NEWEA 2024 Annual Meeting

What does pyrolysis do to PFAS in biosolids? Distinguishing removal from transformation.

Patrick McNamara, Ph.D., P.E.
Hari Santha, P.E, Lynne Moss, P.E. BCEE, Scott Carr, P.E. BCEE

BLACK & VEATCH

Marquette University

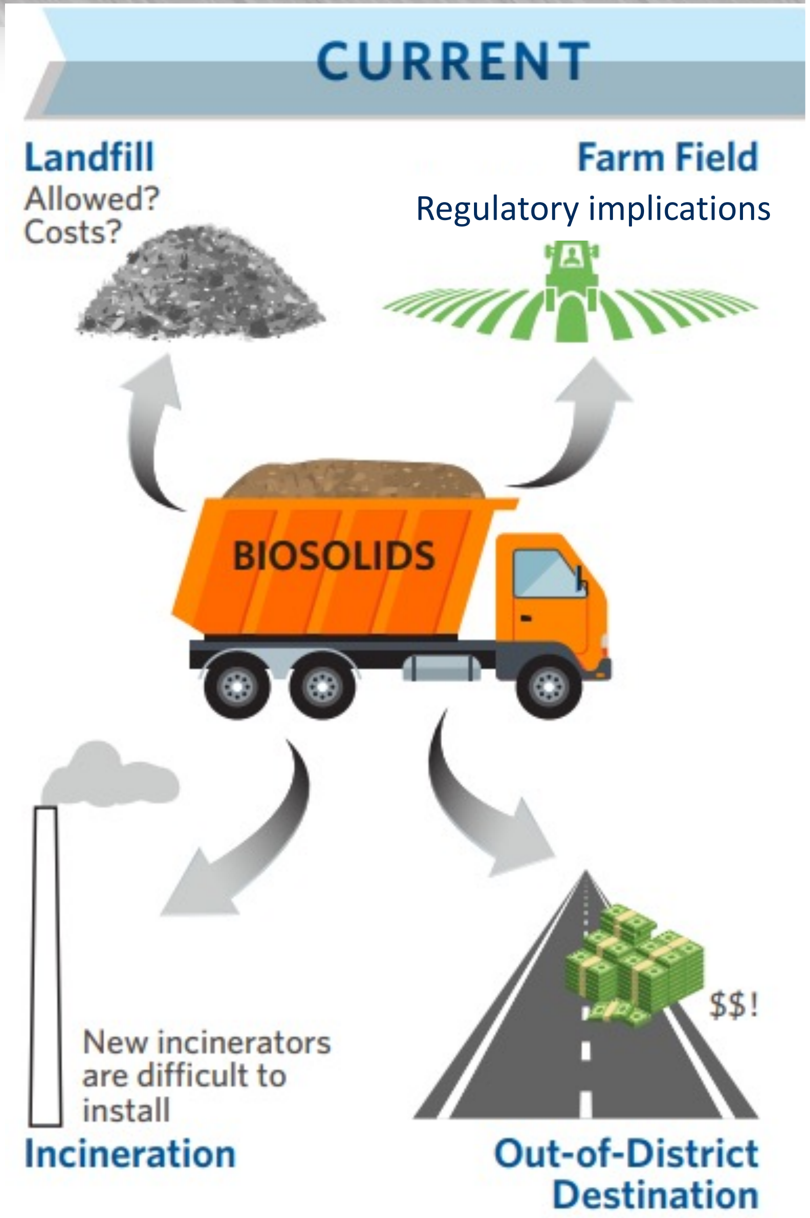
January 22, 2024

WRF Project #5211

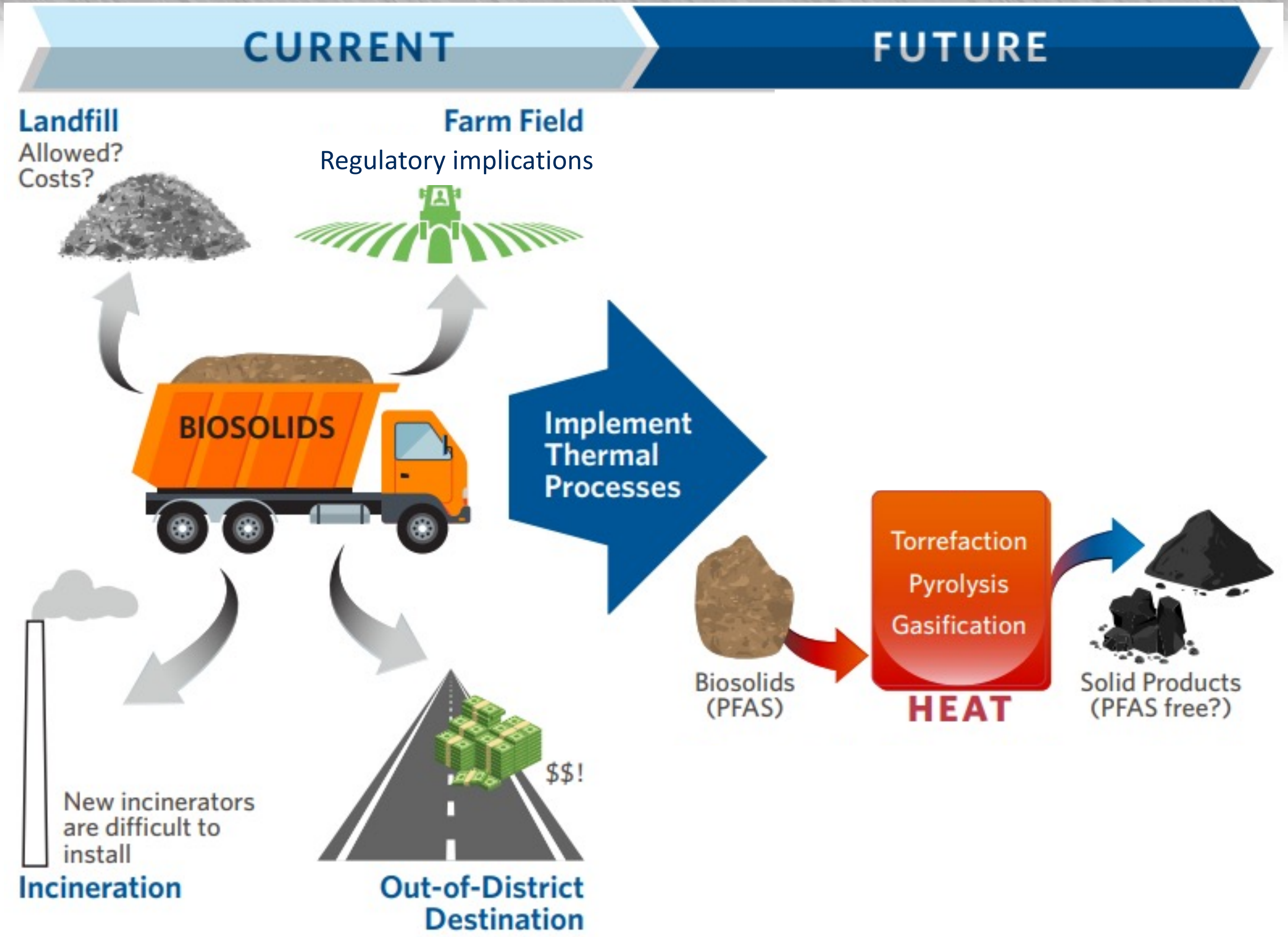
Understanding the Value Proposition of Thermal Processes to Mitigate PFAS in Biosolids

Principal Investigator – Patrick McNamara Ph.D (BV / Marquette)
Co PI – Greg Knight (BV)

