PFAS Characteristics, Fate and Challenges in Waste Management

Linda S Lee

Agronomy

Environmental & Ecological Engineering

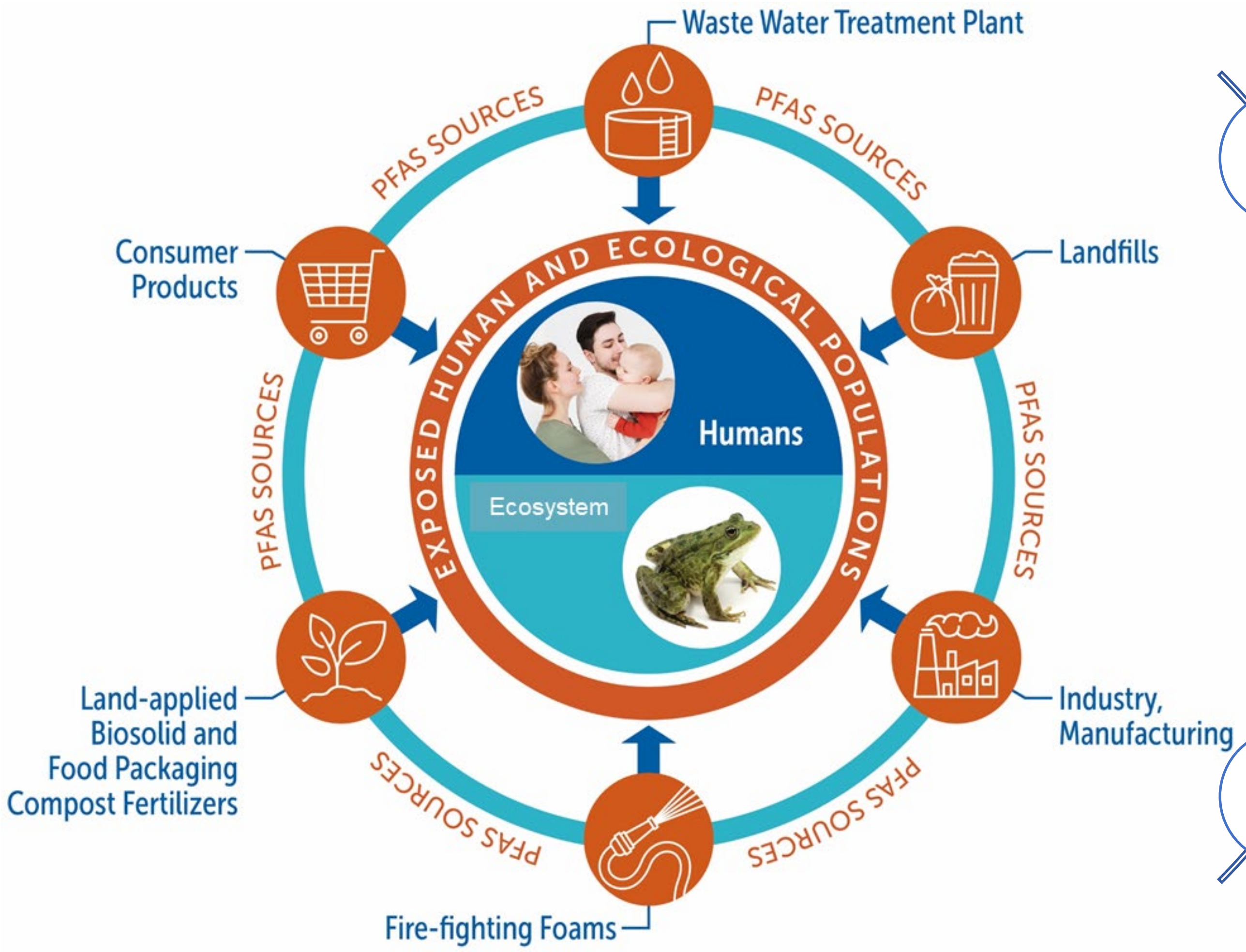
Interdisciplinary Ecological Sciences & Engineering Graduate Program

PURDUE UNIVERSITY®

2021 Emerging Contaminants in the Environment Conference

April 27-28, 2021

PFAS Characteristics, Fate and Challenges in Waste Management



Today

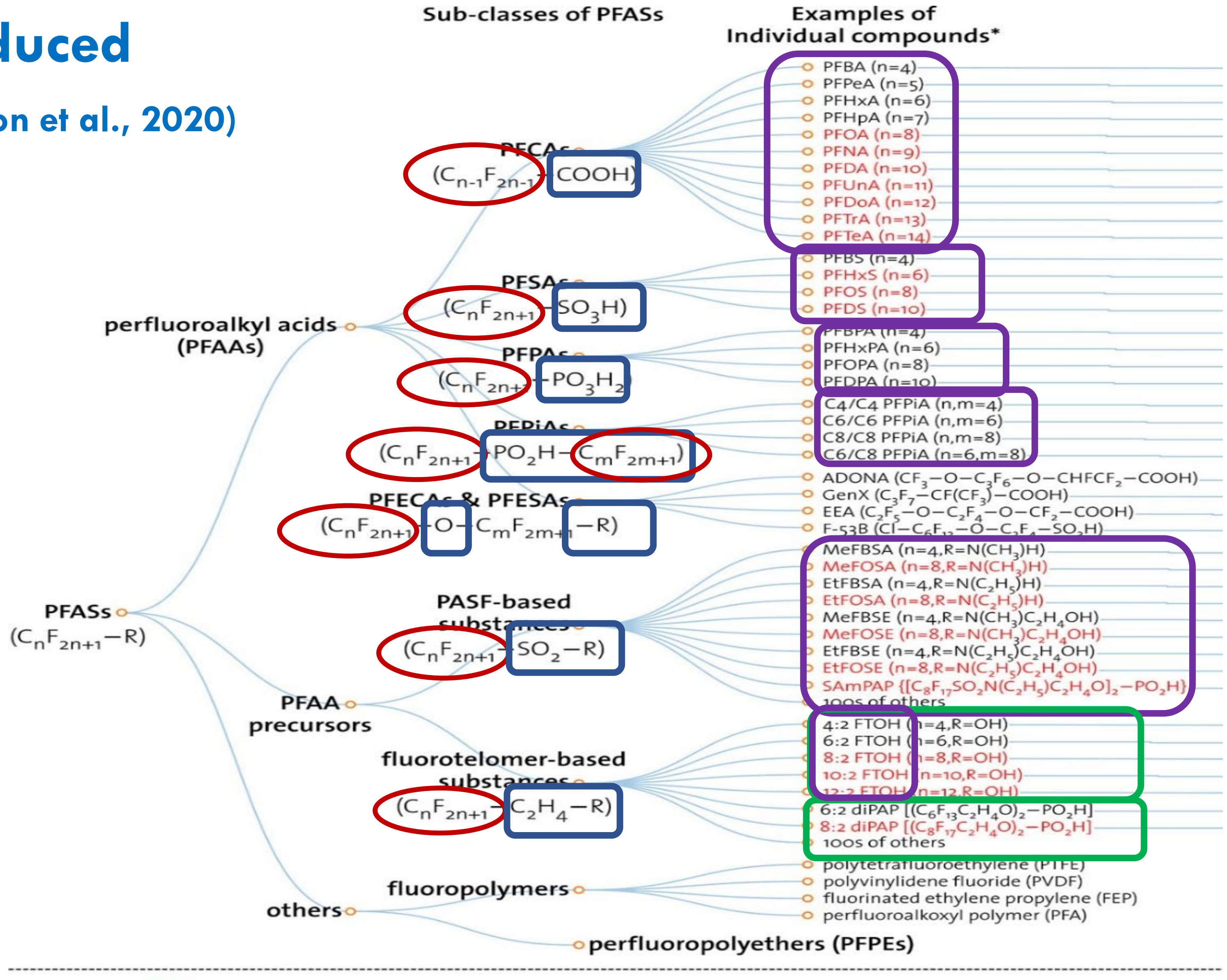
- A few PFAS basics
- Waste-based soil amendments
- Guidance levels
- Biosolids treatment
- Perspective and path forward

What are PFAS - Per and Polyfluoroalkyl substances?

Currently > 4,800 PFAS produced

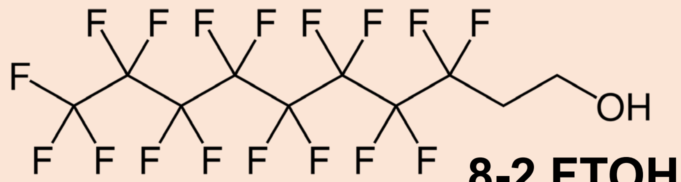
New estimate: >7000* PFAS (*Johnson et al., 2020)

- All have at least one 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!

