pubs.rsc.org/en/content/articlelanding/2020/em/d0em00291g#!divAbstract>

“PFAS are used in almost all industry branches and in many consumer products. Some consumer products even have multiple applications of PFAS within the same product. A cell phone for example may contain fluoropolymer-insulated wiring, PFAS in the circuit boards/semiconductors, and a screen coated with a fingerprint-resistant fluoropolymer.”

Regulations at background levels: Even septic systems may violate standards.

Cape Cod, MA groundwater and drinking water was impacted, only by septic systems, at low ppt levels; no industrial sources nearby.



* Schaider et al., 2016. Septic systems as sources of organic drinking water wells in a shallow sand and gravel aquifer. Sc

1 ppt = 1 ng/L = 1 ng/kg =
1 second in 31,700 years.

Regulations at background levels.

Leaching from biosolids and even food waste composts may not be able to meet a few states' standards.

MA & VT MCLs and groundwater quality standards:

- 20 ppt for the sum of: PFNA, PFOA, PFOS, PFHpA, PFHxS (plus PFDA in MA)

1 ppt =
1 second in 31,700
years.

Maine (ME) soil screening levels:

- PFOA 2.5 ppb
- PFOS 5.2 ppb

1 ppb =
1 second in
31.7 years.

Variability in regulations... (caused by uncertainties)

- MA drinking water standard (2020):
20 ppt (sum of 6 PFAS)
- CA drinking water notification
levels: PFOA = 5.1 ppt, PFOS = 6.2 ppt
- Canada (Dec. 2018): PFOA = 200 ppt,
PFOS = 600 ppt

There are 2 major sources of PFAS in the environment:

- industrial discharges
- fire-fighting (including training, e.g. at military sites)

These cause 1000s to 1,000,000s+ of ppt in waters.

EPA reaches new C8 deal with DuPont

on January 16, 2017 at 4:54 pm



PARK
U.S. E
DuPo
C8 fro
EPA s
level
neste



PMLVideos

**1 ppt = 1 ng/L = 1 ng/kg =
1 second in 31,700 years.**

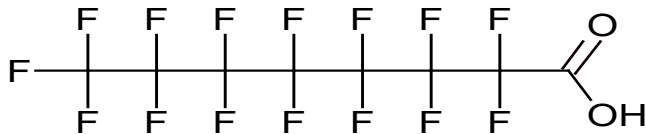
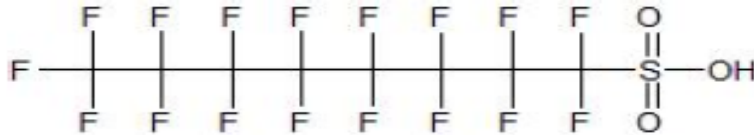
PFAS contamination at industrial site...

Example:

Wolverine Worldwide Kent County tannery dump sites, Rockford, MI

-Highest concentration is **76,000 PPT** (PFOA+PFOS)

Suspected source: This area consists of a former licensed disposal facility owned and operated by Wolverine... and several unregulated dump sites across three townships in northern Kent County.



<https://www.ewg.org/research/update-mapping-expanding-pfas-crisis>

...and then there is ambient background PFAS,



including most wastewater and biosolids and other residuals (e.g. food waste compost, paper mill residuals), septic (onsite) systems, solid waste management activities - these are all receivers of PFAS, not original sources.

When any of these are recycled, the background PFAS go with them.

These cause 10s to 100s of ppt in waters.

Sources of PFAS in soils / on farms

- **Aerial deposition from industry...** Example: Merrimack, NH area, where PFAS were vented from fabric coating industry
- **Groundwater contamination** → farm water impacted... Example: NM dairy
- **Fire-fighting foam use**
- **Lubricants, paints, cleaners, etc.** Example: Floor cleaners & waxes used in schools result in school septic systems & water wells being contaminated.
- **Biosolids and septage** (derived from wastewater treatment)
- **Composts derived from food waste**, especially with compostable foodware

See NEBRA literature review....

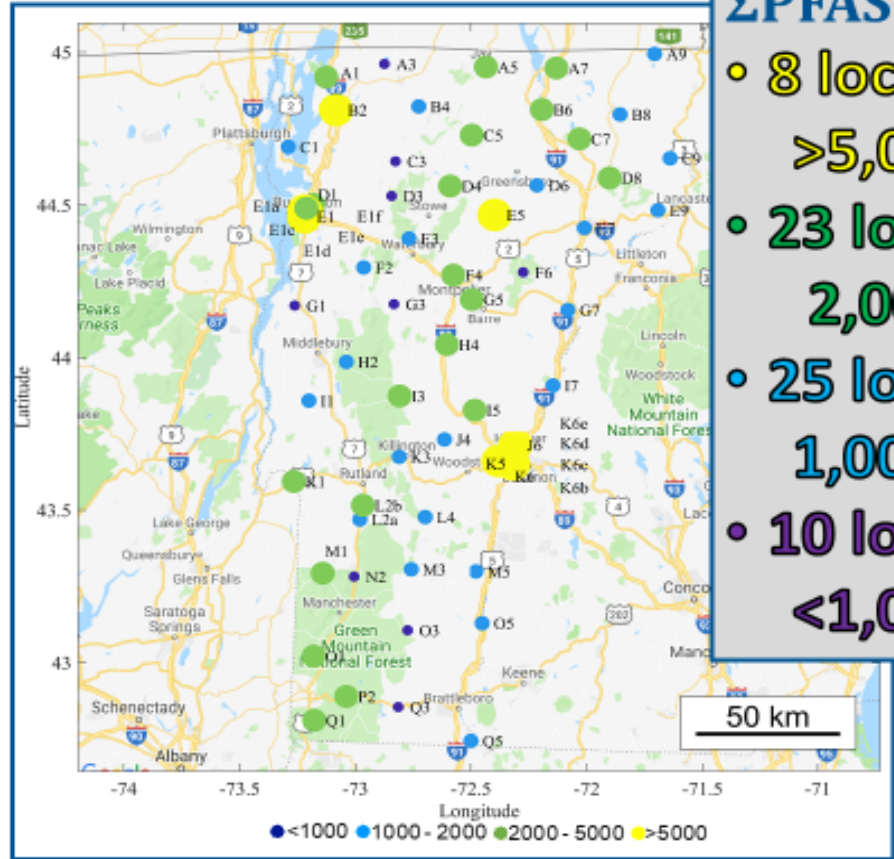
Click to it from the bottom of this page: <https://www.nebiosolids.org/pfas-biosolids>

PFAS in Soils

Study for
VT DEC 2018

PFAS measured
in randomly-
selected sites
with no
obvious PFAS
sources.

PFOS found in
every sample



Σ PFAS (n=66)

- 8 locations >5,000 ng/kg
- 23 locations 2,000-5,000 ng/kg
- 25 locations 1,000-2,000 ng/kg
- 10 locations <1,000 ng/kg

parts per
trillion (ppt)

Why biosolids are used

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Includes “PFAS & Biosolids & Septage on NE Farms” and lit. reviews (click at bottom of page)



Recycled organics: Tools for sustainability.

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PFAS in Biosolids (“sludge”) and Residuals

Recycling organic “wastes” benefits society and the environment.

Throughout the U. S. and Canada, biosolids (treated and tested sewage sludge), septage, paper mill residuals, composts, and other organic residuals are commonly recycled to soils. This recycling does amazing things:

- enhances soil health
- recycles nutrients
- sequesters carbon (mitigating climate change)
- reduces fertilizer & pesticide use
- strengthens farm economies (thousands of farmers choose to use biosolids, because they work)
- restores vitality to degraded lands
- puts to productive use residuals that every community has to manage.
(Wastewater treatment is a vital public health service, and it creates residual solids that have to be managed!)

“Let’s move fast to stop non-essential uses of PFAS. Then let’s work carefully and more slowly on research and balanced regulation.”

— Dr. Linda Lee, Professor of Agronomy, Purdue University, MI WEA Biosolids Conference, Aug. 2020



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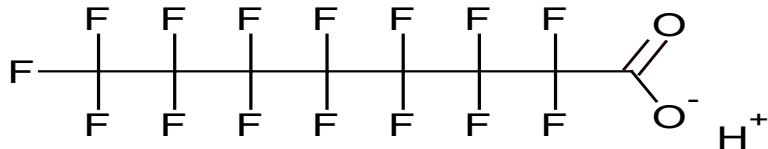


Next...

Analyses & data

PFAS family, chemistry, lab & research data, understanding precursors & fate in biosolids & soils, and data from farm sites

PFOA



1
7

Compare
ppt water
data to:

70 ppt - U. S.
EPA public health
advisory for
drinking water

20 ppt – MA
drinking water &
groundwater
standard for sum
of 6 PFAS

Compare
ppb solids
data to:

~72 ppb - NY
DEC PFOA + PFOS
screening value

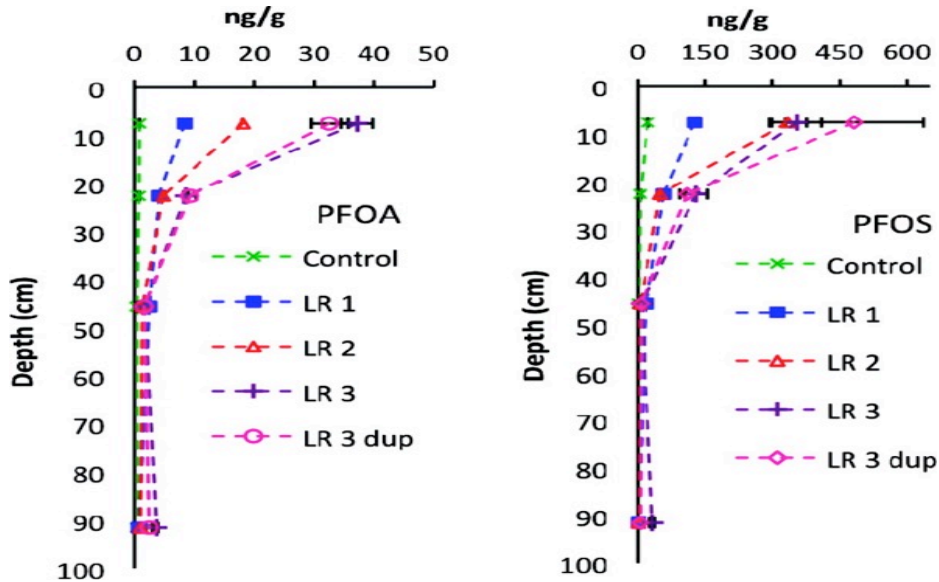
2.5 ppb ME
PFOA screening*

5.2 ppb ME
PFOS screening*

*NEBRA finds these
values inappropriate for
biosolids; ME based them
on modeling leaking
underground tanks.