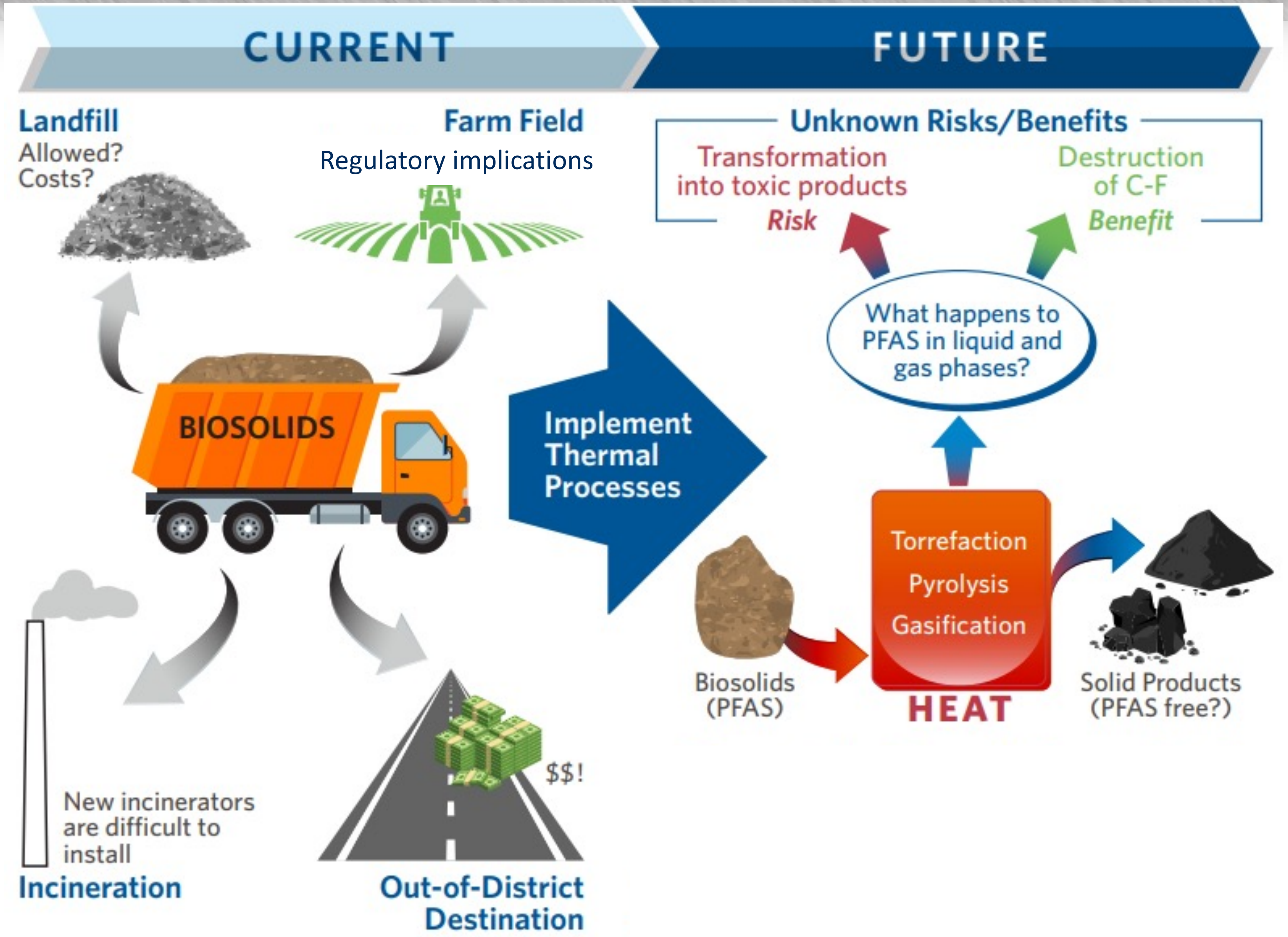
PFAS Risks in Biosolids Management



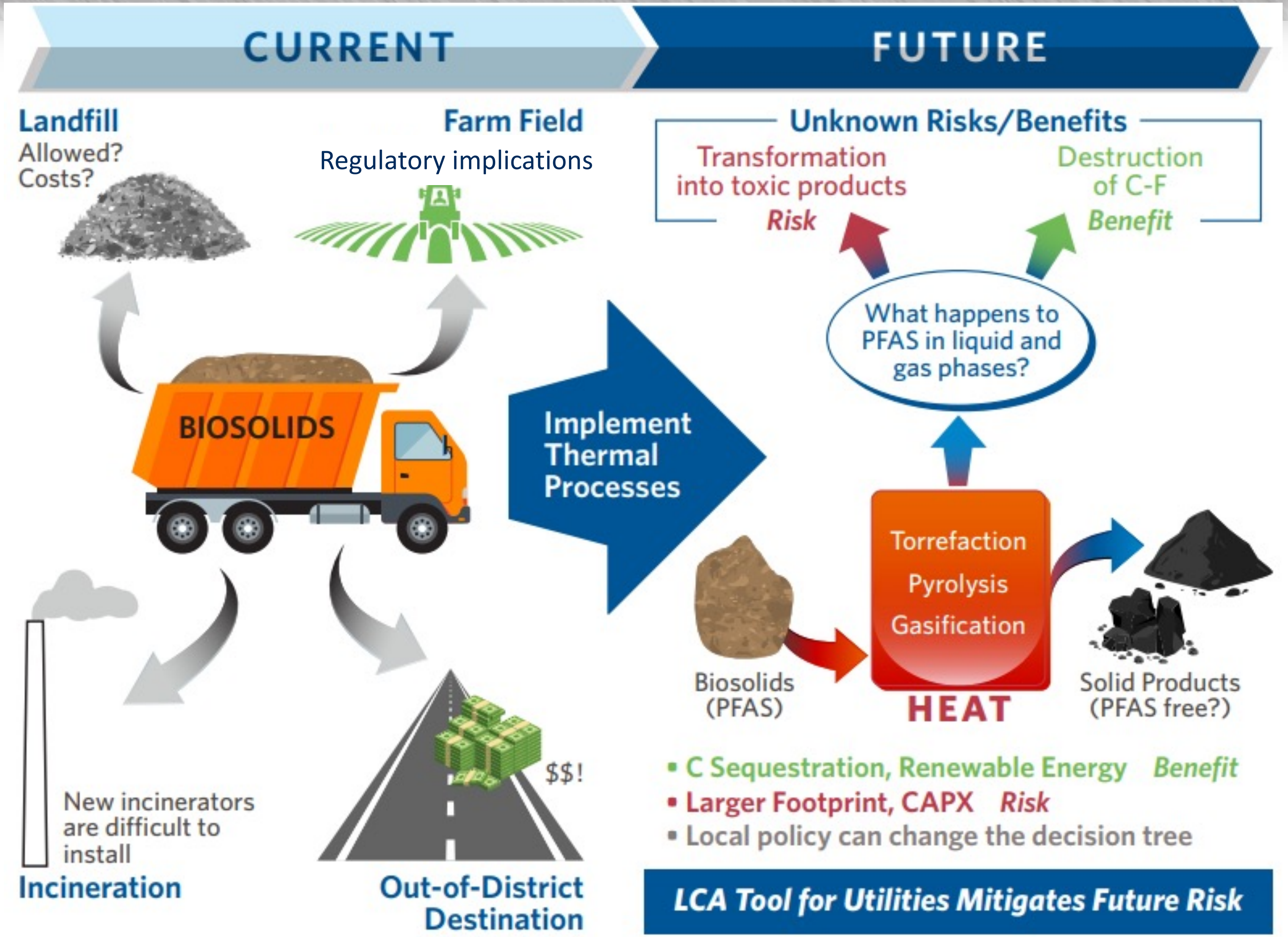
PFAS Risks in Biosolids Management



PFAS Risks in Biosolids Management



PFAS Risks in Biosolids Management



Goal: Provide Tools to Support Biosolids Planning

Tools need to incorporate *broader* potential benefits and costs of installing thermal processes **&** impacts of PFAS that are relevant in a regulatory framework.

This research integrates experimental results with local policy criteria into a practicable **LCA tool** that can be employed by utilities and other WRF subscribers to assess the optimal biosolids management strategies.

Presentation Objectives

1. Know what pyrolysis of biosolids is and what it produces

2. Establish practical aspects (benefits/challenges) that need to be considered for utilities prior to implementation of pyrolysis

3. Understand the potential impacts pyrolysis can have on PFAS

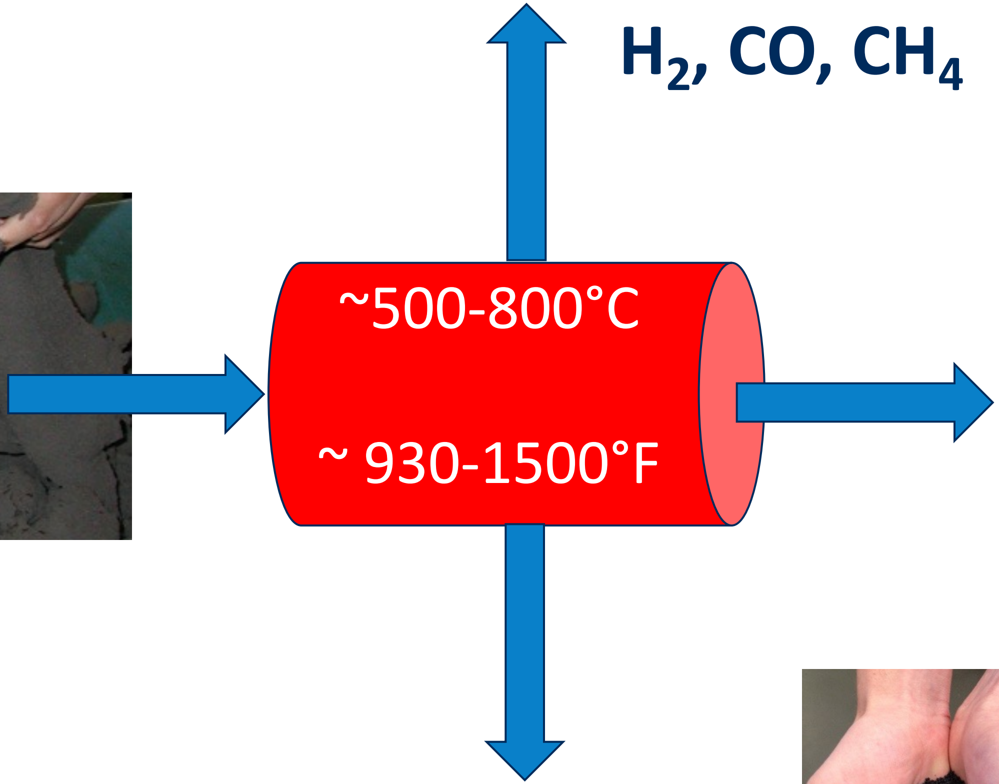
Pyrolysis: Heating without oxygen

Biomass

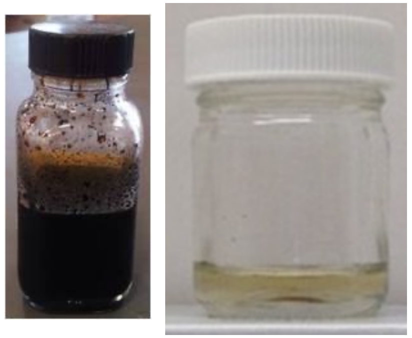
- Wood
- Switchgrass
- Biosolids

Py-gas

H_2, CO, CH_4



Py-liquid



Biochar

Presentation Objectives

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2. Establish practical aspects (benefits/challenges) that need to be considered for utilities prior to implementation of pyrolysis

