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Marquette University

How Does Drying and Pyrolysis Affect PFAS in Biosolids? Distinguishing Transformation from Removal

Patrick McNamara, PhD, PE

April 17, 2024

Presentation Objectives

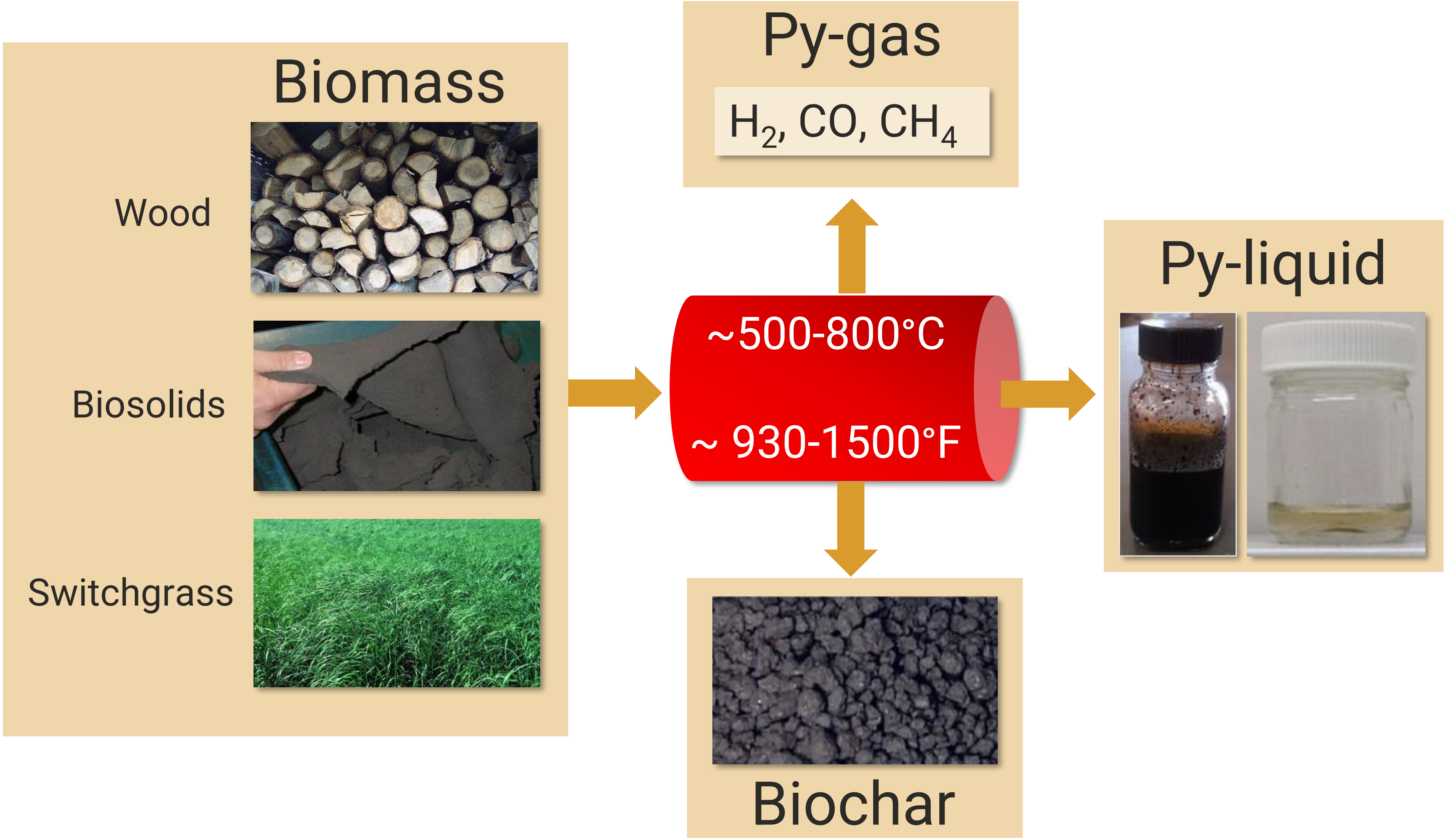
1. Know what pyrolysis of biosolids is and what it produces