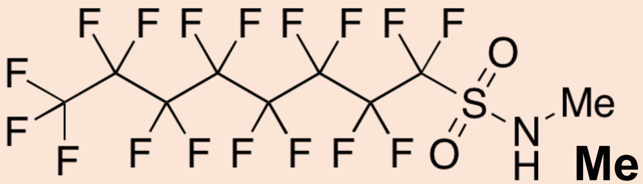
PFAS telomer example



8-2 FTOH

Intermediates

Electrochemical PFAS example



MeFOSA

Intermediates

2 are on the EPA '24' List

Precursors

Multiple steps & pathways

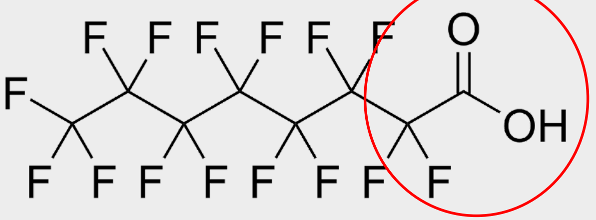
PFAAs

Persistent

Anionic (-), low pK_a

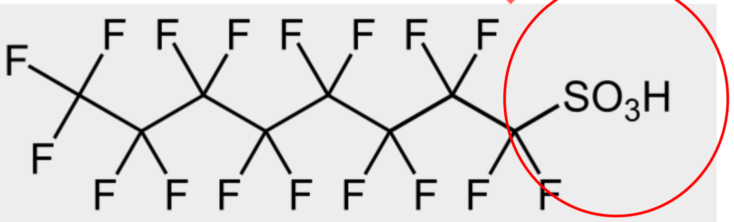
More soluble

More mobile



PFOA C8 + *other PFCAs*

Perfluorooctanoic acid



PFOS C8

Perfluorooctane sulfonic acid

- Perfluoroalkyl carboxylic acid (**PFCA**)
- Perfluoroalkyl sulfonic acid (**PFSA**)

Terminal microbial metabolites: PFCAs + PFSAs = Perfluoroalkyl acids (PFAAs)

Fluorotelomer-based Precursors to Terminal PFAAs

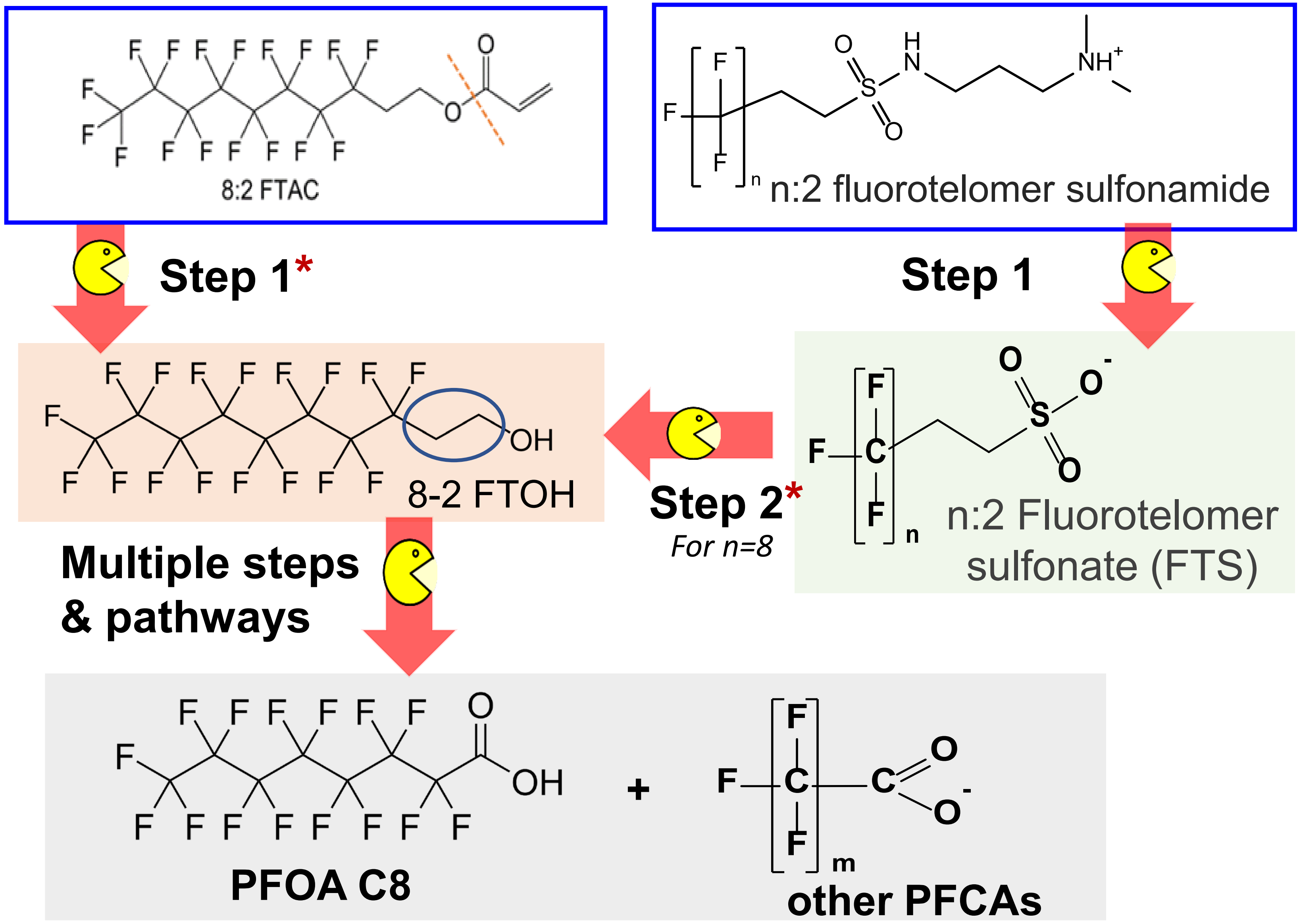
Two examples:

- Rate limiting step varies

- FTOHs have short aerobic half-lives (≤ few days)
- FTS half-lives vary greatly

- PFCA production is high, e.g., up to 40 mol% PFOA yield (plus other PFCAs)

* *rate-limiting step*



Managing PFAS
Wastewater and biosolids Management

PFAS input, multiple sources

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

Wastewater Influent → PFAS* Sorption to Sludge → Effluent* discharge to streams or for irrigation

PFAS* Sorption to Sludge → Biosolids* → Land-application as a soil amendment *aerobic processes*

Treatment process with type and treatment stage

PFAS $t_{1/2}$: anaerobic $\ll$ aerobic

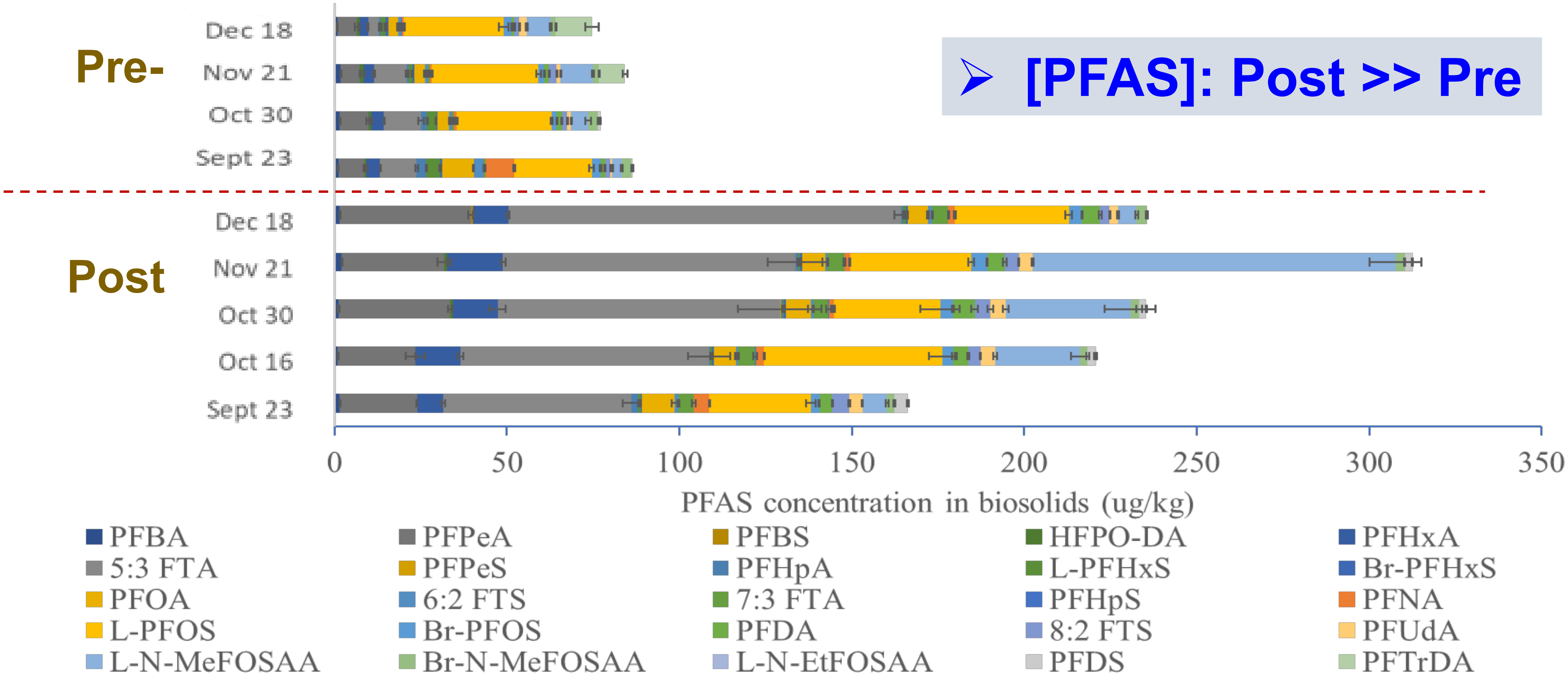
(Not mineralization but PFAS to other FCAS)

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

Biosolids and Biosolid-based Products are not all the Same

- **Production practices vary by utility and if Class A or Class B biosolids**:
  - Aerobic vs anaerobic
  - Temperatures
  - Cycling times
  - Feed composition
  - Microbial populations, etc.
- **Biosolids properties vary and may affect PFAS release**:
  - Moisture content aqueous slurries to moist solids to pellets)
  - 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) and ionic composition
  - % OM (e.g., 17-41%); *Protein content*
  - Polymer additions in the treatment process