Past research: PFAS fate in soils...

Initial finding: PFAS leach to groundwater some...



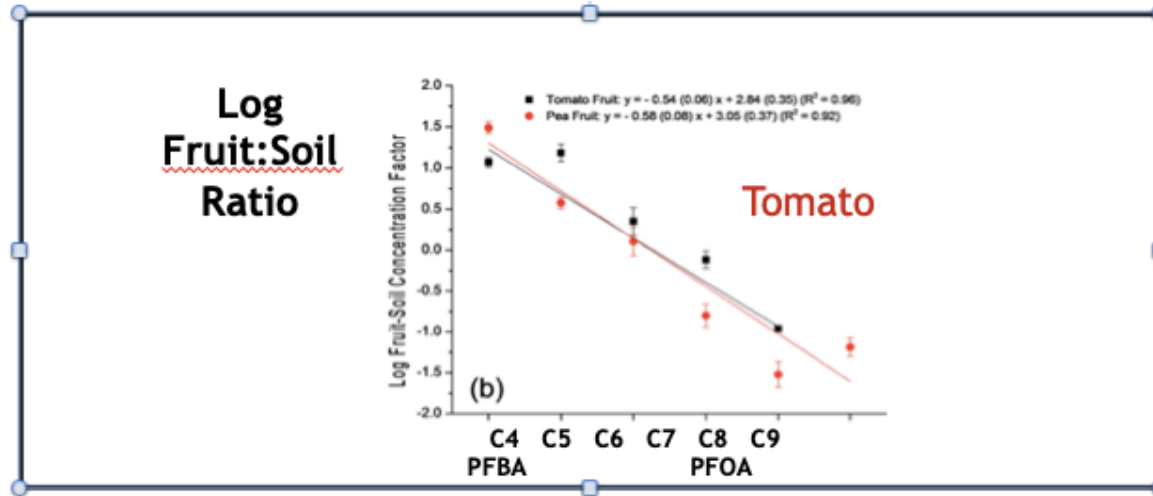
Sepulvado et al;
Environ. Sci. Technol. 2011,
45, 8106-8112

Concentrations of PFOA and PFOS with depth in the long-term plots at various loading rates. Control = 0 Mg/ha, LR 1 = 553 Mg/ha, LR 2 = 1109 Mg/ha, and LR 3 and LR 3 dup = 2218 Mg/ha (on dry weight basis).

Past research: PFAS plant uptake...

Initial finding:

Short-chain PFAS show plant uptake, less with long-chain PFAS...



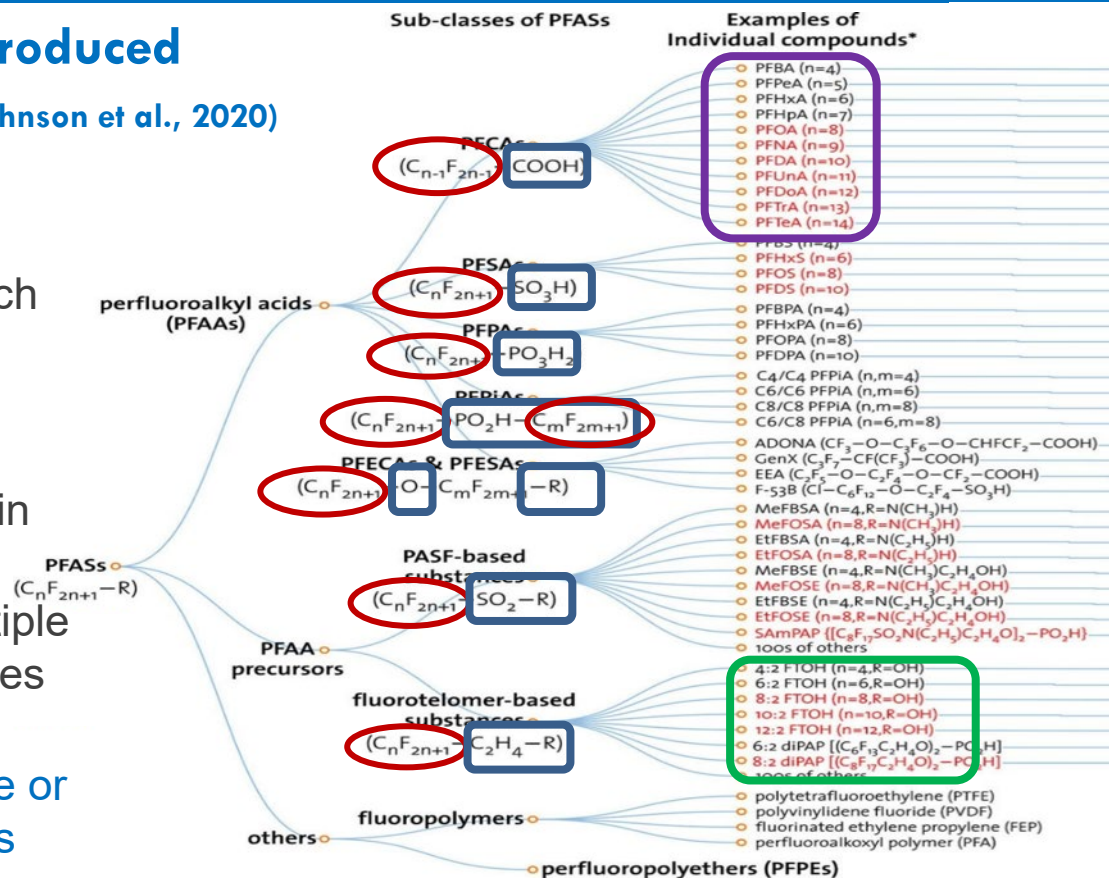
Blaine, A., Rich, C., Sedlacko, E., Hundal, L., Kumar, K., Lau, C., Mills, M., Harris, K., and Higgins, P., 2014. Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils. Environmental Science & Technology, (2014) 48, 7858–7865.

The PFAS Family – more than just the ones you hear about the most

Currently > 4,800 PFAS produced

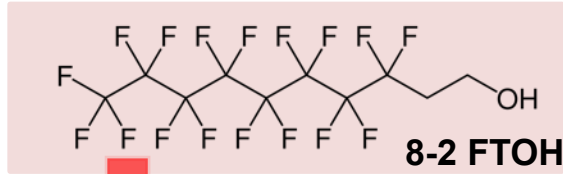
New estimate: >7000* PFAS (*Johnson et al., 2020)

- All have a perfluoroalkyl chain of varying length
- Numerous classes/subclasses, each with a unique differentiating characteristic
- Each subclass includes PFAS with several different perfluoroalkyl chain lengths
- An individual PFAS may have multiple isomers (linear versus different types of branching)
- Each class either does not degrade or degrades to another class/subclass

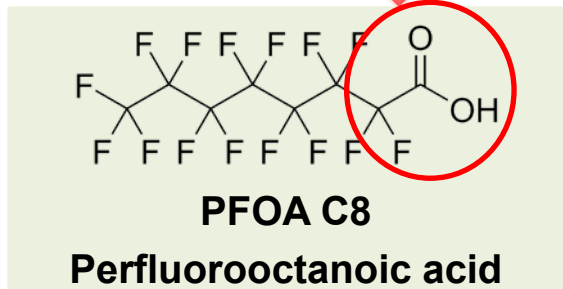


PFAS 'Biodegradability' is not mineralization, but transformation to other PFAS!

PFAS example from the telomerization process

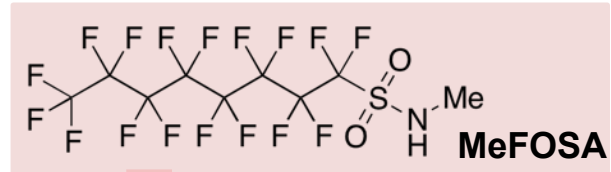


↓ 
Intermediates



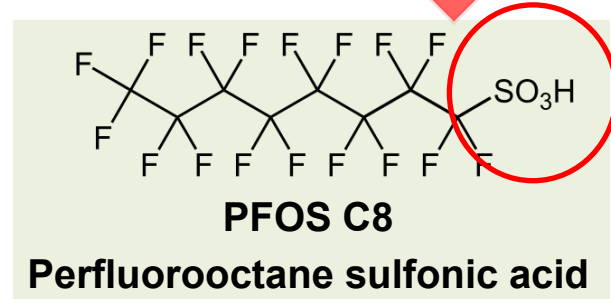
➤ Perfluoroalkyl carboxylic acid (**PFCA**)

PFAS example from the electrochemical process



↓ 
Intermediates

2 are on the EPA '24' List



➤ Perfluoroalkyl sulfonic acid (**PFSA**)