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

4. Understand the potential impacts drying can have on PFAS

Pyrolysis: Heating without Oxygen



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Potential Challenges

Drying Costs

Pyrolysis Liquid

Few Installations

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Pyrolysis Liquid

Few Installations

Who should consider pyrolysis? Analyze drying costs first

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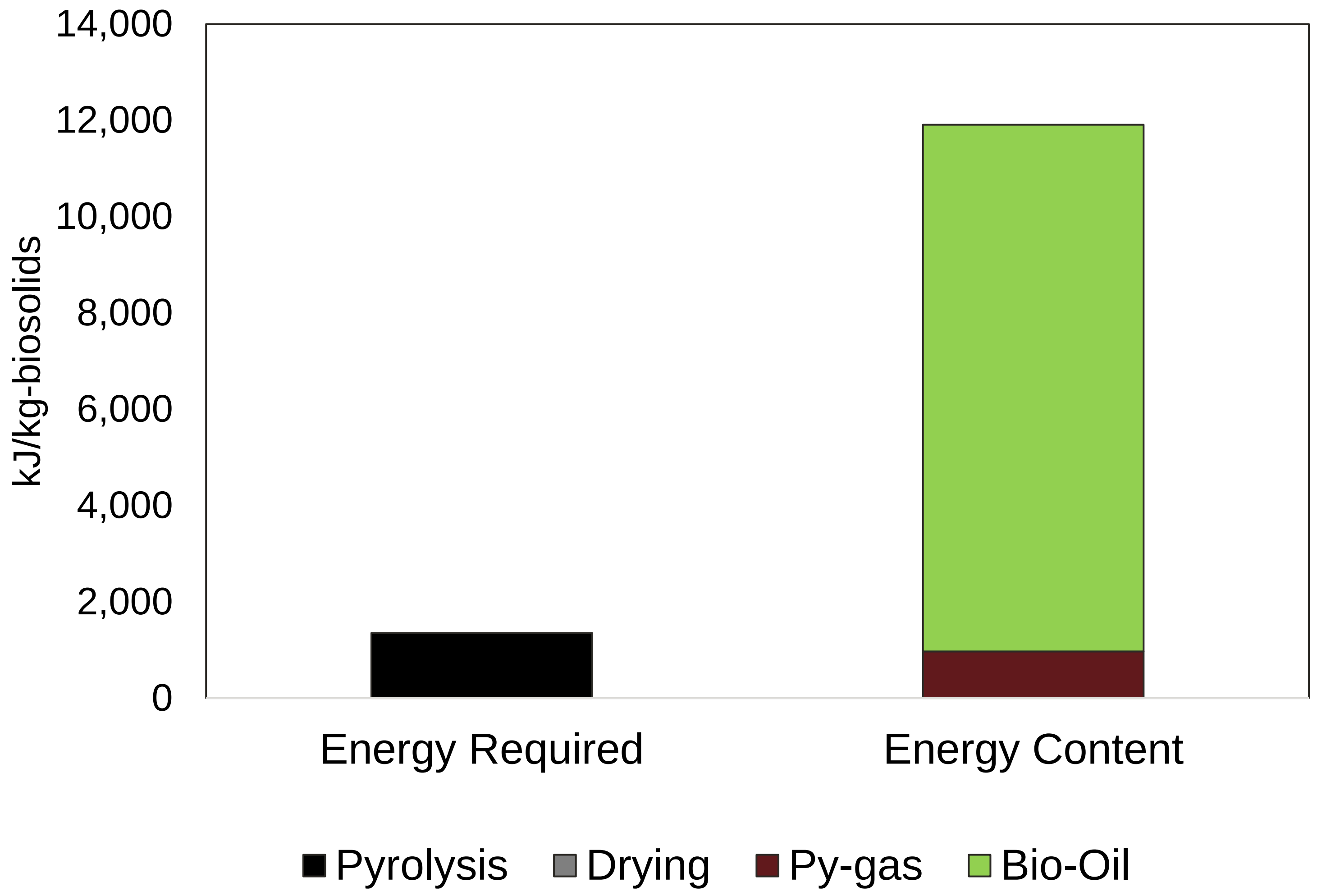
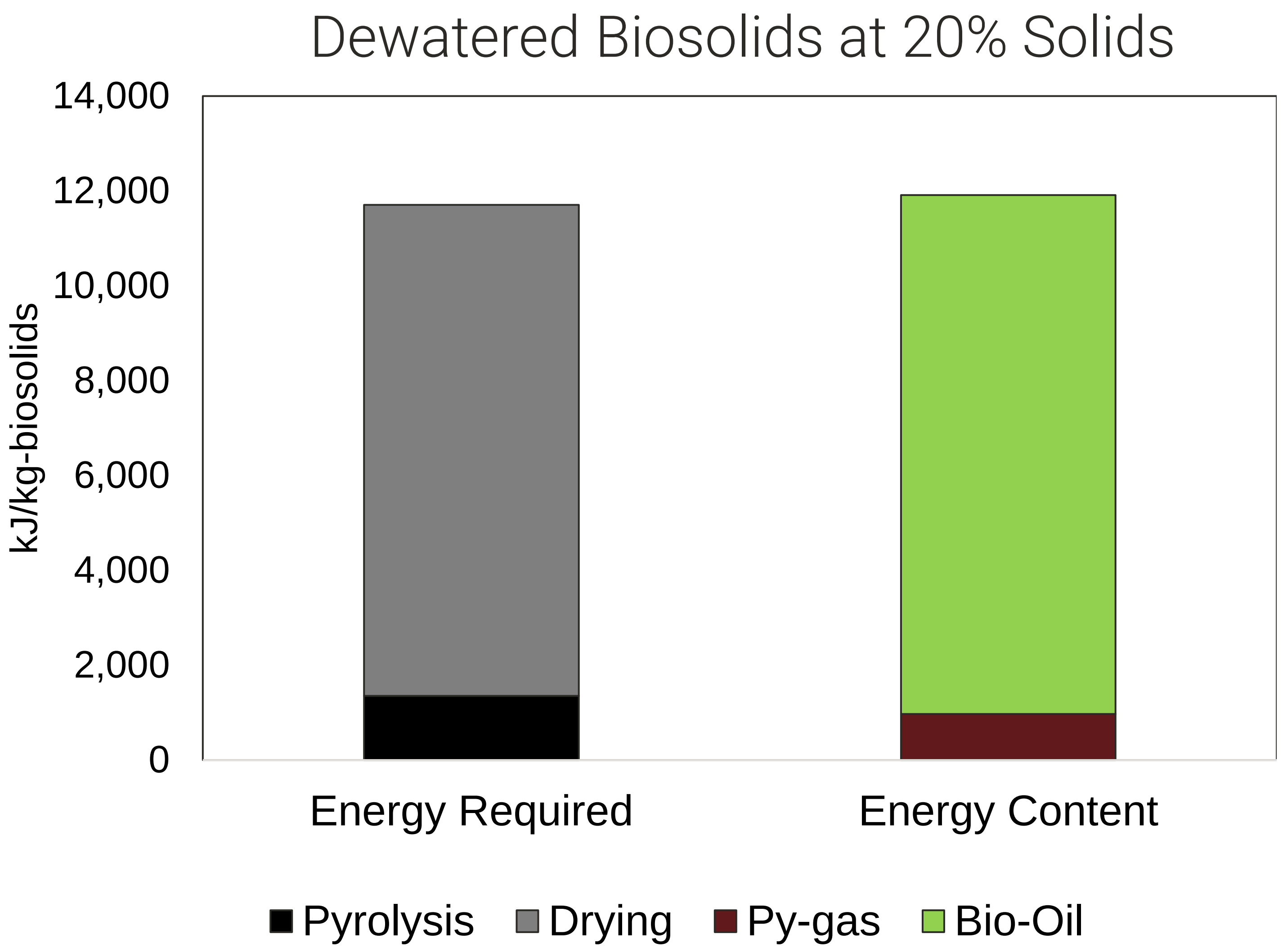