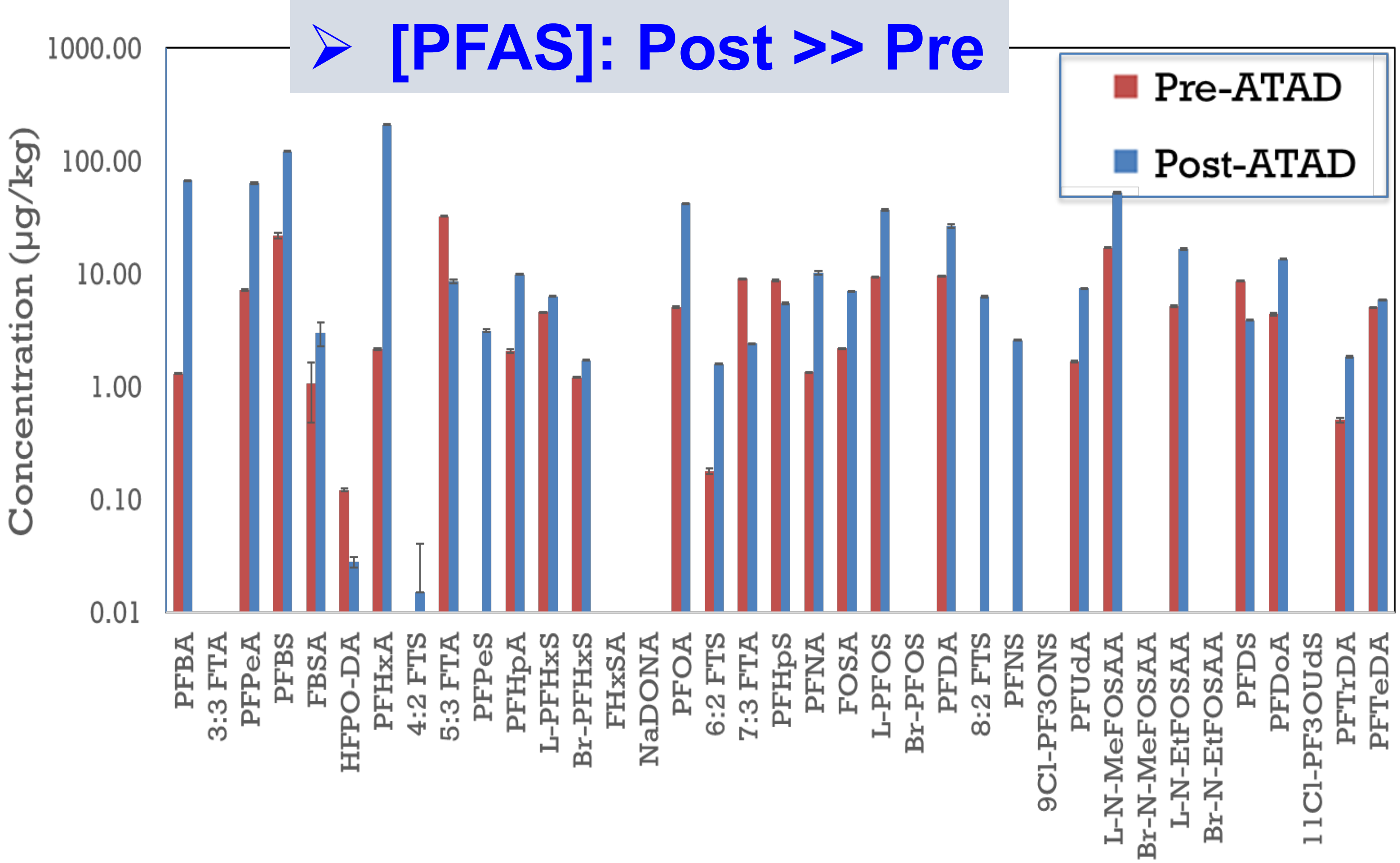
Pre and Post a Typical Anaerobic Treatment Process



➢ [PFAS]: Post >> Pre

- PFAAs increased x ~2.5
- Microbial metabolites 7:3 FTCA ~14x↑, 5:3 FTCA~10x↑
- 6:2 FTS decreased
- Mass reduction ~ 48%

Pre & Post an Autothermal Aerobic Digestion (ATAD) Process



Chain	ATAD	ΣPFCAs (µg/kg)	ΣPFSAs (µg/kg)
Short	Pre	10.7	26.4
	Post	340	132
Long	Pre	10.7	26.4
	Post	110	48.6

Pre vs Post*

- Short PFCAs ~33 x ↑
- Long PFCAs: ~10 x ↑
- Short PFSAs ~5 x ↑
- Long PFSAs: ~2 x ↑

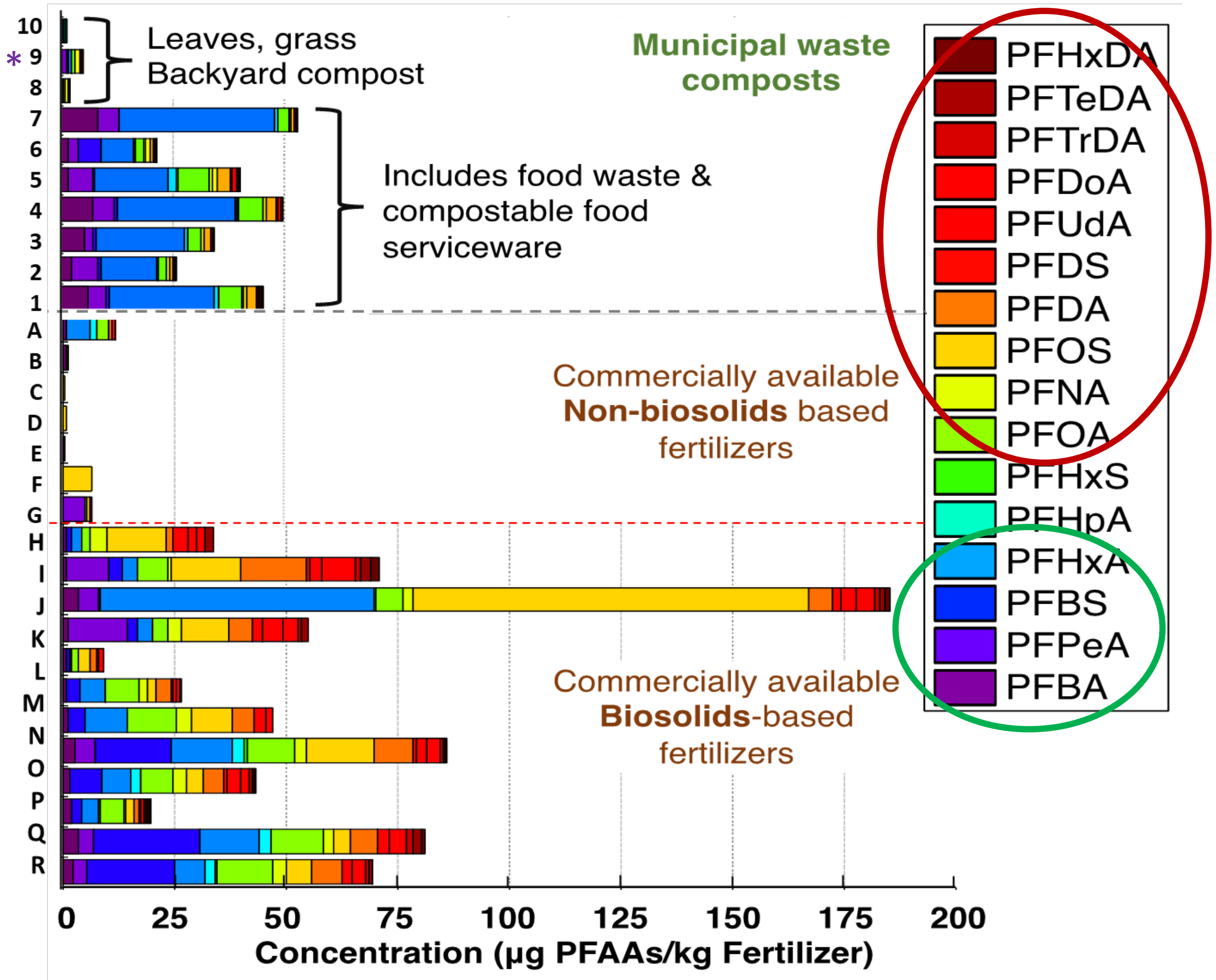
* ***Mass reduction*** *accounts for a ~2-fold concentration*

- Quantifiable PFAS concentrations increase due to precursor breakdown
- Higher transformation in aerobic vs anaerobic treatment

General Analytical Approach for PFAS Evaluations

- **Extraction of solids with addition of mass-labeled surrogates**
- **Targeted PFAS quantification –** initial work focused on 17 PFAAs
  - 13 PFCAs (C4 to C18): $CF_3(CF_2)_nCOOH$
  - 4 PFSAs (C4, 6, 8,10): $CF_3(CF_2)_nSO_3^-$)
  - Subsequent work included up to 60 PFAS
- **Evaluate the presence of precursors**
  - Total oxidizable precursor (TOP) assay
  - Suspect and nontarget screening of other PFAS
- **Evaluate PFAS release to porewater**

