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PFAS and Biosolids- Current Issues and a Look Forward

Todd O. Williams, PE,BCEE
Jacobs Residuals Resource Recovery Global Technology Leader

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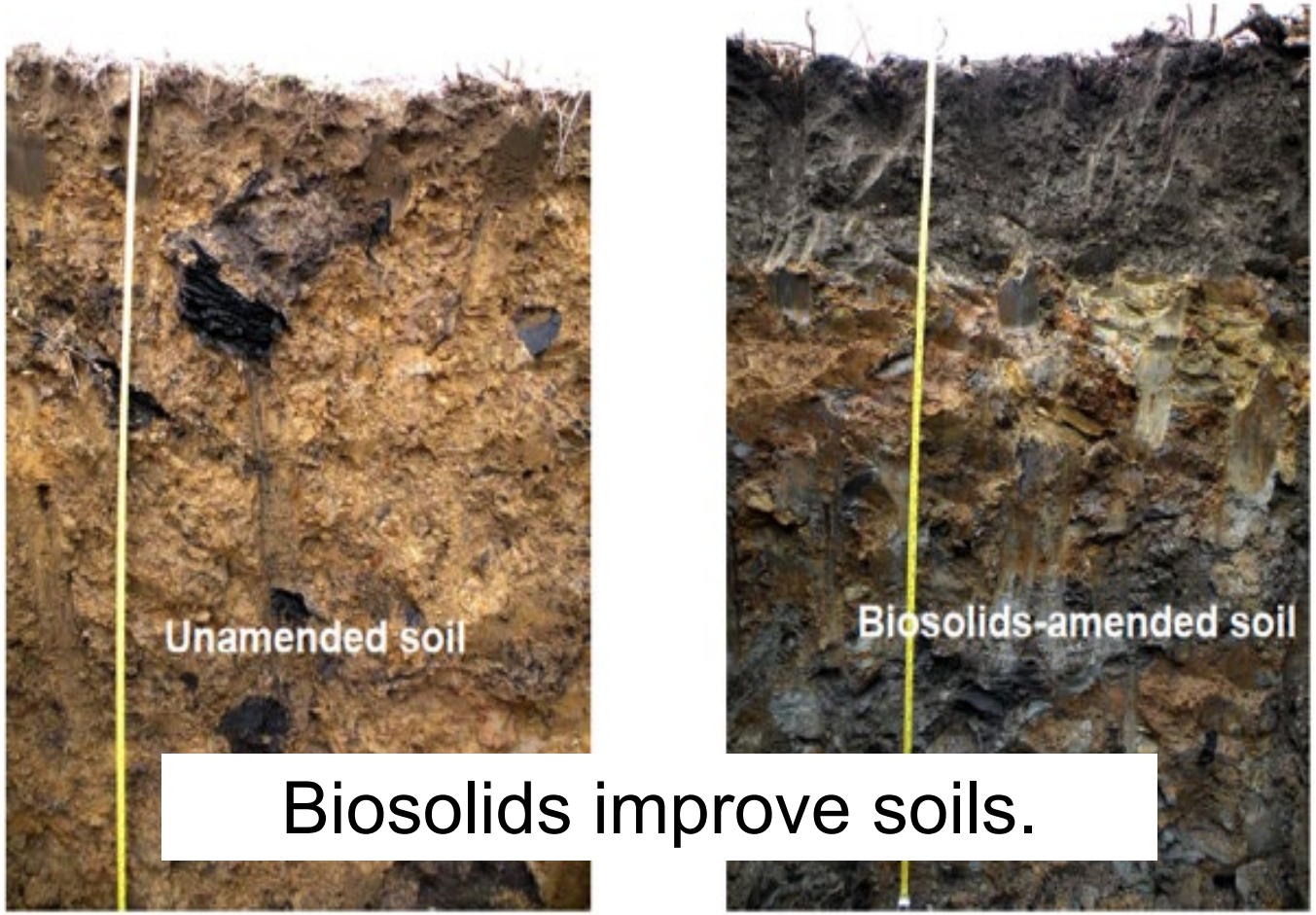
Land Application of Biosolids – Substantiated Benefits for Decades

Biosolids & other organic residuals are treated, tested, regulated, and recycled to soils routinely – and have been for decades. This does amazing things:

- enhances soil health
- recycles nutrients – macro & micro
- 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
- productive use of residuals that every community must manage
- is part of the circular economy

45+ Years of Research

…has shown the benefits & manageable risks



Biosolids improve soils.

Biosolids & soils: Remarkable media for managing CECs!

CECs / Microconstituents: PFAS Are Not Our First Rodeo…

- Dioxins/Furans
- PPCPs
  - Medicine – hormones, drugs for disease & pain management, homeopathic drugs, vitamins & other health supplements, etc.
  - Hygiene – soaps, detergents, hand sanitizers, etc.
- Microbeads
- And now PFAS
  - With over 85,000 known chemical compounds in commerce, unlikely to be our last CEC.

Rationale for managing CECs through biosolids recycling:

- Landfilling & incineration have impacts &/or energy issues.
- Healthy, microbially-active soils are the best medium for treatment of traces of organic chemicals.
- Significant impacts to biota have been measured in aquatic environments, <u>but not in biosolids-amended soils</u>.
- Risk to human health through biosolids-application-to-soil pathways appear to be negligible. Far greater human exposure to most are through daily use of products.
- Source reduction is the most cost-efficient way to address CECs and should focus on persistent compounds with known or potential toxicity.

What Are PFAS?

- Per- and poly-FluoroAlkyl Substances
- Thousands of man-made compounds, no natural occurrence
- Used since the 1950s in many products
  - Heat resistant
  - Flame retardant
  - Oil resistant
  - Water resistant
  - Found in blood of people, animals, and fish worldwide
- Properties which make these compounds useful also result in their persistence in the environment


firefighting foam


paints and stains


stain – resistant carpets


water – repelling fabrics


nonstick cookware

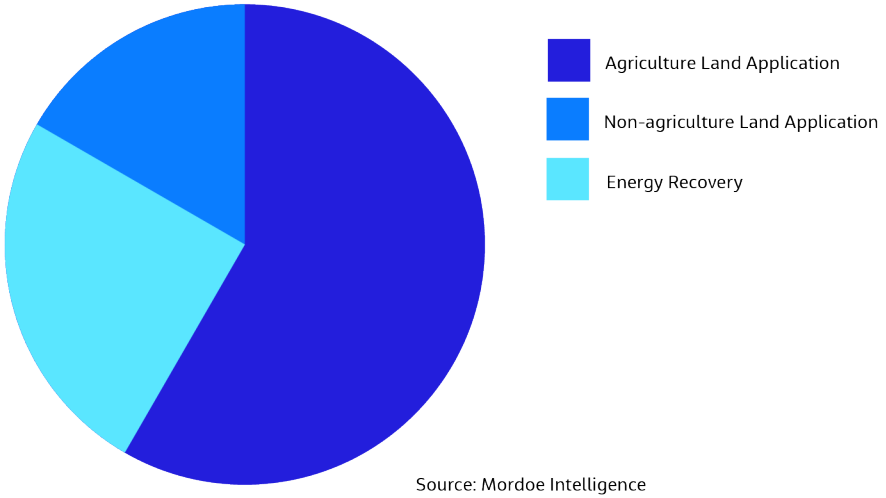

food packaging

PFAS in Biosolids– Why should we care?

- Land application makes up 60% of the global biosolids market
- In the US, half of the 7.2 M dry tons per year of WWTP biosolids are land applied.
- The US biosolids land application market is valued at $600M/year and growing 4% per year or more

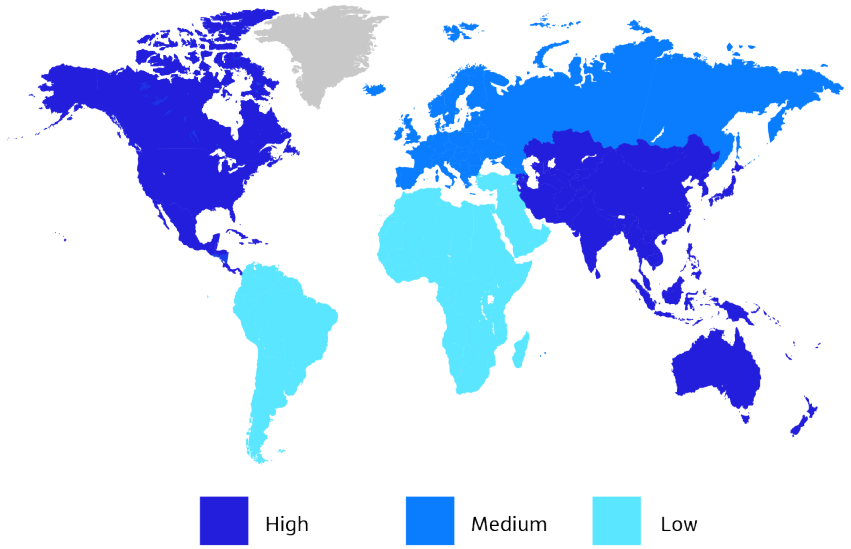
- Problems with landfills is forcing even more biosolids to land application
- What are the concerns?
  - Surface water, ground water, plant uptake
- What do farmers think?

Biosolids Market, Volume (%), by Application, Global 2018



Source: Mordoe Intelligence

Biosolids Market – Growth Rate by Region, 2019-2024



PFAS Source Impacts– the big three

- Industrial
  - Metal platers, coatings, AFFF
  - Chemical, Paint and Paper Manufacturers
- Landfill leachates
- Residential/ Commercial

Impacts to treatment plants are a function of mass loading

Are there regulations related to PFAS in biosolids?

US EPA Biosolids PFAS Rule-Making Progress

- Focus is on PFOS and PFOA where there is the most data
- PFAS in Biosolids Action Plan Developed
  - Problem Formulation by 12/2020
- Screening and Risk Assessment of Emerging Chemicals of concern in 2021 including PFOA and PFOS
- Modeling presented to the Science Advisory Board in 2021
- Risk Assessment to be completed by the end of 2024
  - If there are constituent limits…the 503 rule will be updated
  - Mitigation options will be included
  - Peer review and public comment period will occur

Soil / Biosolids Values are Being Developed for Protection of Groundwater

Entity	µg/Kg (ppb)		
	PFOA	PFOS	PFBS
US EPA (Soil Screening Level)	6.10	0.378	1.94
State values *	0.6 – 350	0.22 - 25	53 – 910
Maine (Biosolids Specific Screening)**	2.5	5.2	1900

- *Current states: AK, MI, NE, NC, TX. Enforceable value in AK.
- ** Maine banned all biosolids land application on 4/20/22

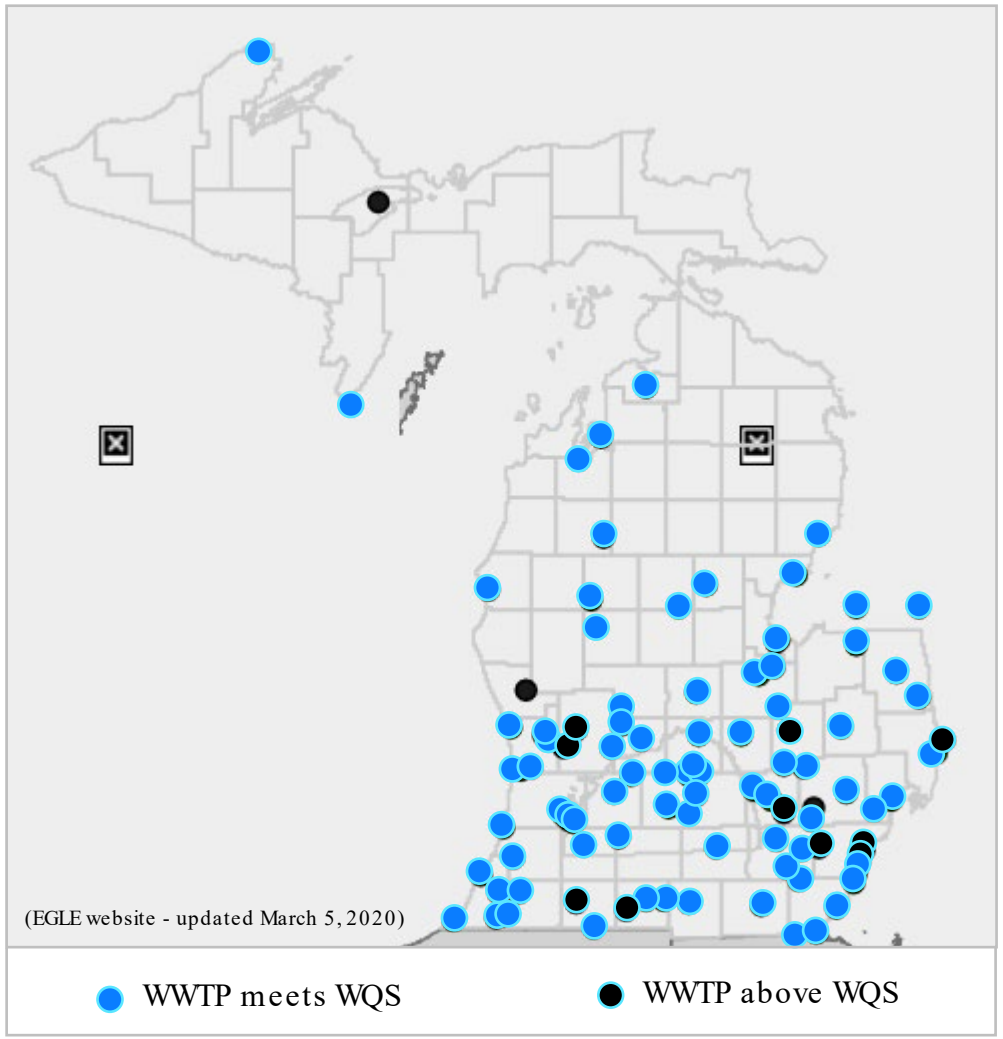
States are Approaching Standards Independently