McNamara, P.J., Koch, J.D., Liu, Z., Zitomer, D.H., 2016. Pyrolysis of Dried Biosolids Can Be Energy Positive. *Wat. Env. Res.* 88 (9), 804-810

Who should consider pyrolysis? Analyze drying costs first



- 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 Challenges

Drying Costs

Pyrolysis Liquid

Few Installations

BioForceTech – Full Scale Installation at SVCW

- In operation since 2017
- Two step process:
  - ➢ Biodryer – batch operation to remove moisture from ~20% DS to achieve 70-75% DS
  - ➢ Pyrolysis reactor to generate py-gas and biochar
- Py-gas is burned in a flameless burner and recovered heat is used for the process

Potential Benefits

Energy Recovery from Biosolids (py-gas)

Value-Added Product & Carbon Sequestration (Biochar)

Solids Reduction

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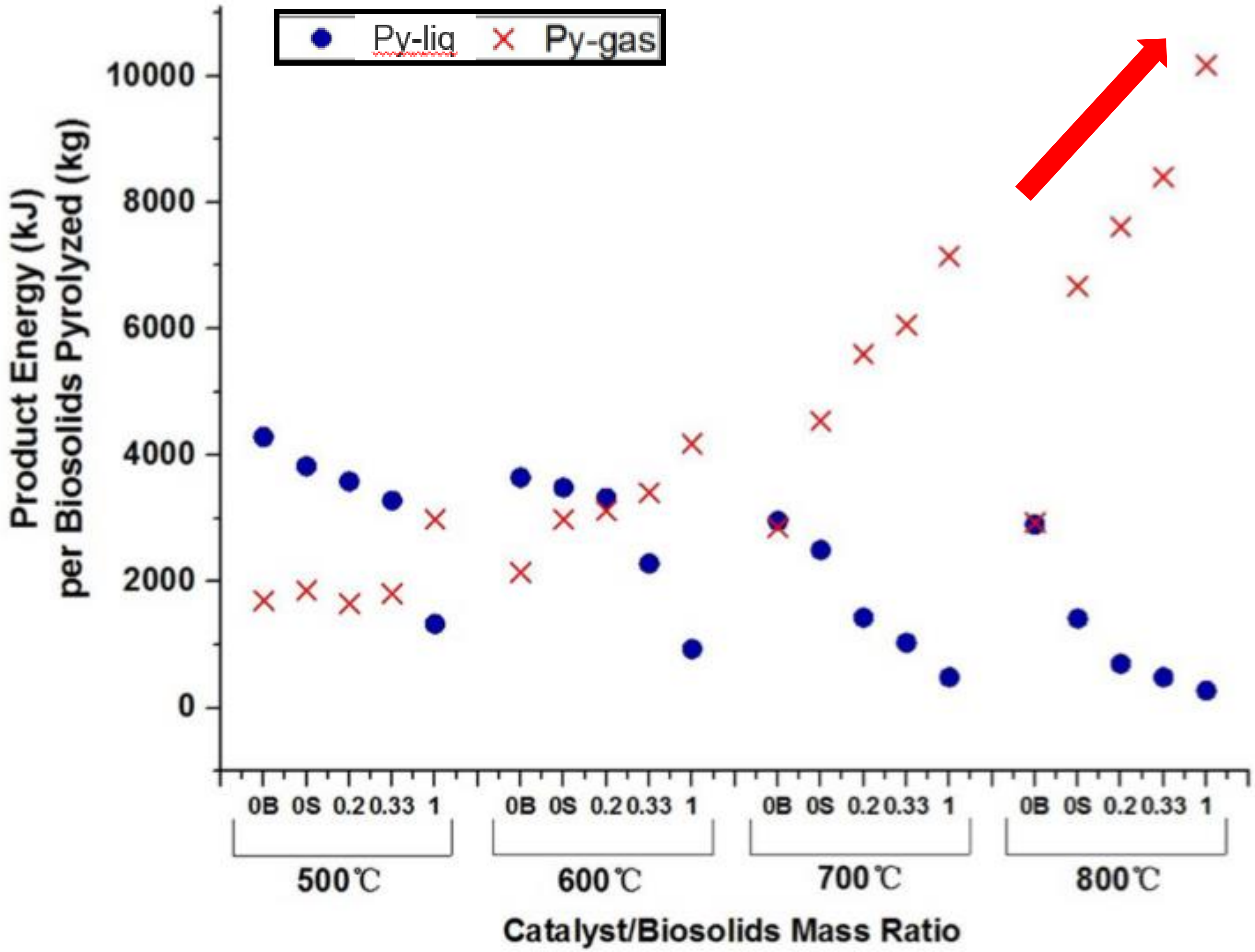
Using Biochar as a Catalyst Increases Energy in the Py-Gas



Liu, Z., McNamara, P., Zitomer, D. 2017. Autocatalytic pyrolysis of wastewater biosolids for product upgrading. *Environmental Science & Technology,* 51 (17), 9808–9816.

