

41st Spring Biosolids Symposium

Effect of Heat Treatment on Fate of PFAS in Biosolids

Patrick McNamara, Ph.D., P.E.



BLACK & VEATCH



Marquette University

March 19, 2024

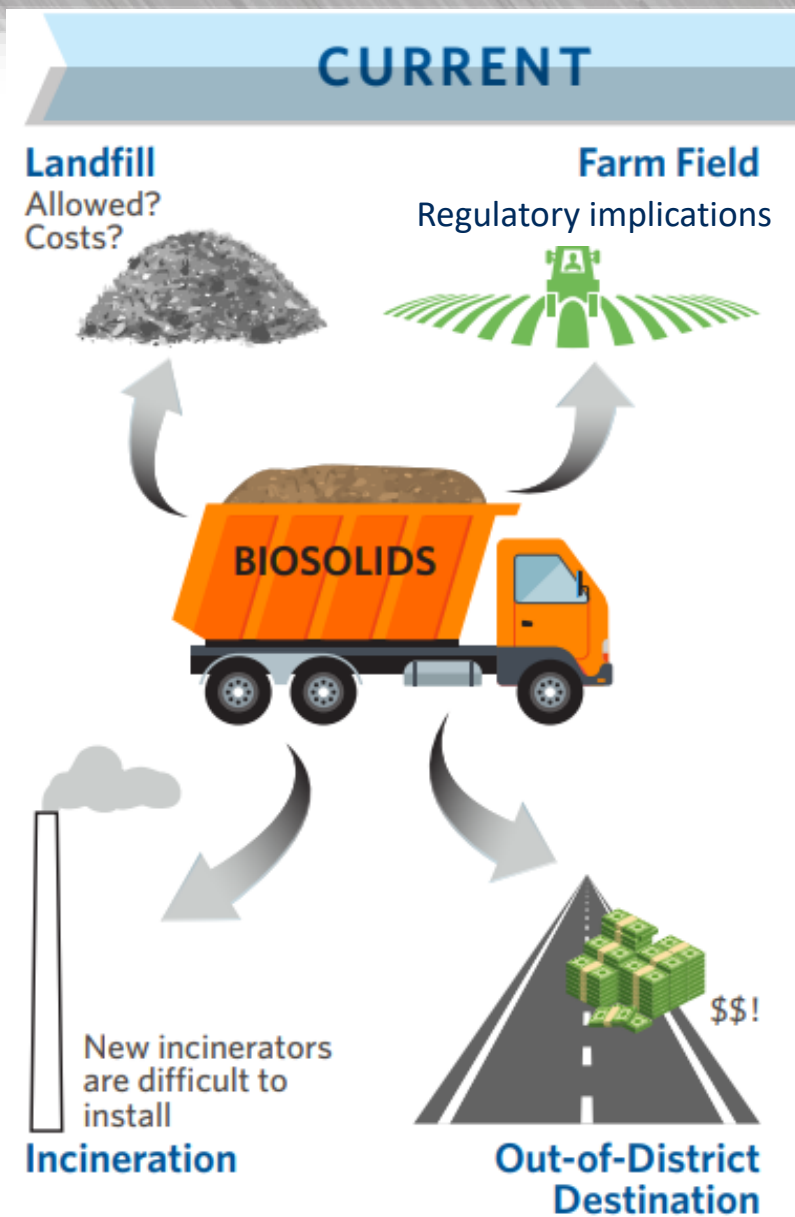


WRF Project #5211

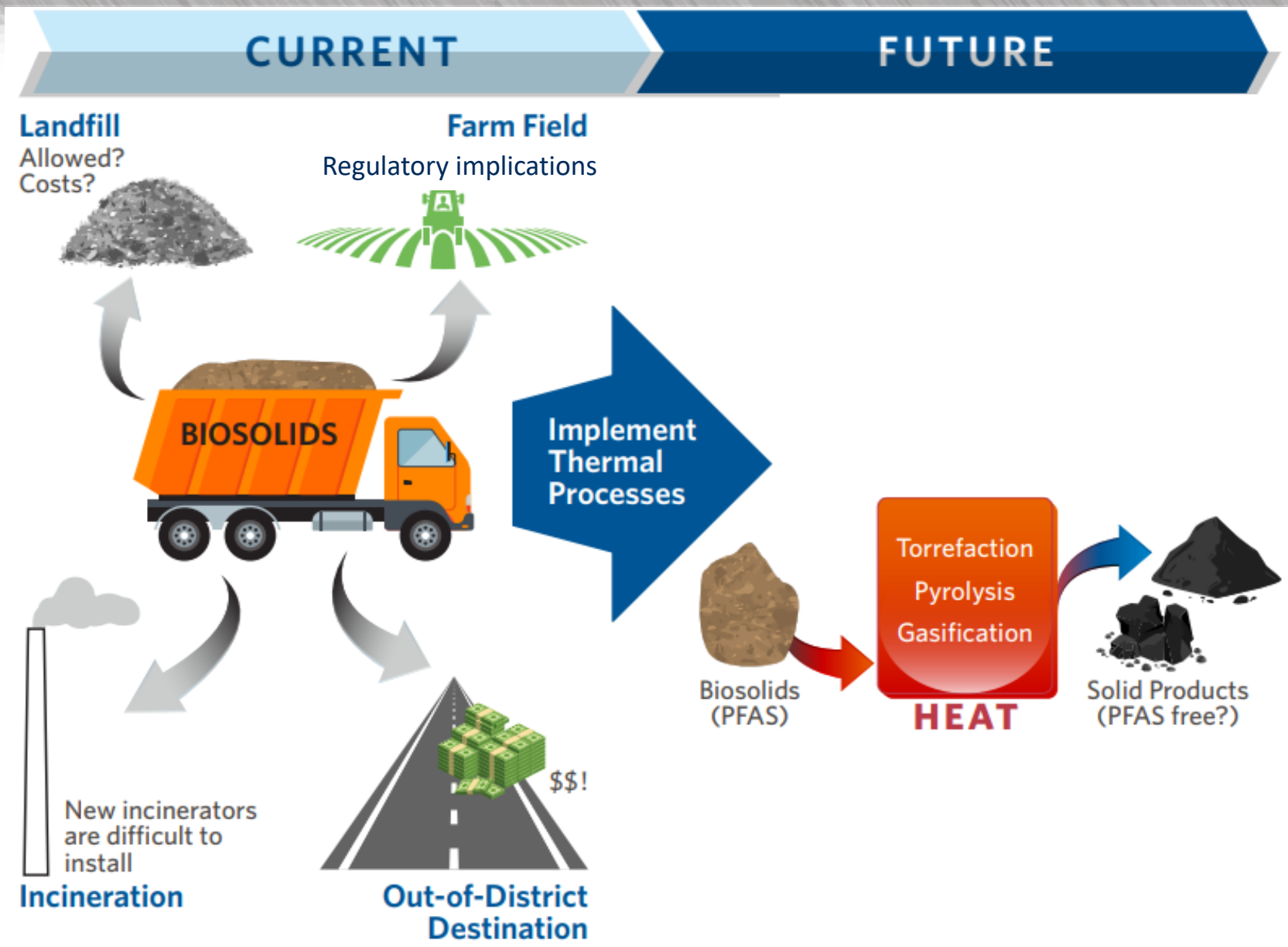
Understanding the Value Proposition of Thermal Processes to Mitigate PFAS in Biosolids