- **California**
  - PFAS investigation plan (March 6, 2019)
  - Orders to sample POTW's (began Q4 2020)
  - Orders to sample POTW biosolids (began Q4 2020)
- **Maine**
  - WWTPs need to test for the PFAS in biosolids used as fertilizer
  - Ban on land application of biosolids signed into law on April 20, 2022
- **Michigan**
  - Leveraging IPP program against surface water quality standards
  - Established an interim guidance for land application of biosolids in Q2 2021

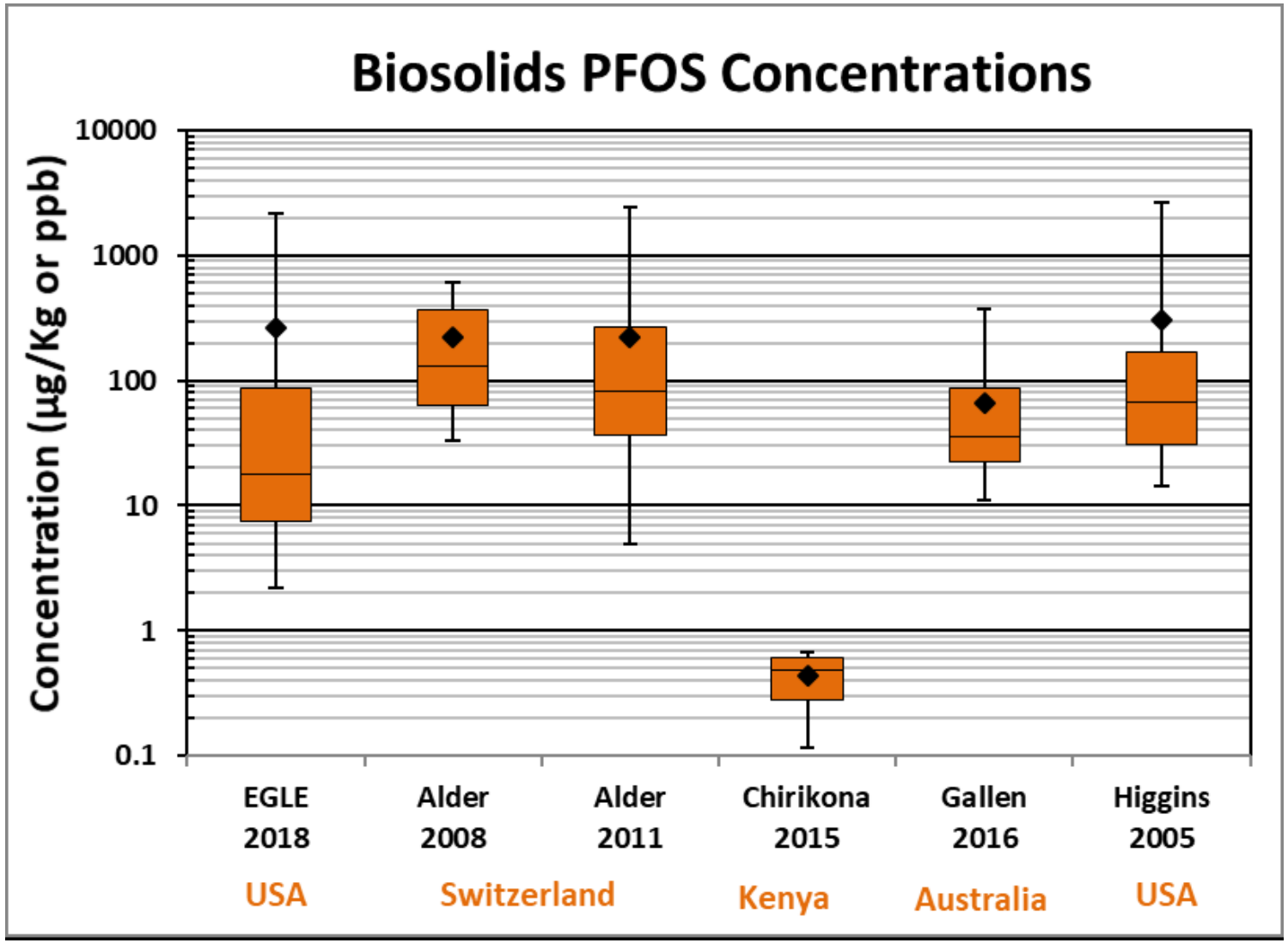
Michigan's Approach to Managing PFAS in Biosolids

- EGLE required sampling and testing for PFOS and PFOA of effluent at WWTPs with IPP's in 2018
  - PFOA of influent and effluents at all plants below current water quality standard
  - Tier 1 – WWTP effluent < 12 ppt PFOS
    - No action needed
  - Tier 2 – WWTP effluent 12-50 ppt PFOS
    - Work towards source control and monitor effluent quarterly
  - Tier 3 – WWTP effluent > 50 ppt
    - Implement source control
    - Monitor effluent quarterly
    - Monitor biosolids quality
- Biosolids interim land application guidelines established

Michigan Surface Water – Rule 57		
Entity	ng/l (ppt)	
	PFOA	PFOS
Non-potable Surface water	12,000	12
Potable Surface water		11

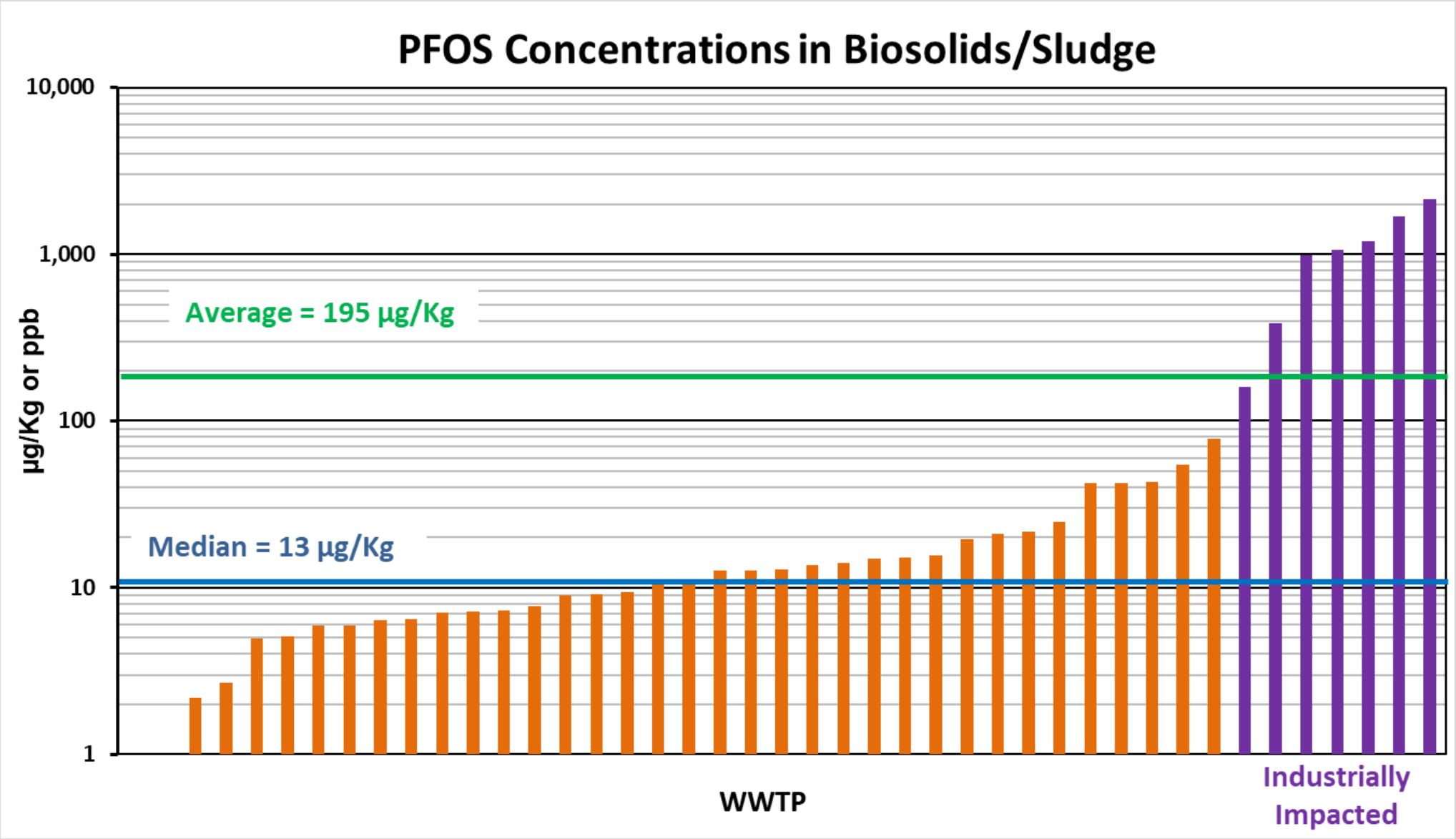


PFOSBiosolids Concentrations in Michigan and Published Literature



Source: EGLE June 2020 Initiatives to Evaluate the Presence of PFAS in Municipal Wastewater and Associated Residuals Report

Michigan Statewide Study of PFOSin Biosolids in 2018



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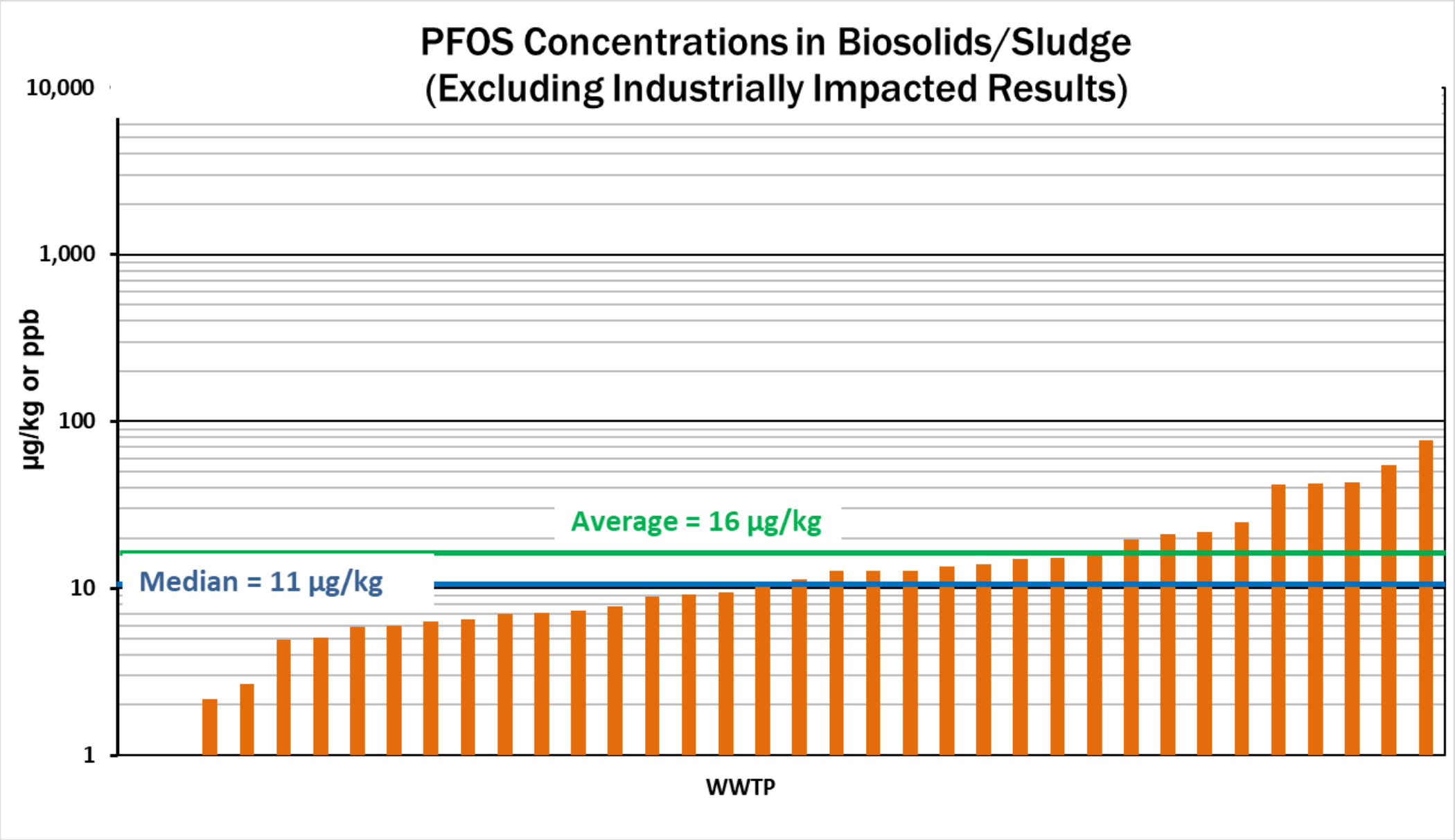


Source: EGLE June 2020 Initiatives to Evaluate the Presence of PFASin Municipal Wastewater and Associated Residuals Report

Example of Biosolids Land Application Analyses in Michigan in 2018

WWTPConcentrations		Soil	Groundwater	Surface Water
Effluent	Biosolids			
2-5	3-90	ND-9	ND-2	ND - 5
169-635	1,060-2,150	1-172	ND - 18	1–2,060