Potential Benefits

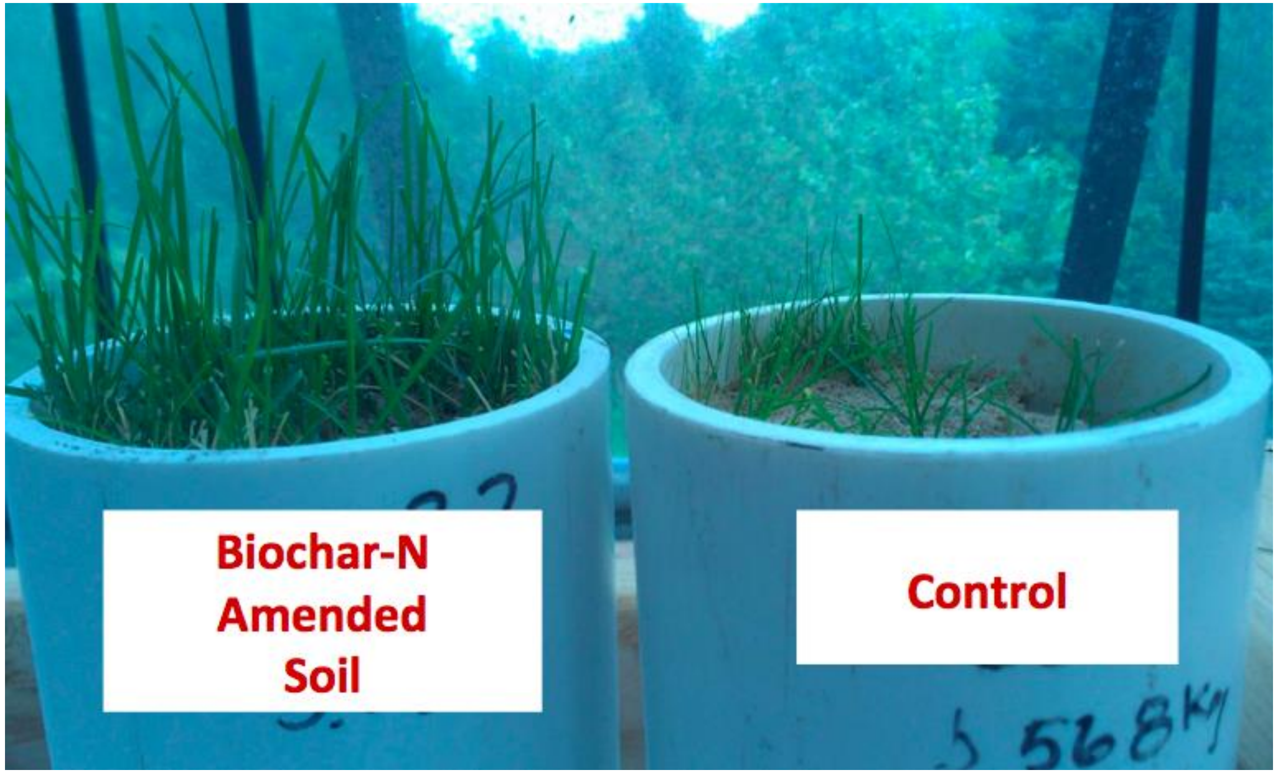
Energy Recovery from Biosolids (py-gas) (Py-Gas)

Value-Added Product & Carbon Sequestration (Biochar)