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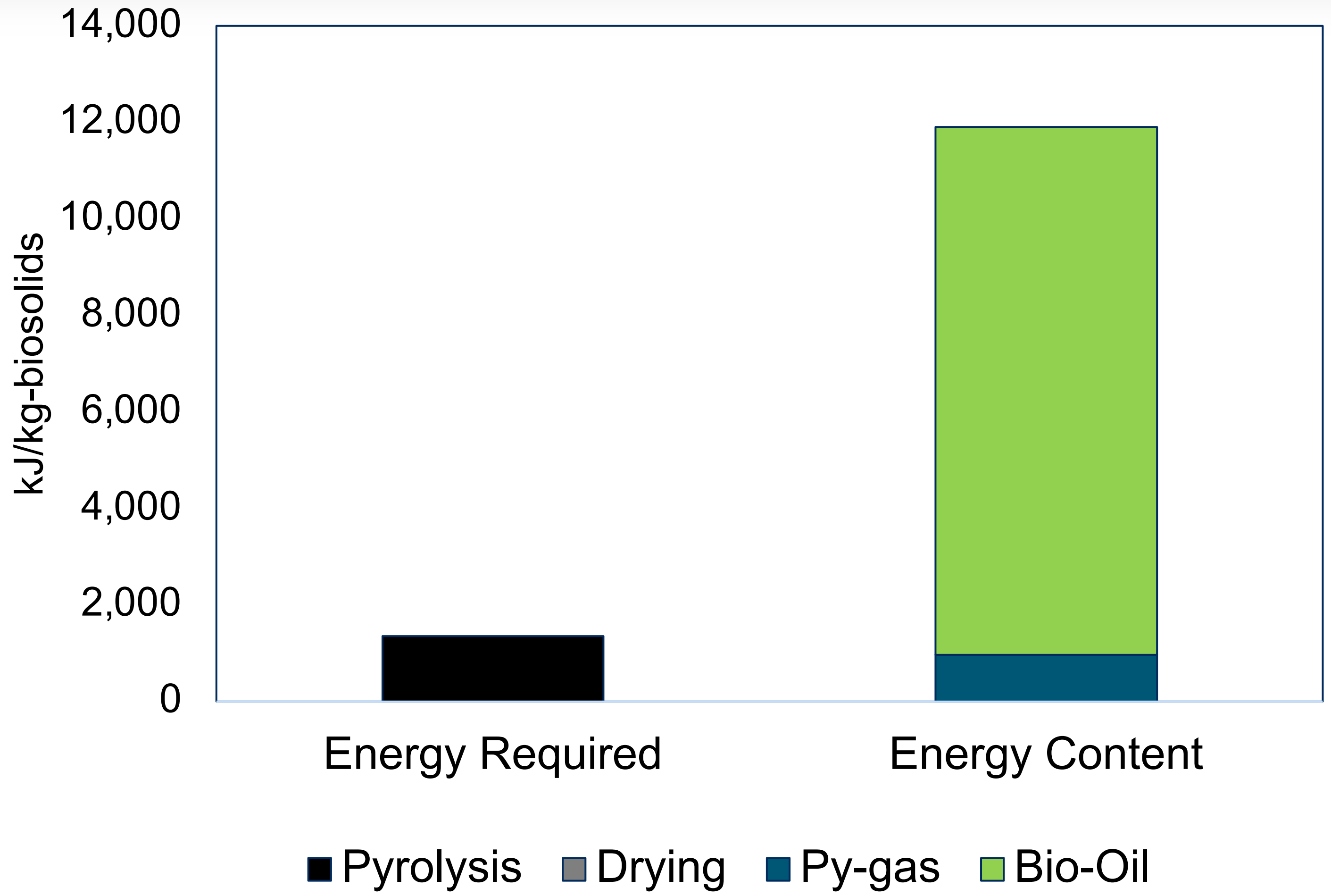
Potential Challenges

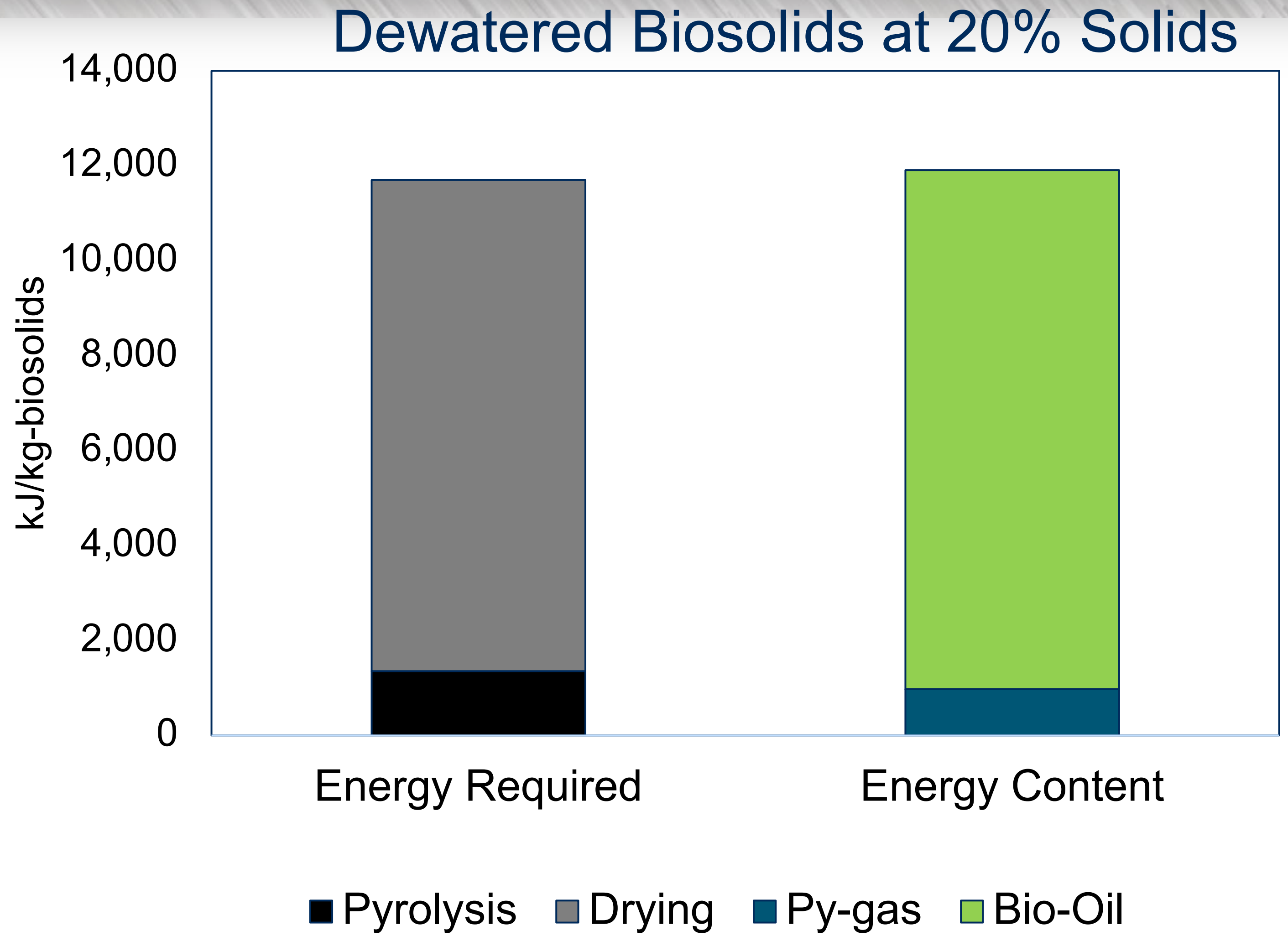
- Drying Costs
- Pyrolysis Liquid
- Nutrient Mass Balance
- Few Installations

Energy Balance



McNamara, P.J., Koch, J.D., Liu, Z., Zitomer, D.H., 2016. Pyrolysis of Dried Biosolids Can Be Energy Positive. *Wat. Env. Res.* 88 (9), 804-810

Energy Balance – Drying is energy intensive



- Assuming 70% energy recovery, energy in products < energy required for pyrolysis & drying

- **Take-home message**: If you already dry, pyrolysis could be used to offset some drying energy costs

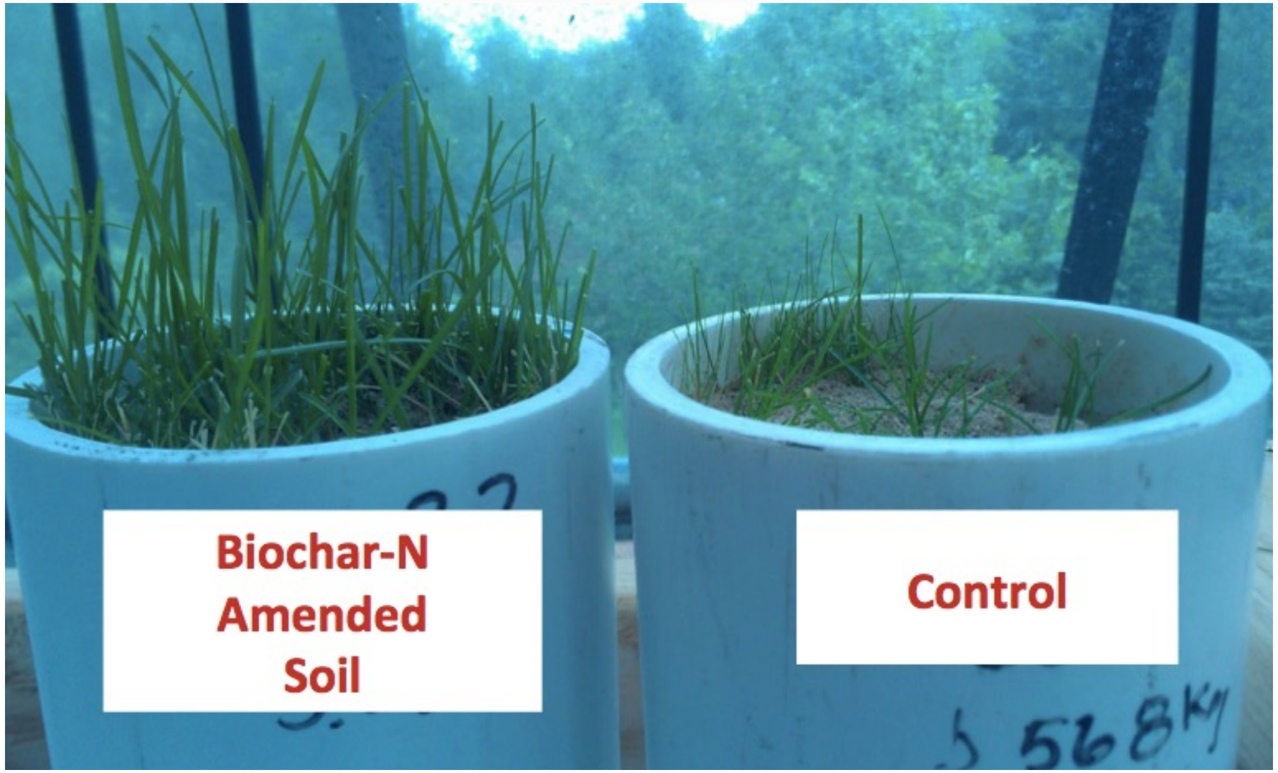
McNamara, P.J., Koch, J.D., Liu, Z., Zitomer, D.H., 2016. Pyrolysis of Dried Biosolids Can Be Energy Positive. *Wat. Env. Res.* 88 (9), 804-810

Potential Benefits

- Energy Recovery from Biosolids (Py-Gas)
- Value-Added Product & Carbon Sequestration (Biochar)
- Solids Reduction
- PFAS Removal

Biochar as a soil amendment

- Moisture holding capacity
- Carbon sequestration
- Less water extractable P than biosolids



"Biochar-N" with belt filter press filtrate

Carey D.E., McNamara, P.J., Zitomer, D.H. 2015. Biochar from Pyrolysis of Biosolids for Nutrient Adsorption and Turfgrass Cultivation. *Wat. Env. Res.* 87 (12), 2098-2105.