PFAA Precursors

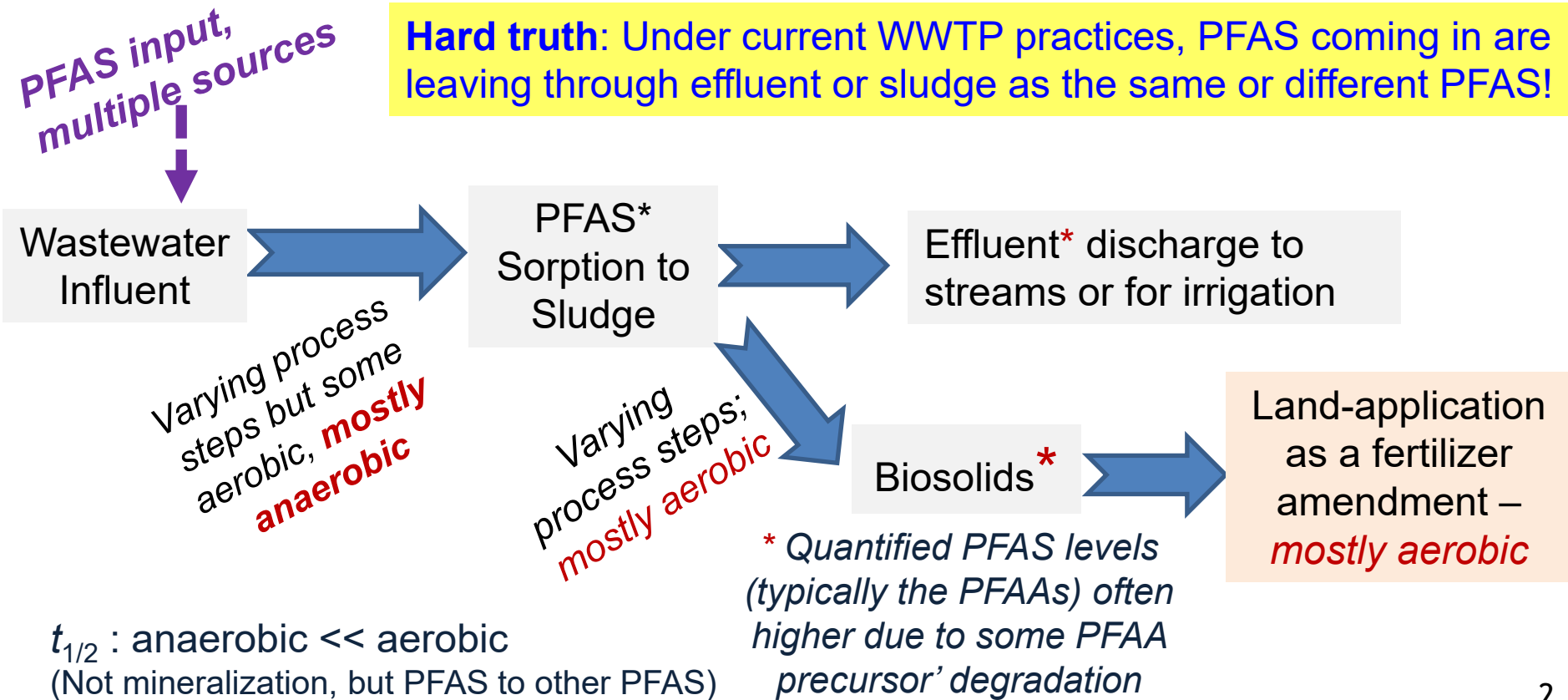
Multiple steps & pathways

PFAAs
Persistent
Anionic (-), low pK_a
More soluble
More mobile

Terminal microbial metabolites: PFCAs + PFSA = PFAAs

Water Resource Recovery Facilities (wastewater treatment plants): PFAS conduits that can lead to more PFAS

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



PFAS Occurrence in Biosolids-based Products and Composts

2014 Commercially Available

A	Food and yard compost
B	Compost with untreated wood products
C	Manure compost
D	Manure and peat compost
E	Mushroom compost
F	
G	Peat/compost based growing mix
H	Heat-dried granular biosolids * 2014, 2016 & 2018
I	
J*	
K	
L	
M	
N	Composted biosolids with woodchips
O	
P	Composted biosolids with municipal solid waste
Q	Composted biosolids with residential yard trimmings
R	Composted biosolids with plant materials

2017 OFMSW Obtained through Zero Waste WA

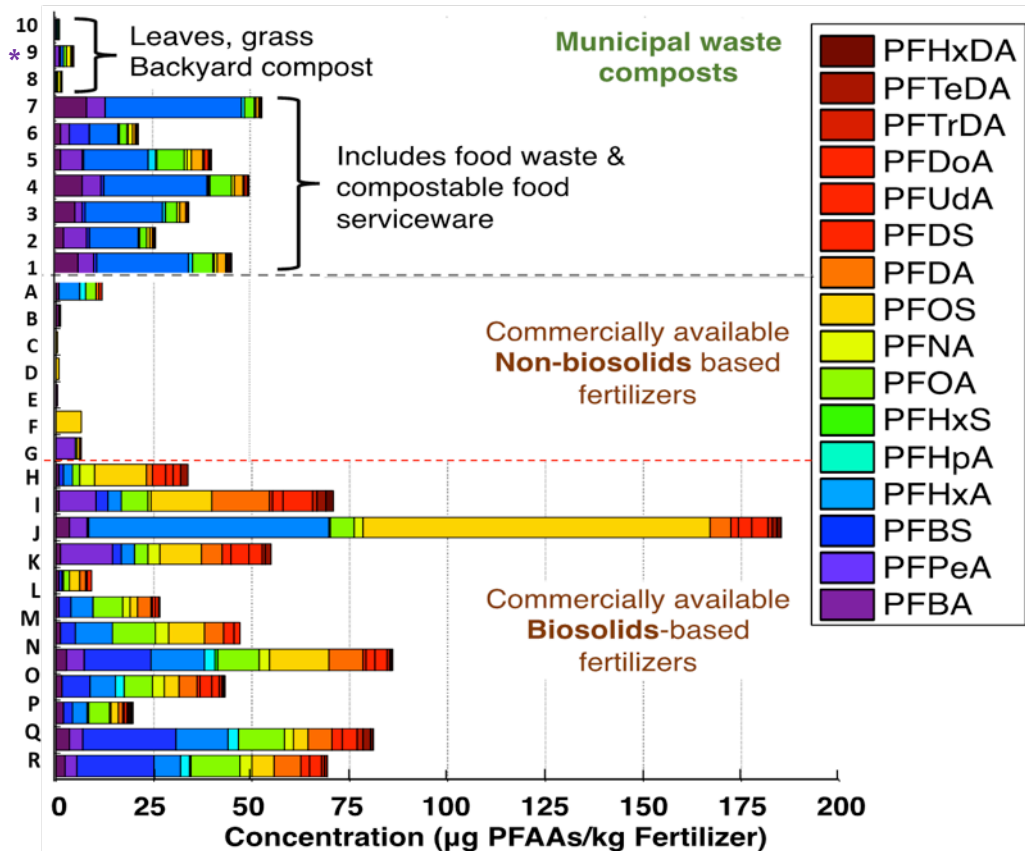
Residential and commercial food waste and yard waste. Allows compostable food packaging.
Municipal food and yard waste and wood products. Allows compostable food packaging.
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Primarily commercial food waste (food scraps, coffee grounds, lobster shells), horse manure and wood shavings. Allows compostable food packaging.
Leaves and grass from municipalities.
Backyard Waste Compost Bin. Includes yard trimmings, food waste and unbleached coffee filters. No compostable serveware or other paper products.
Primarily leaves from municipalities.

General Analytical Approach Used

- **Extraction of solids with addition of mass-labeled surrogates**
- **Targeted PFAS quantification in 2019-2020 publications for soil amendments focused on perfluoroalkyl acids (PFAAs)***
 - 13 PFCAs (C4 to C18): $\text{CF}_3(\text{CF}_2)_n\text{COOH}$
 - 4 PFSAAs (C4, 6, 8, 10): $\text{CF}_3(\text{CF}_2)_n\text{SO}_3^-$
- **Evaluated the relative presence of PFAA precursors**
 - Total oxidizable precursor (TOP) assay- persulfate oxidation at high pH with heat
 - Screened for 30 precursors
- **Evaluated PFAS release to porewater**

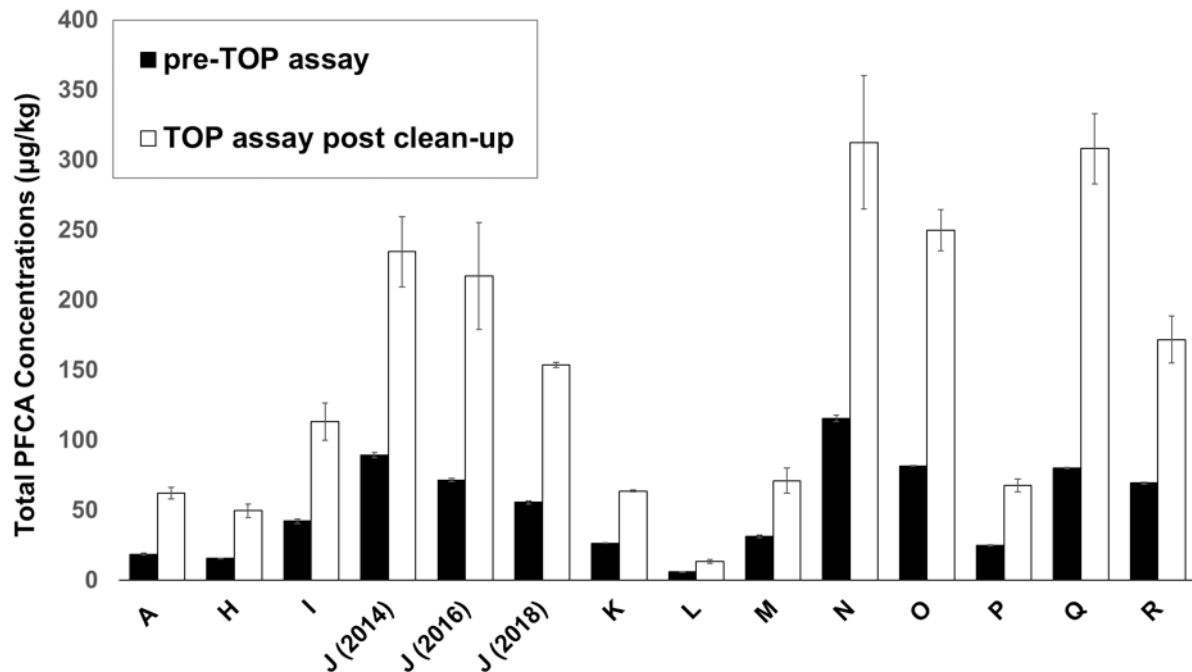
**Our current approach includes 44 PFAS for quantitation with analytical standards (and growing), and target and nontarget screening using a Sciex QToF, SWATH analysis and an ever growing PFAS library.*