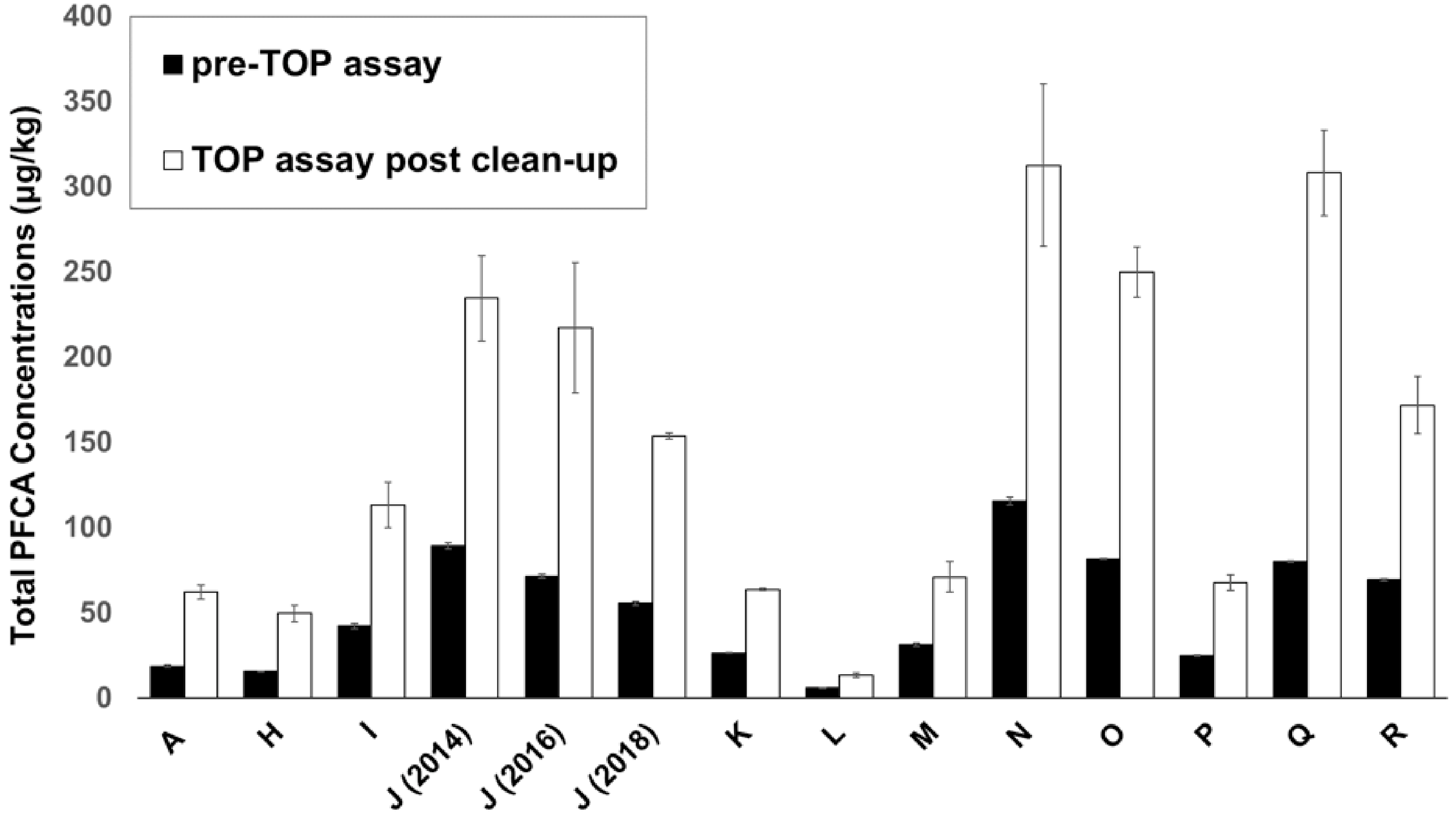
PFAA Occurrence in Biosolids-based Products and Municipal Composts



- Higher PFAA loads in biosolids-based products
- Biosolid-based products: 30-185 μg/kg
- $CF_n \geq 6$ (long-chain) dominant in 2014 biosolid-based products
- $CF_n \leq 6$ (short chain) 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.

Choi, Lee et al. *ES&T Letters*, 6 (6):372–377 https://doi.org/10.1021/acs.estlett.9b00280
Kim-Lazcano, Lee et al. *ES&T* 54(14):8640-8648. https://doi.org/10.1021/acs.est.9b07281

What about other PFAS - *hidden* PFAA sources?
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

- TOP assay can reveal additional PFAA sources
- Largest increase observed in TOP assay was for *PFHxA (not necessarily 1:1 precursor to PFAA)*

Total Oxidizable Precursor (TOP) Assay
One semi-quantitative approach:

Houtz and Sedlak (2012) ES&T, 46:9342-9349

- TOP assay assumes ALL precursors degrade to PFCAs; conversion efficiency varies
- Electrochemical fluorination (ECF) precursors degrade to a single PFCA
- Fluorotelomers degrade to multiple PFCAs at the same time
- TOP assay still needs investigation/optimization, but still useful for exploring precursor abundance
- Does not account for precursors that were not extracted

starting precursor compound	Δ[PFBA]/[precursor]$_0$	Δ[PFPeA]/[precursor]$_0$	Δ[PFHxA]/[precursor]$_0$	Δ[PFHpA]/[precursor]$_0$	Δ[PFOA]/[precursor]$_0$	Δ[PFNA]/[precursor]$_0$
N-EtFOSAA ($n = 7$)					92% ± 4%	
N-MeFOSAA ($n = 8$)					110% ± 8%	
FOSA ($n = 8$)					97% ± 3%	
6:2 FtS ($n = 8$)	22% ± 5%	27% ± 2%	22% ± 2%	2% ± 1%		
8:2 FtS ($n = 9$)	11% ± 4%	12% ± 4%	19% ± 3%	27% ± 3%	21% ± 2%	3% ± 0.1%
6:2 diPAP[b] ($n = 6$)	27% ± 3%	47% ± 3%	33% ± 2%	15% ± 3%		
8:2 diPAP[b] ($n = 6$)	10% ± 2%	17% ± 1%	24% ± 1%	43% ± 2%	38% ± 2%	13% ± 1%

At unadjusted pH, pH quickly becomes acidic (< 3) and can lead to complete mineralization of PFCAs but NOT PFSAs

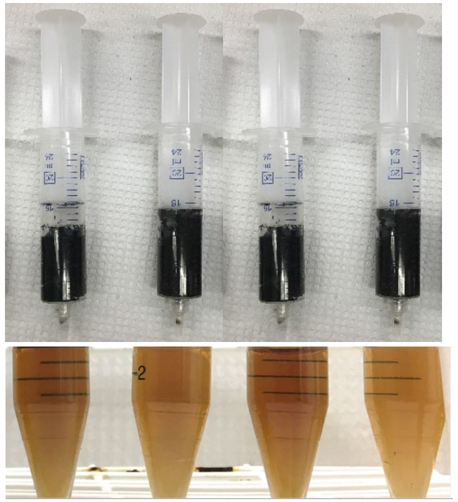
Suspect Screening for Precursors (QToF/MS)

- Precursors in **2014 biosolid-based products & Municipal Composts**
  - 3 sulfonamide-containing PFAS (EtFOSAA, FOSA and FOSAA)*
  - 6:2 and 8:2 FTS*
  - diPAPs (6:2/6:2, 6:2/8:2,8:2/8:2, 8:2/10:2) **

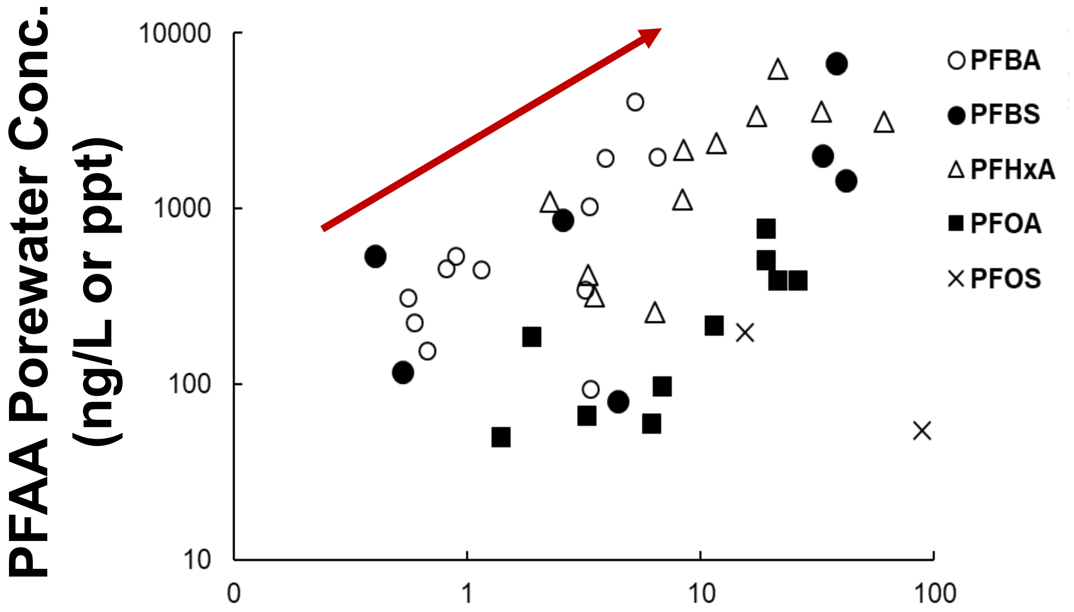
*	***Level 1: Confirmed structure*** by reference standard	MS, MS^2, RT, Reference Std.
**	***Level 2: Probable structure*** a) by library spectrum match b) by diagnostic evidence	MS, MS^2, Library MS^2 MS, MS^2, Exp. data

Confidence Levels 1-5: Schymanski et al. (2014) *EST*

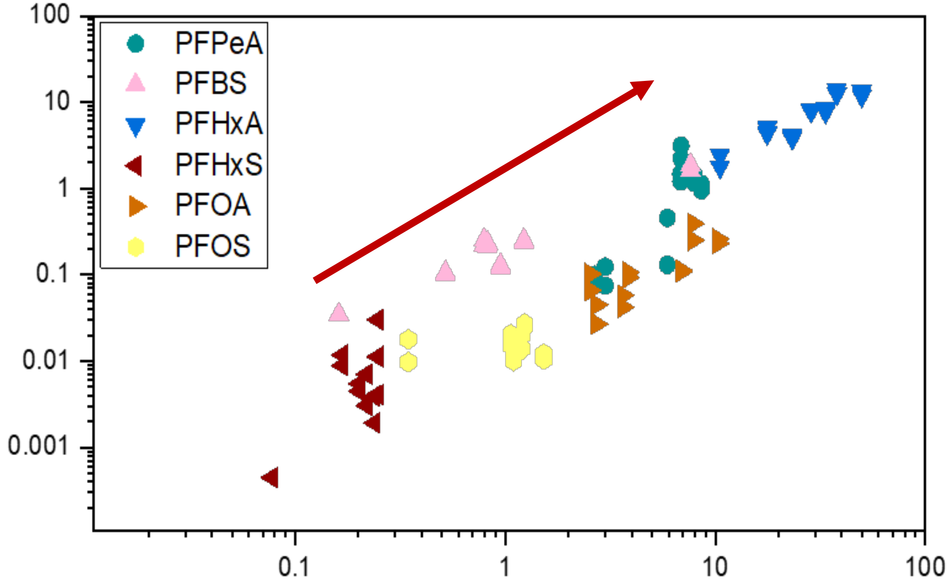
Release to porewater (leachability) from saturated media: Exemplified for a subset of PFAA Pore-water Concentrations



Biosolids-based Composts



OFMSW Composts



PFAA Conc. (μg/kg or ppb) in the Product

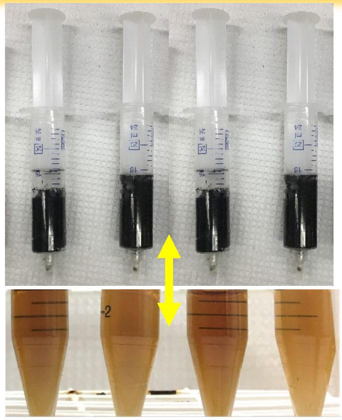
- Overall trend: increasing PFAA ‘release’ concentrations with increasing PFAA loads in the products regardless of source.
- While some PFAA pore-water concentrations **>>** regulatory or provisional guidance levels, PFAAs will be ***diluted*** and ***attenuated*** depending on the application site characteristics, management and chain length.