Biochar as a Beneficial Soil Amendment

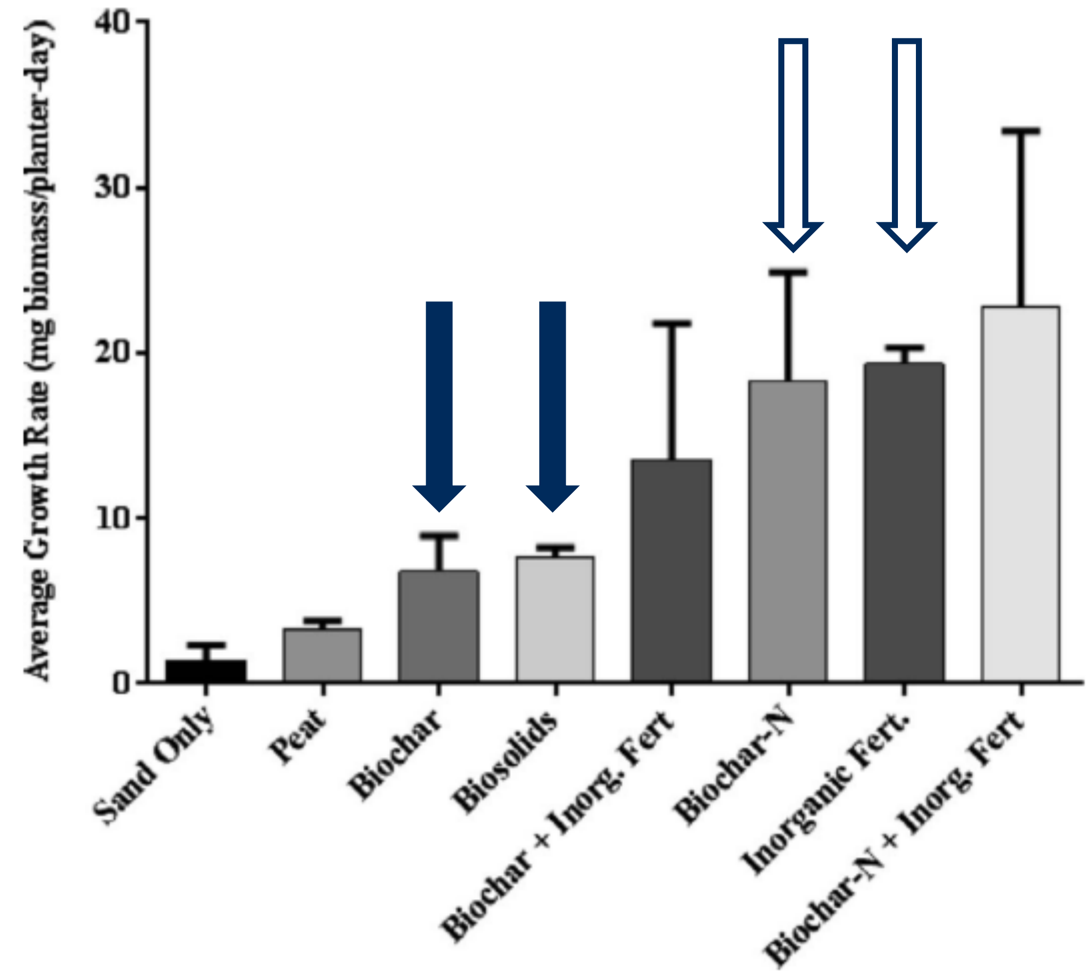


Figure 3—Average growth rate of Kentucky bluegrass biomass. Biomass was measured immediately after trimming to a height of 1 in.

- Biochar is a different product than biosolids
- Need to test specific biochar with specific application

Carey D.E., McNamara, P.J., Zitomer, D.H. 2015. Biochar from Pyrolysis of Biosolids for Nutrient Adsorption and Turfgrass Cultivation. *Wat. Env. Res.* 87 (12), 2098-2105.

Pyrolysis Overview

STRENGTHS

- Non-burning
- Sludge mass converted to energy
- Reduction in GHGs/emissions

WEAKNESS

- Few installations
- High investment w/drying
- Long-term operational feasibility unproven

THREATS

- Unclear regulatory framework
- Air pollution control (APC) requirements unknown

OPPORTUNITIES

- Potential funding
- Removal of PFAS from solids
- Value-added products

McNamara, P., Liu, Z., Tong, Y., Santha, H., Moss, L., Zitomer, D. Pyrolysis-A tool in the wastewater solids handling portfolio, not a silver bullet: Benefits, drawbacks, and future directions. *Wat. Env. Res.* 2023 (https://doi.org/10.1002/wer.10863).

Presentation Objectives

1. Know what pyrolysis of biosolids is and what it produces

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What Does Pyrolysis Do to PFAS? Start with Fate Definitions

Removal

- Compound is no longer present in its original phase

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Transformation

- Compound reacts to form new compound with modified chemical structure

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Destruction

- Compound is mineralized (C-F bonds are broken), inorganic fluoride remains and simple forms of carbon (e.g., CO_2)

How could we know if transformation occurs?

Total Oxidizable Precursor Assay, a.k.a. TOP Assay

A → B

Precursor

Unknown chemical that could be converted to a known PFAS

Oxidation process that converts A to B

PFAS

Specific PFAS we can measure

How could we know if transformation occurs?

Total Oxidizable Precursor Assay, a.k.a. TOP Assay

A → B

Why do we care about a process that occurs under extreme lab conditions?

- The process happens in treatment plants and the environment
- Allows us to know extent of PFAS in sample

Environmental Science & Technology

pubs.acs.org/est Article

Underestimation of Per- and Polyfluoroalkyl Substances in Biosolids: Precursor Transformation During Conventional Treatment

Jake T. Thompson, Nicole M. Robey, Thabet M. Tolaymat, John A. Bowden, Helena M. Solo-Gabriele, and Timothy G. Townsend*

Cite This: https://doi.org/10.1021/acs.est.2c06189 Read Online

TOP Allows Us to Know Extent of PFAS in Samples

If you measure your influent and do not see a specific PFAS, you cannot assume it won't be in your effluent

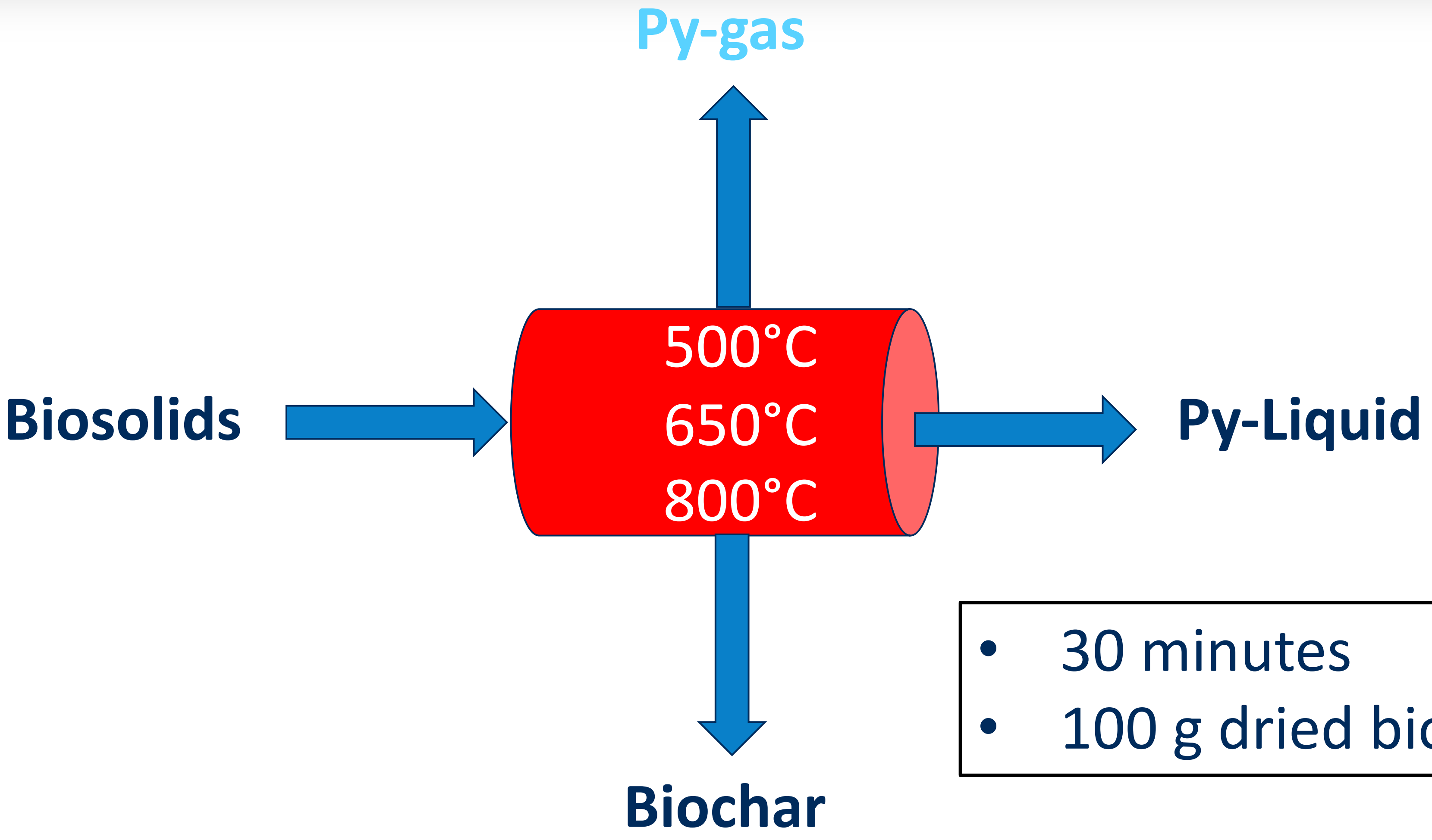
PFAS could be in your effluent that were not in your influent