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

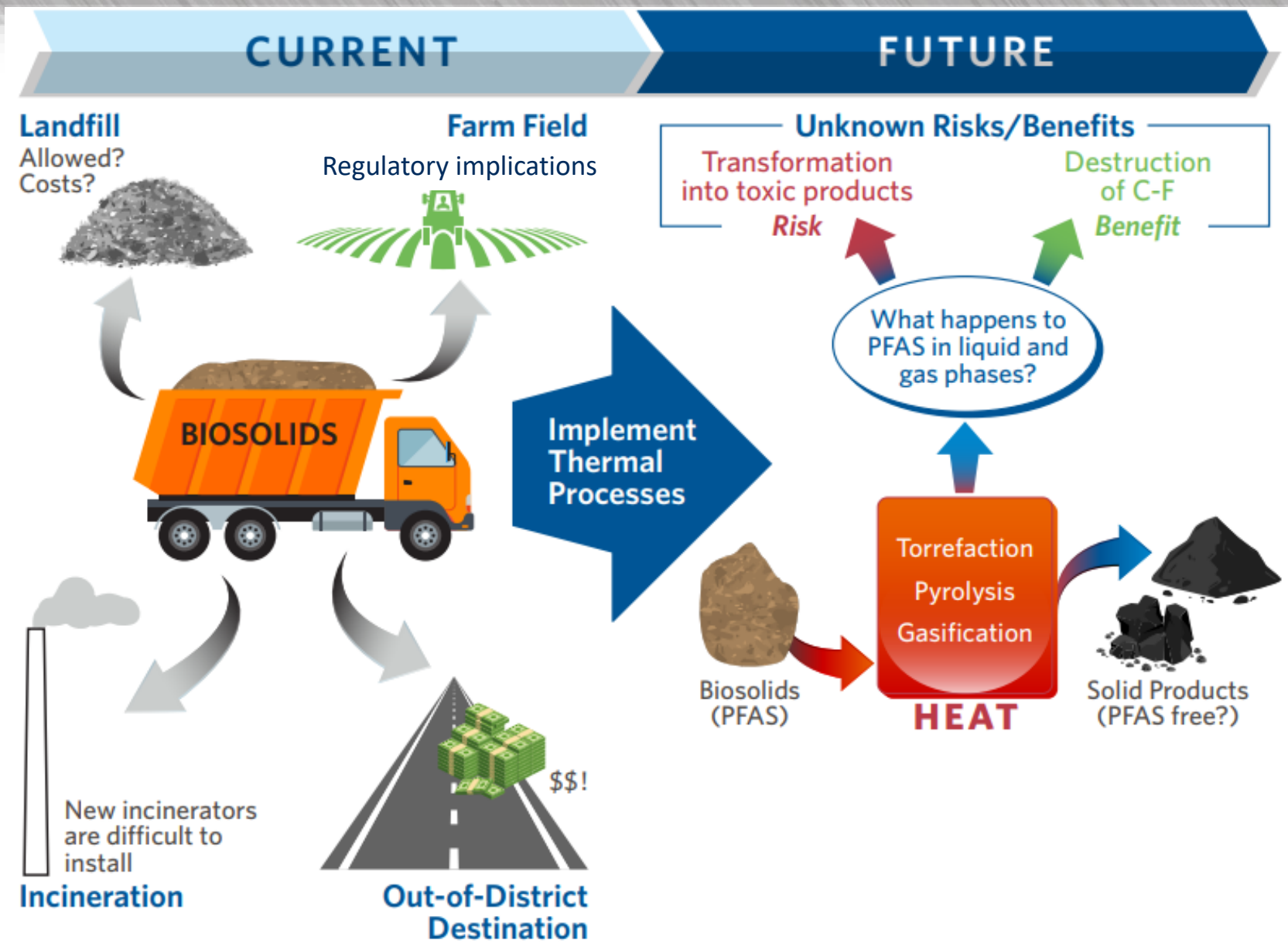
PFAS Risks in Biosolids Management



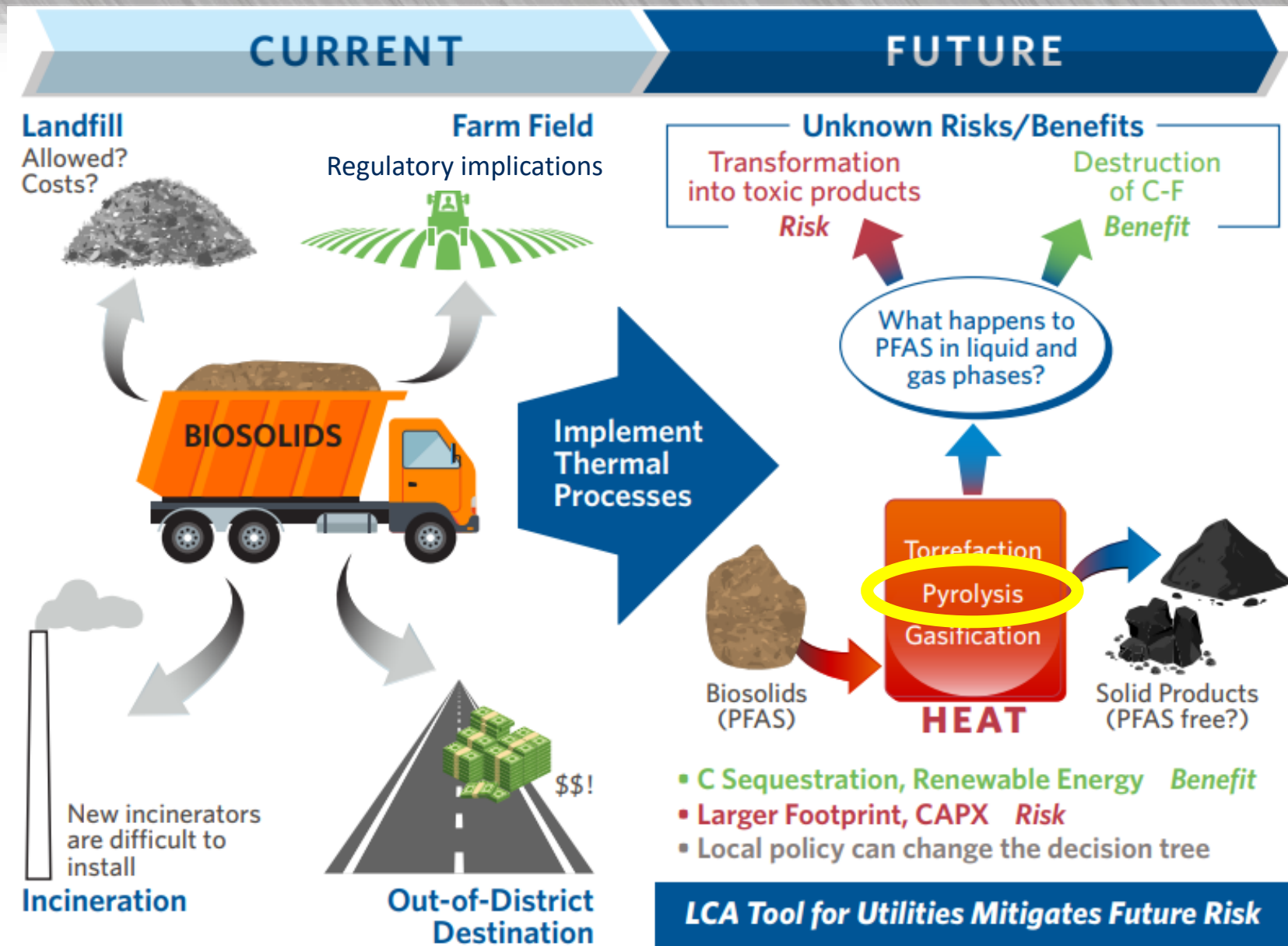
PFAS Risks in Biosolids Management



PFAS Risks in Biosolids Management



PFAS Risks in Biosolids Management



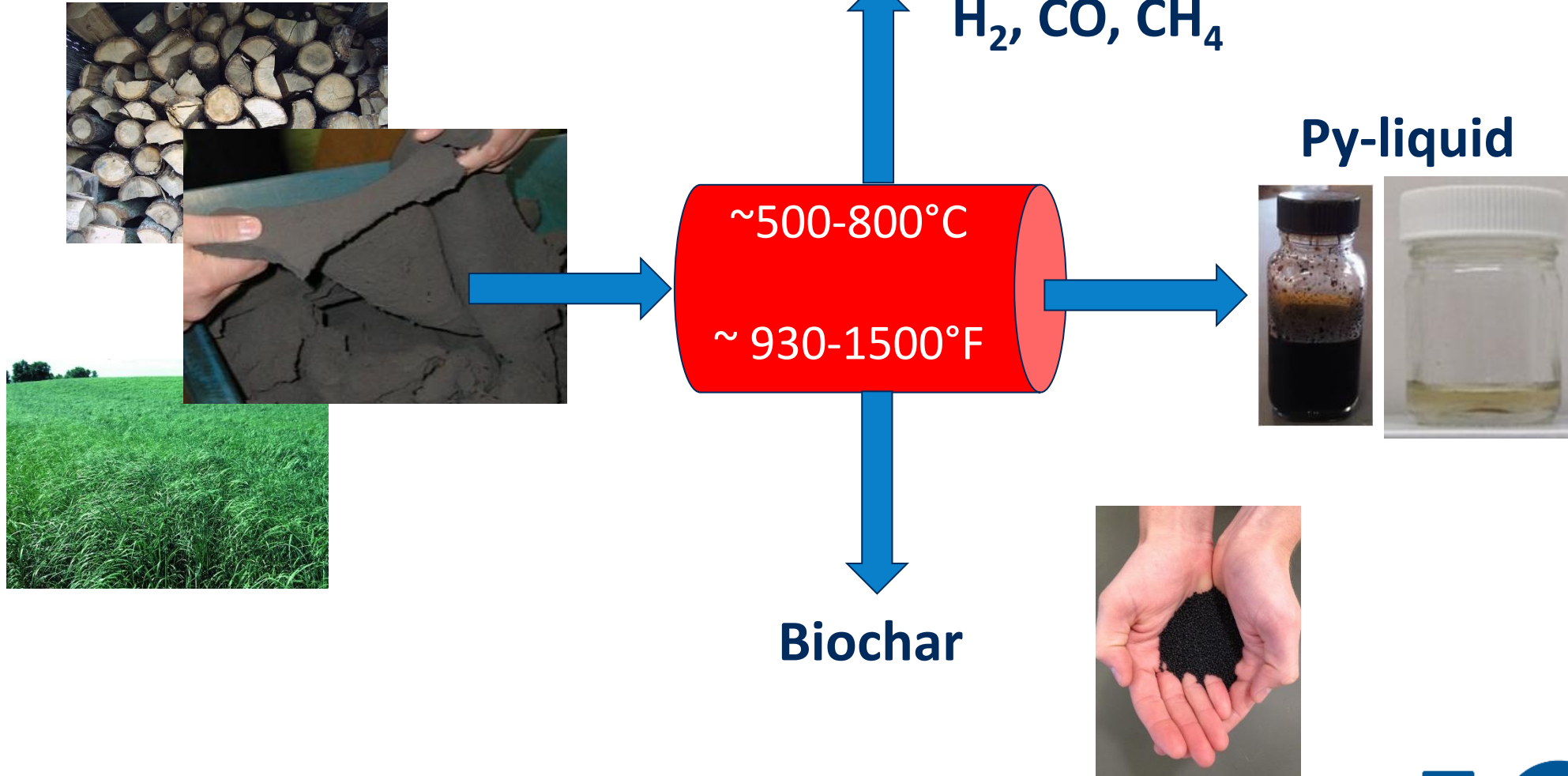
Pyrolysis Presentation Objectives

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