Solids Reduction

Biochar as a soil amendment

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

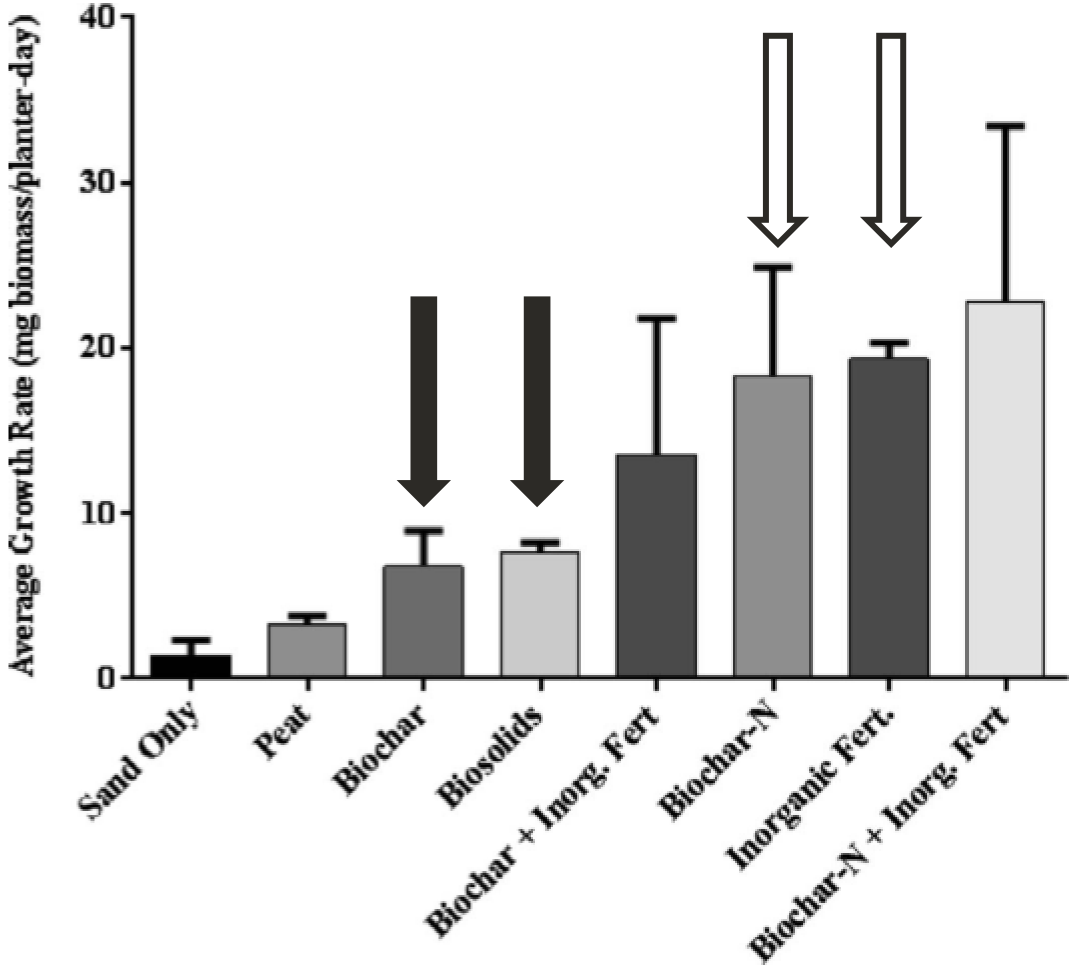


Figure 3—Average growth rate of Kentucky bluegrass biomass. Biomass was measured immediately after trimming to a height of 1 in.

- 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.

Potential Benefits

Energy Recovery from Biosolids (py-gas) (Py-Gas)

Value-Added Product & Carbon Sequestration (Biochar)

Solids Reduction

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).

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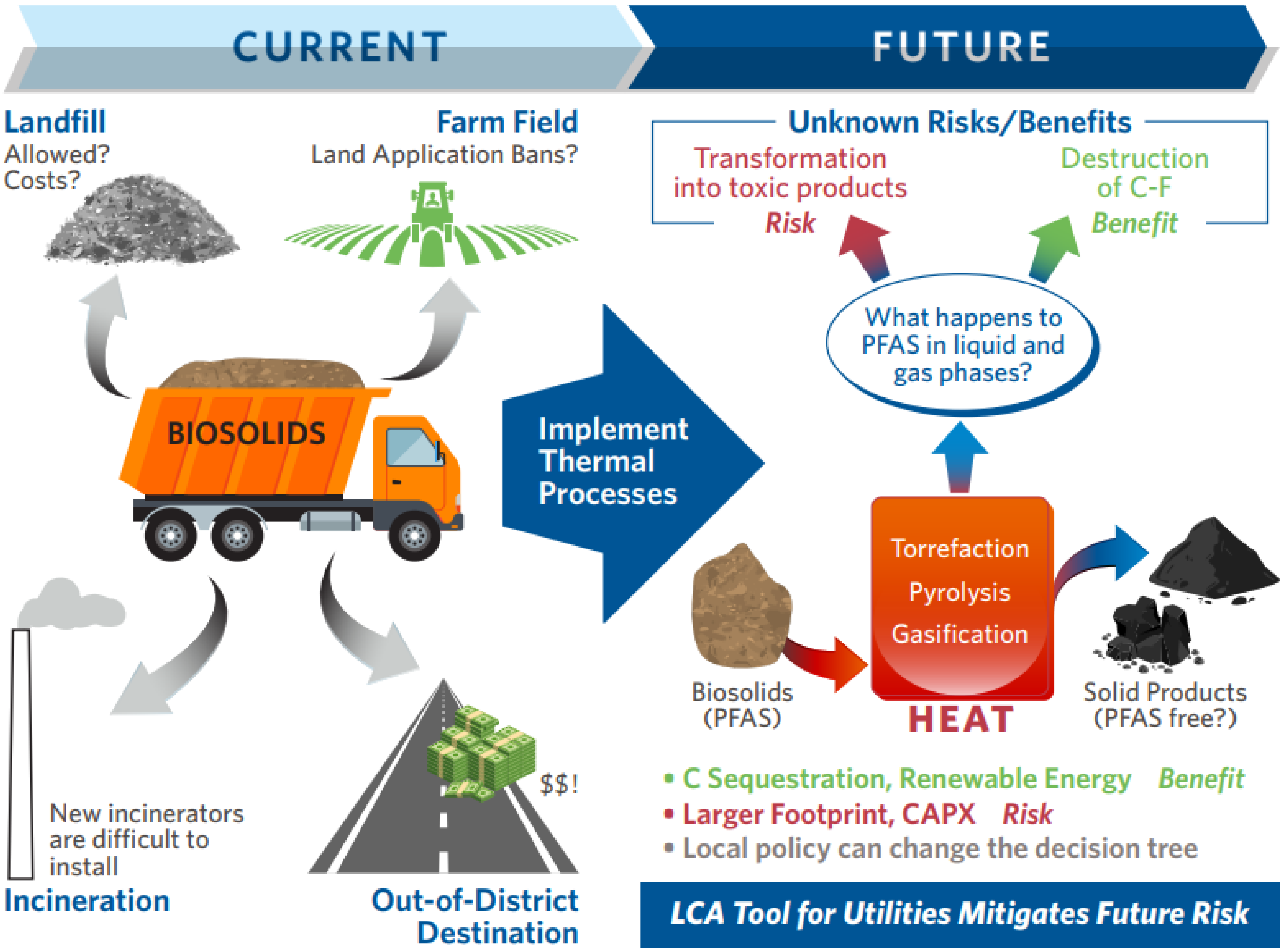
WRF Project #5211

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



What Does Pyrolysis Do to PFAS?