Initial Research Questions

1. Does pyrolysis **remove** PFAS from biosolids?

2. Does pyrolysis **transform** PFAS?

Experimental Approach: Triplicate Batch Experiments



- 30 minutes
- 100 g dried biosolids

Results

Environmental
Science
Water Research & Technology

ROYAL SOCIETY OF CHEMISTRY

PAPER

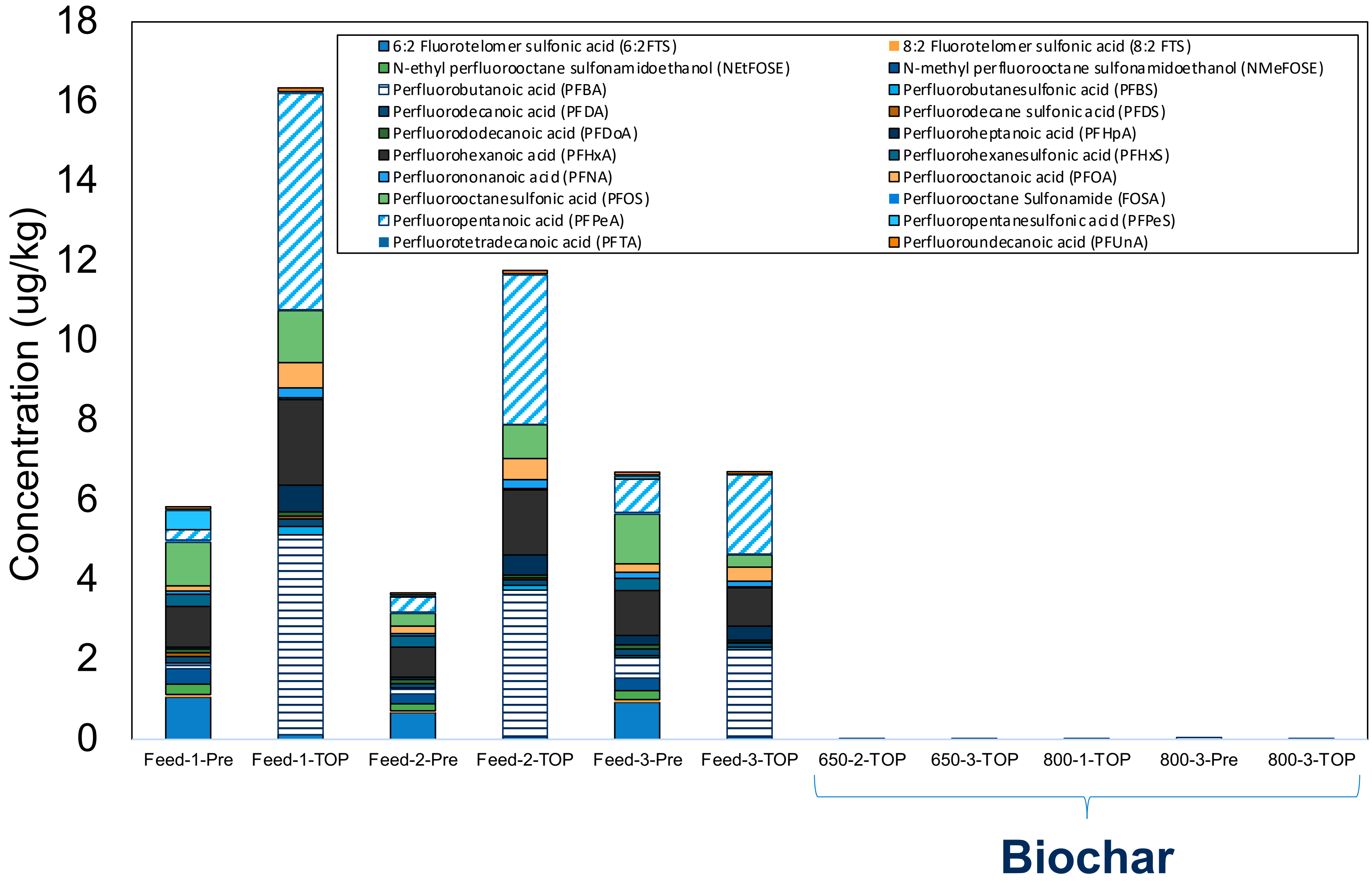
Check for updates

Cite this: *Environ. Sci.: Water Res. Technol.*, 2023, **9**, 386

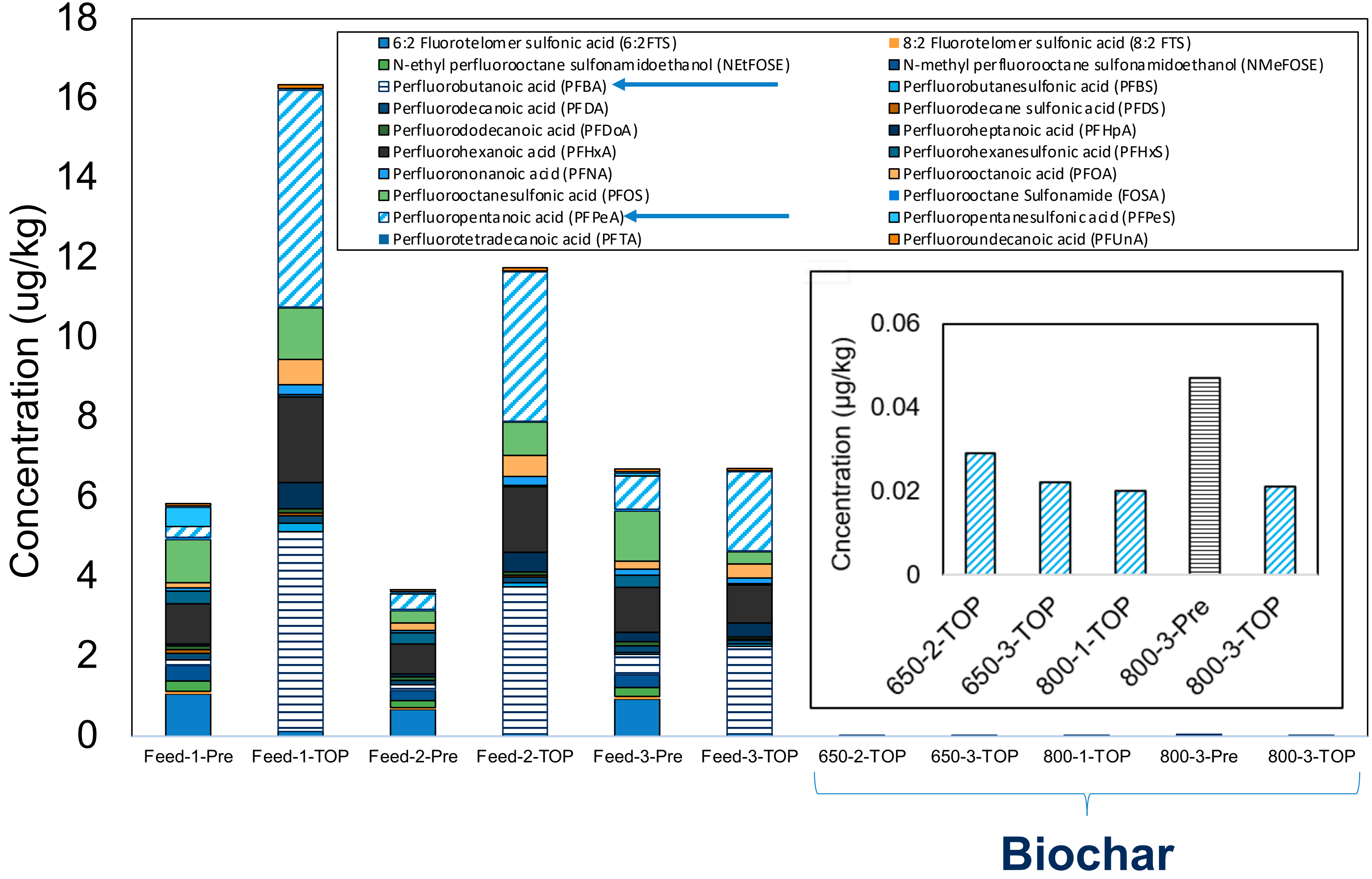
Pyrolysis transports, and transforms, PFAS from biosolids to py-liquid†

Patrick McNamara, *[ab] Melvin S. Samuel,[b] Sandeep Sathyamoorthy,[a] Lynne Moss,[a] Danny Valtierra,[d] Hugo Cortes Lopez,[d] Nick Nigro,[c] Stephen Somerville[c] and Zhongzhe Liu[d]

Pyrolysis removes PFAS from biosolids



Pyrolysis removes PFAS from biosolids



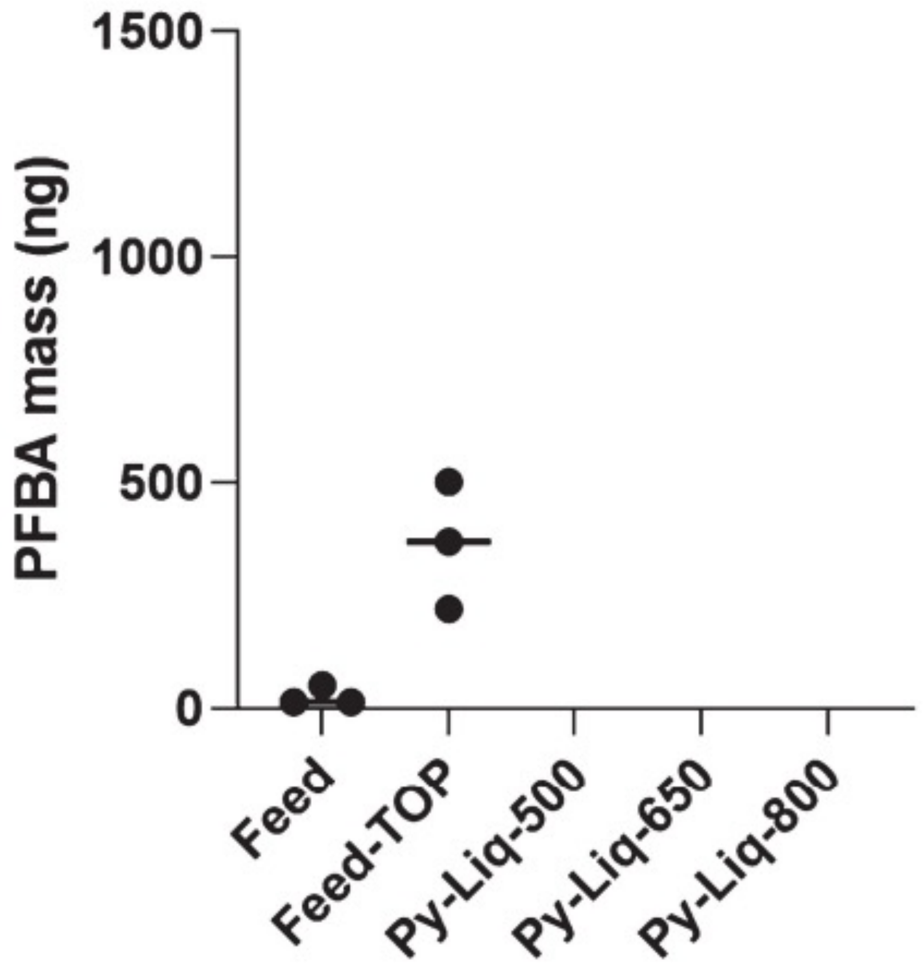
Pyrolysis removes PFAS from biosolids

- 22 PFAS detected in biosolids
- >99% removal in biochar

Removal occurs…what happens to PFAS?