PFAS Occurrence in Biosolids-based Products and Composts



- Higher PFAA loads in biosolids-based products
- Range for the biosolid-based products: 30 – 185 $\mu\text{g/kg}$ (ppb)
- Longer chains ($\text{CF}_n \geq 6$) dominant in 2014 biosolid-based products versus $\text{CF}_n \leq 6$ in 2017 municipal waste composts
- Higher [PFAA] in municipal waste composts with compostable food packaging (#1-7)
- * #9 included food wastes, coffee grounds, unbleached coffee filters
- Background levels include atmospheric deposition, insecticides, and contaminated water.

What did the Total Oxidizable Precursor (TOP) assay reveal about *hidden* PFAA sources in **2014** Commercially Available Organic Soil Amendments?



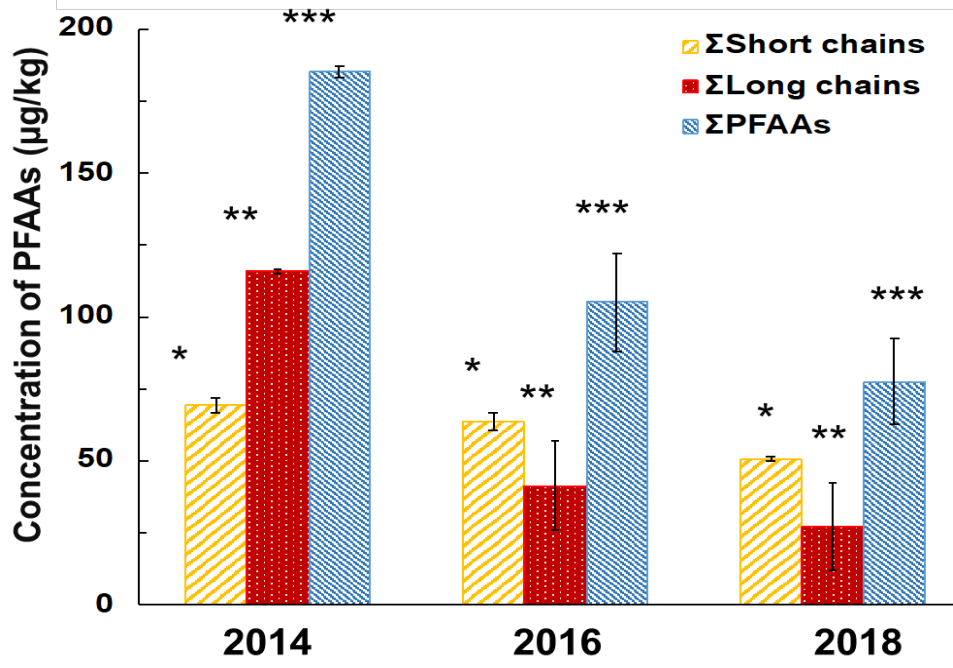
↑ Increases in Total PFAA concentration after TOP treatment reveals *hidden* precursors

↓ Precursor degradation after land application can contribute to increases in available PFAAs for transport

- Largest increase observed in TOP was for *PFHxA* (note: not necessarily 1:1 precursor to PFAA)
- ENVI-Carb clean-up step prior to the TOP assay is necessary; otherwise conversion efficiency reduced due to dissolved organic matter.

Temporal Trends May Vary (*Example 1: PFAS Decreasing*)

2014, 2016, & 2018 Milorganite - heat-treated biosolid-based fertilizer



(*,**&*** statistically different at $p < 0$)

Milorganite commonly used in home gardens, golf courses, community gardens, etc.

From 2014 to 2018:

- **~80% PFOS (C8) reduction**
- **~30% PFHxA (C6) reduction**

Keep in mind:

- Only 17 PFAAs were analyzed.
- Source and process dependent

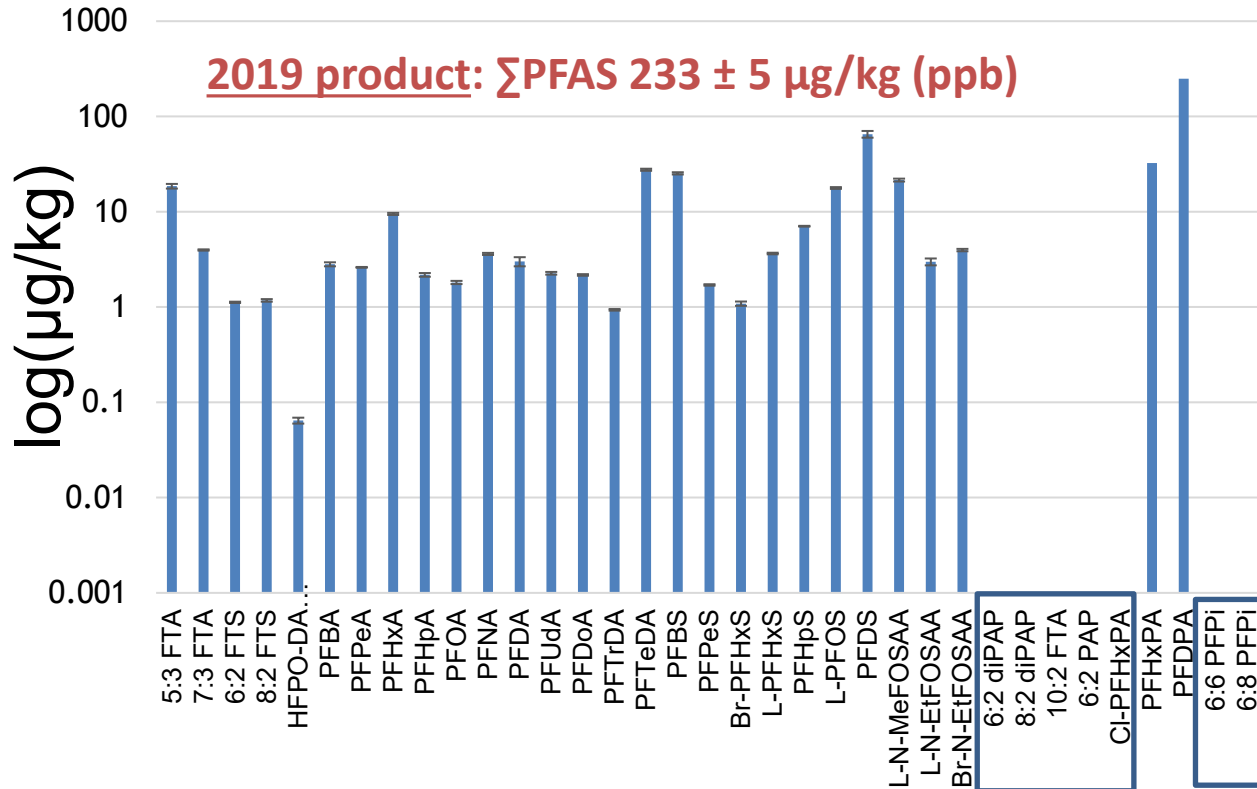
Temporal Trends May Vary (Example 2: PFAS Increasing)

2014 vs 2019 Product - heat-treated biosolid-based fertilizer

2014 $\Sigma 17$ PFAAs 35 $\mu\text{g}/\text{kg}$ VS **2019** $\Sigma 17$ PFAAs 210 $\mu\text{g}/\text{kg}$