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Potential Challenges



Drying Costs



Pyrolysis Liquid

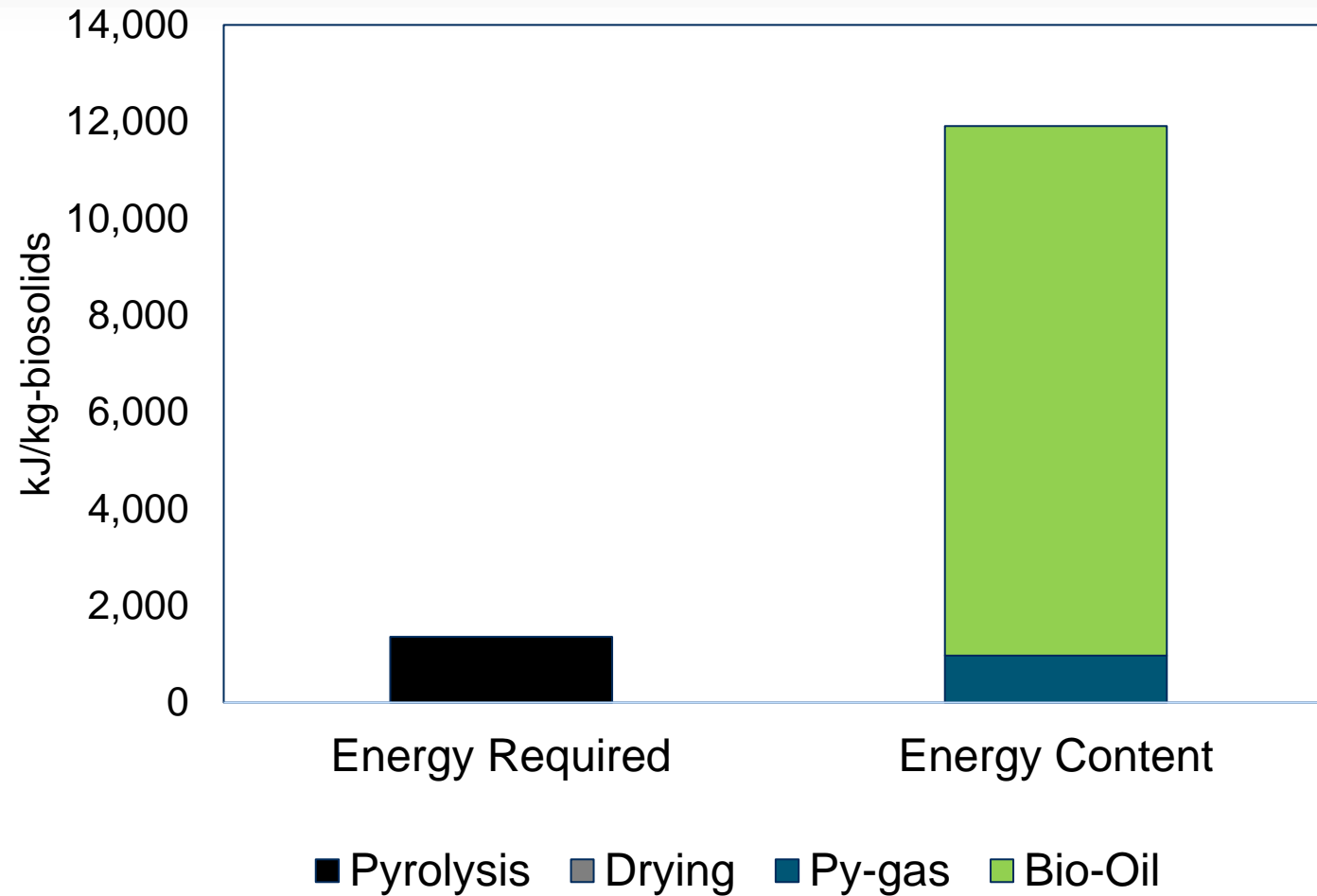


Nutrient Mass Balance



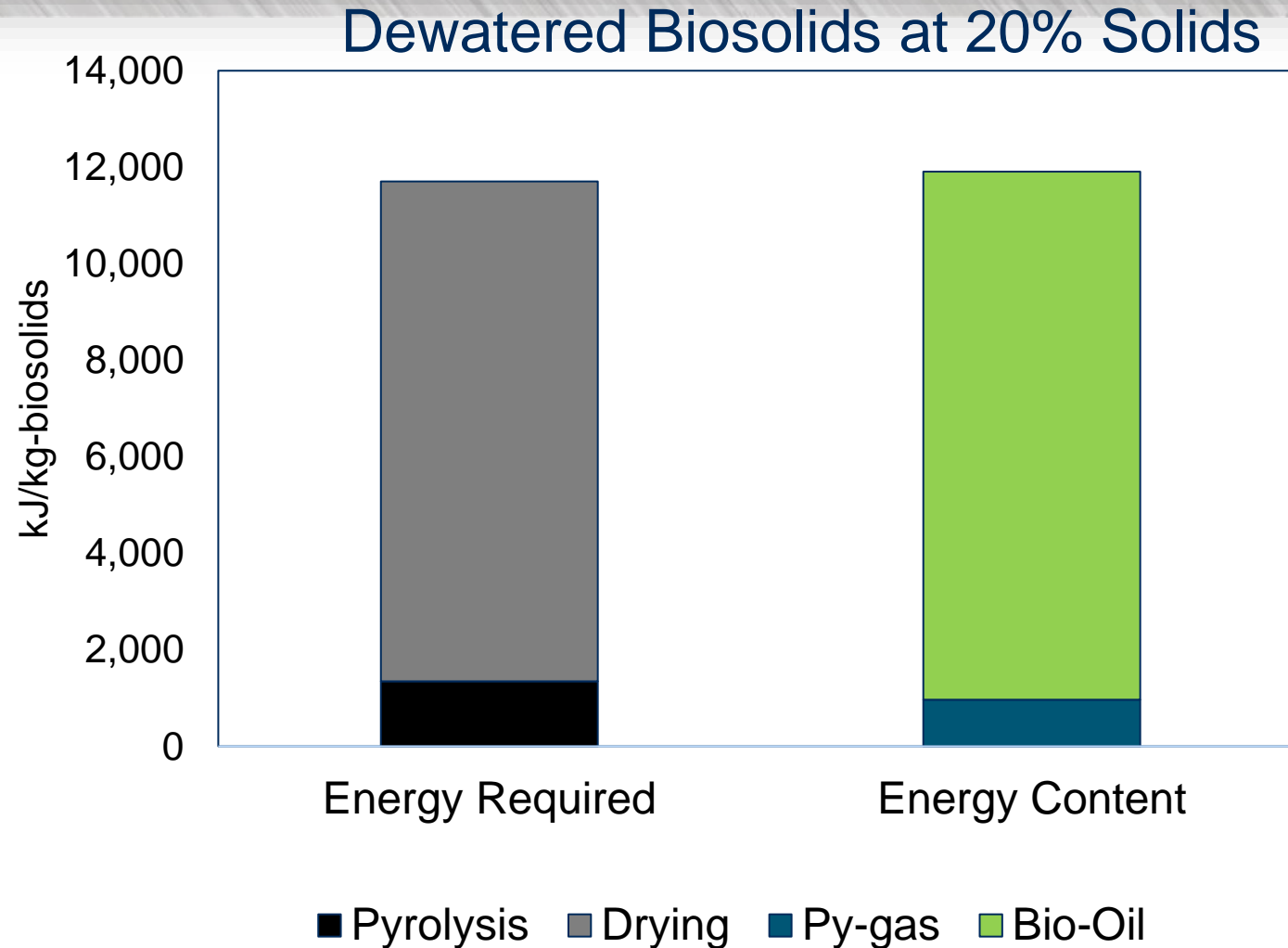
Few Installations

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

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

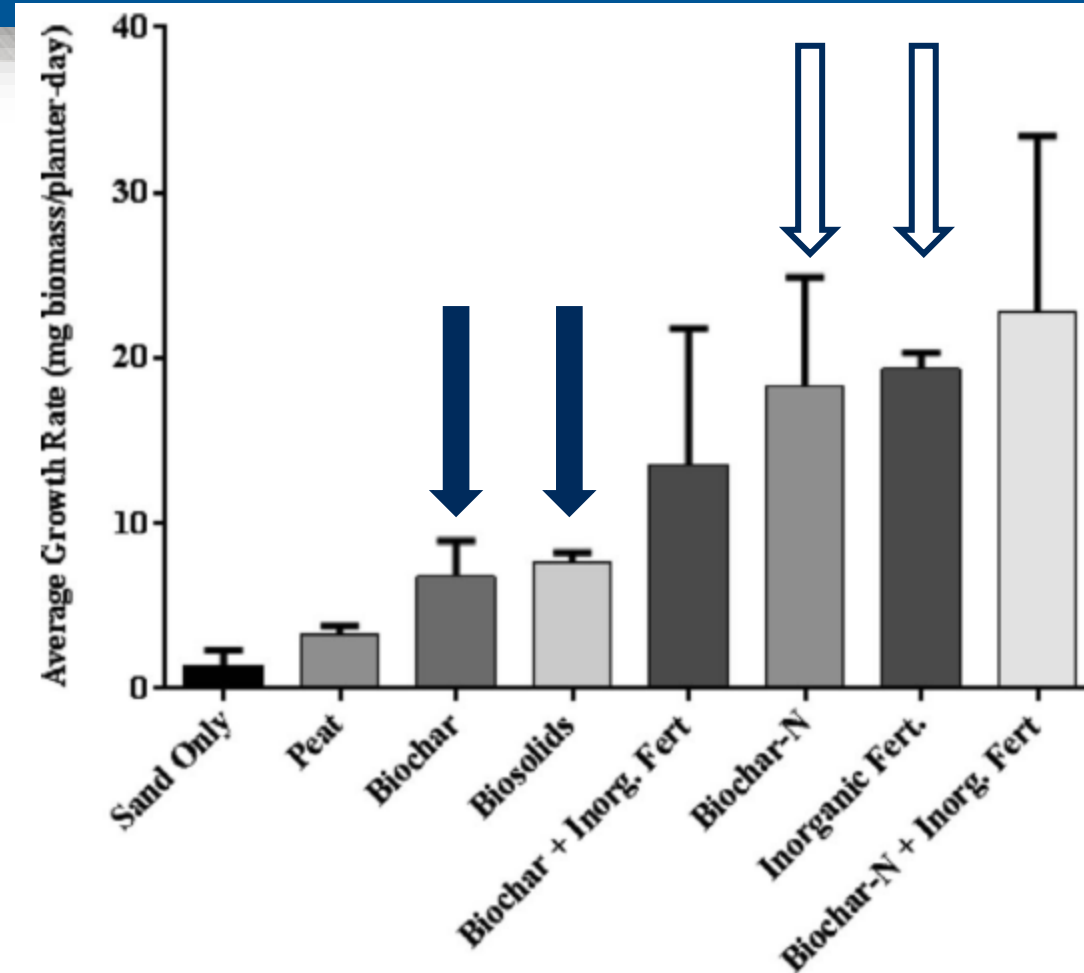
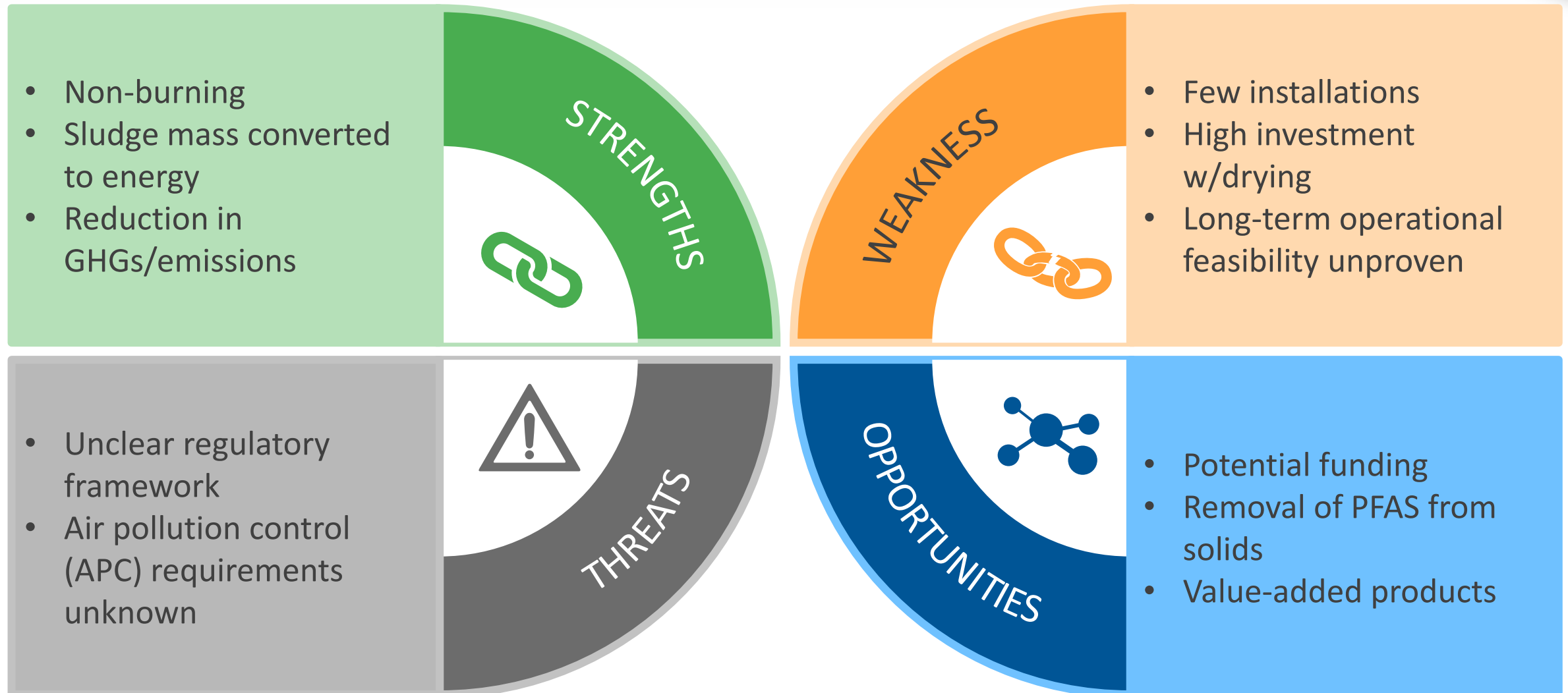