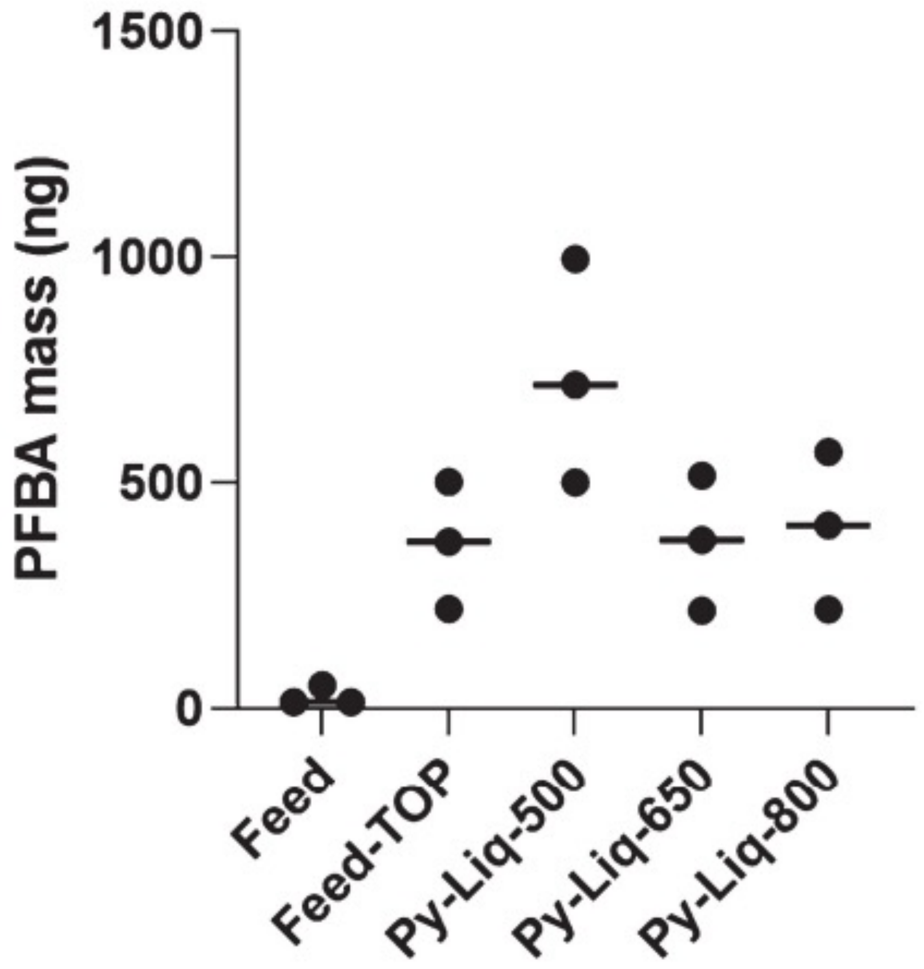
PFBA Precursors are in Biosolids

- Total Oxidizable Precursors (TOP) assay measures all the precursor compounds that could transform to PFBA

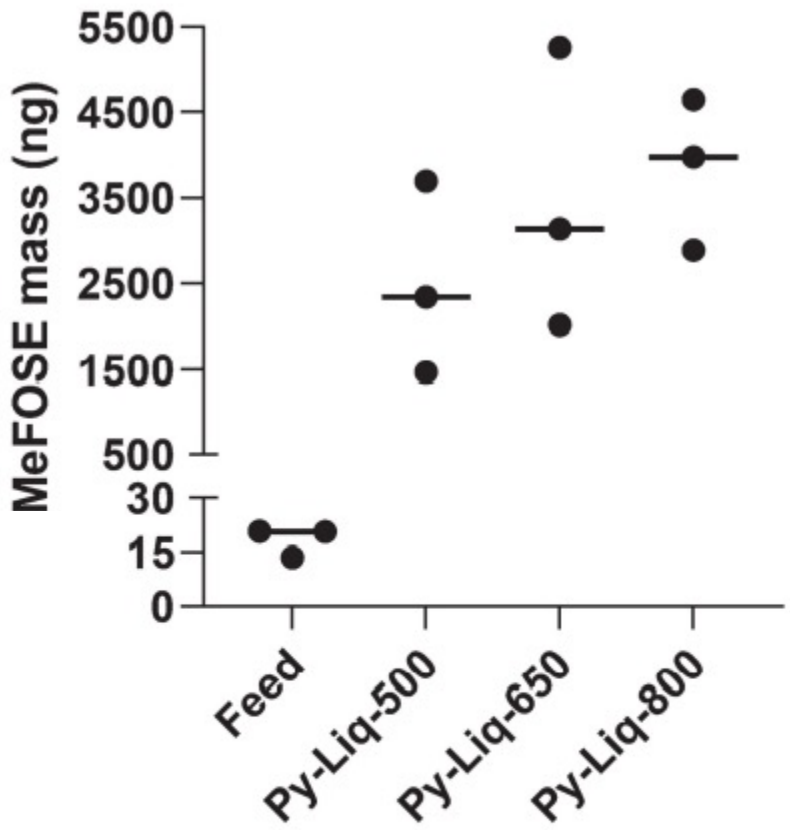


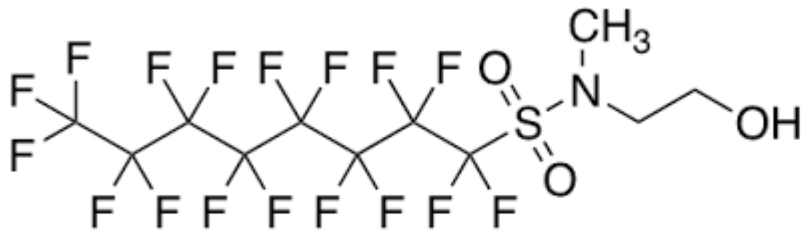
PFBA Precursors are in Biosolids

- Total Oxidizable Precursors (TOP) assay measures all the precursor compounds that could transform to PFBA
- PFBA detected at much higher levels in py-liquid than in the feed
- **Precursor compounds can be converted to PFAS during pyrolysis**



Pyrolysis forms MeFOSE (via transformation)





MeFOSE

Answers to Research Questions

1. Does pyrolysis **remove** PFAS from biosolids? ***Yes***

2. Does pyrolysis **transform** PFAS? ***Yes***

3. Does pyrolysis **destroy** PFAS? *We do not know yet, but at least not entirely because PFAS were observed in the liquid*

What about drying?

Drying temperatures are too low to affect PFAS, right?

- We tested samples from 3 utilities
- Dried in oven over night
- Measured PFAS in wet and dry samples

Drying Affects PFAS Profile

Name	A Wet	A Dry	B Wet	B Dry	C Wet	C Dry
PFBA		1				1
PFPeA		1		1		1
PFHxA		1		1		1
5:3 FTCA	1	1	1	1	1	1
6:2 FTCA	1		1		1	1
PFHxS	1					
PEPA		1				
PFOA	1	1	1	1	1	1
6:2 FTS	1	1				
7:3 FTCA	1	1	1	1	1	1
PFNA	1	1	1	1		1
8:2 FTCA	1		1		1	
FOSA	1					
PFOS	1	1	1	1	1	1
PFDA	1	1	1	1		1
8:2 FTS	1	1	1	1		
NMeFOSE	1	1	1	1	1	1
PFUnA	1	1	1	1	1	1
NMeFOSAA	1	1	1	1	1	1
NEtFOSE		1				1
NEtFOSAA	1	1	1	1	1	1
PFDS		1				
PFDoA	1	1	1	1	1	
10:2 FTS			1	1	1	
PFTeA						1
Sum	17	19	15	15	12	16

Precursor Transformation

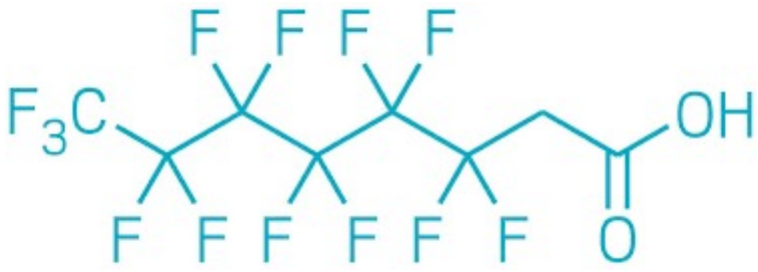
Contents lists available at ScienceDirect

Science of the Total Environment

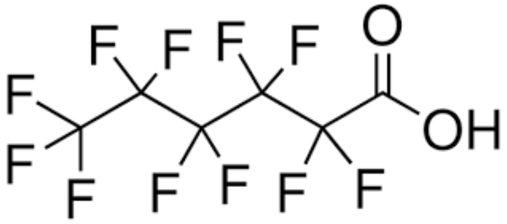
journal homepage: www.elsevier.com/locate/scitotenv

Using regular and transcriptomic analyses to investigate the biotransformation mechanism and phytotoxic effects of 6:2 fluorotelomer carboxylic acid (6:2 FTCA) in pumpkin (*Cucurbita maxima* L.)