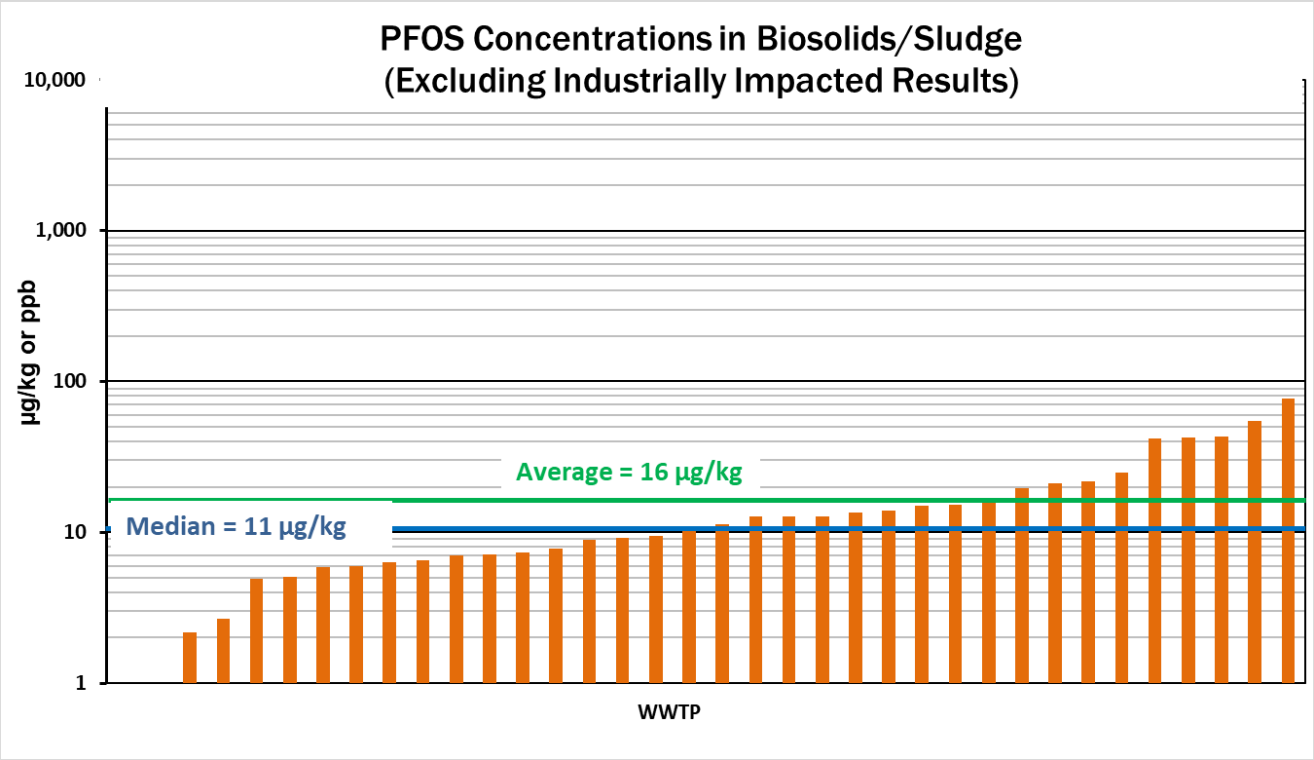
PFOS: Aqueous = ng/L or ppt
Solid = ug/Kg or ppb

"Typical" non-industrially impacted biosolids with PFOS < 90 ppb

Non-typical industrially impacted biosolids with PFOS > 1000 ppb

Michigan EGLE Biosolids Land Application Interim Strategy Effective 7/2021

- **PFOSconcentration > 150 µg/Kg, ppb**
  - Land application not allowed! Alternative disposal (landfilling) required.
  - Investigate source reduction of PFAS
- **PFOSconcentration > 50 and <150 µg/Kg, ppb**
  - Land application allowed at no more than 1.5 DT/acre
  - Investigate source reduction of PFAS
- **PFOSconcentration < 50 µg/Kg, ppb**
  - Land application is allowed
  - If PFOS > 20 ppb, consider investigating sources



Source: Michigan EGLE Land Application of Biosolids Containing PFAS; Interim Strategy, March 2021

Wisconsin DNR Biosolids Land Application Draft Interim Strategy as of 9/2021

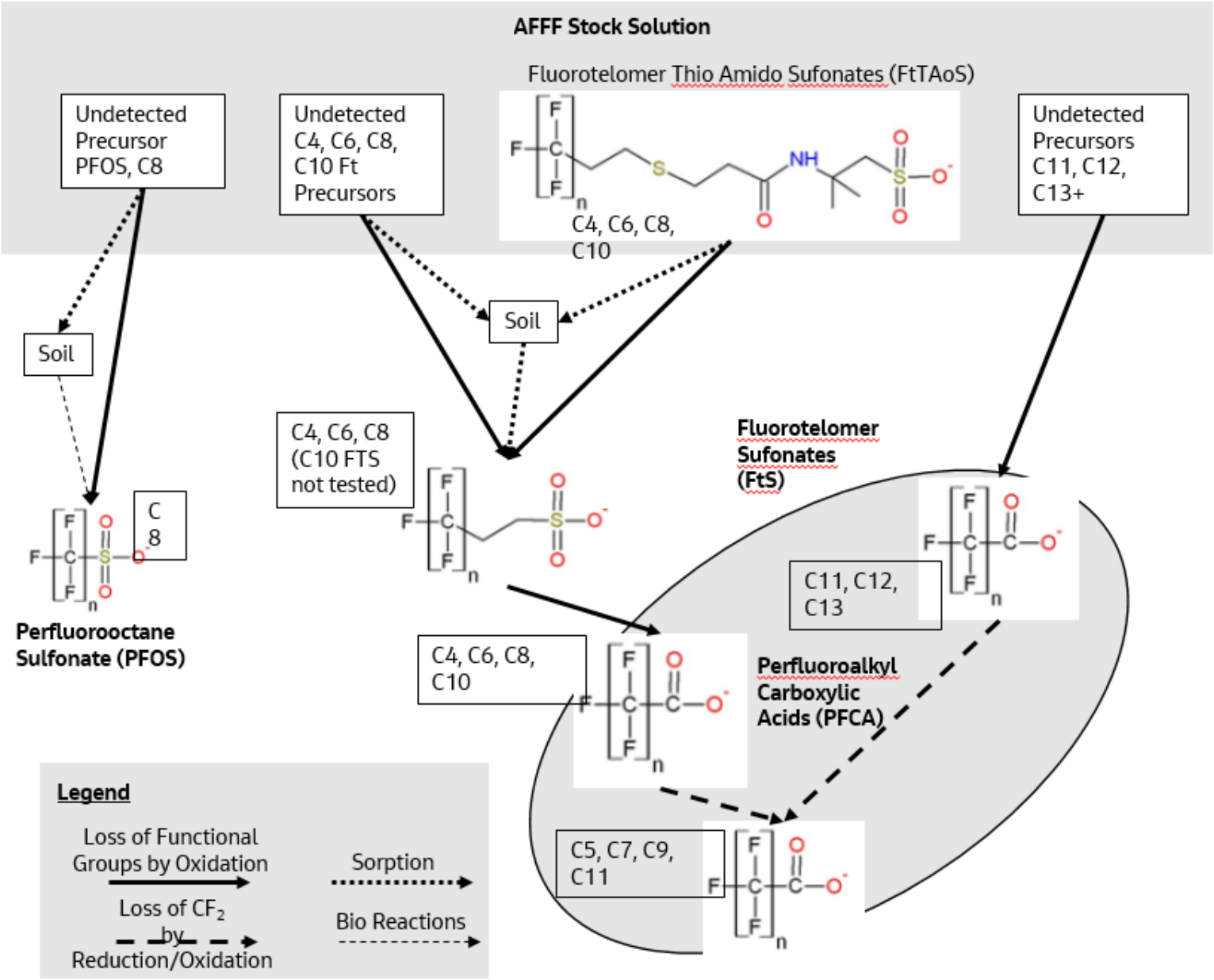
- **Sum of PFOA/PFOSconcentration > 150 µg/Kg, ppb**
  - Immediately notify DNR
  - Land application not allowed! Alternative disposal required (landfill or incineration)
  - Investigate source reduction of PFAS
- **Sum of PFOA/PFOSconcentration > 50 and <150 µg/Kg, ppb**
  - Land application allowed at no more than 1.5 DT/acre
  - Investigate sources and develop source reduction of PFAS
- **Sum of PFOA/PFOSconcentration < 50 µg/Kg, ppb**
  - Land application allowed
  - If PFOA/ PFOS > 16 ppb
    - Implement source investigation and reduction
    - Provide landowners with PFAS data PRIOR to land application

Source: Wisconsin DNR Website 2021

How can PFAS in biosolids be treated?

PFASPrecursor Biotransformation Background

Interpretation of AFFF degradation pathways

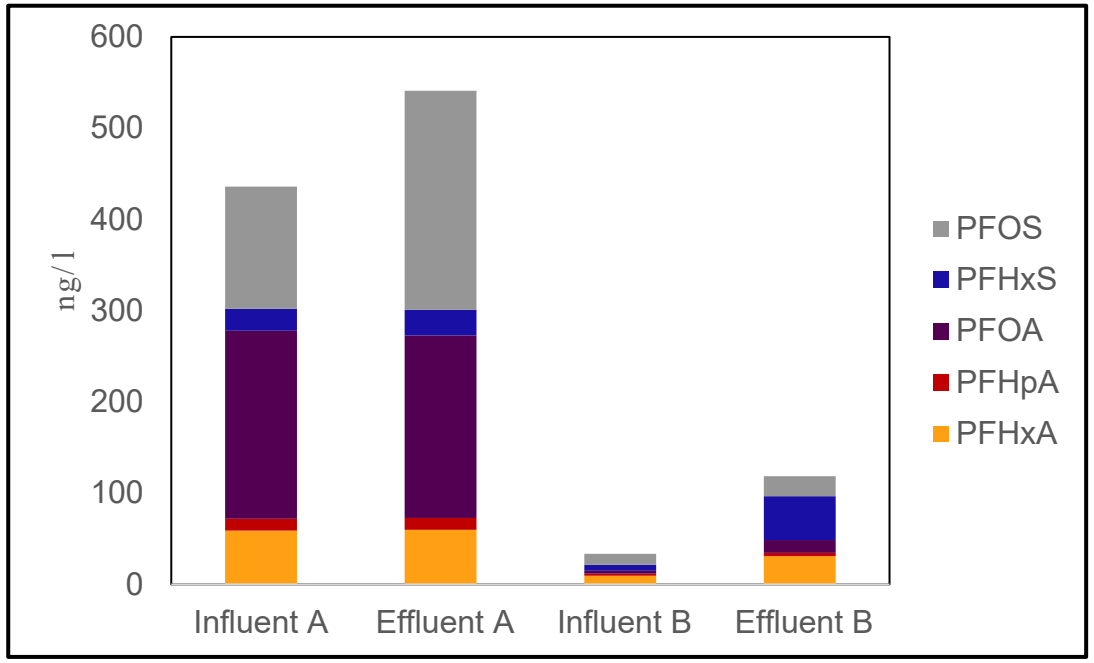


Reference:

James Hatton, Dusty Rose Berggren, Jeremy Bishop and Bill Diguiseppi. “Treatability Test: Oxidation Technologies for Destruction of PFASCompounds”. CH2M Hill Innovation Grant Technical Memorandum December 2014

PFAS Concentrations Within Wastewater Facilities are Highly Variable (ng/l)

Plant	Location	PFHxA	PFHpA	PFOA	PFHxS	PFOS	Total
A	Influent	59	13	206	24	134	444
	Effluent	60	13	200	28	240	560
B	Influent	9.7	2.2	3.1	6.6	12	35
	Effluent	31	3.7	14	48	22	120

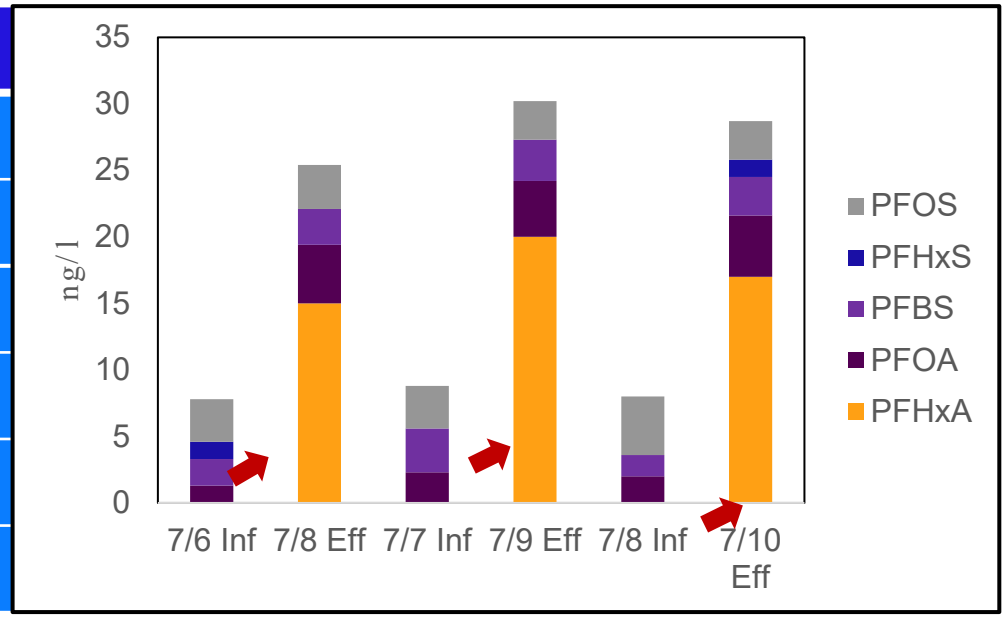


- Measured PFAS pass through WWTP with limited/no reduction
- Precursors discharged to WWTP cause detectable PFAS to increase across aeration
- PFAS also leaves plant through biosolids