Figure 3—Average growth rate of Kentucky bluegrass biomass. Biomass was measured immediately after trimming to a height of 1 in.

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

Pyrolysis Overview



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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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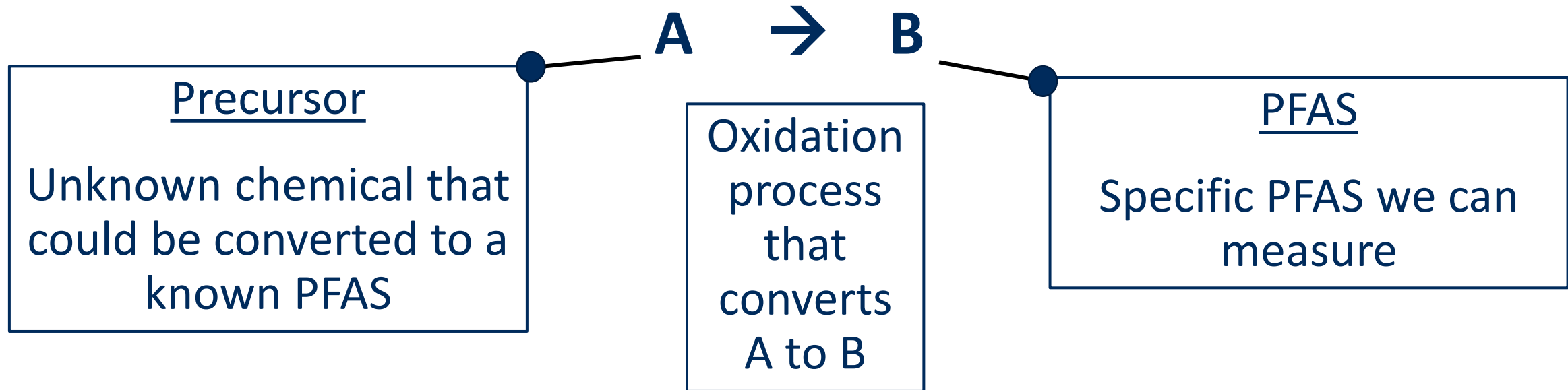
- Compound reacts to form new compound with modified chemical structure

Destruction

- Compound is mineralized (C-F bonds are broken), inorganic fluoride remains and simple forms of carbon (e.g., CO₂)

How could we know if transformation occurs?

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



How could we know if transformation occurs?

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



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

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

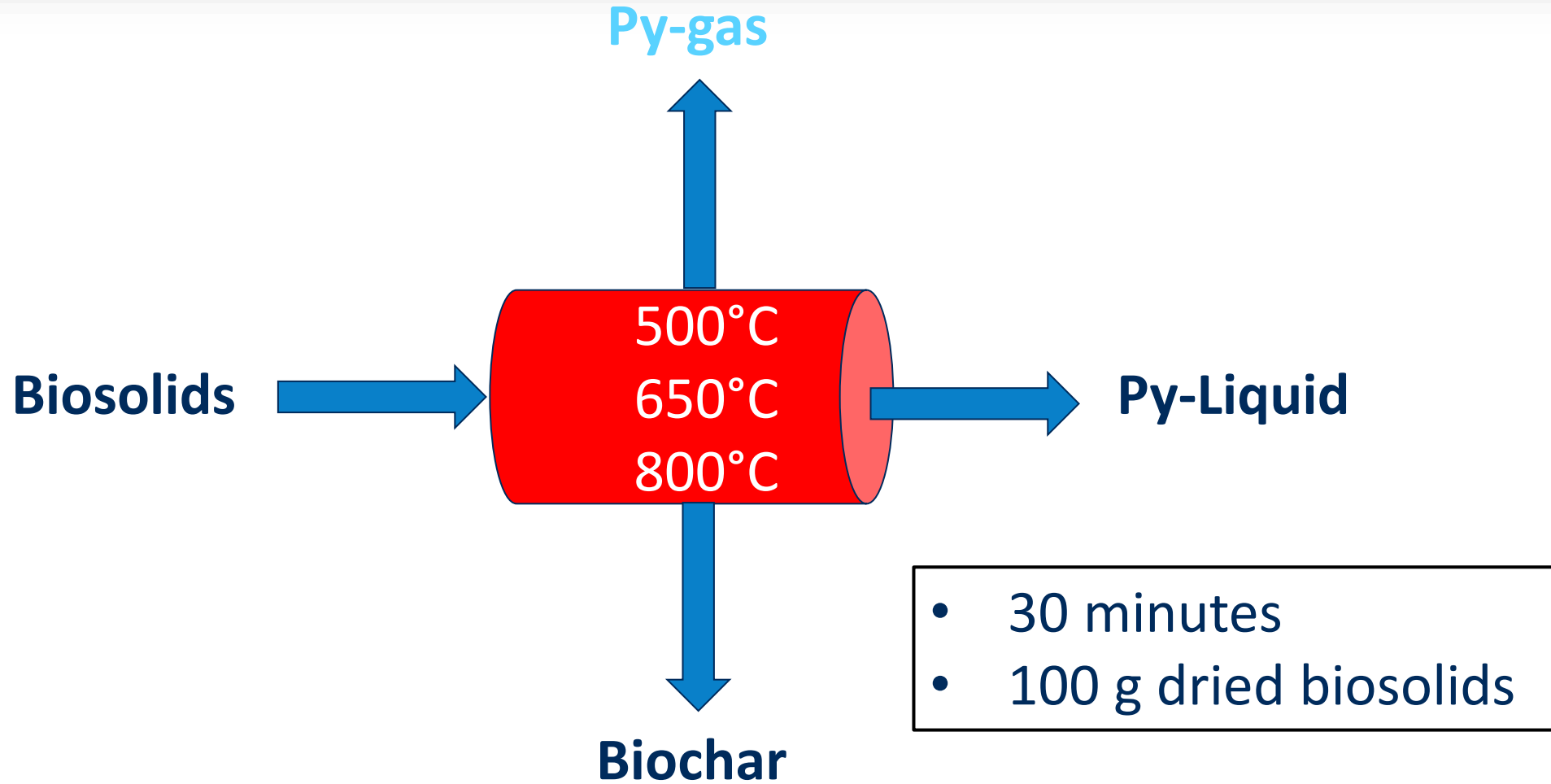
If you measure your influent and do not see a specific PFAS, you cannot assume it won't be in your effluent