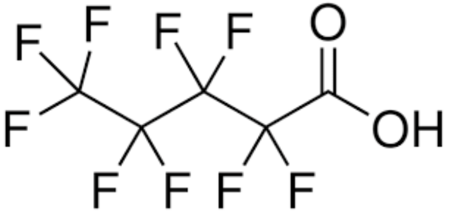
Fanghui Chi [a,1], Jingyan Zhao [a,1], Liping Yang [b], Xiaojing Yang [a], Xv Zhao [a], Shuyan Zhao [a,*], Jingjing Zhan [a]



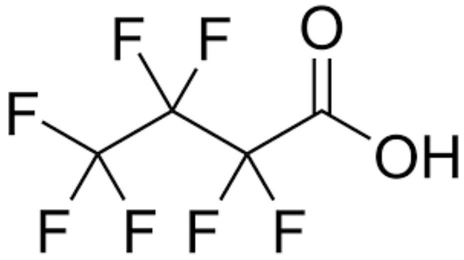
6:2 FTCA



PFHxA



PFPeA



PFBA

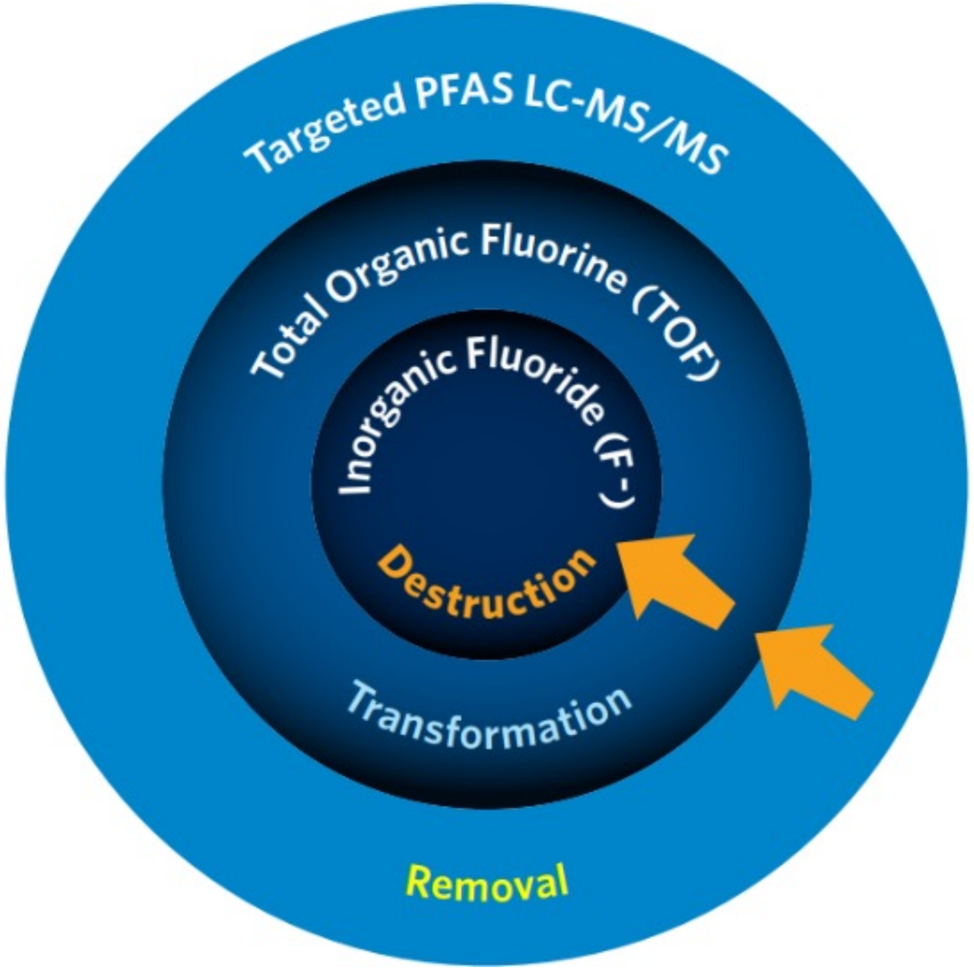
Answers to Research Questions

Drying can also lead to transformation reactions

Moving Forward with WRF: Filling in Research Gap

To know what happens to PFAS we need analytical methods:

- Gas phase and liquid phase
  - Specific PFAS
  - Total organic fluorine (TOF)
  - Inorganic Fluoride



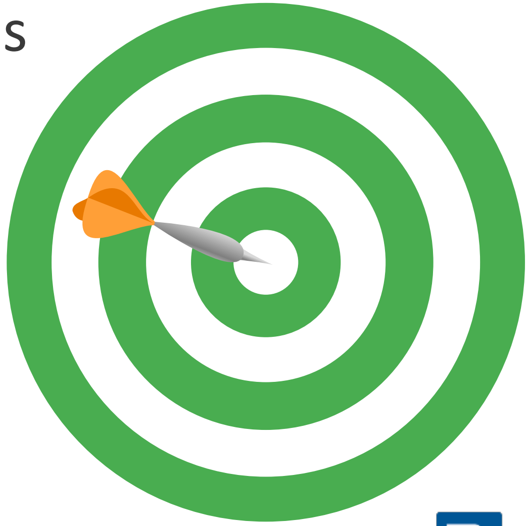
WRF Project Objectives

Objective 1. Develop methods to quantify PFAS in the effluent liquid and gas phases of thermal processes.

Objective 2. Determine the impact of thermal processes on fate of PFAS from biosolids.

Objective 3. Conduct Life Cycle Assessment (LCA) on Thermal Processes

Objective 4. Final Report



Objective 1 – Method Development

- Eurofins Technical Team:
  - *Taryn McKnight (Co-PI)*
  - *William Anderson, Ph.D. (Source Air Specialist)*
  - *Eric Redman (VP of Technical Services)*
- Gas Phase Development
  - Collection: Methanol impinger
  - Analysis: CIC-TOF with chemical pretreatment to knock-out inorganic fluoride
- Liquid Phase Development
  - Separate aqueous phase liquid
  - Non-aqueous phase liquid

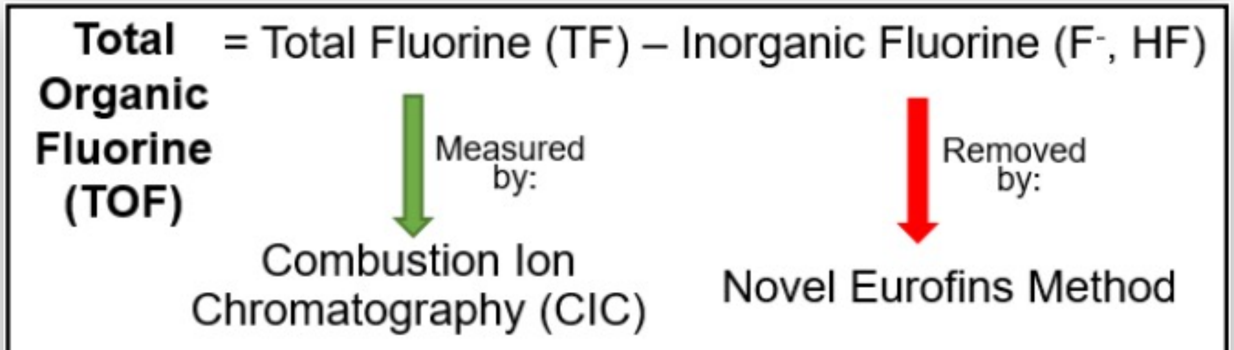
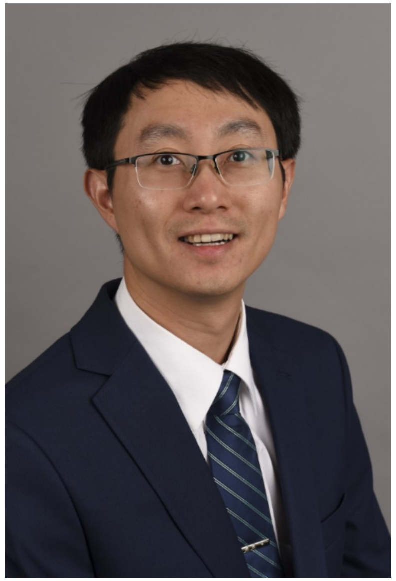


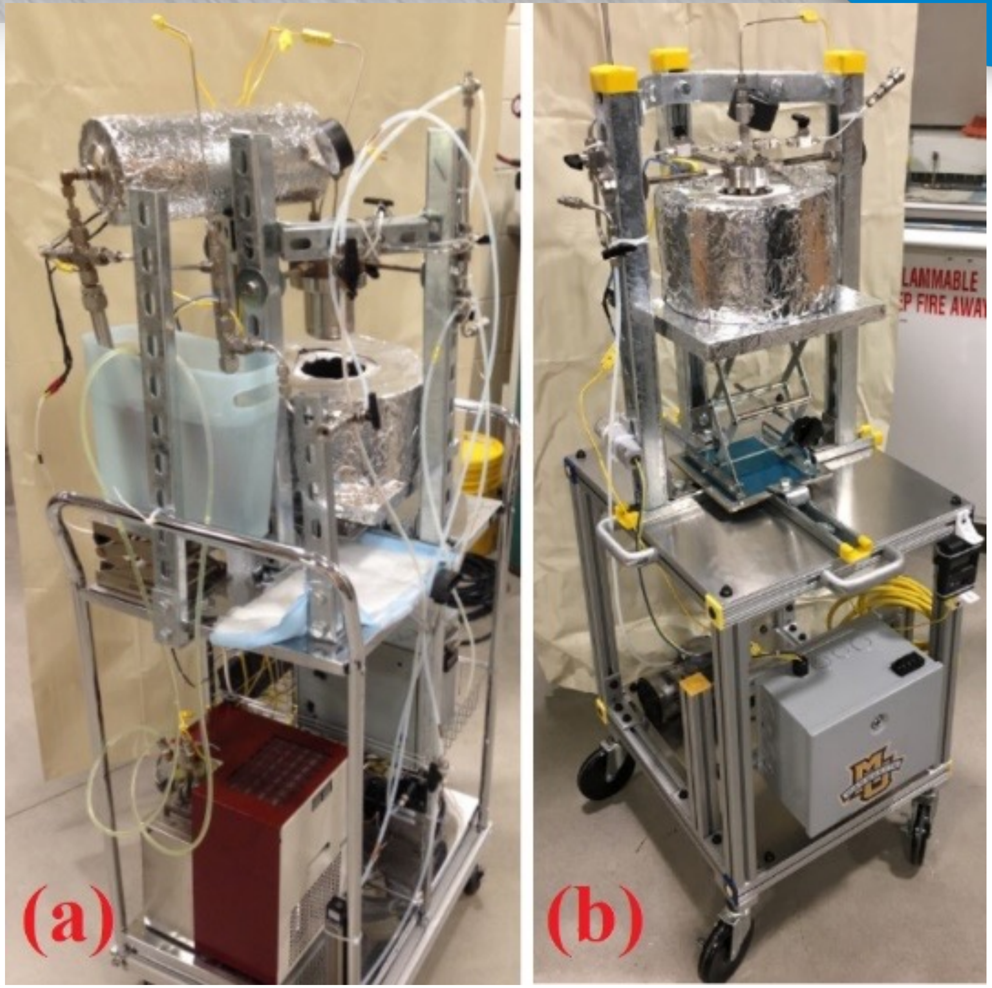
Figure 3-4. Analytical Approach to Determine TOF