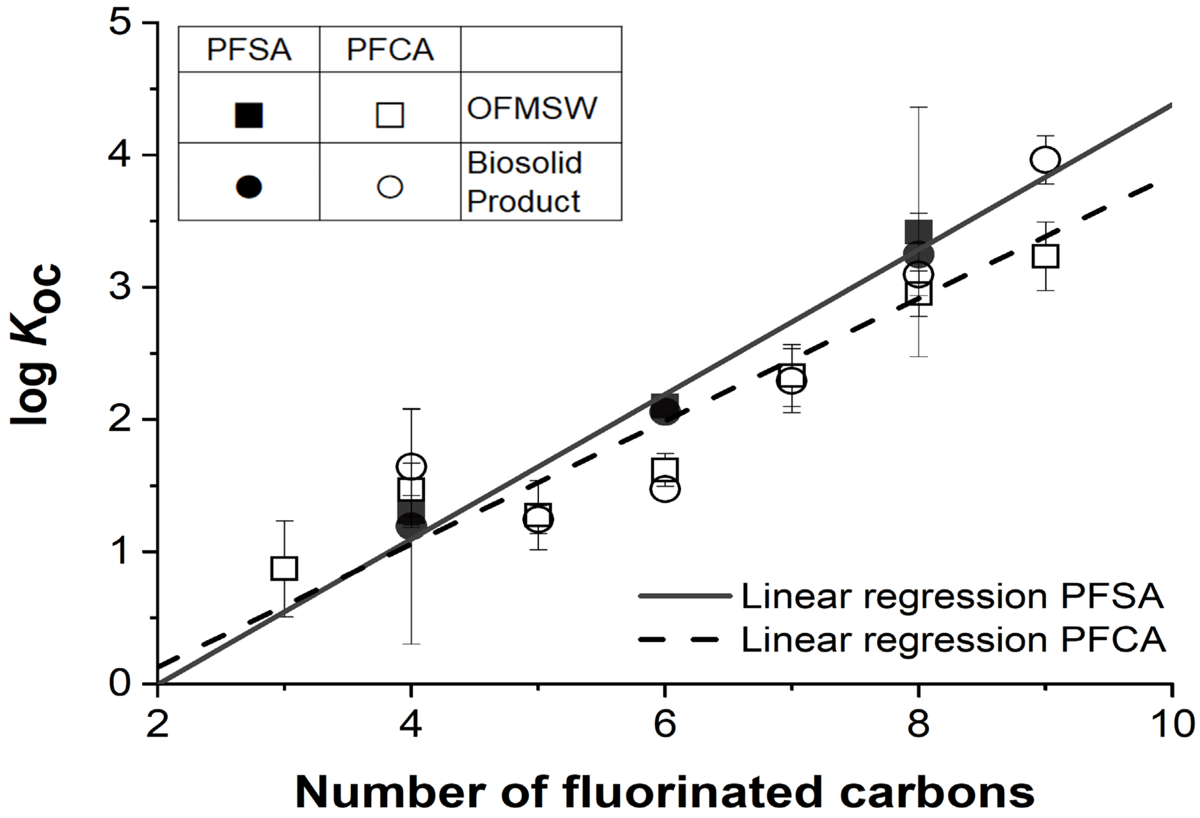
Biosolids and Biosolid-based Products are not all the Same

- **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*)

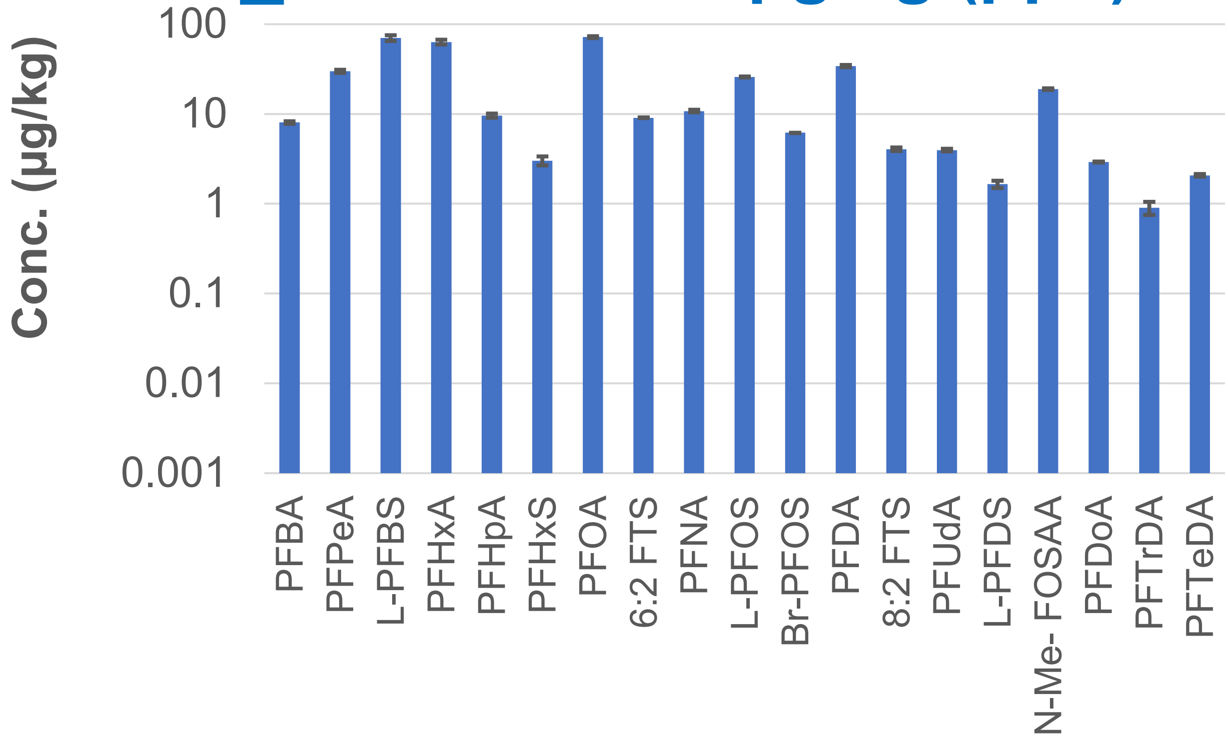


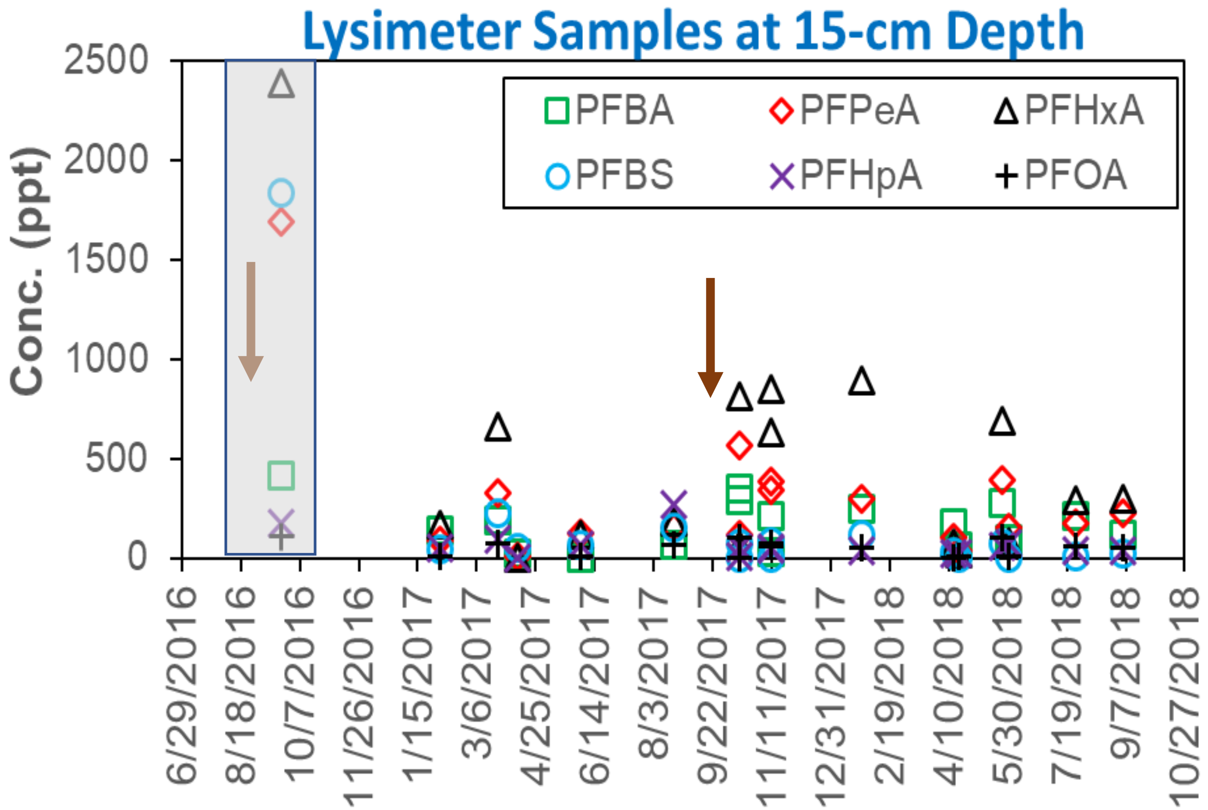


- *K_{oc}* strongly correlated to PFAA chain length and similar for all organic-based amendments
- Slope for PFSAs *slightly higher* even on a CF_2 basis versus chain length
- *K_{oc}* values have NOT proven adequate for PFAA soil-water partitioning across soils (OC in soils < compared to OC in biosolids)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