Start with Fate Definitions

Removal

- Compound is no longer present in its original phase

Transformation

- Compound reacts to form new compound with modified chemical structure

Destruction

- Compound is mineralized (C-F bonds are broken), inorganic F remains and simple forms of C (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 in 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

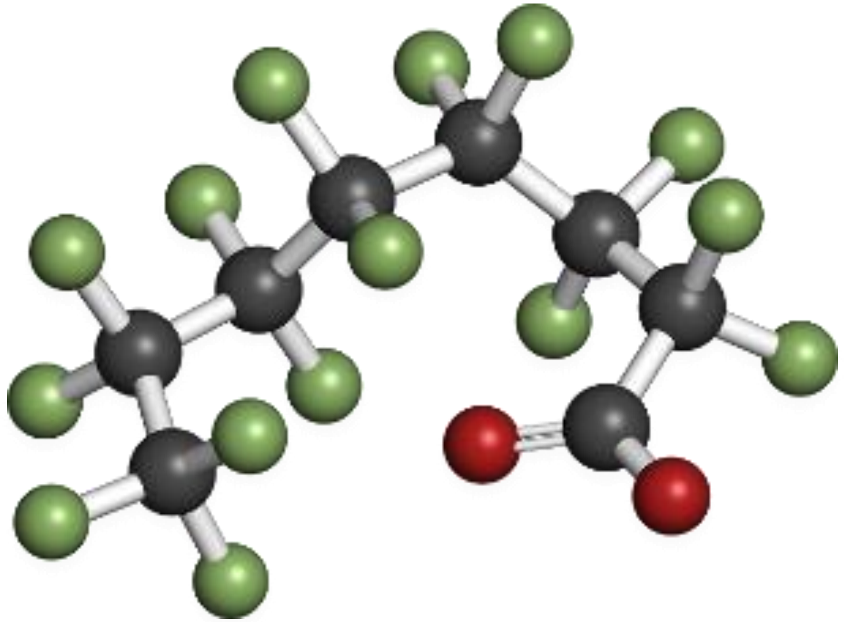
If you measure your influent and do not see a specific PFAS, you cannot assume it won't be in your effluent

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

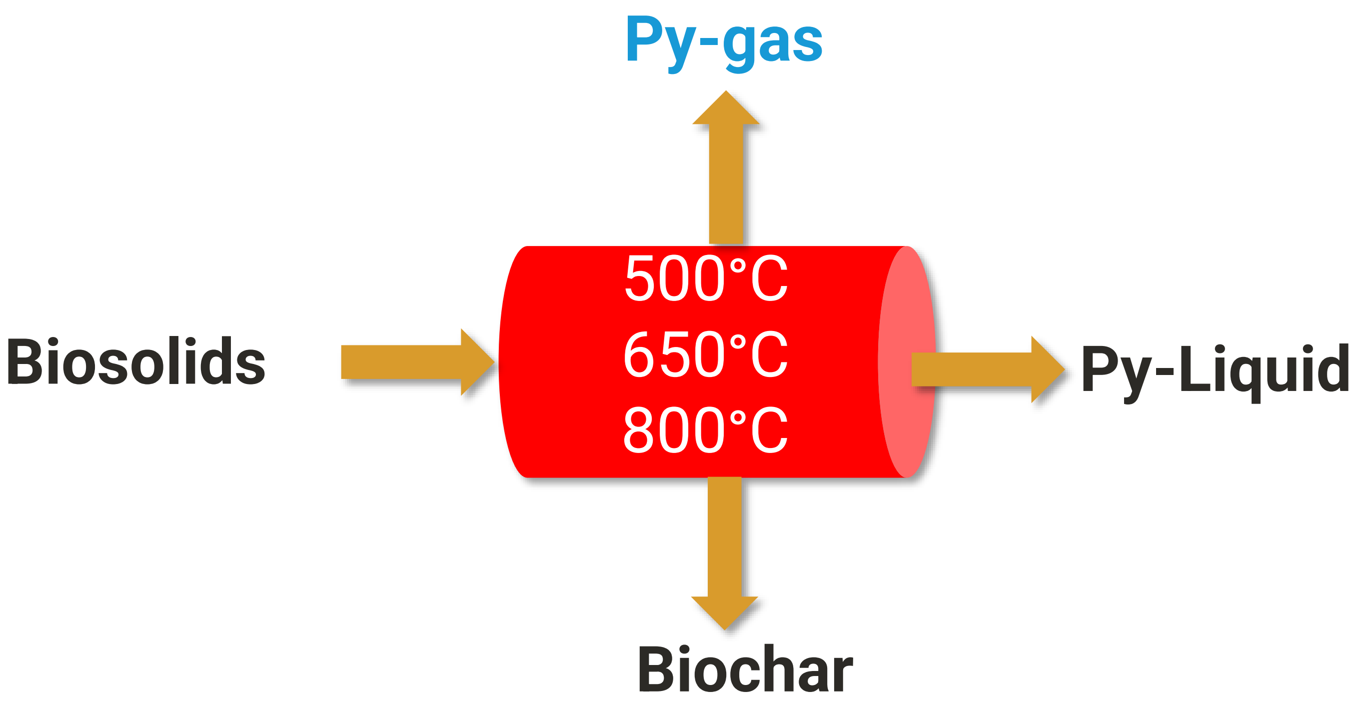
WRF 5211: Initial Research Questions

Does pyrolysis **remove** PFAS from biosolids?

Does pyrolysis **transform** PFAS?