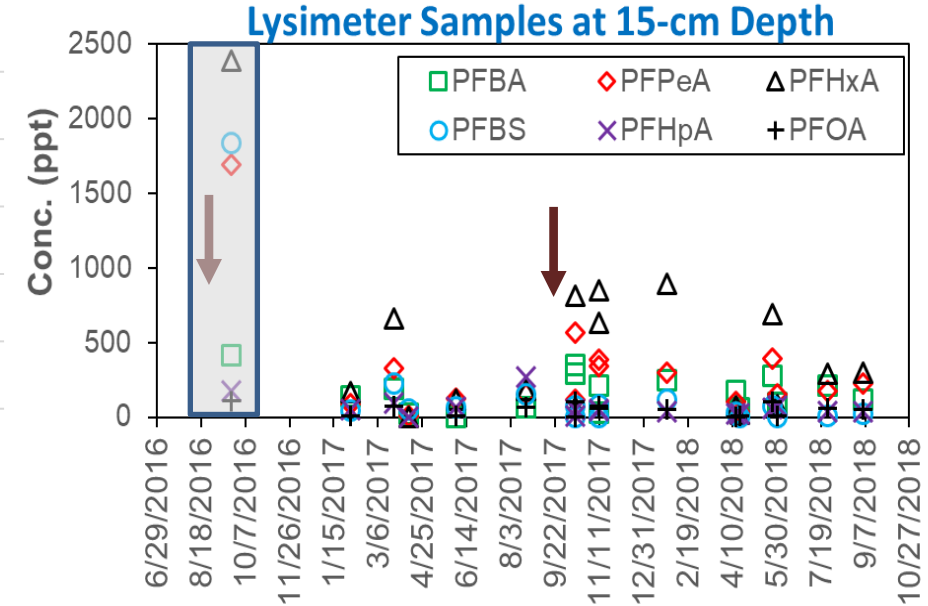
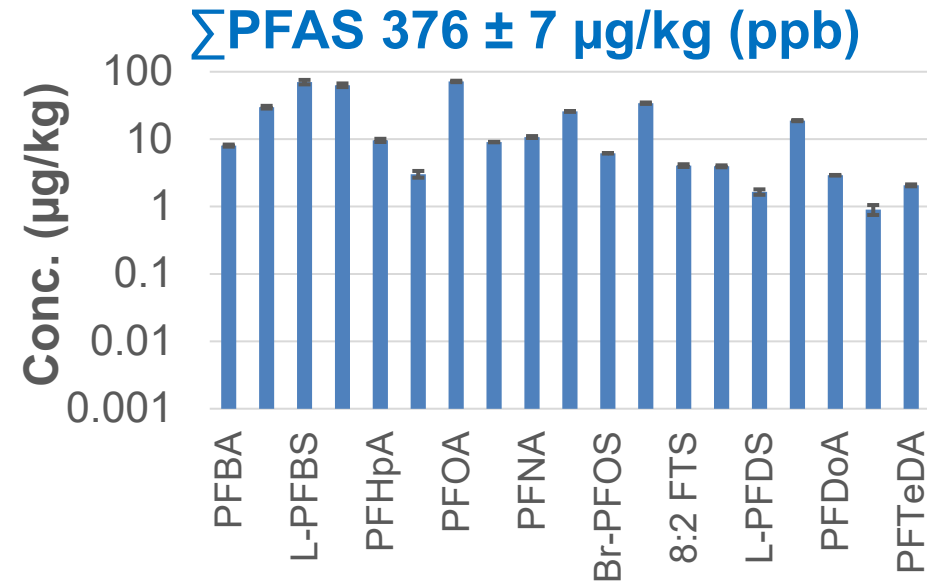
2019 product: Σ PFAS 233 \pm 5 $\mu\text{g}/\text{kg}$ (ppb)

Concentration



- Σ PFAAs:
2014 \ll 2019
- TOP Assay & Nontarget screening revealed additional PFAS in 2014 product, but estimated Σ PFAS still \ll 2019 product
- Method modifications, e.g., increased PFAS targeted, improved extraction procedure (long chains and precursors)

2016 Land Reclamation Study (5x agricultural rate) Leached PFAS Concentrations to the 15-cm Depth

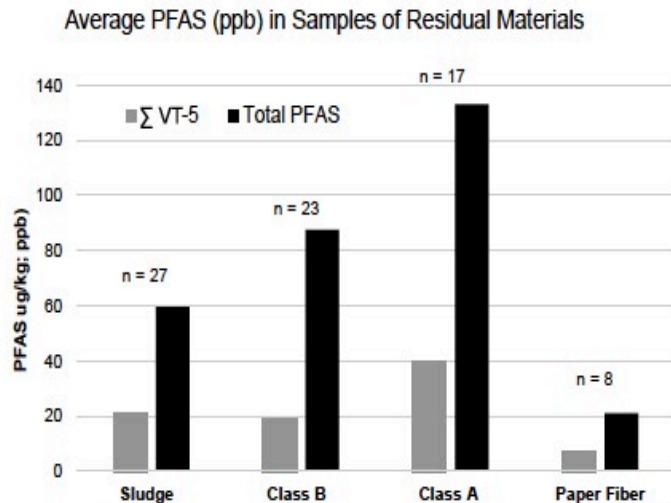


- High concentration in first ≥ 2.5 cm rain event likely due to new site establishment period
- PFAA concentration rise associated with heavy rain months
- Leaching mostly short chains (C4-C6), which were also generally present at higher product conc.
- *Remember*, significant dilution and attenuation will occur prior to reaching groundwater

Biosolids and Biosolid-based Products are not all the Same

- Production practices vary by utility and if Class A or Class B biosolids:

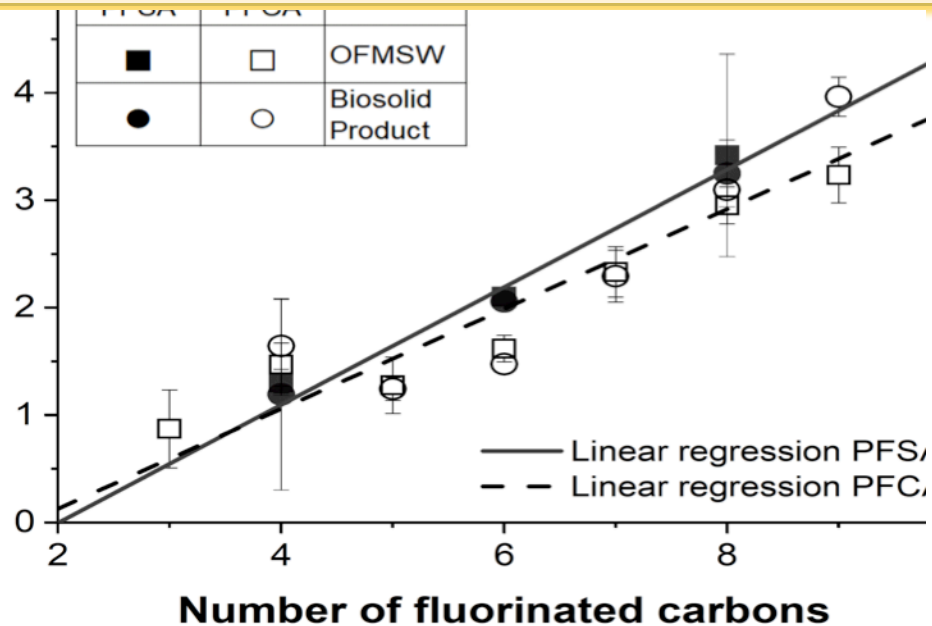
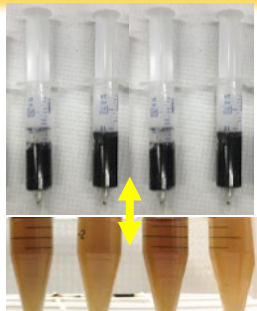
- Temperatures
- Cycling times
- Feed composition
- Microbial population
-



Biosolids and Biosolid-based Products are not all the Same

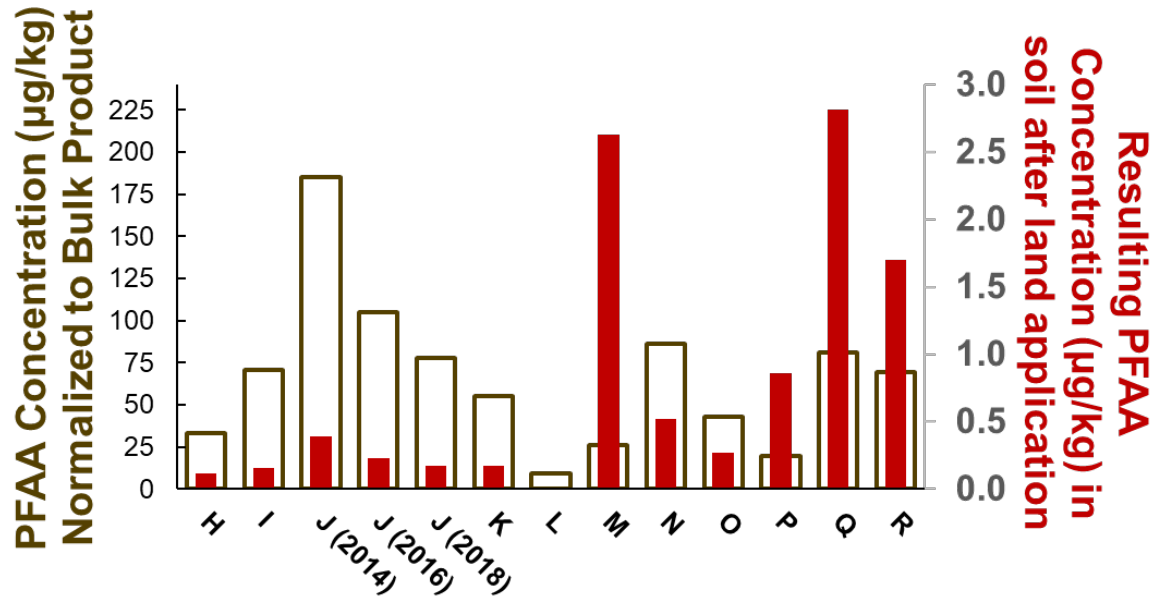
- Production practices vary by utility and if Class A or Class B biosolids:
 - Temperatures
 - Cycling times
 - Feed composition
 - Microbial populations, etc.
- **Biosolids properties vary and may affect PFAS release:**
 - Al content (e.g., 1,400 to 57,300 mg/kg)
 - Fe content (e.g., 1,575 to 299,000 mg/kg)
 - pH (e.g., 6.5 to 8)
 - % OM (e.g., 17-41%)
 - Polymer additions in the treatment process
 - *Protein content may also vary and correlate to PFAS release*

OC-normalized media-water sorption coefficients (K_{oc}) strongly correlated with PFAA chain length (CF_2 groups)



- K_{oc} strongly correlated to PFAA chain length and similar for all organic-based amendments
- Slope for PFSA *slightly higher* even on a CF_2 basis versus chain length
- K_{oc} values have NOT proven adequate for PFAA soil-water partitioning across soils (OC in soils < compared to OC in biosolids) especially in trying to predict vadose-zone transport

Putting PFAA in Biosolids in Perspective (*Example*)