Objective 2: Lab-Scale Experiments on Thermal Processes

Temp (^{o}C)	Process
100	Drying
300	Torrefaction
500	Low Temp Pyrolysis
800	High Temp Pyrolysis
800	Gasification



Zhongzhe Liu, Ph.D.
Assistant Professor
CSU-Bakersfield



Lab-scale thermochemical conversion systems
(a) pyrolyzer (b) gasifier

Objective 3: LCA

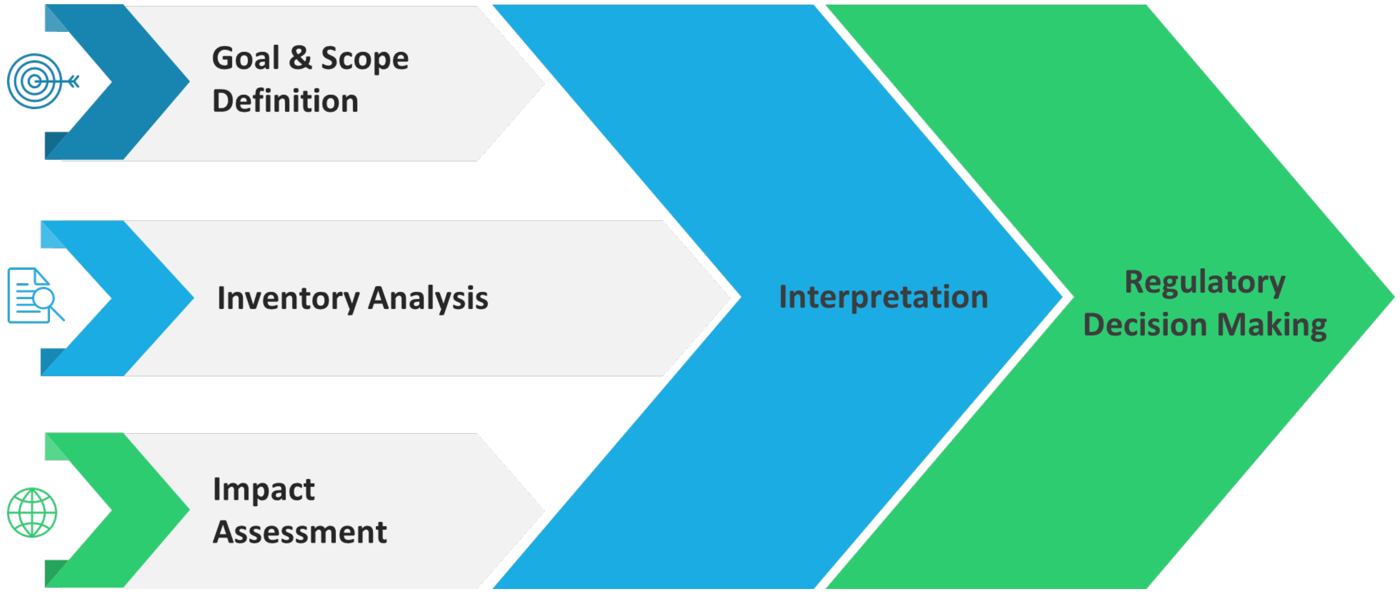
Rationale: Understand the environmental impacts and benefits of adopting gasification, pyrolysis, and torrefaction as different treatment approaches for biosolids.

Scenarios:

- ➢ Nominal small facility
- ➢ Nominal large facility

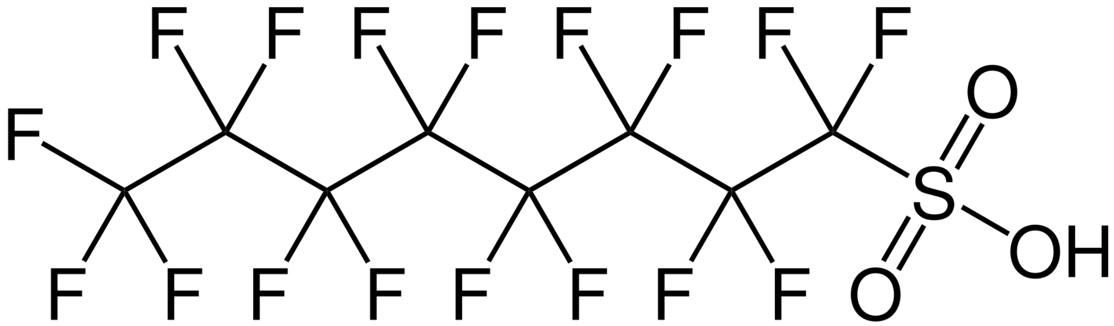
Treatment approaches:

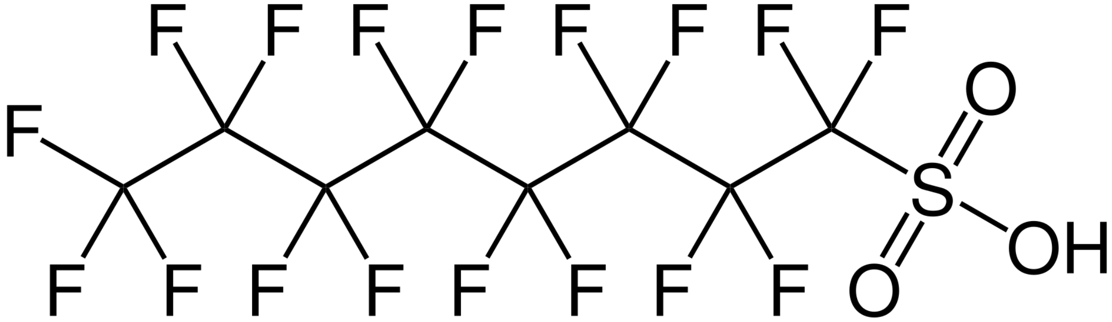
- ➢ Thermal drying => Class A
- ➢ Thermal drying + gasification
- ➢ Thermal drying + pyrolysis
- ➢ Thermal drying + torrefaction



Greg Knight (lead), Andrew Shaw, Ph.D., Francesca Cecconi, Ph.D.

Final Thoughts





Acknowledgements

WRF Project 5211

- BV (Lynne Moss)
- Eurofins (Taryn McKnight)
- CSU-B

BV – PFAS Research

- Research & Innovation Platform BV
- Pace® Analytical Services
  - Nick Nigro
- Cal State Students
  - Hugo Cortes Lopez, Danny Valtierra

Marquette Pyrolysis Research

- Lead Collaborators – Dr. Daniel Zitomer & Dr. Zhongzhe Liu
- Graduate Students – John Ross (MS), Yiran Tong (PhD), Dan Carey (PhD),
- Collaborators – Dr. Brooke Mayer, Dr. Simcha Singer
- Funders – MMSD, NSF WEP, OCOE Seed Grant

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Thank You

Questions, or interest in collaboration?

McNamaraP@BV.com

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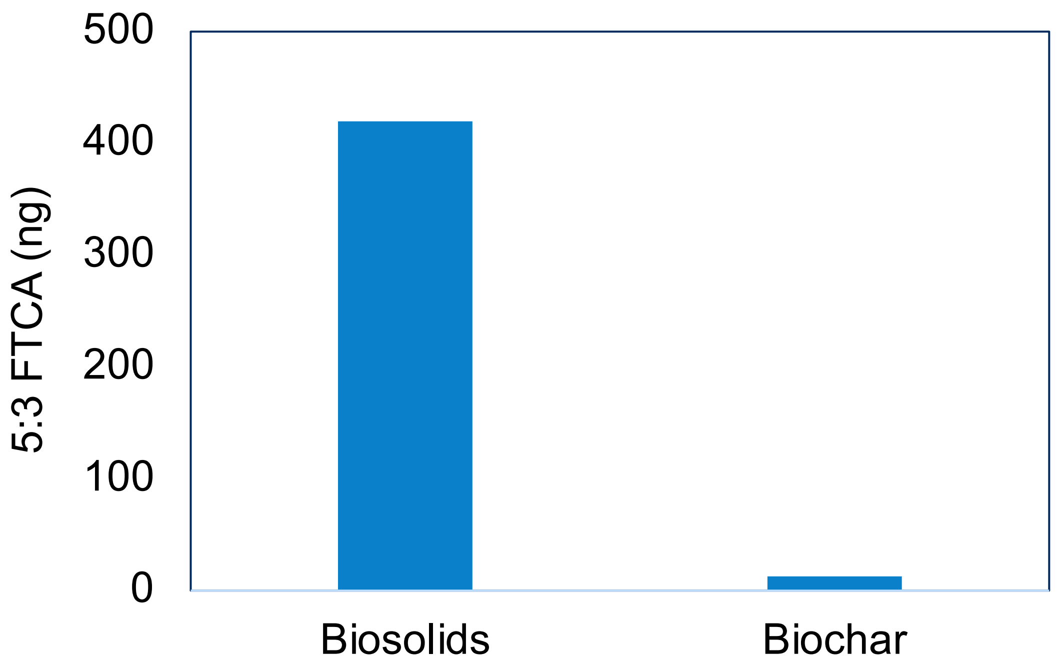
Marquette University

New Experiment, Same Idea



New Experiment, Same Idea - PFAS in Py-Liquid