Source: Gallen et. al., 2018, *Chemosphere*

A Conventional Wastewater Facility PFAS Concentrations (ng/L)

Sample	Location	PFHxA	PFOA	PFBS	PFHxS	PFOS	Total
7/6 Inf 7/8 Eff	Influent	ND	1.3	2.0	1.3	3.2	7.8
	Effluent	15	4.4	2.7	ND	3.3	26.4
7/7 Inf 7/9 Eff	Influent	ND	2.3	3.3	ND	3.2	8.8
	Effluent	20	4.2	3.1	ND	2.9	30.2
7/8 Inf 7/10 Eff	Influent	ND	2.0	1.6	ND	4.4	8.0
	Effluent	17	4.6	2.9	1.3	2.9	28.7

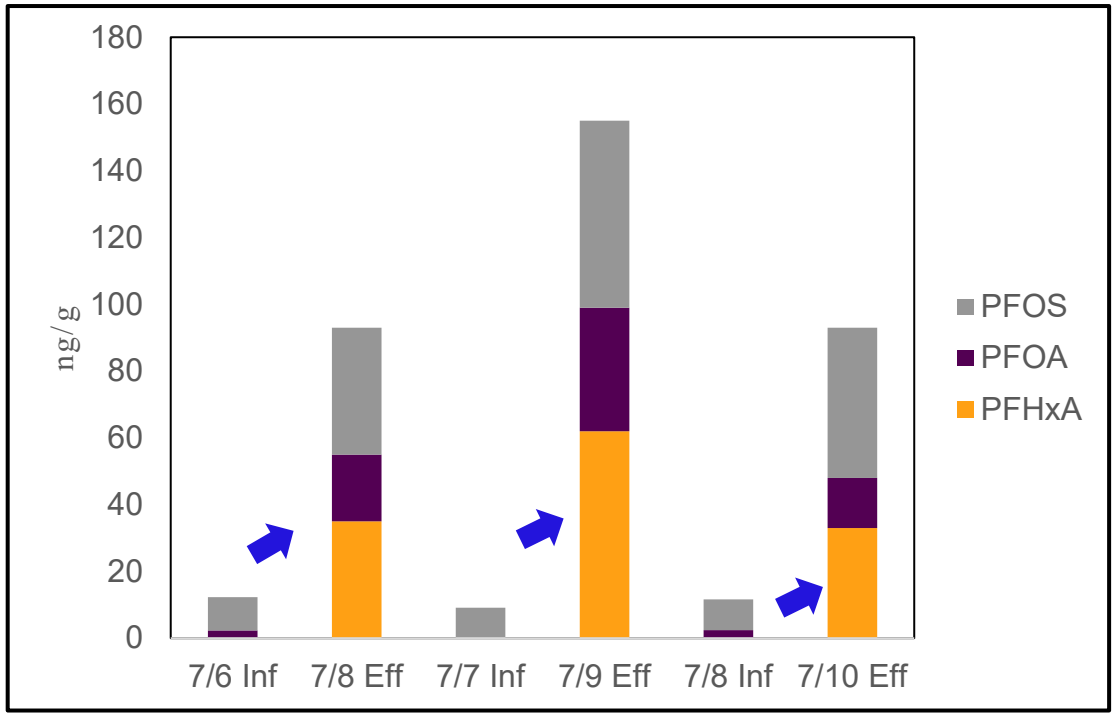


- Low concentrations of PFAS detected
- Often see detectable concentrations due to wastewater source:
  - Domestic products
  - Landfill leachate
  - Human excretion
- Does not appear to have "significant" industrial contribution
- Increase across aeration commonly observed from "precursor" conversion

Source: Jacobs, 2019

A Conventional Wastewater Facility Biosolids PFASConcentrations (ng/g)

Sample	Location	PFHxA	PFOA	PFOS	Total
7/11 DI 7/6 BS	Digester Inf	ND	2.3	10	12.3
	Biosolids	35	20	38	93
7/13 DI 7/8 BS	Digester Inf	ND	ND	9.1	9.1
	Biosolids	62	37	56	155
7/15 DI 7/10 Eff	Digester Inf	ND	2.4	9.2	11.6
	Biosolids	33	15	45	93
Average	Digester Inf	ND	2.4	9.4	11.8
	Biosolids	43.3	24	46.3	114



- 100% Waste Activated Solids treated through Autothermal Aerobic Digestion (ATAD) system
- PFBS and PFHxS not detected
- Increase across digestion from aerobic "precursor" conversion and/or changes in % solids

Source: Jacobs, 2019

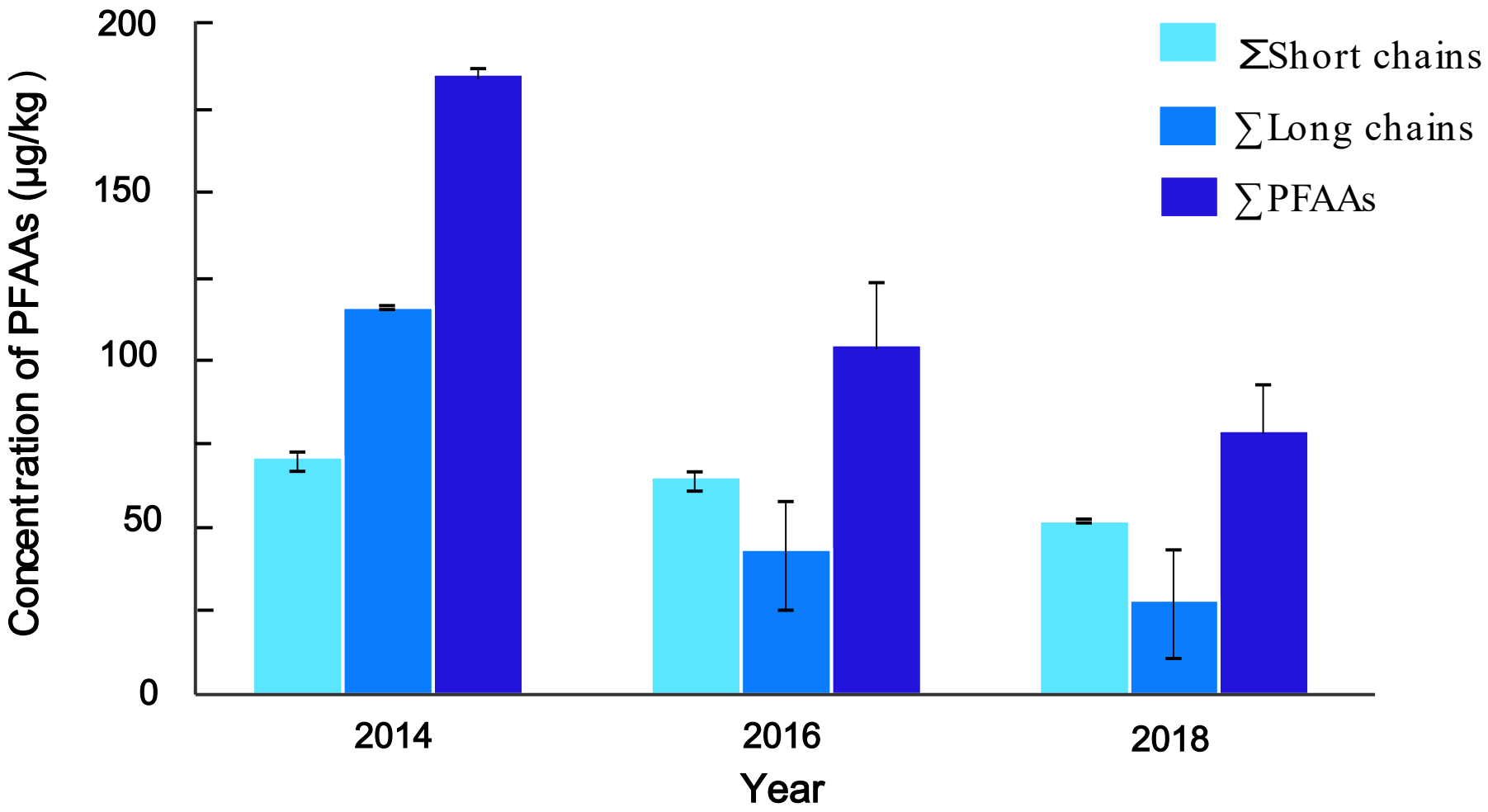
Drying Wastewater Solids and its Impact on PFAS Concentrations

- Data from various studies

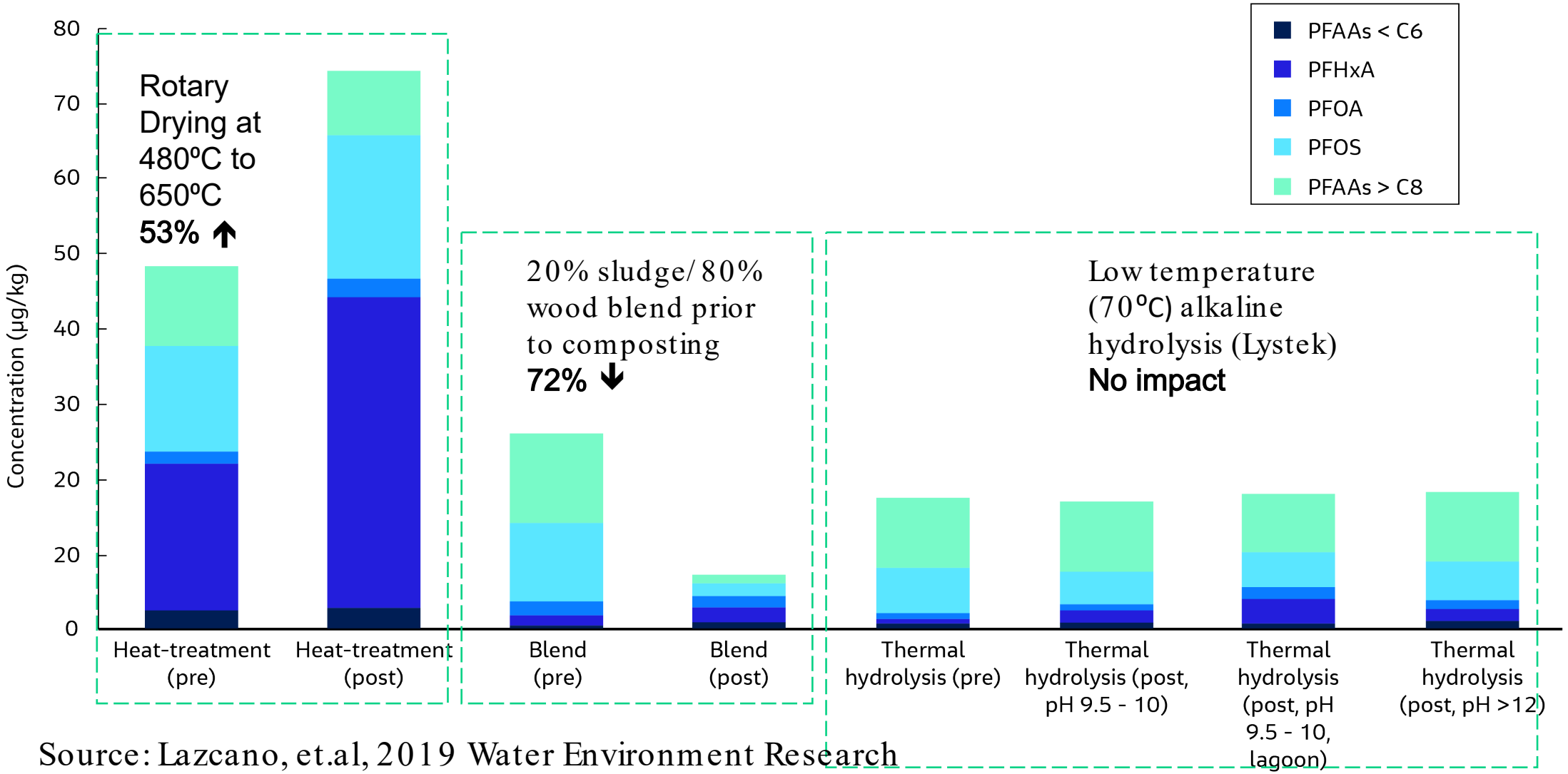
Drying Technologies Differ

	Rotary Drum	Belt Dryer	Indirect Dryer
Benefits	- Class A Biosolids - High Product quality	- Class A Biosolids - Moderate product quality	- Class A Biosolids - Less product quality
PFAS Impact	- Single pass - Multiple pass	- Single pass	- Single pass - High temperature surfaces

PFAA concentrations in biosolids have dropped as PFOS and PFOA were phased out of production in the US (one dried biosolids case study)