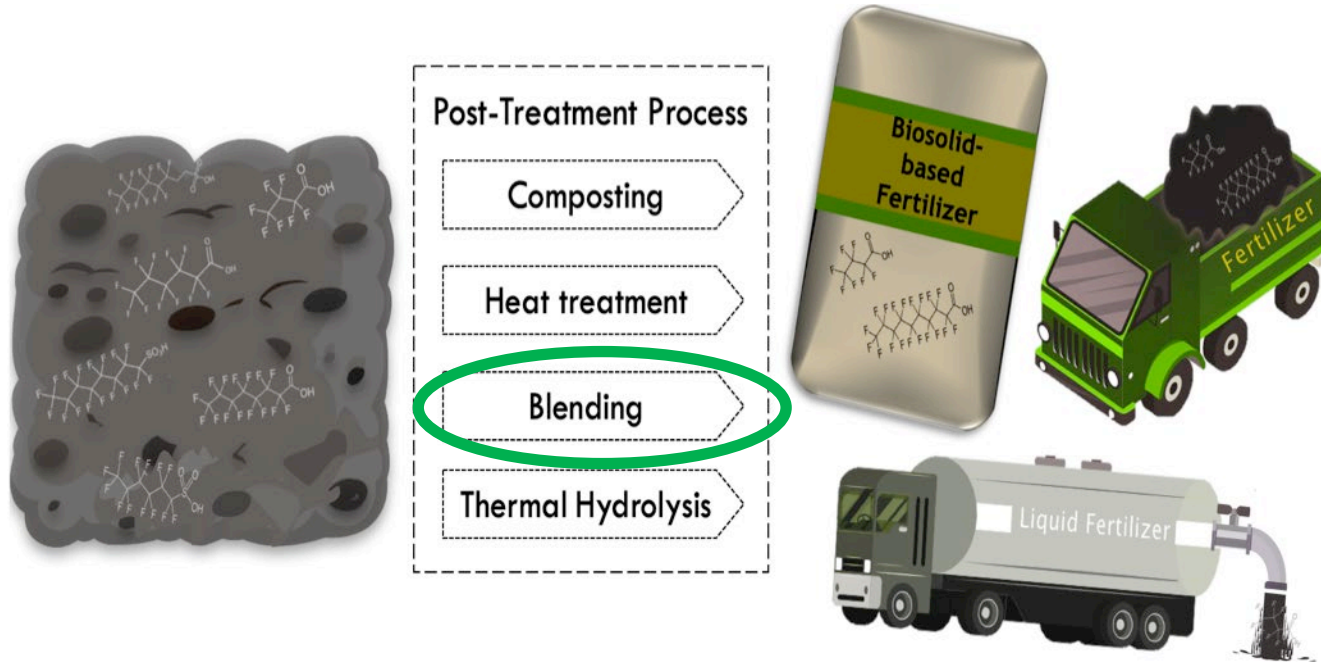


PFAAs in soil after an initial application based on N recommendations at the start of the growing season

- Soil amendments/fertilizers are often applied based on N requirements
- Products low in N could lead to higher PFAS loads with a single application
- ALSO biosolids that are offered free to the public from their local municipality are often over applied unlike use in commercial agriculture where regulations are in place
- Plant uptake in home gardens may be a greater concern than commercially grown products

Impact of Common Biosolid Treatment Processes on PFAA levels (prior to land-application or use in gardens)

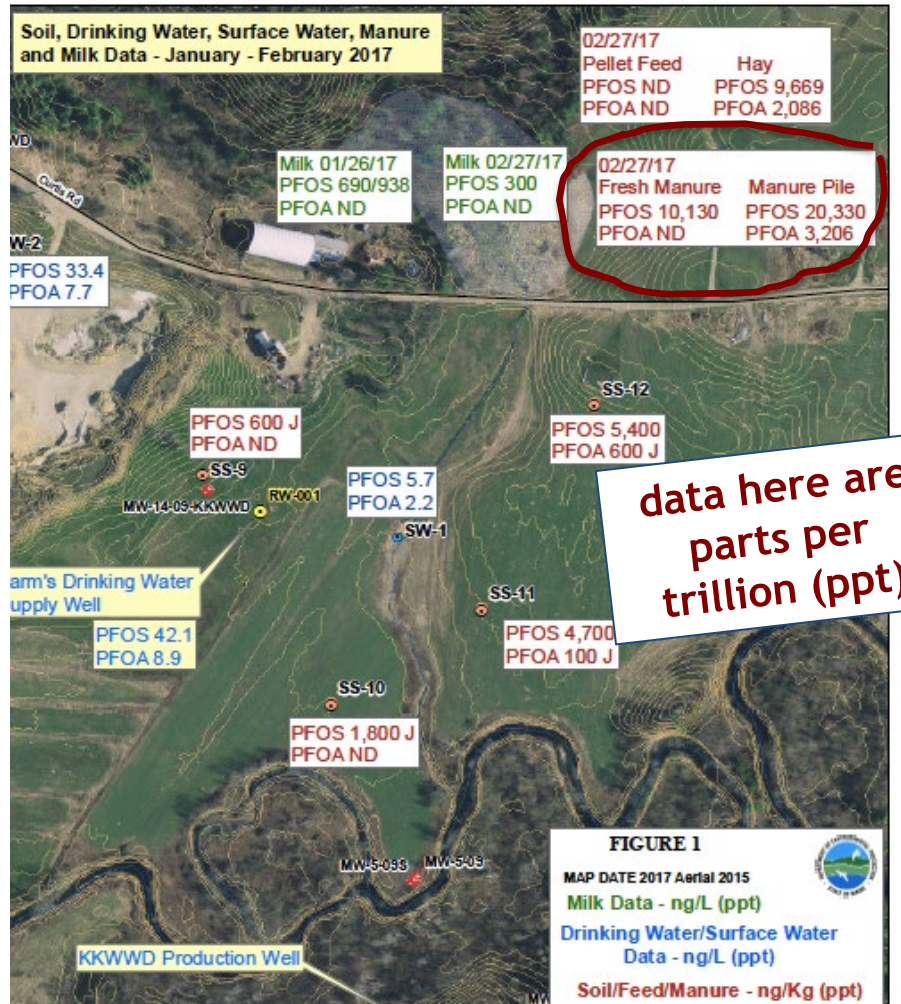
Only blending decreased PFAS loads due to dilution



(Kim Lazcano et al., 2019, *Water Environ. Res.*, doi:10.1002/wer.1174)

Current field data: PFAS in manure?

- Yes, where there are high soil levels from industrial sources
- Minimal data
- PFAS can cycle in manure - soil - (plant?) - cow system
- *Example:* industrially-impacted Maine farm with manure up to 20 ppb (see right →)



Current field data:

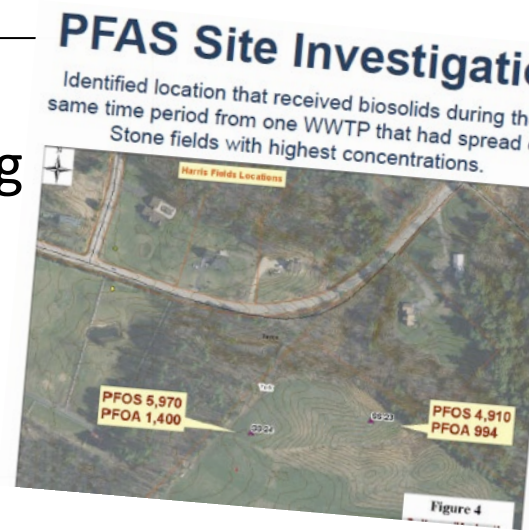
Biosolids-Amended Soil Sampling Data

Maine, 2019

29 fields, 1 sample each, multiple years of biosolids application
ug/kg (ppb)

Biosolids = typical, not-industrially impacted

	Mean	Maximum	Minimum	Screening
PFOA	3.06	12.90		1.05
2.5				
PFOS	8.76	20.90		2.13
5.2				



Current field data:

Industrially-impacted farms...Vermont

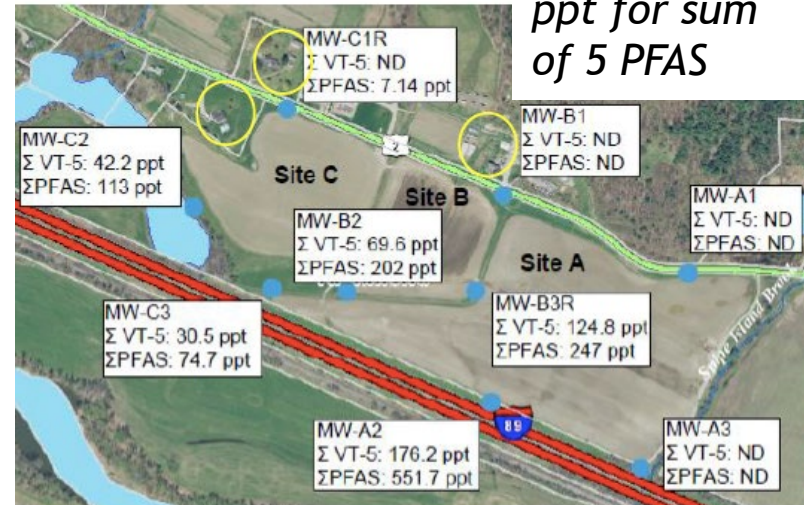
“Sewage sludge spreading leads to farm groundwater PFAS contamination:” (April 12, 2020)

<https://vtdigger.org/2020/04/12/sewage-sludge-spreading-leads-to-farm-groundwater-pfas-contamination/>

*Below:
long-term
septage land
application;
Vermont
groundwater
standard = 20
ppt for sum
of 5 PFAS*

But...

- Only a few long-term biosolids sites showed levels of potential concern.
- These levels are far lower than industrial & firefighting (e.g. max. of 176 ppt in data here →)
- No significant impacts on farm products
- Biosolids are “worst-case”; food waste composts have PFAS, just less.