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



Environmental Science Water Research & Technology




PAPER

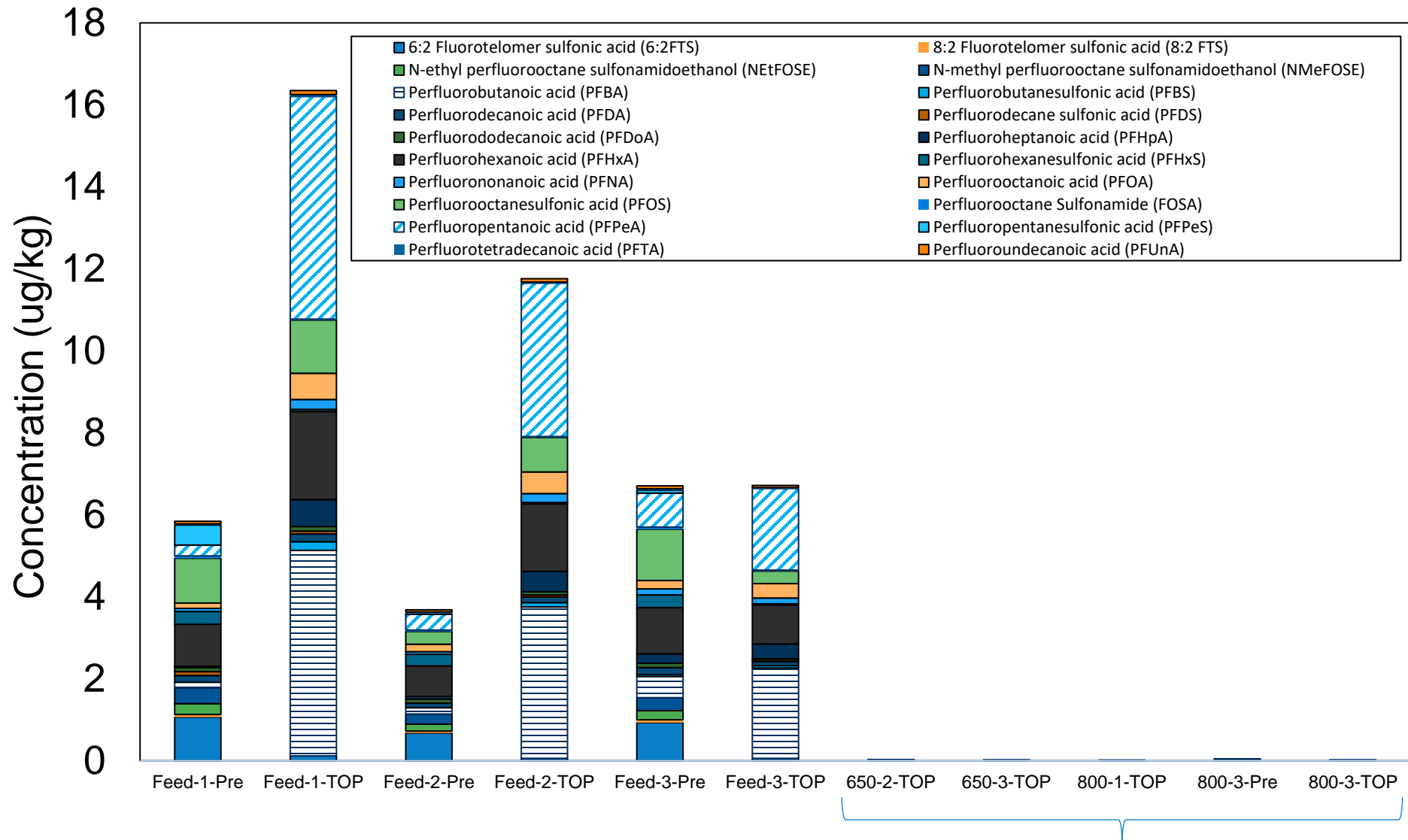
 Check for updates

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

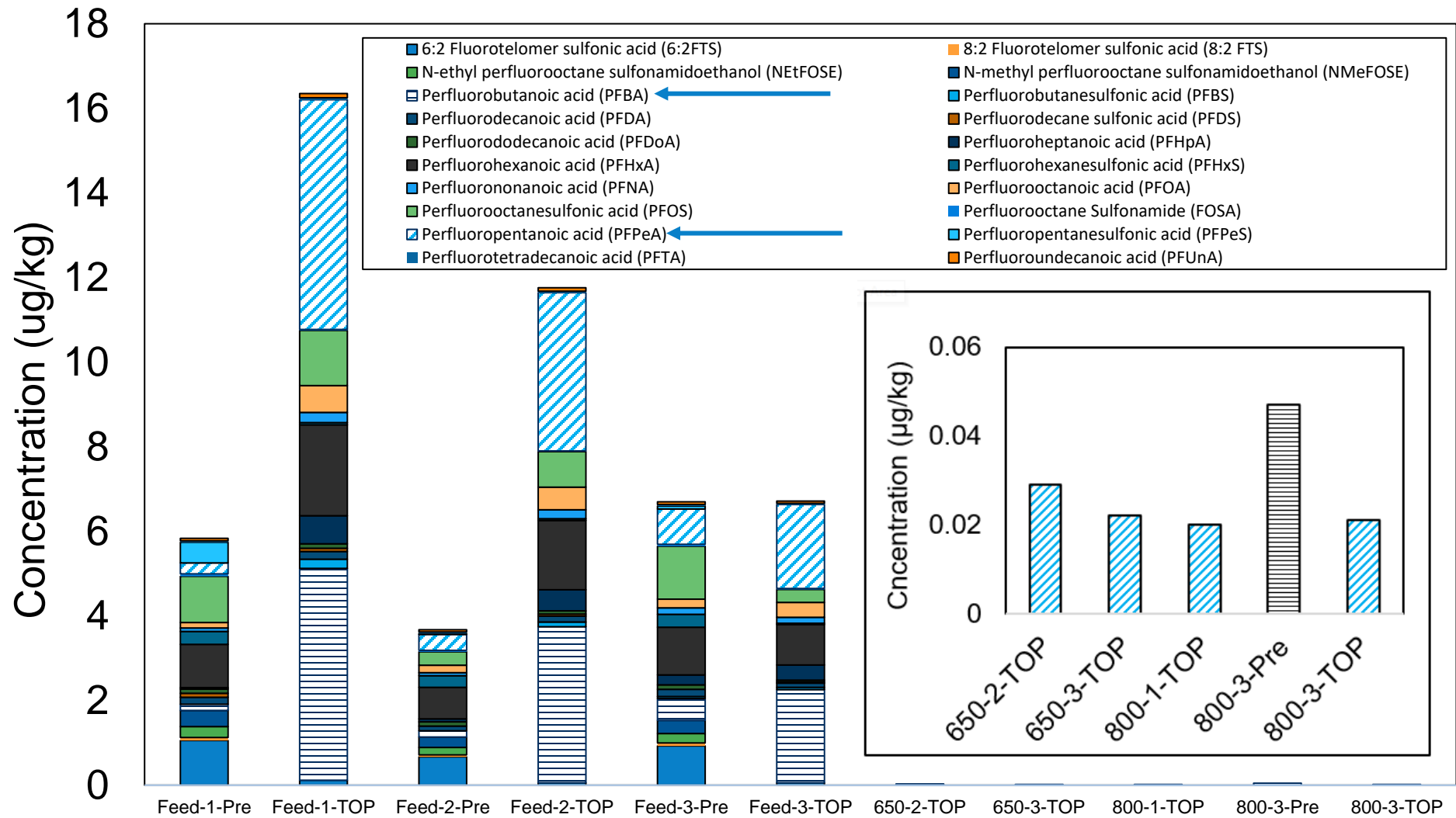
Pyrolysis transports, and transforms, PFAS from biosolids to py-liquid†

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



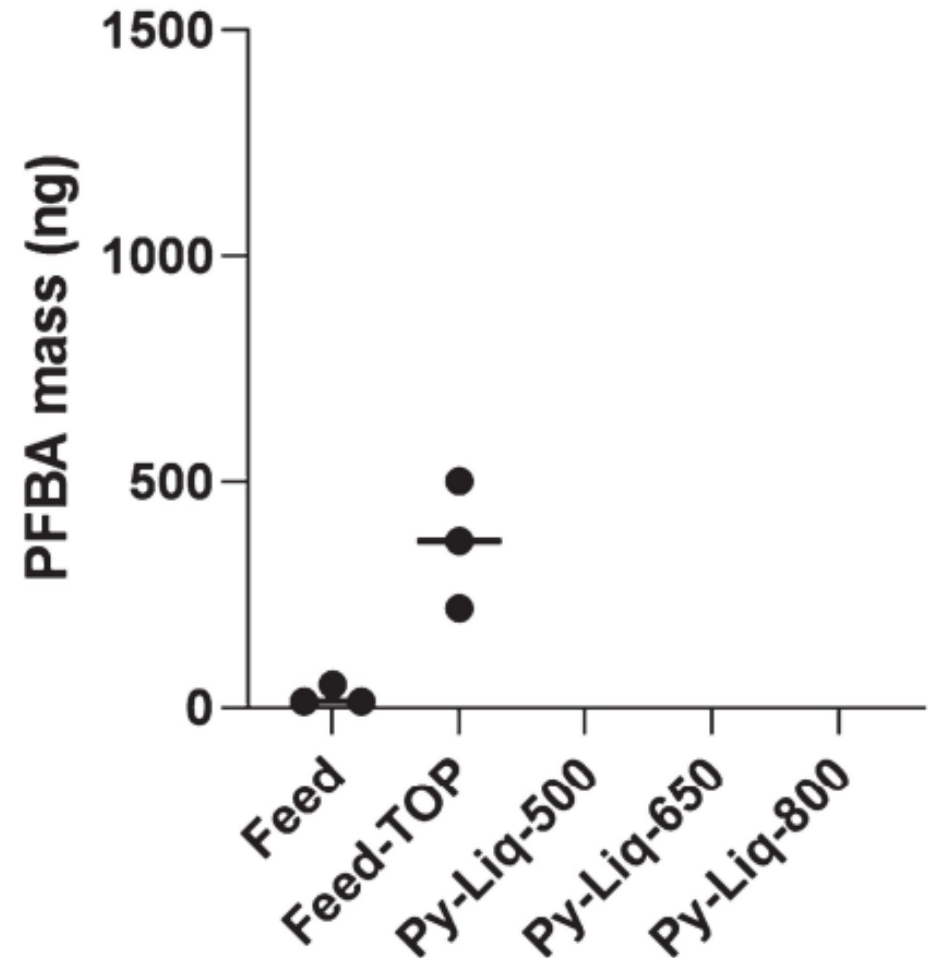
Pyrolysis removes PFAS from biosolids

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

Removal occurs...what happens to PFAS?