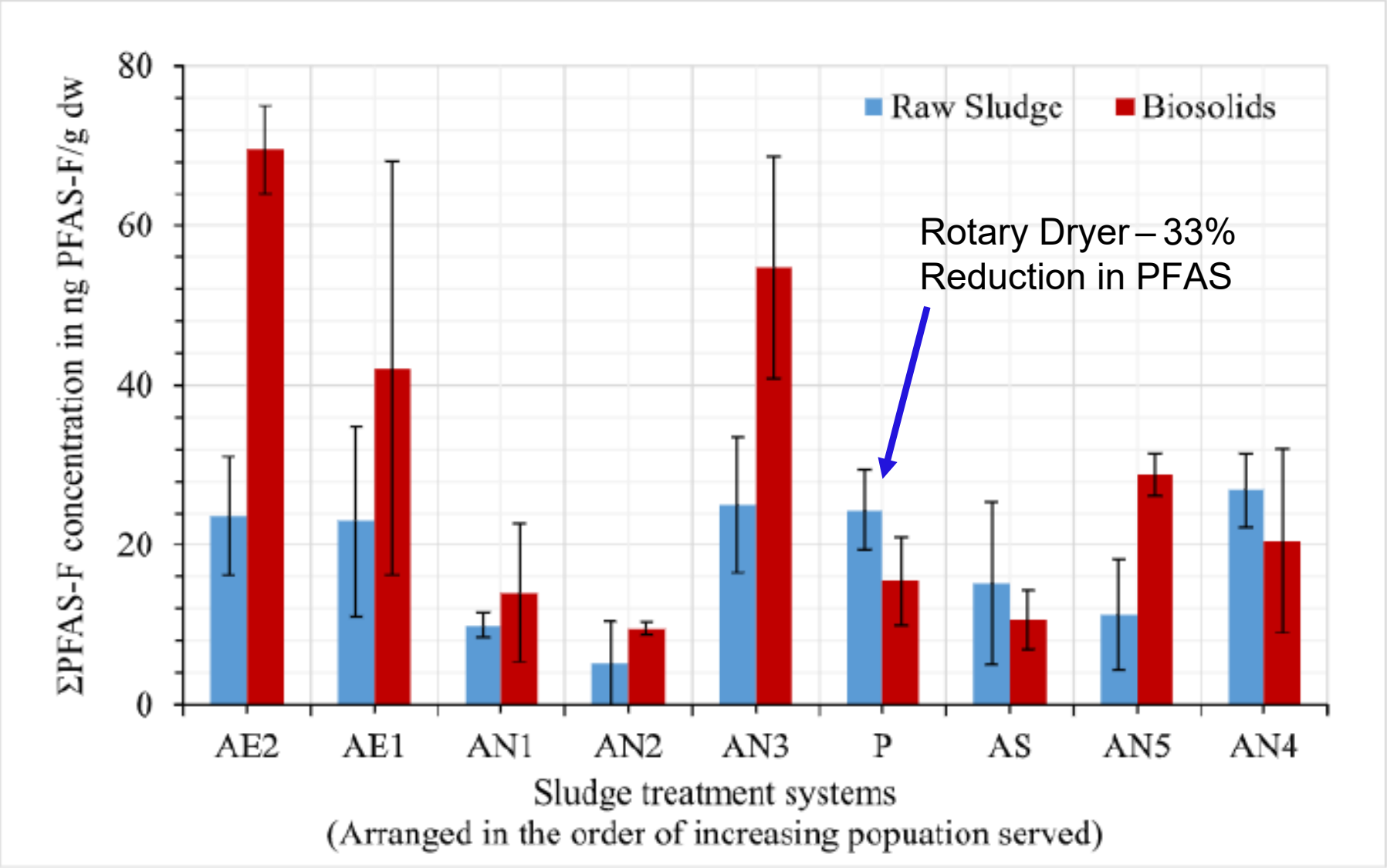


Impact of thermal drying, blending with bulking agent, and chemical/thermal hydrolysis treatment (not THP)



Source: Lazcano, et.al, 2019 Water Environment Research

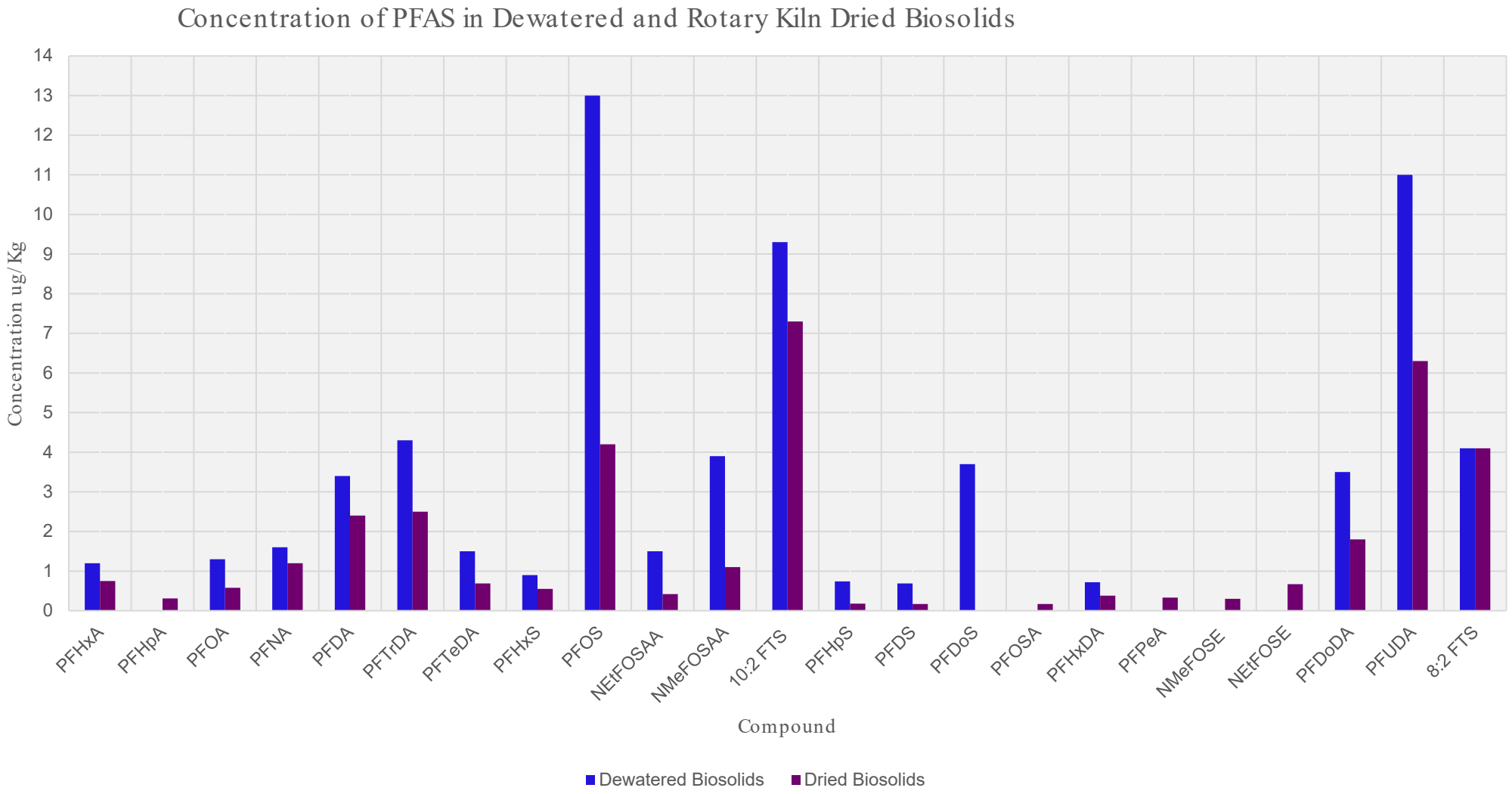
Canadian Sludge Treatment Systems Impact on PFAS



Source: Lakshminarasimman, et.al, 2021 Science of the Total Environment

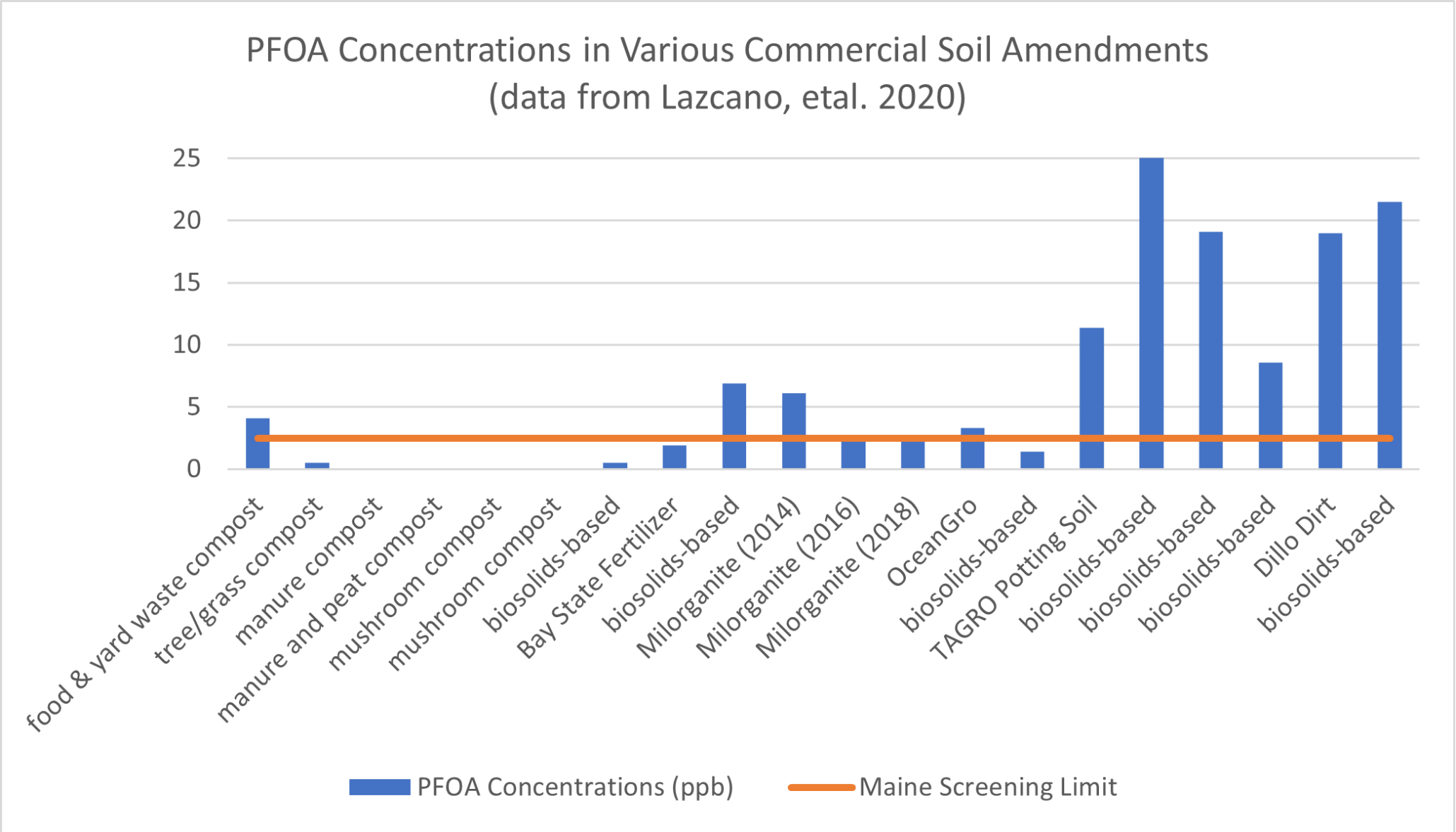
Rotary Kiln Dried Undigested Biosolids PFAS Testing

- 45% Reduction of Measured PFAS (Range 25-75% reduction)