Industrially-impacted farm... Wisconsin

- April 15, 2020: PFAS found in 7 of 98 drinking water wells near Marinette, WI where industrially-impacted biosolids were applied...
- But...
only 1 result is above EPA health advisory (70 ppt):
 - <https://www.wbay.com/content/news/More-wells-in-Marinette-County-test-positive-for-elevated-levels-of-PFAS--569683041.html>
Milwaukee Journal Sentinel:
<https://www.jsonline.com/story/news/local/wisconsin/2020/04/14/forever-chemicals-johnson-controls-ordered-deliver-more-homes/2989330001/>
Wisconsin Public Radio: <https://www.wpr.org/listen/1625136>
Wisconsin DNR info: <https://dnr.wi.gov/topic/Contaminants/Marinette.html>

Industrially-impacted farms... Maine **PFOS** - a legacy issue - is what stands out...

- **Maine Stoneridge Farm, 2017:**
 - Soil - PFOS stands out at high level, up to 878 ppb
 - Milk - 176 - 1,420 ppt (but PFOA = ND); likely from soil & manure ingestion
- **2nd Maine Farm, 2020:**
 - Soil - hundreds of ppb Hay - has PFOS in it or on it Corn - minimal
 - Milk - up to 32,000 ppt (!) - under investigation; likely from some industrial residual applied in the 1980s....

For comparison: New England farms using typical biosolids:

- Soil: <10 ppb PFOS
- Milk <100 ppt, compared to ME conservative standard of 210 ppb

But...
Maine
milk is
safe.

<https://www.maine.gov/dacf/ag/pfas/index.shtml>

PFAS Round Two Retail Milk Testing Results 2020, Vista Labs (ND= Not Detected)
Samples of Maine milk processed either: 1) in-state or 2) out-of-state (but sold in Maine)

Sample Number	Sample Date	State in Which Milk was Processed	PFOS Results with Reporting Limit at 25ng/L Method Detection Limit 5.04 ng/L	PFHxS Results with Reporting Limit at 25ng/L Method Detection Limit 5.92 ng/L	PFOA Results with Reporting Limit at 25ng/L Method Detection Limit 4.07 ng/L	8:2 FTS Results with Reporting Limit at 25ng/L Method Detection Limit 12.9 ng/L
1	2/10/2020	ME	10.1 J	21.3 J, Q	ND	ND
1-retest	4/01/2020		ND	ND	4.95 J	ND
2	2/10/2020	ME	10.8 J, Q	10.7 J	ND	ND
3	2/10/2020	ME	65.7 Q	ND	ND	ND
3-retest	4/01/2020		55.4	ND	6.06 J	22.6 J
4	2/10/2020	ME	ND	ND	ND	ND
5	2/10/2020	ME	5.55 J, Q	ND	ND	ND
6	2/11/2020	ME	ND	ND	ND	ND
7	2/10/2020	ME	11.9 J, Q	11.3 J	ND	ND
8	2/11/2020	ME	9.02 J, Q	9.50 J, Q	ND	ND
9	2/12/2020	ME	12.2 J, Q	11.0 J	ND	ND
10	2/10/2020	NY	ND	ND	ND	ND
11	2/10/2020	NH	ND	ND	ND	ND
12	2/10/2020	MA	ND	ND	ND	ND
13	2/10/2020	MA	26.7 Q	ND	ND	ND
13-retest	4/01/2020		24.6 J,Q	ND	ND	ND
14	2/11/2020	ME	ND	ND	ND	ND
15	2/11/2020	ME	ND	ND	ND	ND
16	2/10/2020	ME	8.72 J, Q	ND	ND	ND
17	2/10/2020	ME	ND	ND	ND	ND
18	2/18/2020	VA	ND	ND	6.27 J	ND
19	2/18/2020	VA	ND	10.9 J	5.55 J	ND
20	2/18/2020	NY	ND	11.6 J, Q	ND	ND

J Result qualified by the laboratory as detected below the laboratory reporting limit.

Q Results further qualified by the laboratory as not meeting laboratory analytical criterion.

Industrially-impacted biosolids - Michigan

MI showed how to efficiently address PFAS in biosolids.

- PFAS source control upstream of wastewater plants has reduced PFAS levels 90+% in biosolids.
- Smart focus on source control & pretreatment = biggest risk reduction for the cost.
- Collaborative effort of Michigan EGLE & MPART (ag dept.), et al.

NEBRA coverage:

<https://www.nebiosolids.org/michigan-shows-effective-approach-to-pfas-in-wastewater-biosolids>

Michigan EGLE:

https://www.michigan.gov/pfasresponse/0,9038,7-365-88059_91299---,00.html

Municipal WWTP	PFOS, Effluent (ppt, most recent**)	PFOS Reduction in Effluent (highest to most recent)	Actions Taken to Reduce PFOS
Ionia WWTP*	<14.96	99%	Treatment (GAC) at source (1)
Lapeer*	20	99%	Treatment (GAC) at source (1)
Wixom*	36	99%	Treatment (GAC) at source (1)
Howell	6	95%	Treatment (GAC/resin) at source (1)
Bronson*	13	96%	Treatment (GAC) at source (1)
Kalamazoo	3.1	92%	Treatment (GAC) at source (2), change water supply
K.I. Sawyer*	18	83%	Eliminated leak PFOS-containing fire-fighting foam
GLWA (Detroit)	5.7	62%	Treatment (GAC) at sources (8)
Belding	7.2	49%	Restricted landfill leachate quantity accepted

**as of October 15, 2019

*Effluent exceeds WQS of 12 ng/L or ppt

PFAS: Many unknowns; research ongoing.

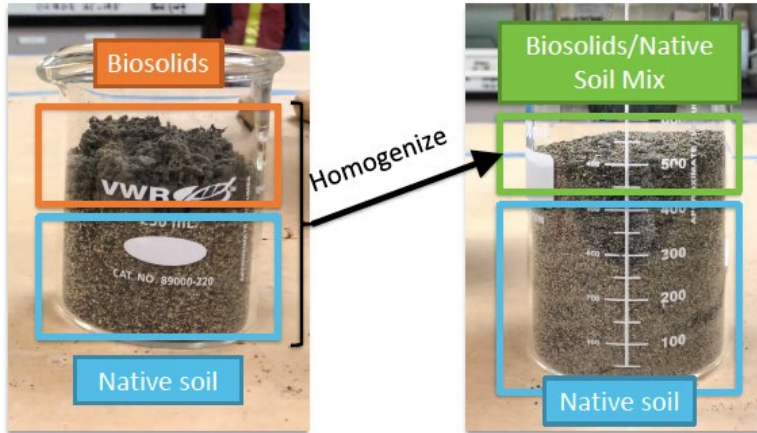
- Sampling requires care because of widespread use of PFAS.
- Formal EPA analytical methods still in development for solids, soils, & dirty water.
- Uncertain:
 - Plant uptake: not likely in corn; maybe in grass?
Seems minimal in vegetables
 - Fate in soil: long-chain PFAS migrate less than short-chain
 - Precursors play important role & evolve over time
- Certain:
 - Exposure for most of us is through use of consumer products (e.g. food packaging, raingear, etc.)
 - FDA testing shows little current concern for overall food quality.
 - Concern if drinking water and food are contaminated at high levels because of nearby industry or fire-fighting activity, etc.



Water Research Foundation Project #5042 (CDM Smith, Purdue)

Assessing PFAS Release from Finished Biosolids

Test Setup Weathering in field-aged mesocosms



Biosolids added at a rate of 3% by mass to the top 1/3 of the mesocosm

- 6-month study (4/27-10/20)
- 7 biosolids
- 140 to 450 $\mu\text{g}/\text{kg}$ PFAS
- 28 pore volumes passed
- Leached PFAS concentrations varied
- Precursor transformation evident

**Decreasing polyfluoroalkyl substances (PFAS) in municipal wastewater effluent
and minimizing release from land-applied biosolids**

L.S. Lee (PI, Purdue), J. Judy (co-PI, UF) & B. Chaplin (co-PI, UI-Chicago)

Overarching Goals (6 Objectives)

Goal 1 (Objectives 1-3):

Reduce PFAS loads in the Water Resource & Recovery Facilities (WRRFs) by treating PFAS in the landfill leachate entering the WRRF and in the centrate that gets returned to the basins within the WRRF, which will also reduce PFAS loads in the subsequent biosolids.