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

∑PFAS 376 ± 7 µg/kg (ppb)

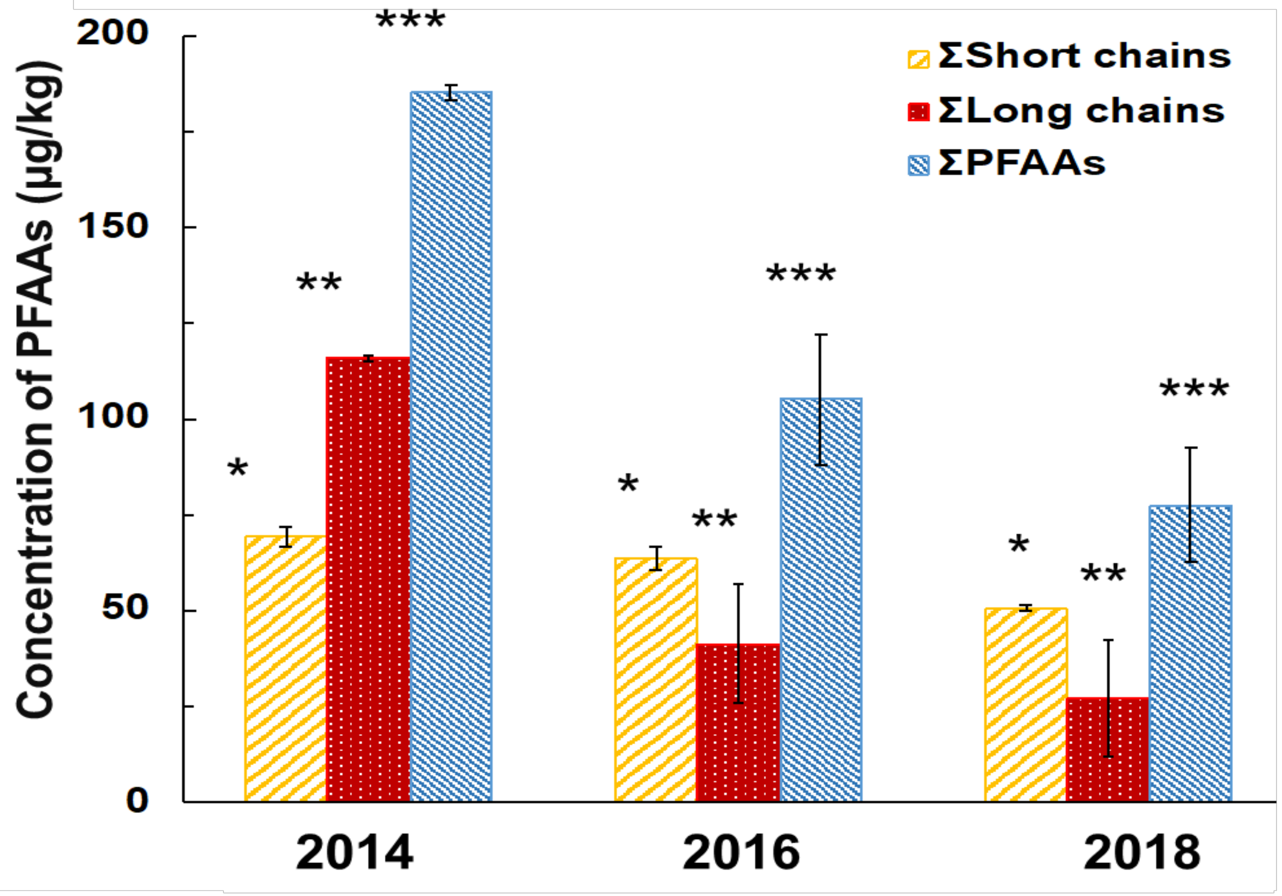




- High concentration in first ≥ 2.5 cm rain event likely due to new site establishment period *(and in the range predicted by our pore-water assay correlations – considering load and OM)*
- Leaching mostly short chains (C4-C6); also generally present at higher conc. in the biosolids
- *Remember,* significant dilution and attenuation will occur prior to reaching groundwater

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

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



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

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

From 2014 to 2018:

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

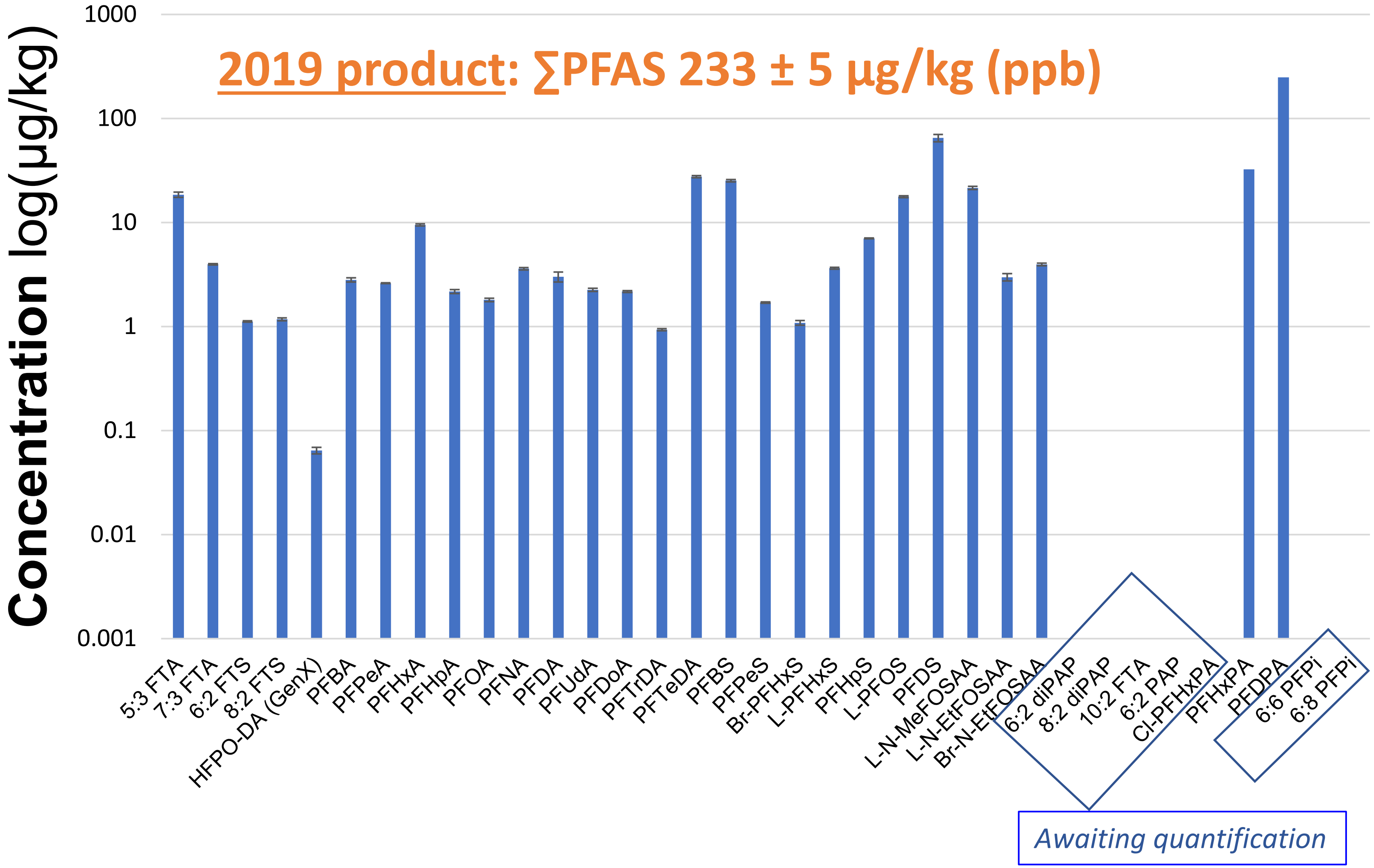
- Differences may be due to variation in inputs and possibly process
- *Note: Only 17 PFAAs were analyzed.*

Kim-Lazcano, Lee et al. *ES&T* 54(14):8640-8648.
https://doi.org/10.1021/acs.est.9b07281

Temporal Trends May Vary *(Example 2: PFAS Increasing)*

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

2014 ∑17 PFAAs 35 µg/kg VS **2019 ∑17 PFAAs 210 µg/kg**



- ∑PFAAs: 2014 << 2019
- TOP Assay & Nontarget screening revealed additional PFAS in 2014 product, but estimated ∑PFAS still << 2019 product
- Some difference may be due to improved extraction procedure
- Most differences like due to variation in inputs to the WWTP

PFAS Content in 2019 Biosolids

	2019 Biosolids (n=9) µg/kg	Maine Guidelines µg/kg
Total PFAS	190 - 870	
PFOA	3.3 - 26.6 (9.95)*	2.5
PFOS	5.2 – 127 (59.3)*	5.2
PFBS	9.9 – 131 (51.2)*	1900

* Average

- Despite regional, size, property, and process differences among the utilities and biosolids, total PFAS concentrations fall within a relatively narrow concentration interval although specific PFAS vary over 1-2 orders of magnitude
- All would fail to meet Maine guidelines

Example PFAS Concentration Ranges (μg/kg)

	PFAS	~Min	~Max
PFAAs (terminal metabolites)	PFOS	5	130
	PFHxS	5	50
	PFOA	3	30
	PFHxA	5	30
PFAA precursors but also intermediates from other precursors	6:2 FTS	1	15
	8:2 FTS	1	30
	MeFOSAA	10	100
	EtFOSAA	1	50
	7:3 FTCA	10	40
	5:3 FTCA	0	220

Some Additional Precursors

PFAS	~Min	~Max
6:2 diPAP	13	400
8:2 diPAP	0	200
6:2 PAP	23	340
6:6 PFPI	0	2
6:8 PFPI	0	3