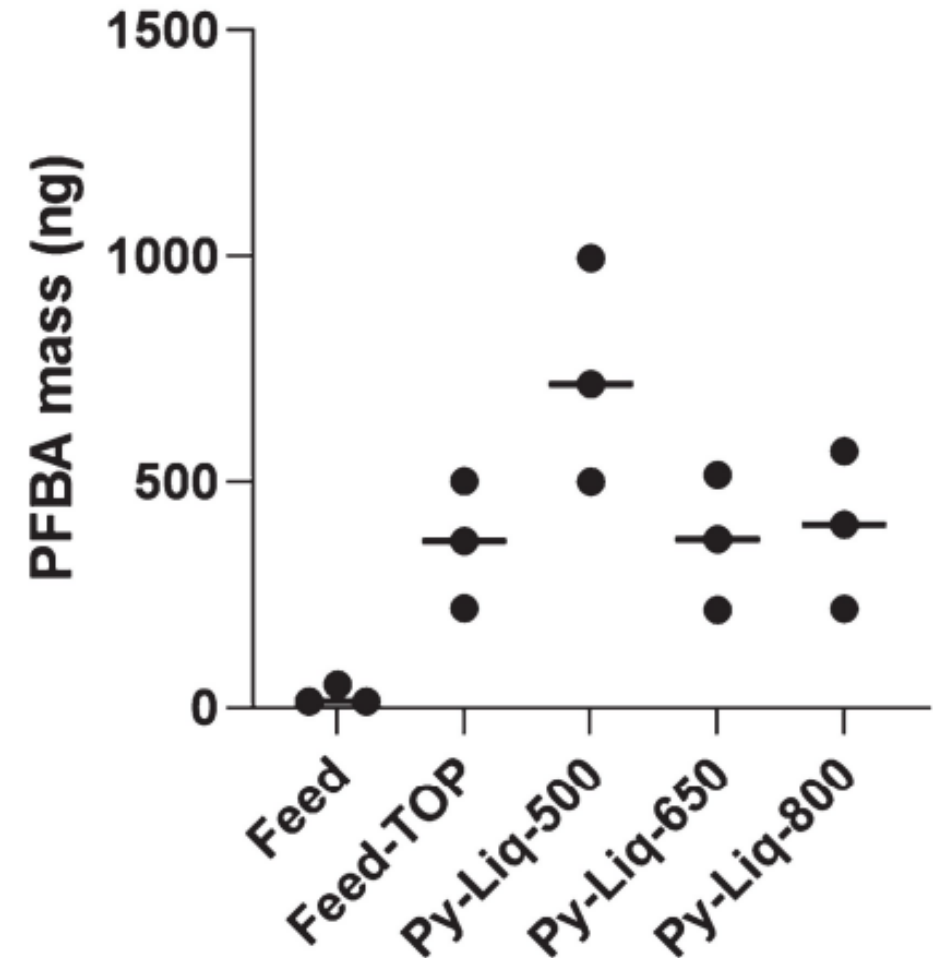
PFBA Precursors are in Biosolids

- 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**



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		B		C	
	Wet	Dry	Wet	Dry	Wet	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



ELSEVIER

Contents lists available at [ScienceDirect](https://www.sciencedirect.com)

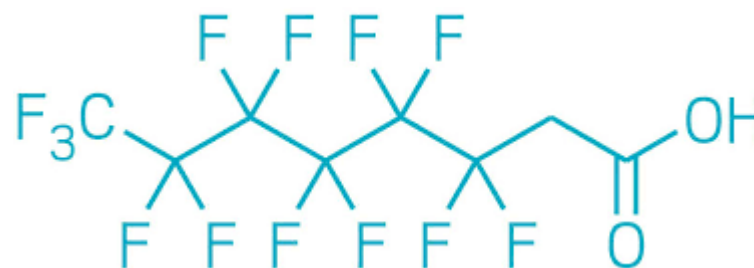
Science of the Total Environment

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

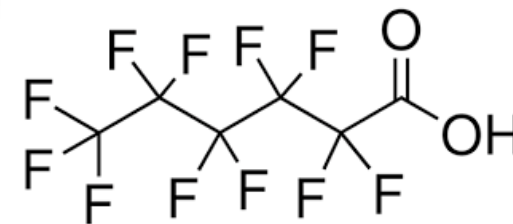


Using regular and transcriptomic analyses to investigate the biotransformation mechanism and phytotoxic effects of 6:2 fluorotelomer carboxylic acid (6:2 FTCA) in pumpkin (*Cucurbita maxima* L.)

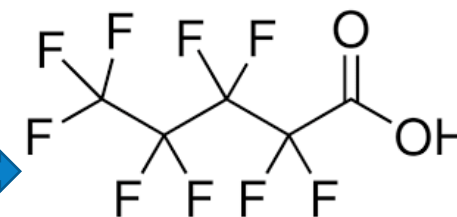
Fanghui Chi^{a,1}, Jingyan Zhao^{a,1}, Liping Yang^b, Xiaojing Yang^a, Xv Zhao^a, Shuyan Zhao^{a,*}, Jingjing Zhan^a



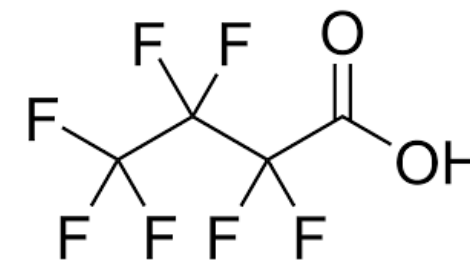
6:2 FTCA



PFHxA



PFPeA



PFBA

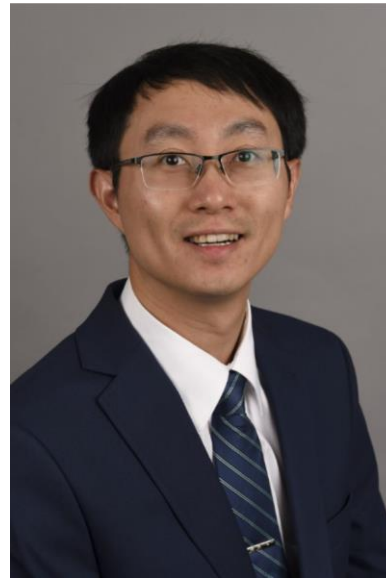


Answers to Research Questions

Drying can also lead to transformation reactions

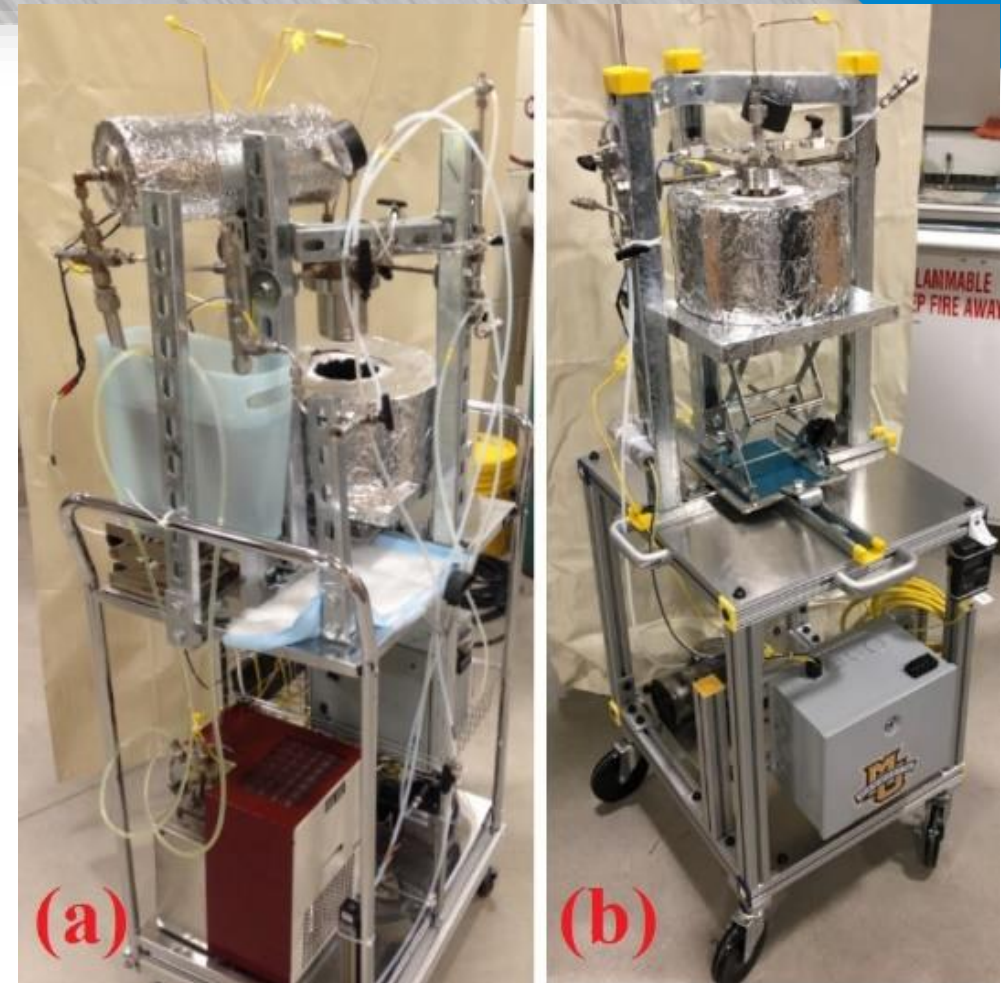
Full List of Experiments

Temp (°C)	Process
100	Drying
300	Torrefaction
500	Low Temp Pyrolysis
800	High Temp Pyrolysis
800	Gasification



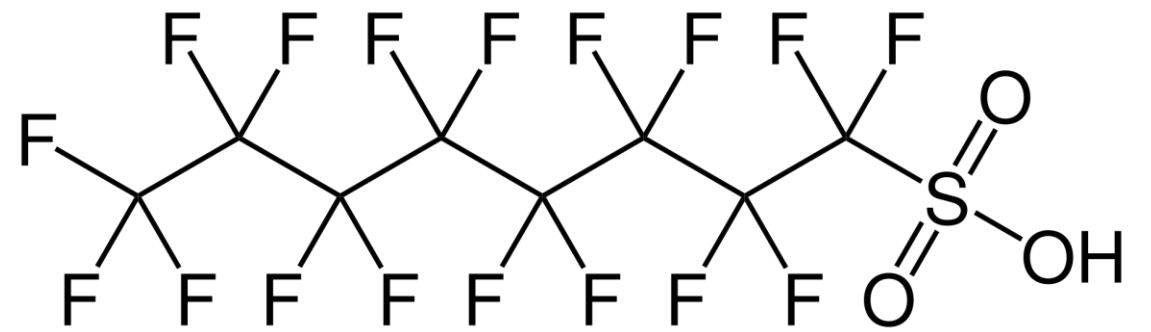
Zhongzhe Liu, Ph.D.