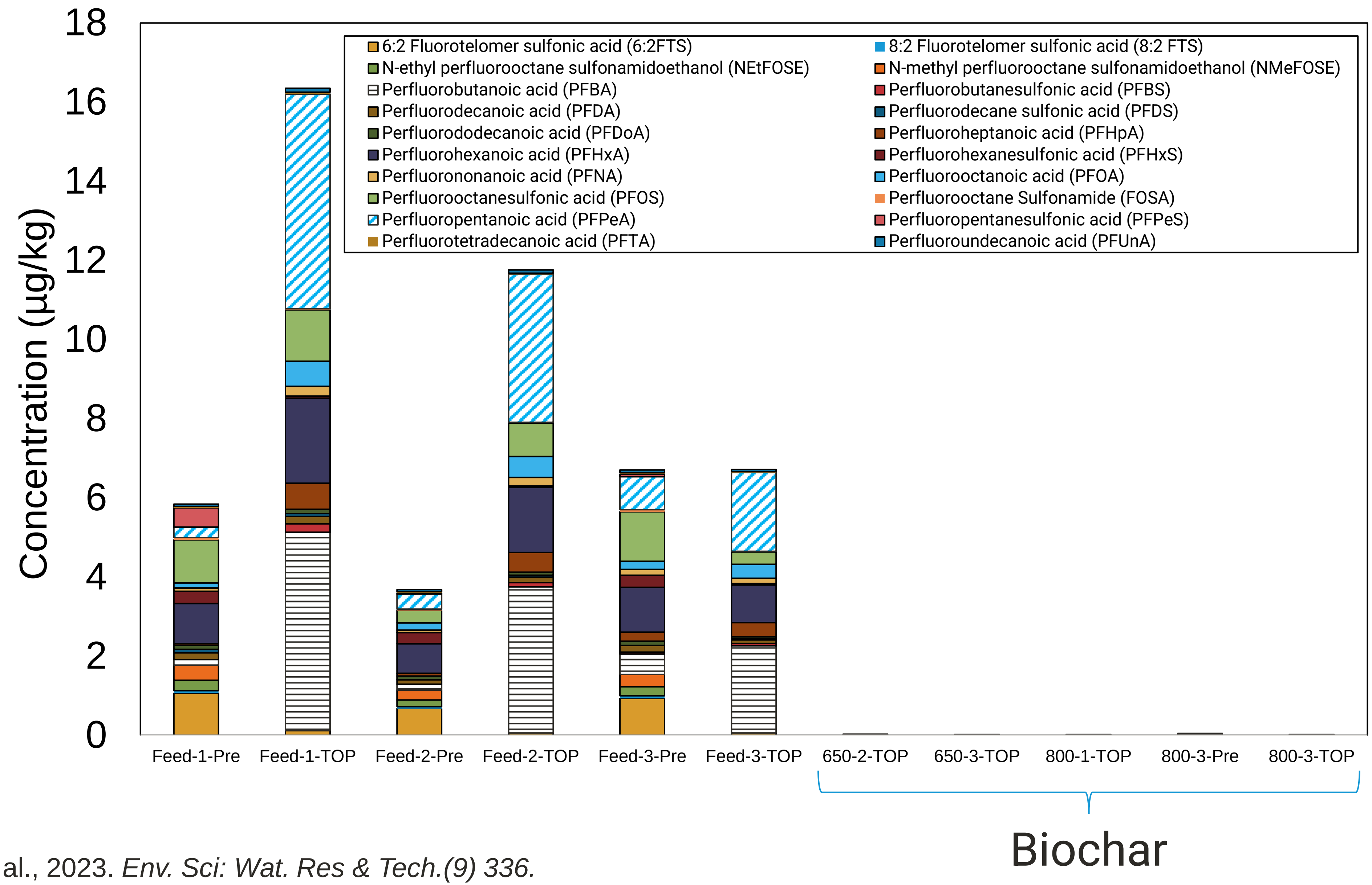


Experimental Approach: Triplicate Batch Experiments



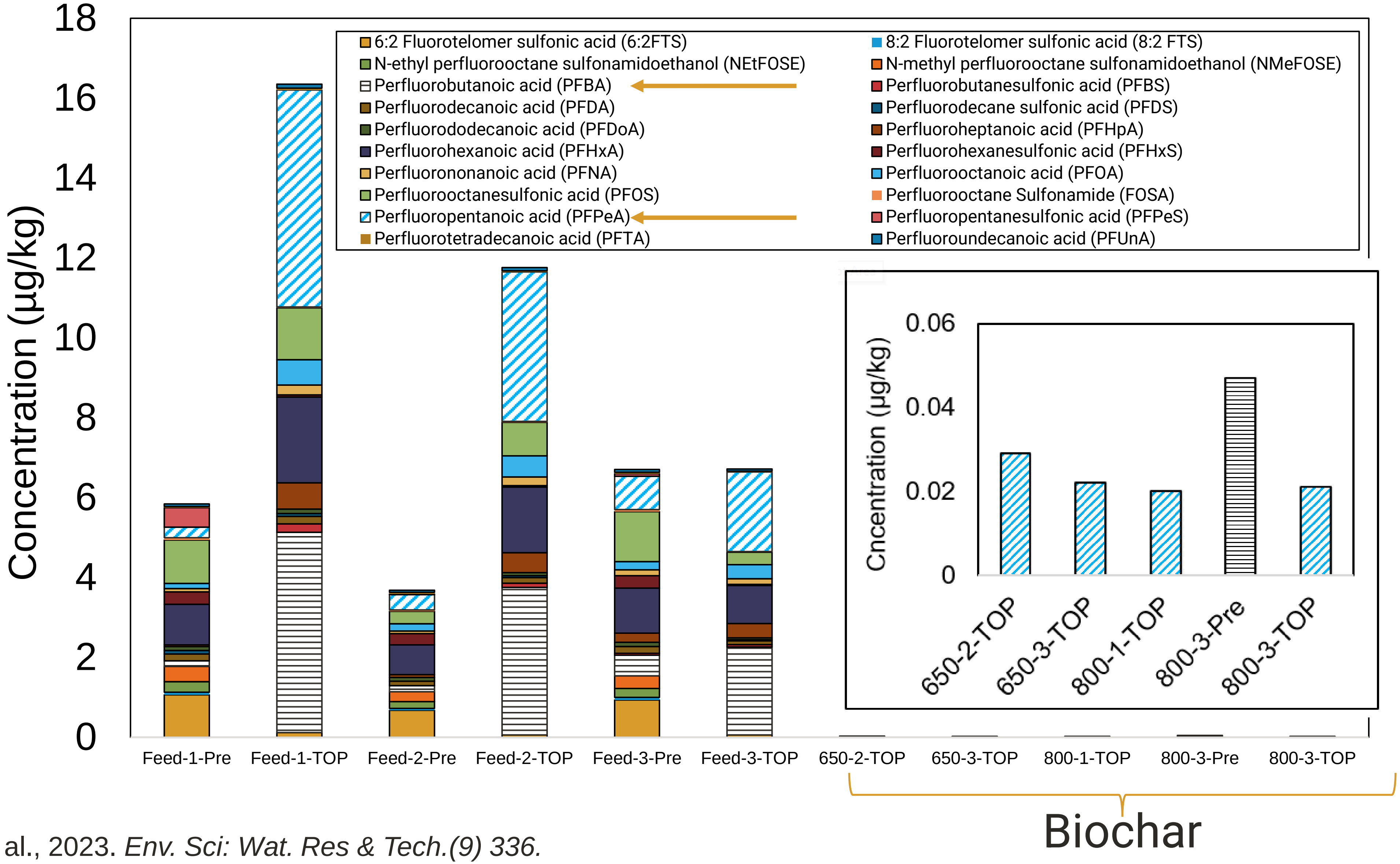
- 30 minutes
- 100 g dried biosolids

Pyrolysis Removes PFAS from Biosolids



McNamara, P.J., et al., 2023. *Env. Sci: Wat. Res & Tech.(9) 336.*