- For most utilities, identified precursors are a substantial fraction (up to ~50%) of the overall PFAS fluorine mole balance
- **Larger precursors that are not extracted are also likely present**

State Reactions to Acceptable PFAS Levels Vary Greatly

- Michigan (drinking water)
  - 8 ppt PFOA, 6 ppt PFNA, 16 ppt PFOS, 51 ppt PFHxS, 420 PFBS, 370 ppt GenX, 400,000 PFHxA for dw
- Maine & Vermont (groundwater)
  - 20 ppt total of 5 or 6 PFAS (PFNA, PFOA, PFOS, PFHpA, PFHxS (plus PFDA in MA)
- California (drinking water notifications)
  - 5.1 ppt PFOA and 6.2 ppt PFOS
- *compared to* Canada
  - 200 ppt PFOA, 600 ppt PFOS

State Reactions Vary Greatly

- Michigan (drinking water)
  - 8 ppt PFOA, 6 ppt PFNA, 16 ppt PFOS, 51 ppt PFHxS, 420 PFBS, 370 ppt GenX, 400,000 PFHxA for dw
- Maine & Vermont (groundwater)
  - 20 ppt total of 5 or 6 PFAS (PFNA, PFOA, PFOS, PFHpA, PFHxS (plus PFDA in MA)
- California (drinking water notifications)
  - 5.1 ppt PFOA and 6.2 ppt PFOS
- *compared to* Canada
  - 200 ppt PFOA, 600 ppt PFOS

State reactions to acceptable PFAS levels biosolids and soils led by drinking water guidance

- Alaska, 2016
  - Proposed migration-to-groundwater soil cleanup levels:

    PFOA: 1.7 μg/kg (ppb)

    PFOS: 3 μg/kg

- New York DEC interim preliminary screening level for one specific permit:

    PFOA + PFOS: 72 μg/kg

Typical biosolids *can* meet this.

- Maine - sludge/biosolids program licensees and sludge/biosolids composting facilities

    PFOA: 2.5 μg/kg

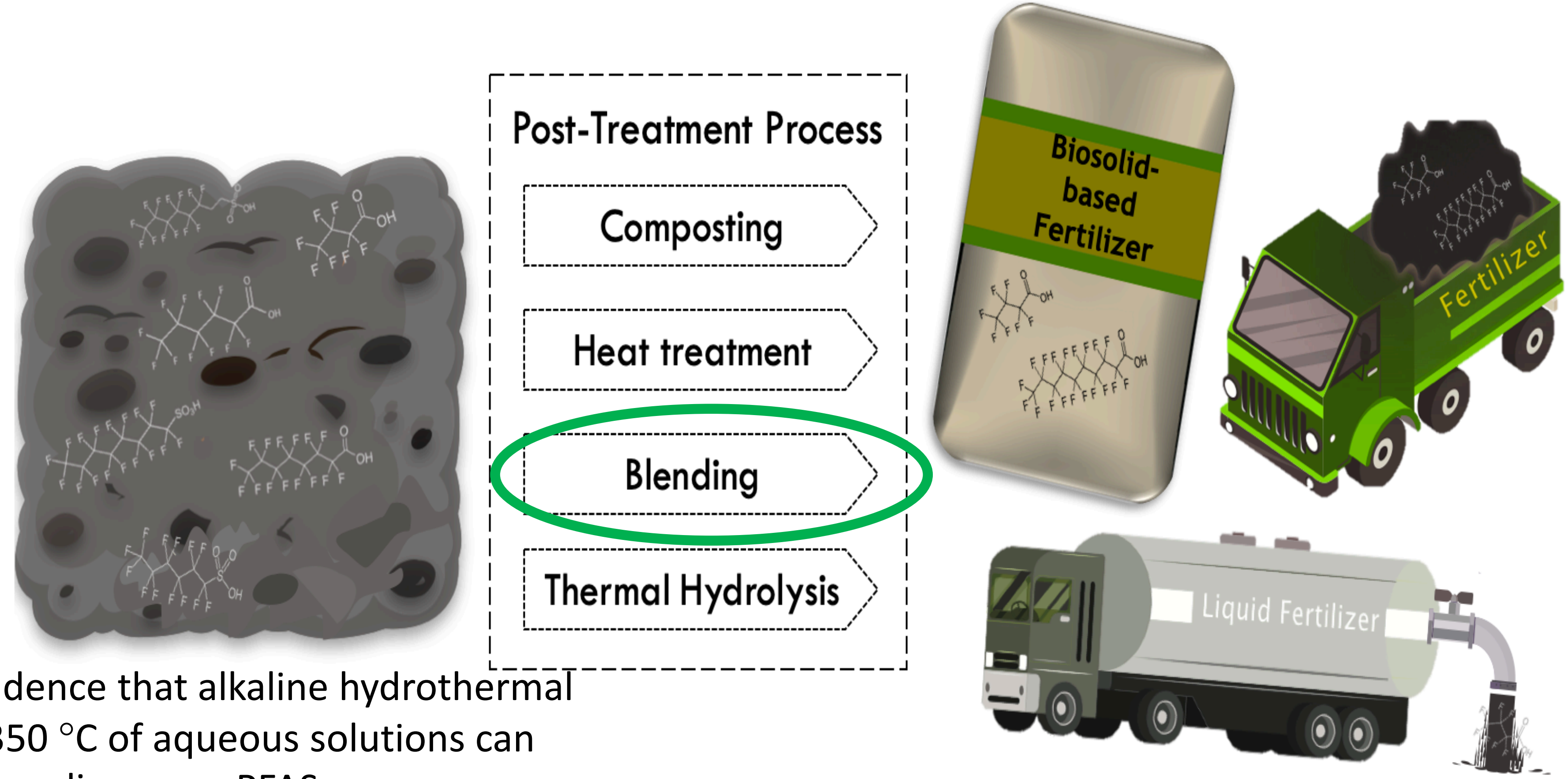
    PFOS: 5.2 μg/kg

    PFBS: 1900 μg/kg

Typical biosolids and even municipal solid waste composts *frequently will not* meet these levels.

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

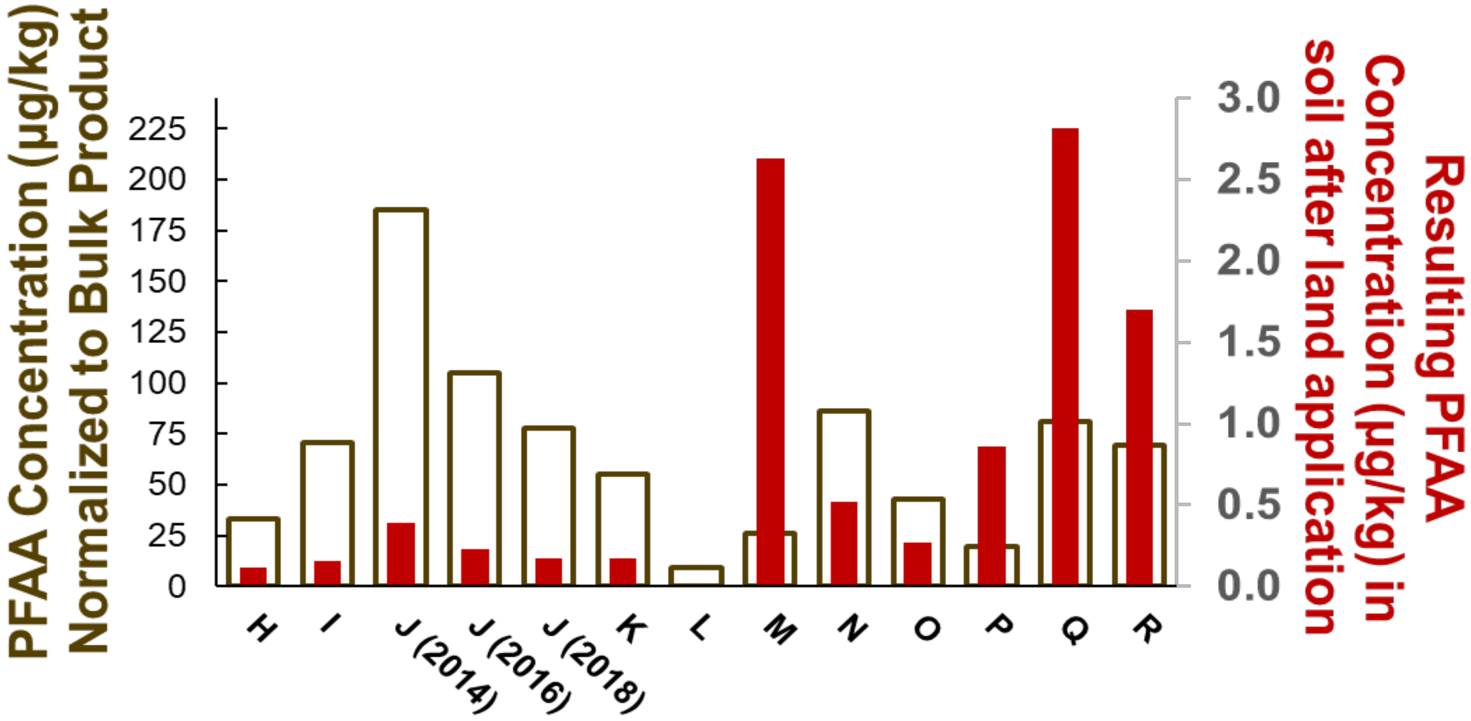


Note: There is evidence that alkaline hydrothermal reactions at ≥ 350 °C of aqueous solutions can mineralize some PFAS.
(Wu, Strathmann et al. 2019. ES&T Let. 6:630–636)