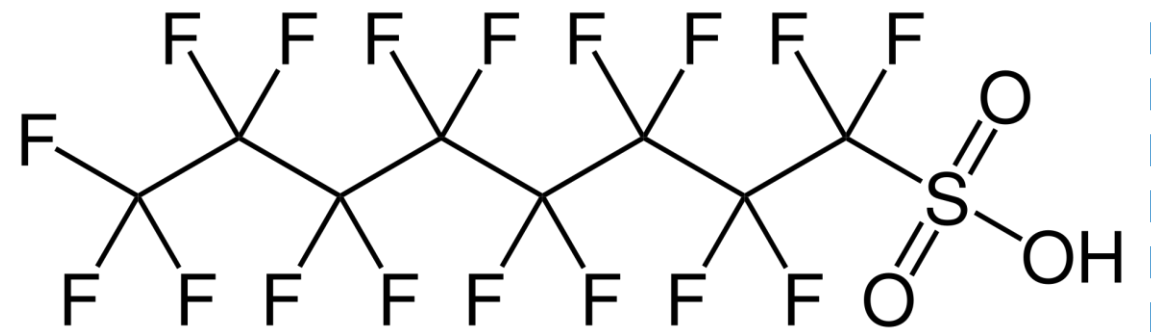
Assistant Professor
CSU-Bakersfield



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

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

41st Spring Biosolids Symposium

Thank You

Questions, or interest in
collaboration?

McNamaraP@BV.com



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Marquette University



Goal: Provide Tools to Support Biosolids Planning

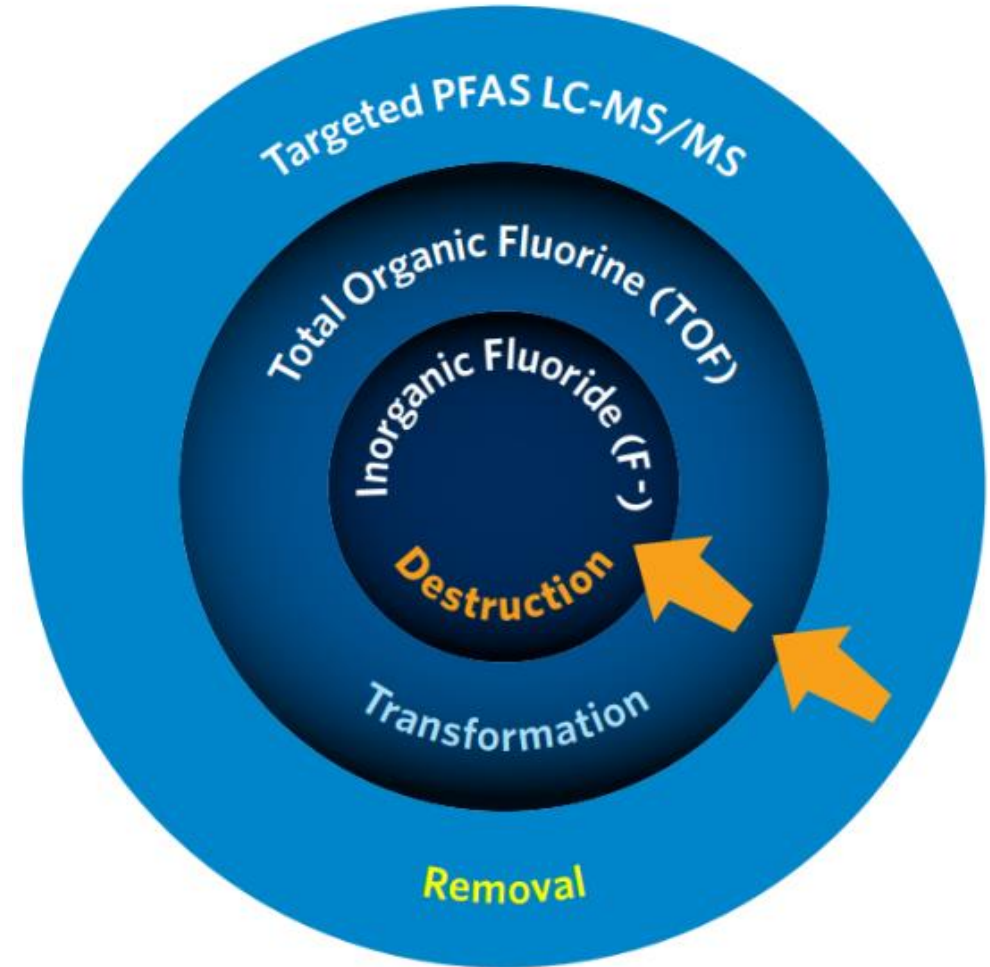
Tools need to incorporate *broader* potential benefits and costs of installing thermal processes & impacts of PFAS that are relevant in a regulatory framework.

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.

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



Objective 3: LCA

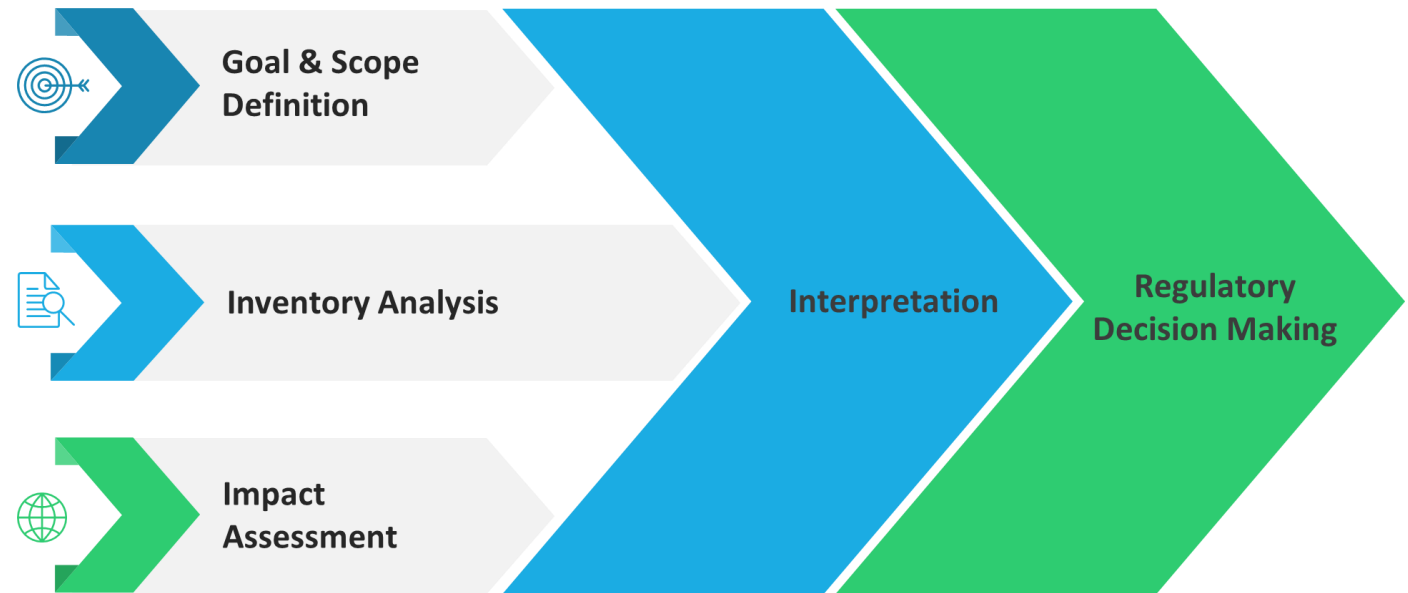
Rationale: Understand the environmental impacts and benefits of adopting gasification, pyrolysis, and torrefaction as different treatment approaches for biosolids.

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.

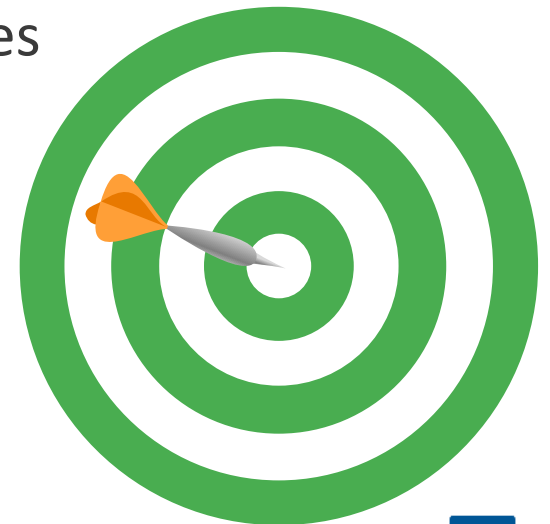
WRF Project Objectives

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.