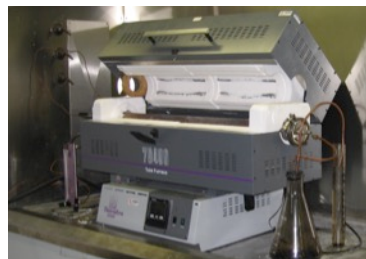
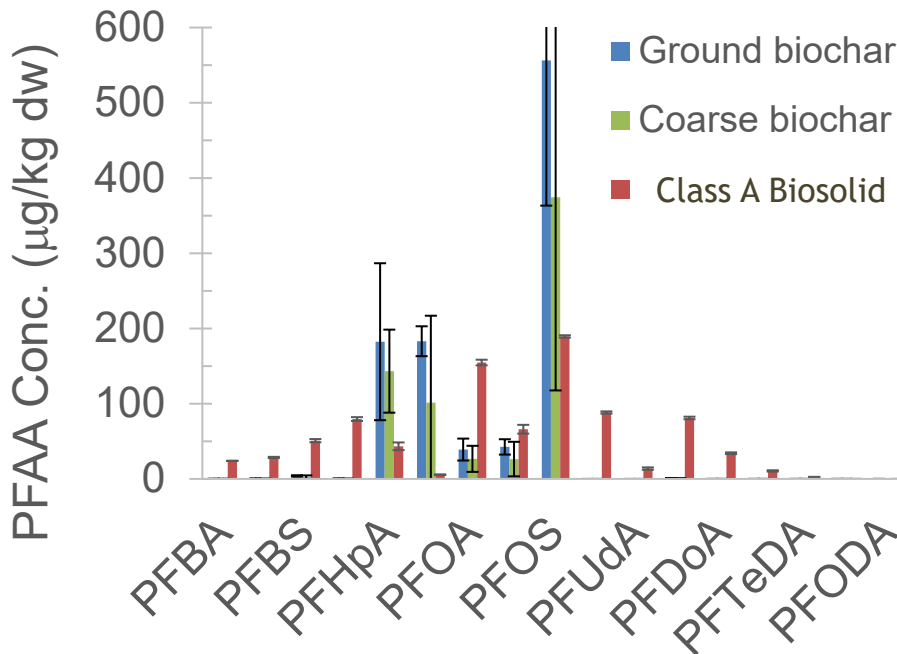
Goal 2 (Objectives 4-6):

Simultaneously protect the beneficial use of biosolids and water quality by reducing the mobility of PFAS that may be present in biosolids

- Anaerobic digestion train: 2-2.5 time increase in typically quantified PFA
- Anerobic thermophilic digestion train: ~5 times increase
- Pyrolyzed biosolids reduce PFAS leaching

Low Temperature (350 °C, Low O₂) Pyrolysis of Biosolids (Obj. 5)

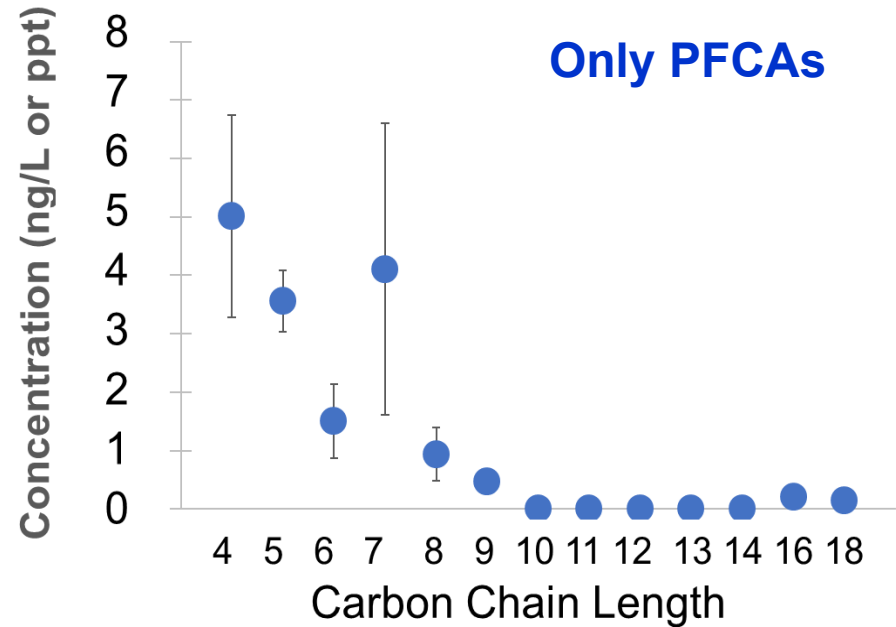
- Pyrolysis leads to volume & mass reduction
- Grinding material affects extraction efficiency
- Most PFAAs concentrations decreased with pyrolysis
- PFAA loss could be due to volatilization, thus may be in the syngas/oil product
- Apparent increases or negligible change for some PFAAs may be due to PFAA precursor breakdown or mass reduction greater than volatile losses



Pyrolysis done by Dr. Wei Zheng
Illinois Sustainable Technology Center
University of Illinois at Urbana-Champaign

PFAA Release to Porewater Reduced After Low Temperature (350 °C, Low O₂) Pyrolysis (Obj. 5)

- Only PFCAs observed in porewater
- [PFCA] < 7 ppt)
- In the untreated Class A biosolid, PFAA porewater concentrations ranged from 6 to 1200 ppt
- Pyrolysis reduced leaching of PFAAs even if totals on a mass basis increased
- Next steps - evaluate sorptive capability of biochar for potential mixing with untreated biosolids



Evaluating PFAS Occurrence and Fate in Rural Water Supplies and Agricultural Operations to Inform Management Strategies (R840082) Lead at Purdue University

L.S. Lee (PI, Purdue), H. Preisendanz (co-PI, PSU) & Kurt Pennell (co-PI, Brown University)

Overarching Goal

To address key data gaps in our understanding of the occurrence and fate of PFAS in rural landscapes and agricultural operations and their impacts on rural water supplies and agricultural products.

Overall Approach

- We propose a combination of synergistic field, laboratory and modeling activities.
- We will survey rural water supplies for PFAS in PA, IN, and VA and evaluate data available from other states where plausible to better understand sources to rural waters.

https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/recipients.display/rfa_id/658/records_per_page/ALL

**Where are we on regulations
being imposed on biosolids?**

**What is the best mitigation
strategy?**

Given PFAS are 'Forever' Chemicals, shouldn't we just ban PFAS-containing materials from land-application or stream discharge?

- Banning land application places a **heavy burden on public municipalities**
- Banning could lead to numerous **unintended consequences**
- **Control sources** contributing to PFAA levels in biosolids (e.g., pretreatment of influent from industry or landfills with *high* PFAA levels)
- Focus on **regulating nonessential uses** of PFAS & **ban them from use in food packaging, carpets, etc.** This will go a long way to reducing PFAS loads in municipal wastes including biosolids.



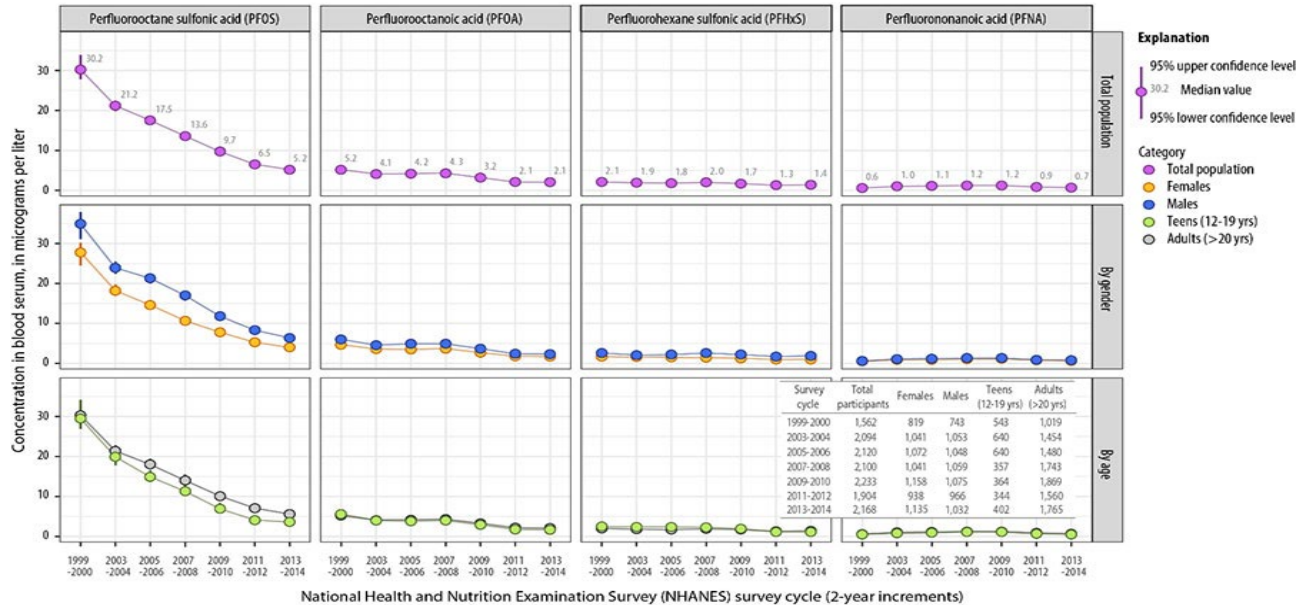
+



Phase out use of most-concerning PFAS.

EPA facilitated the most significant reduction of risk, phasing out PFOA & PFOS → blood serum levels reduced 70%.

Median concentration of selected per- and polyfluoroalkyl substances (PFAS) in blood serum (1999-2014) in the United States



<https://www.atsdr.cdc.gov/pfas/pfas-blood-testing.html>

Data source: Centers for Disease Control and Prevention. Fourth Report on Human Exposure to Environmental Chemicals, Updated Tables, (January 2017). Atlanta, GA: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention. <https://www.cdc.gov/exposurereport/>.
 Note: In January 2006, the eight major PFAS manufacturing companies in the U.S. voluntarily committed to a 95% reduction of emissions and product content for PFOA and selected related PFAS species by 2010 and a complete elimination of these chemicals from emissions and products by 2015 (USEPA, 2010/2015 PFOA Stewardship Program). The major US producer of PFOS phased out production of PFOS precursors by 2002 (Prevedouros et al. ES&T 2006, 40:32-44).



Thank you.



Agronomy

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PFAS & Biosolids: <https://www.nebiosolids.org/pfas-biosolids>

Includes “PFAS and Biosolids and Septage on NE Farms”
Click to lit. review on PFAS in Agriculture at bottom of page.

Summary article in *Country Folks*:
<https://countryfolks.com/pfas-and-agriculture-what-it-means/>

“We can never get to zero...”
<https://www.wastedive.com/news/pfas-chemicals-organics-recycling-compost-biosolids/587044/>



Biosolids
compost for my
raspberries...
I still use it,
knowing it has
PFAS in it. I
believe the
benefits
outweigh risks :)

Acknowledgements & Sources of NEBRA PFAS slides

Inclusion on this list does not imply endorsement.

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