Source: Jacobs confidential client 2022

Research summarized by NEBRA on various biosolids products

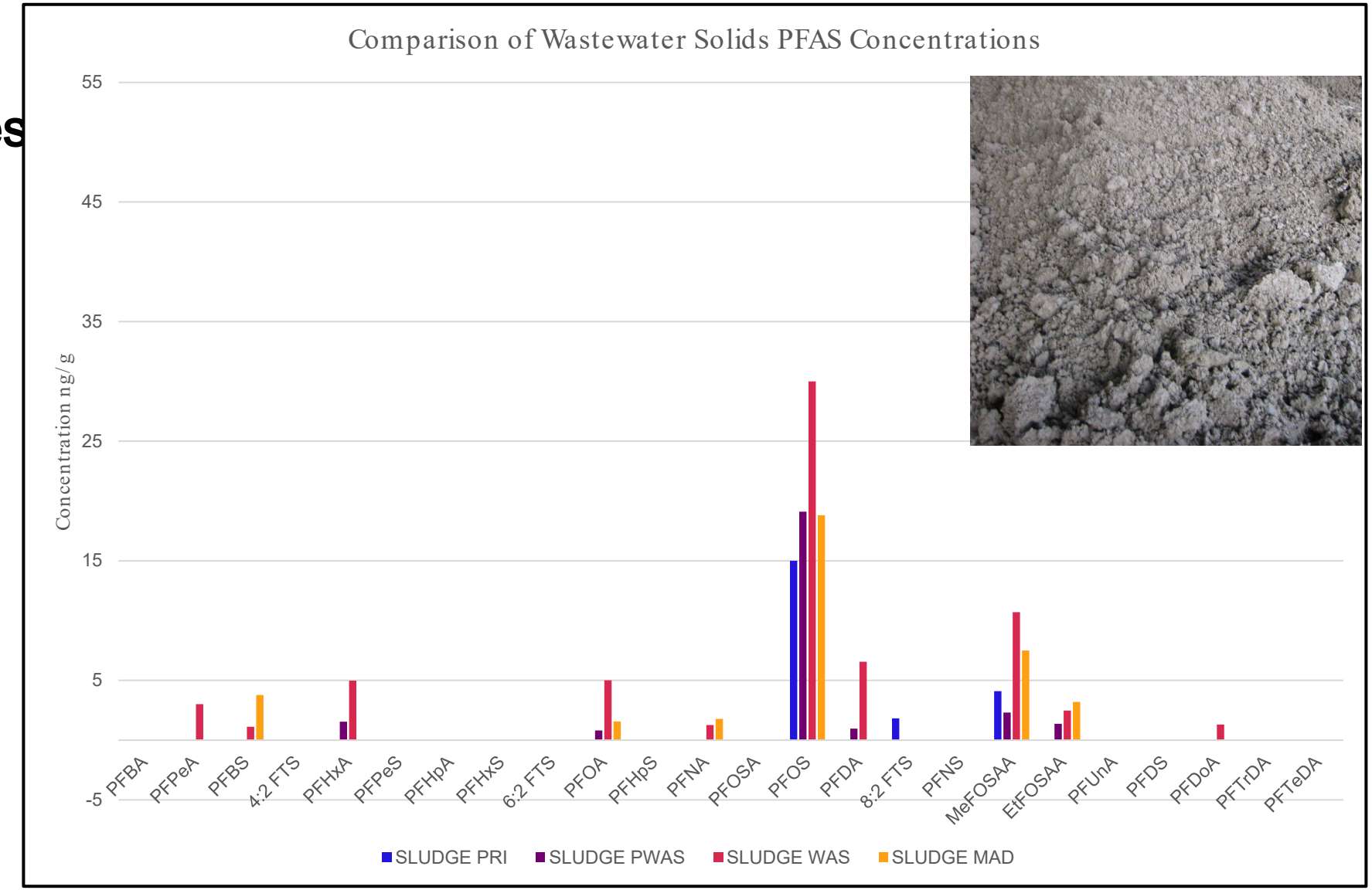


Composting Wastewater Solids and its Impact on PFAS Concentrations

- Jacobs conducted sampling and testing of several biosolids composts in 2020 for analysis of 24 PFAS compounds using isotope dilution/LC-MS/MS method ompliant with Table B-15 of Department of Defense Quality Systems Manual 5.3
- Wastewater treatment systems where compost sampled have minimal industrial contribution
- Wastewater treatment schemes prior to composting included the following:
  - Primary treatment and primary sludge only (PRI)
  - Conventional secondary treatment with nutrient removal, mixture of primary and waste activated sludge (PWAS)
  - Conventional secondary treatment with nutrient removal, waste activated sludge only (WAS)
  - Conventional secondary treatment, mixture of primary and waste activated sludge, then mesophilic anaerobic digestion (MAD)
- All operations sampled utilized the aerated static pile method of composting
- Expectation was that bulking agent dilution effect would reduce concentrations of PFAS in compost compared to input solids. But, what about biotransformation?

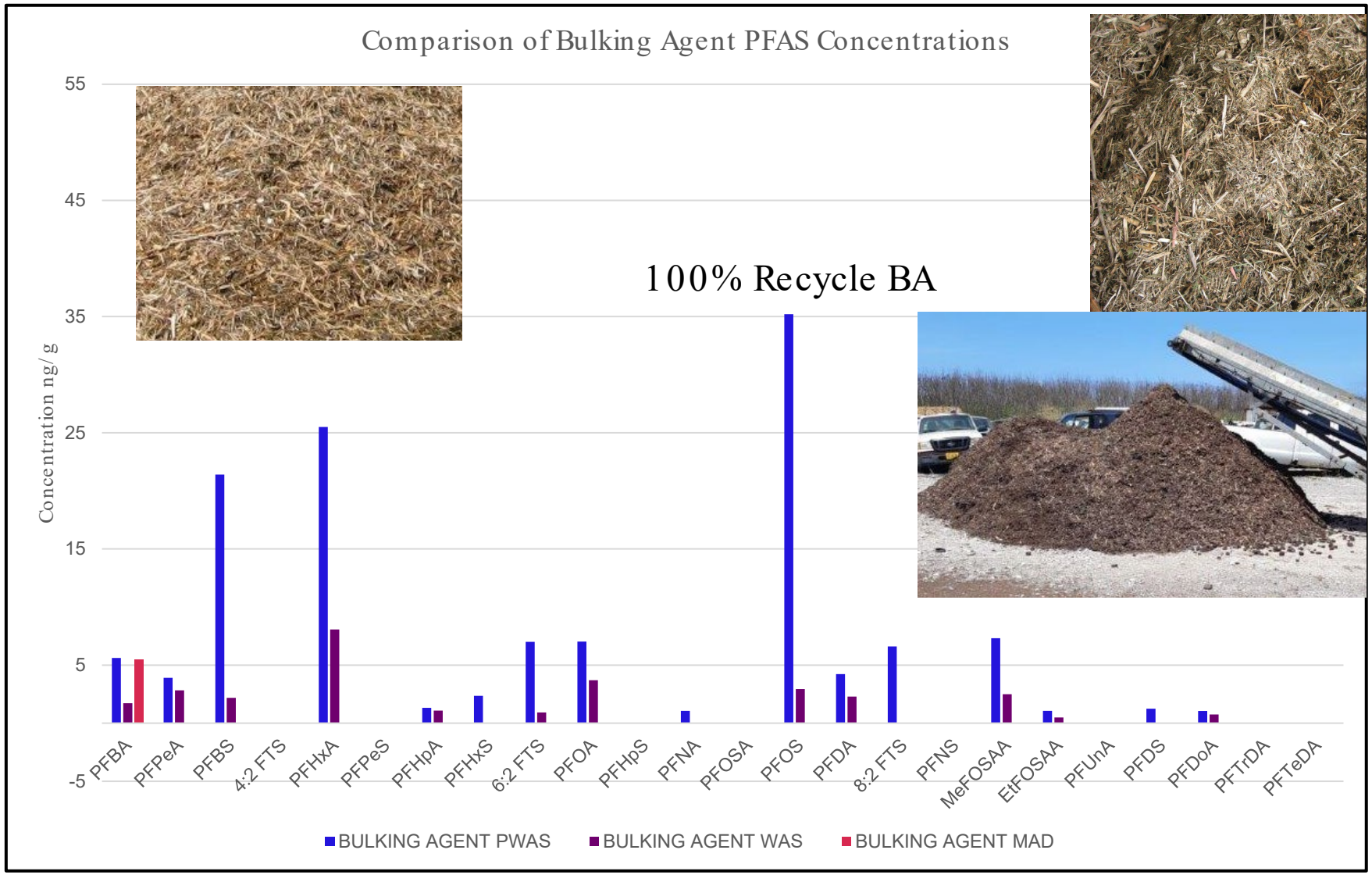
PFAS Concentrations in WWTP Solids Cakes (ng/g dry)

- In general, concentrations in WW solids are not high
- PFOS and MeFOSAA are 2 largest components in WW solids
- MeFOSAA typically degrades to PFOS



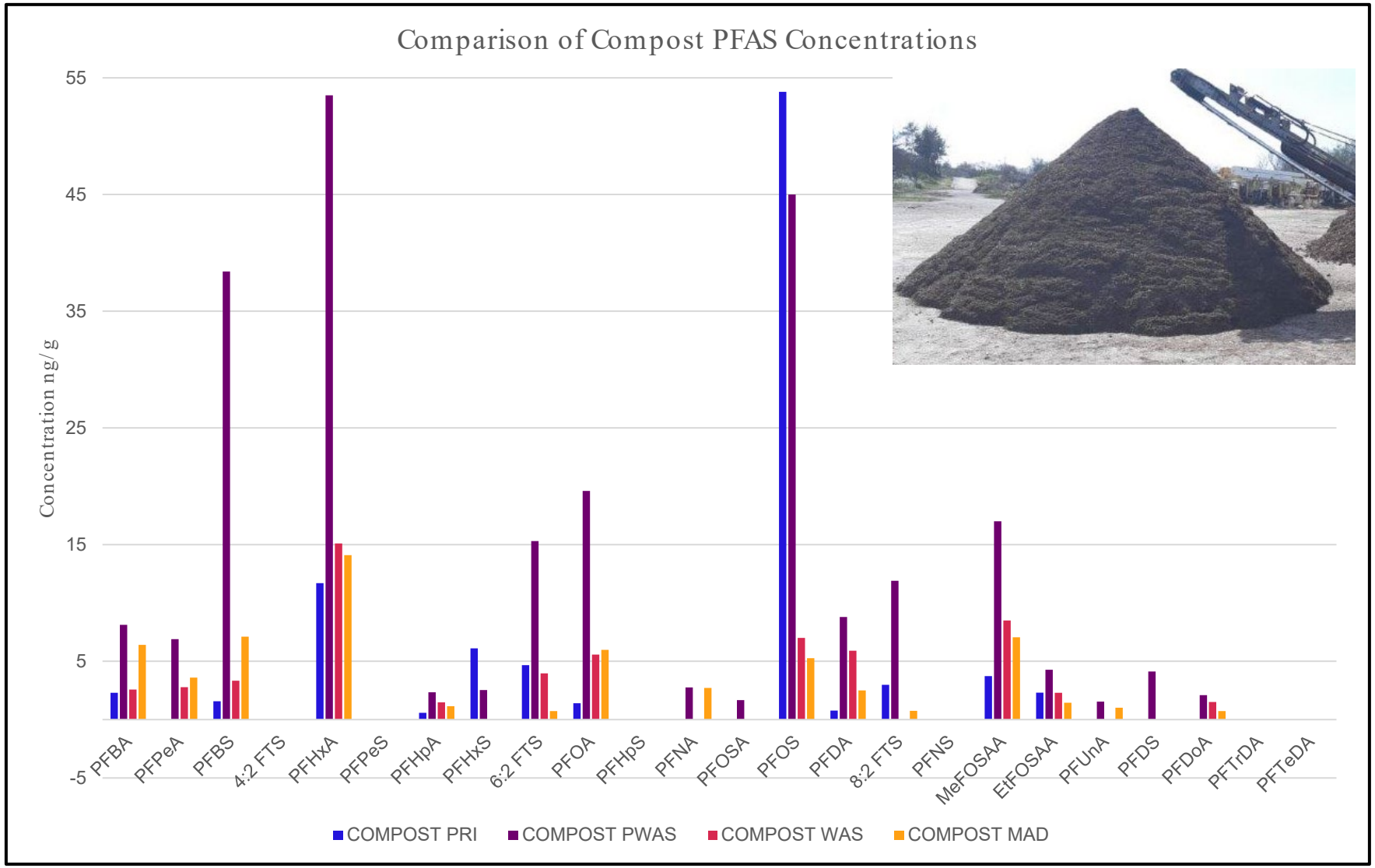
PFAS Concentrations in Bulking Agents (ng/g dry)

- Bulking agents used included wood chips, ground pallets, ground yard waste and recycled screen overs
- Most bulking agent concentrations are very low
- Recycling 100% bulking agent may increase PFAS concentration