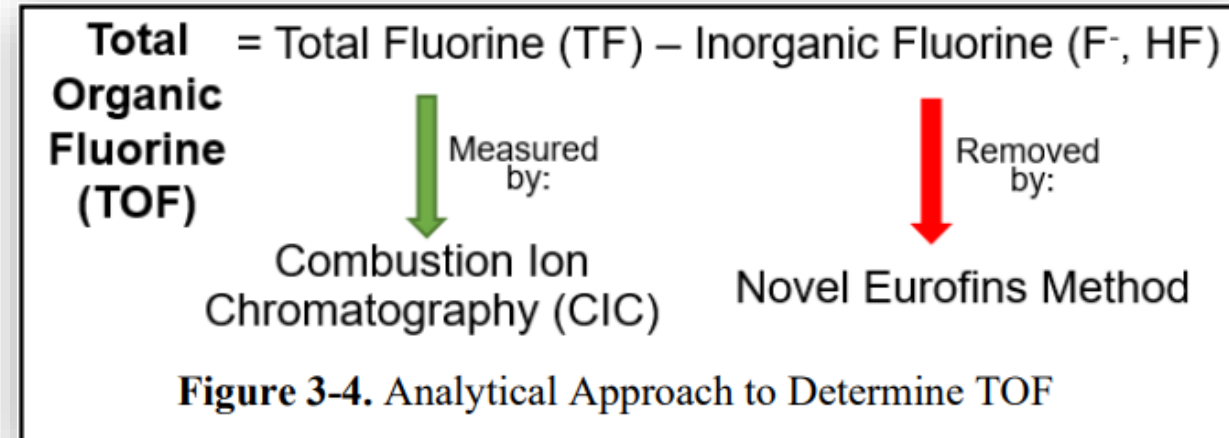
Objective 3. Conduct Life Cycle Assessment (LCA) on Thermal Processes

Objective 4. Final Report

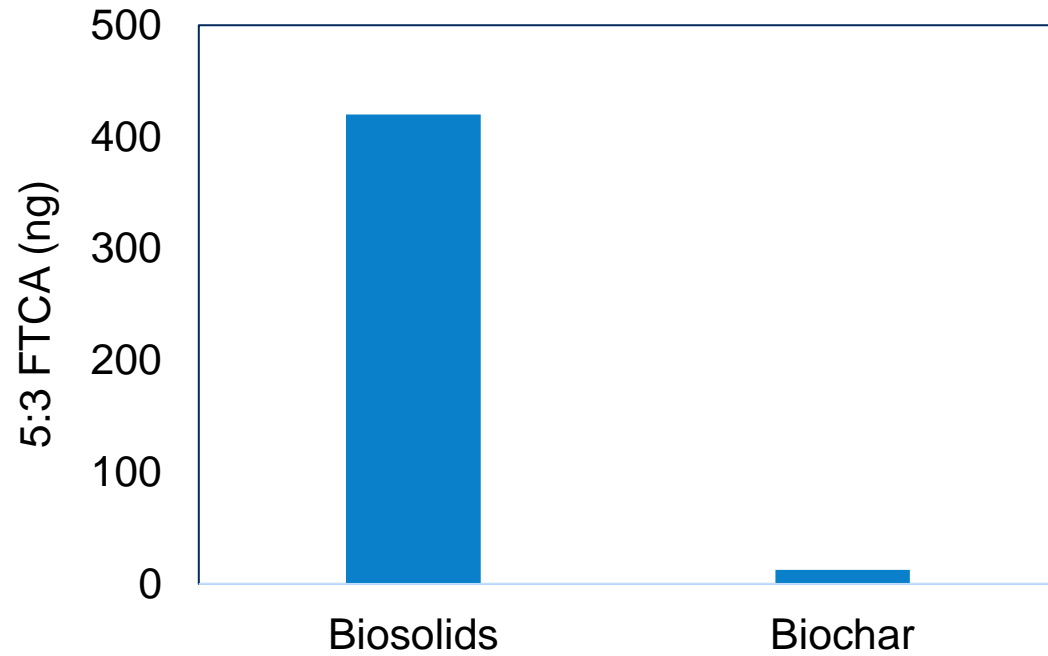


Objective 1 – Method Development

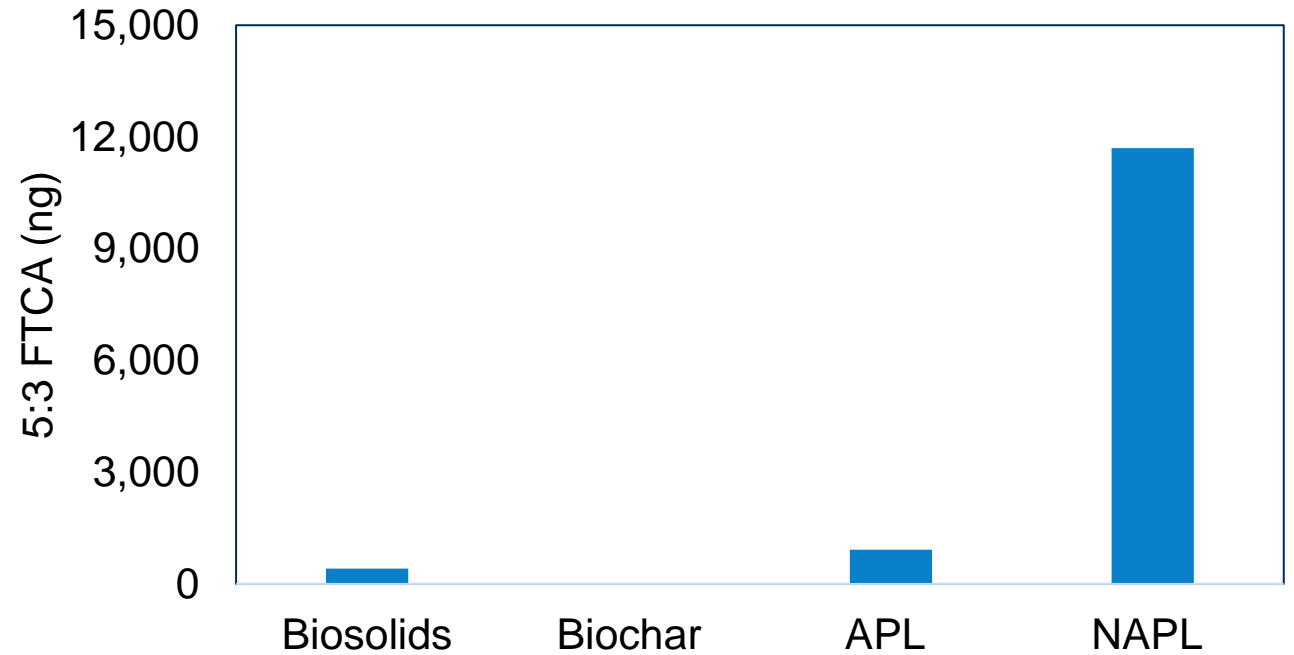
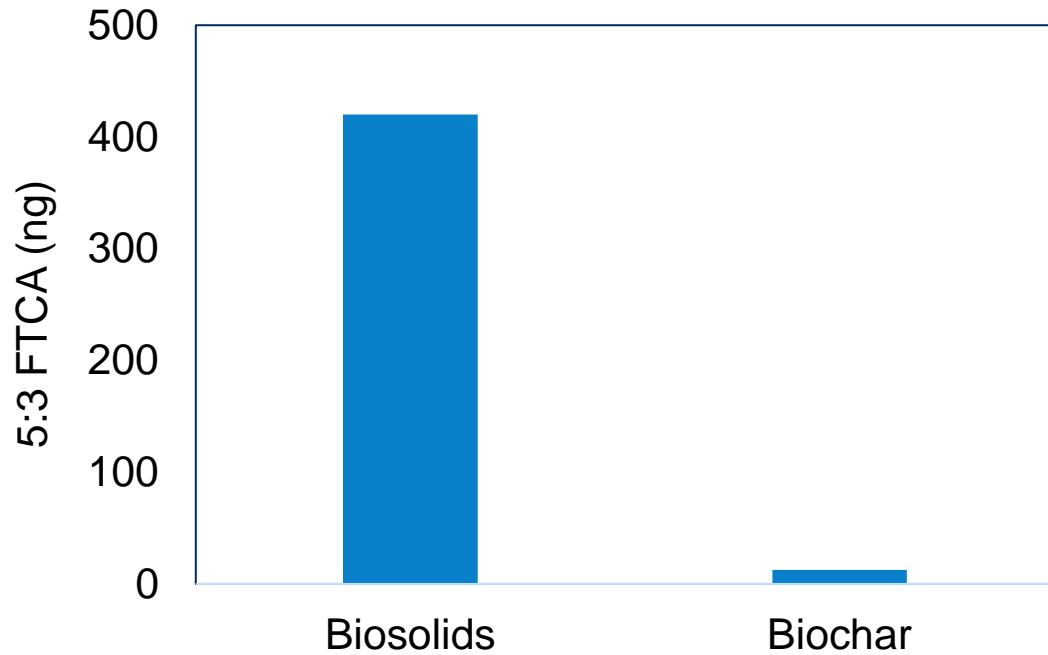
- Eurofins Technical Team:
 - *Taryn McKnight (Co-PI)*
 - *William Anderson, Ph.D. (Source Air Specialist)*
 - *Eric Redman (VP of Technical Services)*
- Gas Phase Development
 - Collection: Methanol impinger
 - Analysis: CIC-TOF with chemical pretreatment to knock-out inorganic fluoride
- Liquid Phase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



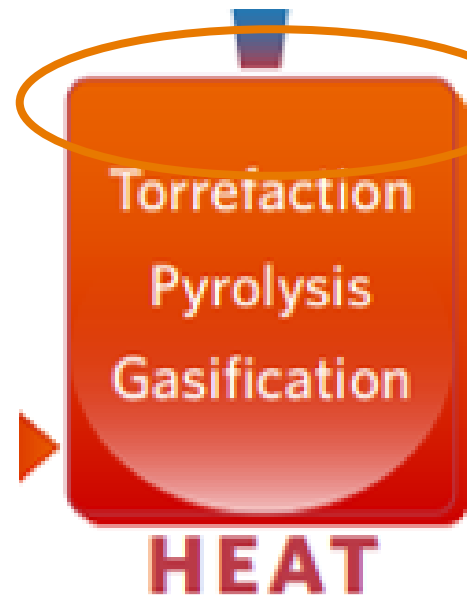
New Experiment, Same Idea



New Experiment, Same Idea - PFAS in Py-Liquid



Heat Treatments



Treatment	Temperature	Air?	
Drying	<105C	Air	
Pyrolysis	500-800C	No Air	
Gasification	>800C	Limited Air	