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

Putting PFAA in Biosolids in Perspective *(Example)*

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



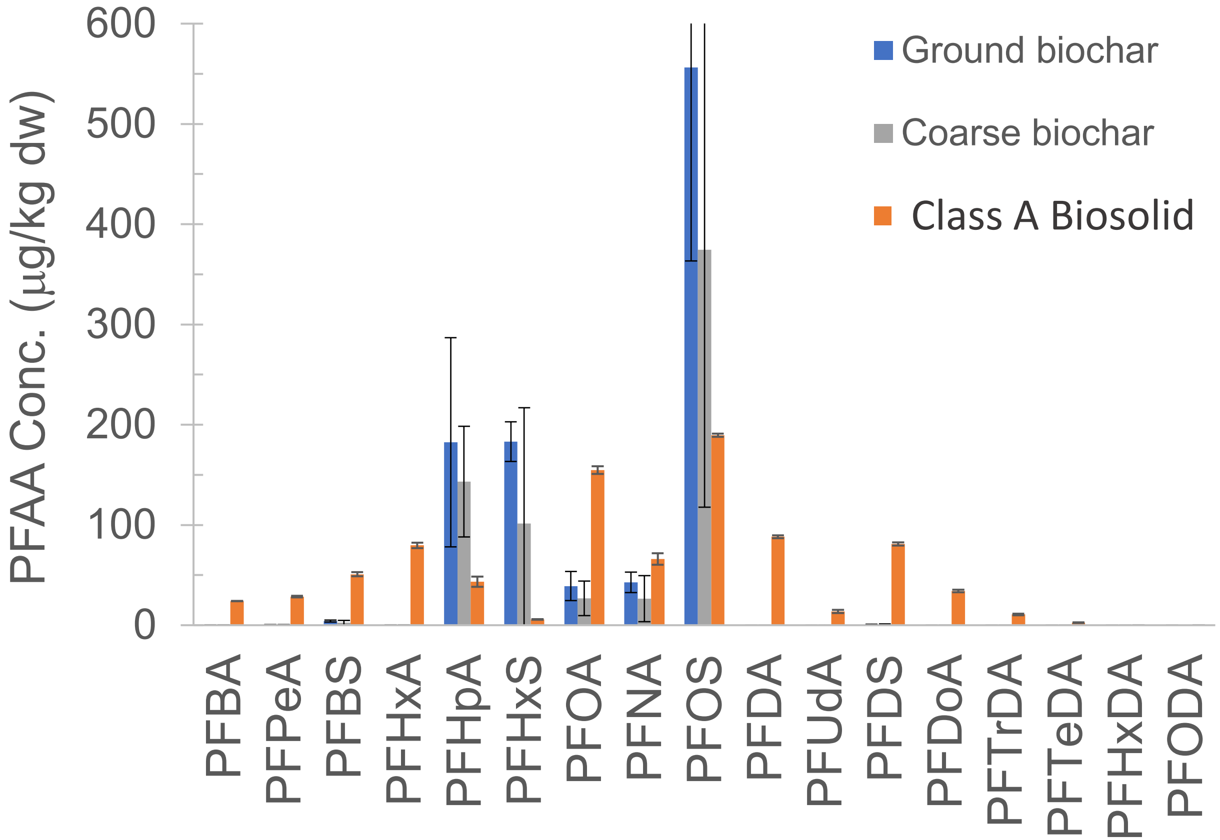
- Soil amendments/fertilizers are often applied based on N requirements
- Products low in N could lead to higher PFAS loads with a single application
- **So 'blending' is a *pragmatic* management strategy for now**

27

Low Temperature (350 °C, Low O_2) 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

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



What happens to PFAS when we Pyrolyze Biosolids?
This case: Low temperature (350 °C) and Low oxygen

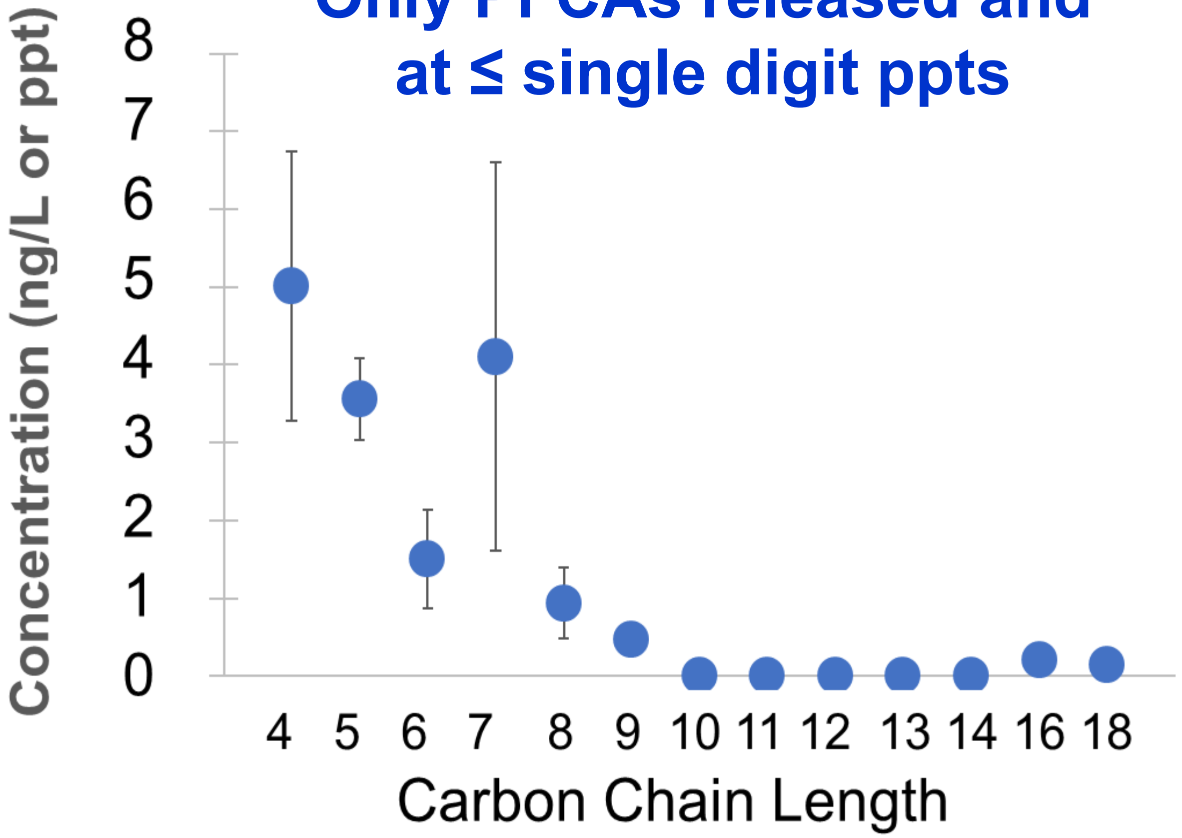
For this Class A biosolids,

- ○ ~900 ppb total PFAAs
- ○ Porewater concentrations 6 to 1200 ppt for the different PFAAs

For pyrolyzed biosolids (~1000 ppb PFAAs):

- ○ Volume & mass reduction, thus PFAA concentrations increased for some
- ○ PFAA concentrations decreased for most PFAAs, but may be in syngas
- • Only PFCAs observed in porewater
- • **Pyrolysis reduced PFAA leaching substantially** – each PFCA] < 7 ppt

Only PFCAs released and at ≤ single digit ppts



Incinerating is a Problem

- Most current incinerators are not designed to mineralize PFAS in wastes and spent consumer products (e.g., carpets)
- Two companies in Indiana now facing suits for incineration of military AFFF stockpiles
- Some states currently have bans on incineration of PFAS-containing materials

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 PFAS 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.

+

→

FINISH LINE
WINNER'S
CIRCLE

What are states doing about PFAS Use?

State of Washington

- **PFAS-containing Food Packaging**
  - Contingent upon the outcome of an alternatives assessment
  - Suitable alternatives identified for several types of packaging but not all (e.g., French fry cartons, clamshells)
  - For those with alternatives, transition must occur by February 2023

A safer alternative must

- Be evaluated for hazard and exposure
- Be practicably & economically (comparable cost) substituted for the original chemical in the product
- Be available in sufficient availability and at comparable cost
- Perform at least as well as PFAS.

What are states doing about PFAS Use?

State of Washington

- **Firefighting foam training ban -** July 1, 2018, use of PFAS-containing Class B firefighting foam for training is prohibited across Washington, no exemptions.
- **Firefighting foam sales ban -** July 1, 2020, the manufacture, sale, and distribution of PFAS-containing Class B firefighting foam will be prohibited with a few exemptions.
- **Firefighting personal protective equipment (PPE) notice -** July 1, 2018, manufacturers and sellers of PFAS-containing firefighting PPE must notify purchasers and why PFAS were used.

What are states doing about PFAS Use?

State of California

Dept of Toxic Substance Control has identified 3 PFAS-containing Products as Priority Products Under Safer Consumer Products

- **PFAS-containing carpets**
- **PFAS use in converted textiles and leathers** (includes stylized garment to any home furnishing product to which PFAS were added)
- **PFAS in food plant fiber-based food packaging**

Current Sustainable Management Options and Path Forward for 'forever' PFAS

- **Continue research** - research at an increased rate is ongoing, including fate, toxicity, development and evaluation of a variety of treatment technologies, and development of acceptable alternatives, which needs to continue.
- Meanwhile, for biosolids, **consider blending** not just for nutrient value but as a pragmatic approach for keep PFAS loads lower in our biosolids
- **Control sources** - **pretreatment** of influent from industry or landfills with *high* PFAS levels)
- **Regulate/ban nonessential uses** (e.g., food packaging, carpets, textiles, etc.)

Acknowledgements

- Dr. Rooney Kim Lazcano (Ph.D. student, Purdue Univ.)
- Dr. Youn Jeong Choi (Post doc., Purdue; Professional, Purdue)
- Caroline Rose Alukkal M.S. (Ph.D. student, Purdue Univ.)
- Dr. Mahsa Modiri-Gharehveran (Post Doc, Purdue Univ.)
- Lynda Peter (Ph.D. student, Purdue Univ.)
- Dr. Youn Jeong Choi (Post doc., Purdue; Professional, P
- Heather Trim on behalf of Zero Waste Washington
- Dr. Michael L. Mashtare (Assist. Prof., Purdue Univ., now at Penn State)

Funding:

- USDA – Agriculture and Food Research Initiative Competitive Grant & Hatch funds
- EPA G2-18-STAR-B1 83964001-0
- EPA National Priority G20B113019085
- Water Research Foundation 5042 with CDM Smith
- VA Hampton Roads Sanitation District (HRSD)
- DuPont