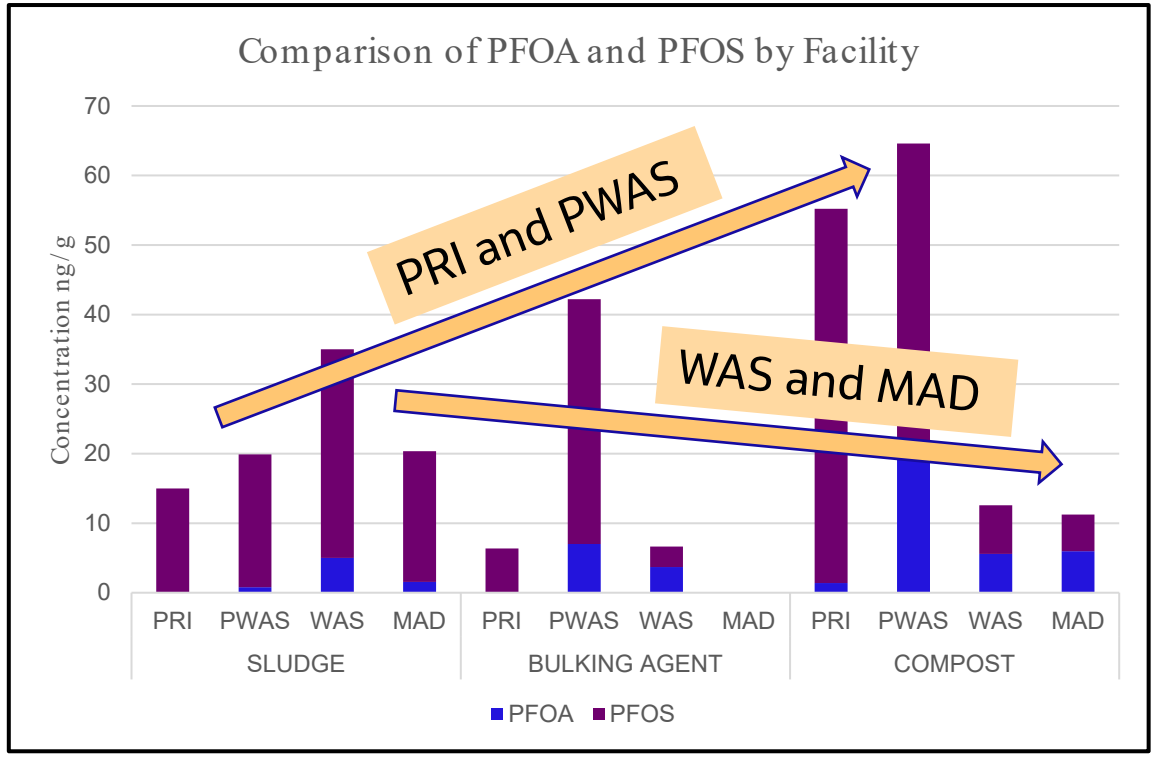


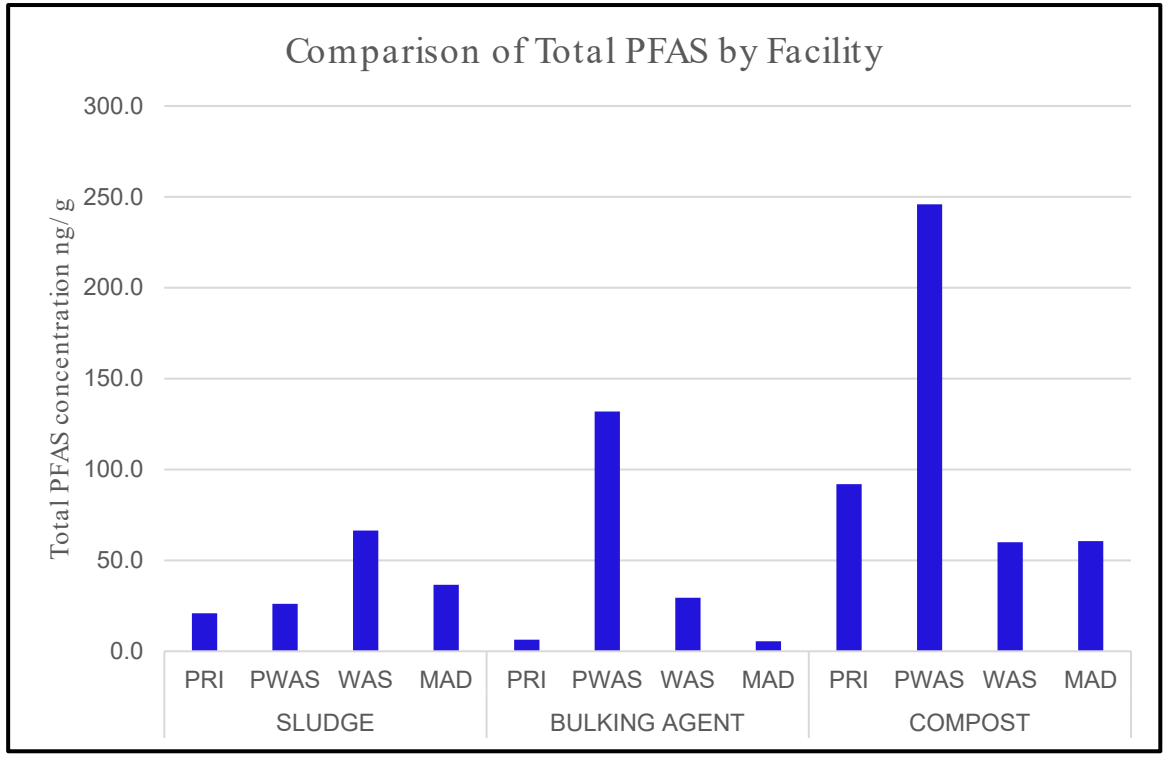
PFAS Concentrations in Composts (ng/g dry)

- PFOS, PFOA, PFHxA, PFBS and MeFOSAA are largest components in composts



PFOA, PFOS and Total PFAS by Facility





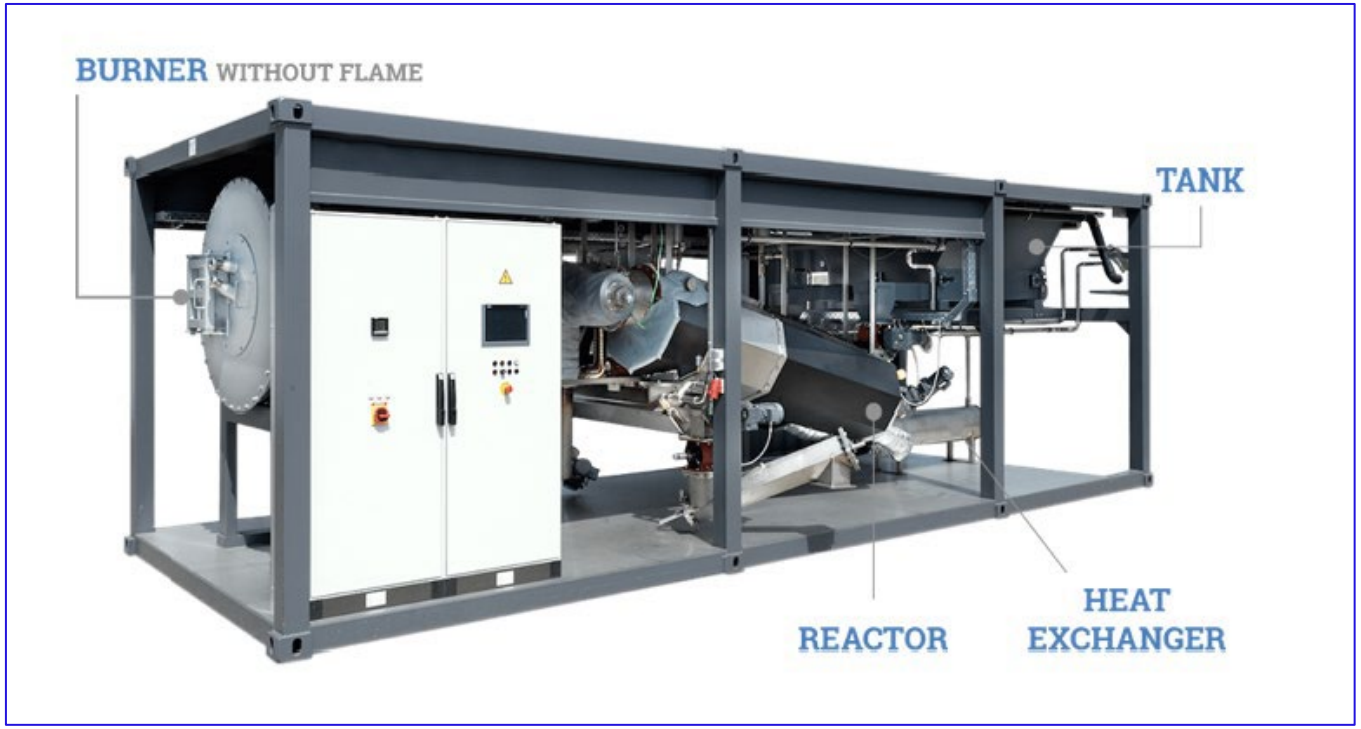
Appears to be more precursor transformation of primary solids vs. waste activated solids or digested solids

WWTP Solids Composting Summary Points

- This is a very small data set. However, there are some observations
- PFOS is the most commonly detected compound in all materials (WWTP solids, bulking agent and composts)
- Primary solids not treated aerobically first appears to be more susceptible to precursor transformation into multiple PFAS terminal compounds through composting
- Aerobically processed solids and anaerobically digested solids may result in less precursor transformation during composting
- Bulking agent recycling may increase PFAS concentration in the bulking agent and the resulting compost
- Every WWTP solids are different…..know what you've got through sampling and testing!

What is Pyrolysis?

- Pyrolysis is a process which occurs by exposing dried biosolids to high temperatures (850ûF – 1300ûF) without oxygen for ~20 minutes to produce a charcoal type product known as biochar which is marketable as a soil amendment



(courtesy of BioforceTech)

Why Consider Transforming Biosolids to Biochar?

- Potential to create a high value product from dried biosolids
- Destruction of contaminants such as estrogens, microplastics, PFAS & pathogens in biosolids
- Biochar is easy to store & handle – dry, stable & odor free
- Volume of biochar is ~50% less than dried biosolids – less trucking
- Potential reduction in GHGemissions and carbon sequestration in the char product
- Biochar is a valuable soil amendment

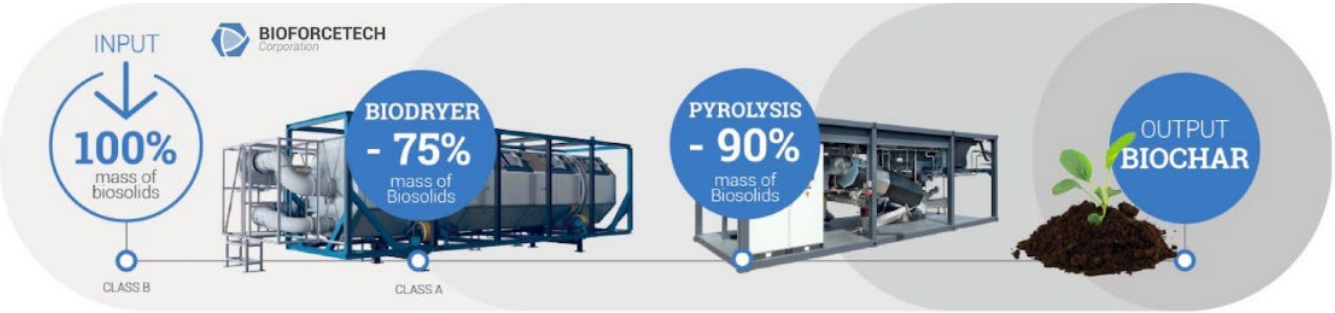
Biochar from Bioforcetech Corp.

- One set of samples 2019, confirmed in 2020
- Pyrolysis at 1100ºF (600ºC)
- We know soil sampling needs to be above 1000ºC for destruction of PFAS

Compound Name	Dry Biosolids (ng/g)	Biochar (ng/g)
PFBA	7.03	Not Detected
3:3 FTCA	ND	Not Detected
PFPeA	5.94	Not Detected
PFBS	2.3	Not Detected
4:2 FTS	ND	Not Detected
PFHxA	33.7	Not Detected
PFPeS	ND	Not Detected
HFPO-DA	ND	Not Detected
5:3		
PF		
AD		
PF		
6:		
PFOA	89.1	Not Detected
PFHpS	ND	Not Detected
7:3 FTCA	40	Not Detected
PFNA	5.3	Not Detected
PFOSA	ND	Not Detected
PFOS	26.3	Not Detected
9Cl-PF3ONS	ND	Not Detected
PFDA	11.3	Not Detected
8:2 FTS	5.68	Not Detected
PFNS	ND	Not Detected
MeFOSAA	23.5	Not Detected
EtFOSAA	19.6	Not Detected
PFUnA	3.39	Not Detected
PFDS	ND	Not Detected
11Cl-PF3OUdS	ND	Not Detected
10:2 FTS	ND	Not Detected
PFDoA	5.85	Not Detected
MeFOSA	ND	Not Detected
PFTrDA	ND	Not Detected
PFTeDA	2.44	Not Detected
EtFOSA	ND	Not Detected
PFHxDA	ND	Not Detected
PFODA	ND	Not Detected
MeFOSE	17.1	Not Detected
EtFOSE	ND	Not Detected

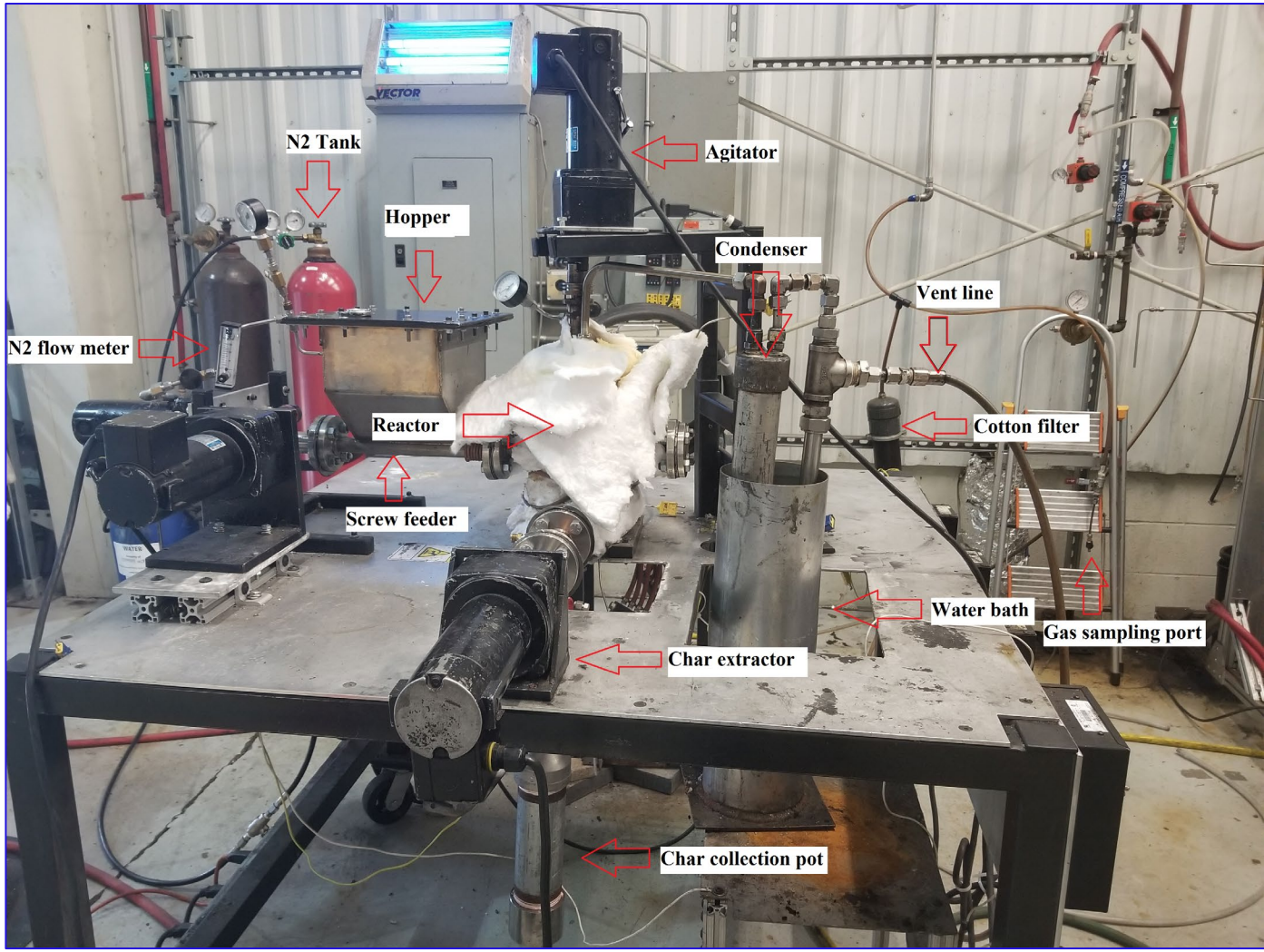
PFOA =89.1 & PFOS= 26.3

All ND @ 2ppb



Jacobs and CharTechBench Scale Pyrolysis Testing in 2020

- A continuously-fed bench-scale pyrolysis kiln unit (known as “Baby MFR”) processing 500 g dried biosolids at 500 °C and 700°C
- Bench study completed at ICFAR (Western University Institute for Chemicals and Fuels from Alternative Resources)
- Biosolids were previously dewatered and subsequently dried in a batch thermal dryer to approximately 95 percent solids
- Biosolids processed in pyrolysis reactor for 20 minutes

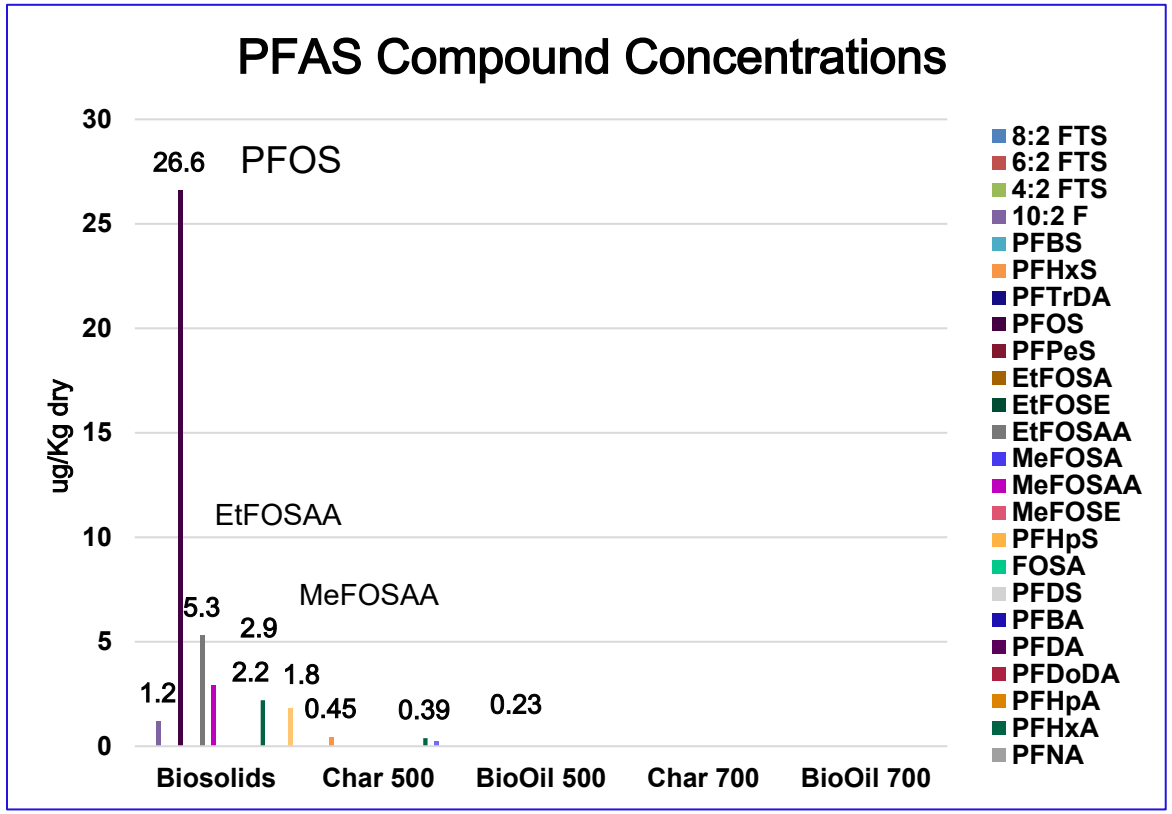


PFASTesting Results

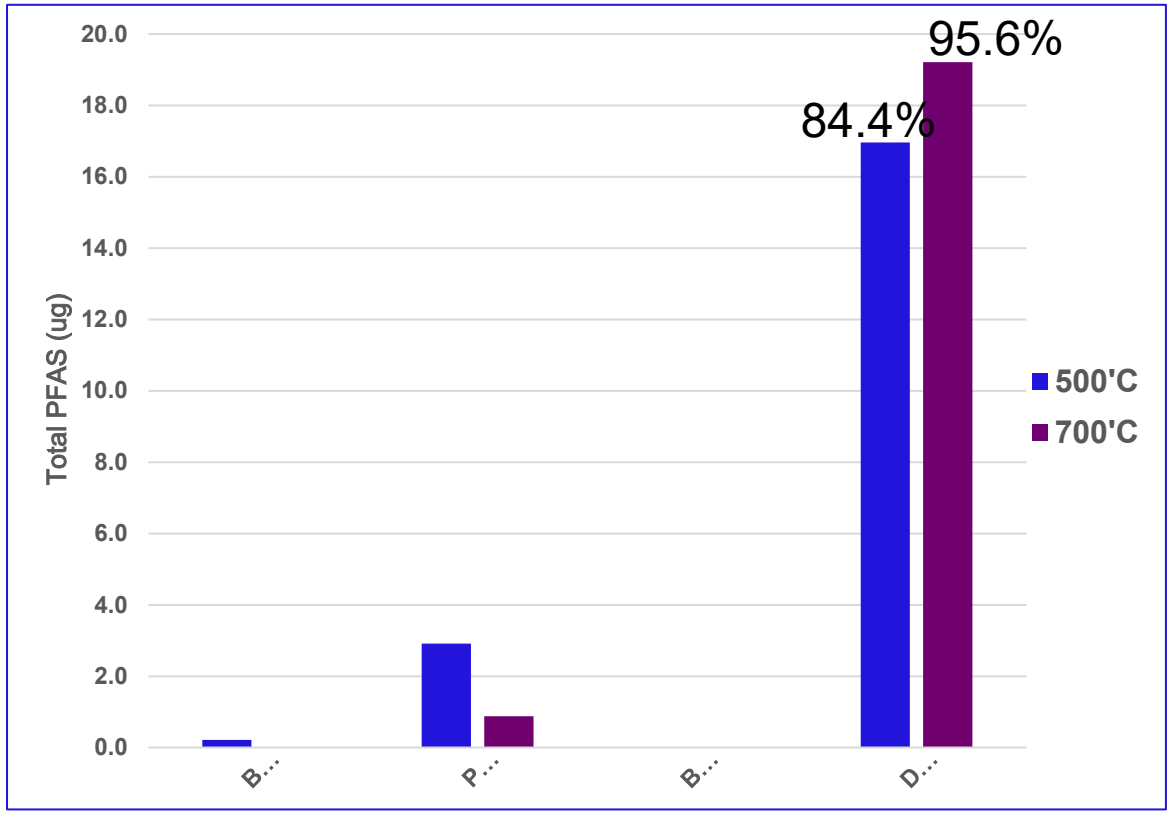
20 ug of PFASdetected in 500 g of 95% dry biosolids

Feedstock/Output		Test 1 - 500°C					Test 2 - 700°C				
	Biosolids	Biochar	PyroGas	Biooil	Destroyed/Converted		Biochar	PyroGas	Biooil	Destroyed/Converted	
Total Mass (g)	500	200	100	200	N/A		150	185	165	NA	
Parameter	(µg)	(µg)	(µg)	(µg)	(µg)	(%)	(µg)	(µg)	(µg)	(µg)	(%)
6:2 Fluorotelomer sulfonic acid(6:2 FTS)	BDL	BDL	0.011	BDL	-2	-2	BDL	0.022	BDL	-2	-2
10:2 Fluorotelomer sulfonic acid(10:2 F)	0.6	BDL	BDL	BDL	0.6	100%	BDL	BDL	BDL	0.6	100%
Perfluorohexane sulfonic acid (PFHxS)	*0.091*	0.09	BDL	BDL	0	0%	BDL	BDL	BDL	0.09	100%
Perfluorooctane sulfonic acid (PFOS)	13.3	BDL	BDL	BDL	13.3	100%	BDL	BDL	BDL	13.3	100%
N-Et PFO sulfonamidoacetic acid(EtFOSAA)	2.65	BDL	BDL	BDL	2.65	100%	BDL	BDL	BDL	2.65	100%
N-Me PFO sulfonamidoacetic acid(MeFOSAA)	1.45	BDL	BDL	BDL	1.45	100%	BDL	BDL	BDL	1.45	100%
Perfluorodecanoic acid (PFDA)	BDL	BDL	BDL	BDL	-2	-2	BDL	0.007	BDL	-2	-2
Perfluorohexanoic acid (PFHxA)	1.1	0.078	1.95	BDL	-0.93	-84.30%	BDL	0.266	BDL	0.8336	75.80%
Perfluorononanoic acid (PFNA)	BDL	BDL	0.168	BDL	-2	-2	BDL	0.224	BDL	-2	-2
Perfluorooctanoic acid (PFOA)	BDL	0.046	0.245	BDL	-2	-2	BDL	0.113	BDL	-2	-2
Perfluoropentanoic acid (PFPeA)	BDL	BDL	0.494	BDL	-2	-2	BDL	0.194	BDL	-2	-2
Perfluoroundecanoic acid (PFUnDA)	0.9	BDL	0.047	BDL	0.85	94.80%	BDL	0.052	BDL	0.8482	94.24%
Total	**20.09**	**0.21**	**2.915**	**0.00**	**16.96**	**84.4%**	**0.00**	**0.878**	**0.00**	**19.21**	**95.6%**

PFASTesting Results Before and After Pyrolysis



PFASMass and % Reductions out of 20 ug PFASin biosolids



W4170 MULTISTATE RESEARCH COMMITTEE RESPONSE TO USEPA OIG REPORT-NOV 29, 2018

Prepared by: USDA National Institute of Food and Agriculture Research Committee W4170

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AUTHORS

Nicholas Basta, Professor of Soil and Environmental Science
School of Environmental Science & Natural Resources, Ohio State University, Columbus, OH

Ian Pepper, Professor of Environmental Microbiology
Director of the Water and Environmental Technology Center (WEST), University of Arizona, Tucson, AZ

Linda S. Lee, Professor of Environmental Chemistry
Purdue University, Department of Agronomy, West Lafayette, IN

Greg Kester, Director of Renewable Resource Programs
CA Association of Sanitation Agencies, Sacramento, CA

Alyssa Zearley, Research Associate
School of Environment and Natural Resources, Ohio State University, Columbus, OH

Two Main Conclusions From this W4170 Response Regarding PFAS in Biosolids Land Application

- Exposures associated with land application of typical biosolids that are not heavily industrially impacted are insignificant compared to the other direct and indirect exposures in modern living environments. Recycling of biosolids to soils has not been a significant contributor to the nearly ubiquitous presence of PFAS in the human population.
- PFAS are released to the environment via land application of biosolids, and evaluation of land application as a pathway for human exposure through the contamination of groundwater and/or surface water and uptake by plants and animals has occurred and is ongoing. Except for a few, rare worst-case scenarios involving industrially impacted biosolids, the literature does not show cases of excessive human exposure associated with the use of biosolids in agriculture.
  - (Blaine et al., 2013; Gottschall et al., 2017; Kowalczyk et al., 2013; Lindstrom et al., 2011; Lupton et al., 2012; X. Zhang et al., 2016).

So What's the Impact of Biosolids Processes on PFAS

- Limited data….but…
  - Digestion may change precursors, but does not reduce overall PFAS levels
  - Short duration thermal drying could increase or decrease PFAS concentrations depending on precursors
  - Addition of bulking agent (composting) can dilute PFAS concentrations depending on sludge type
  - Pyrolysis (and longer duration desorption) can eliminate measurable PFAS
- Research on non-industrially impacted biosolids is progressing
  - Dr. Linda Lee at Purdue and others doing much research in this area
- Studies are being initiated to evaluate other process impacts.
  - Look for more data later this year and next.

Summary Thoughts…

Implications to biosolids land application

- PFOS and PFOA concentrations are decreasing
- EPA is working through risk analysis process for PFAS
- Some states will issue guidance recommendations on land application of biosolids based on concentration levels. MI has already done so. ME has banned all biosolids to land.
- Most data on PFAS impact in field studies has been gathered on impacted biosolids. Very little data on impact (leachability, plant uptake, etc.) in US of PFAS from non-industrially or non AFFF impacted biosolids/ soils
- We are seeing more data on the impact of various biosolids treatment processes on PFAS concentrations
- Studies are being initiated to evaluate various biosolids process impacts. Jacobs is gathering more data this year.

Biosolids PFAS Management Summary Thoughts…

- Follow studies and regulation development
- Update biosolids management plans
- Develop flexible biosolids programs that can be modified as regulations and/or public demand require
- Consider testing biosolids to understand PFAS levels
- Look upstream for industries that may use PFAS (SIC search)
- Prepare for questions from the public as they will come
- Fact sheets are available from several sources
  - https://www.nacwa.org/advocacy-analysis/campaigns/pfas
  - https://pfas-1.itrcweb.org/
  - Jacobs PFAS fact sheet

PFAS FACTSHEET

APWA American Public Works Association
CASA
NACWA
National Waste & Recycling Association
SWANA Solid Waste Association of North America
WateReuse
Water Environment Federation the water quality people
ERIS Environmental Research Institute of the States
ECOS

ITRC
50 F St. NW, Suite 350
Washington, DC 20001
itrcweb.org

ITRC Disclaimer

Jacobs Challenging today. Reinventing tomorrow.

Biosolids and PFAS– Current Issues and A Look Forward

Thank you!

Todd O. Williams, PE,BCEE

Todd.williams3@jacobs.com