Pyrolysis Removes PFAS from Biosolids



McNamara, P.J., et al., 2023. *Env. Sci: Wat. Res & Tech.(9) 336.*

Pyrolysis Removes PFAS from Biosolids

Pyrolysis

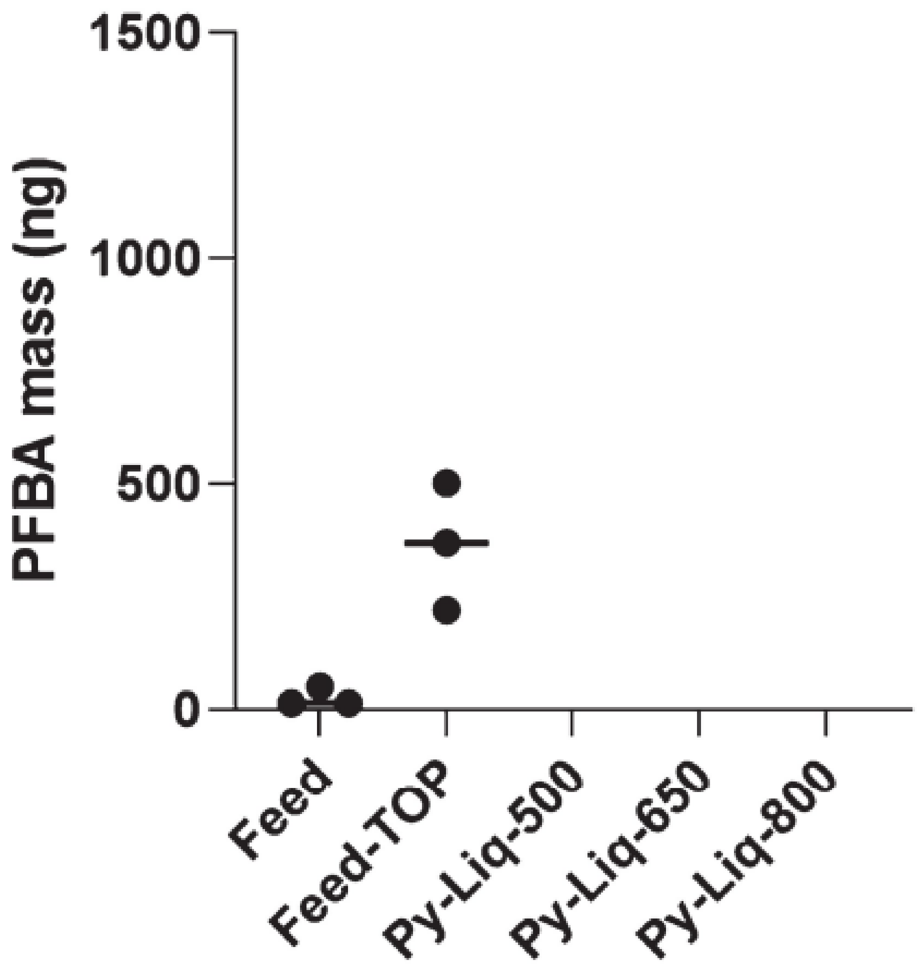
22 PFAS detected

>99% PFAS removal

Removal occurs…what happens to PFAS?

PFBA Precursors are in Biosolids

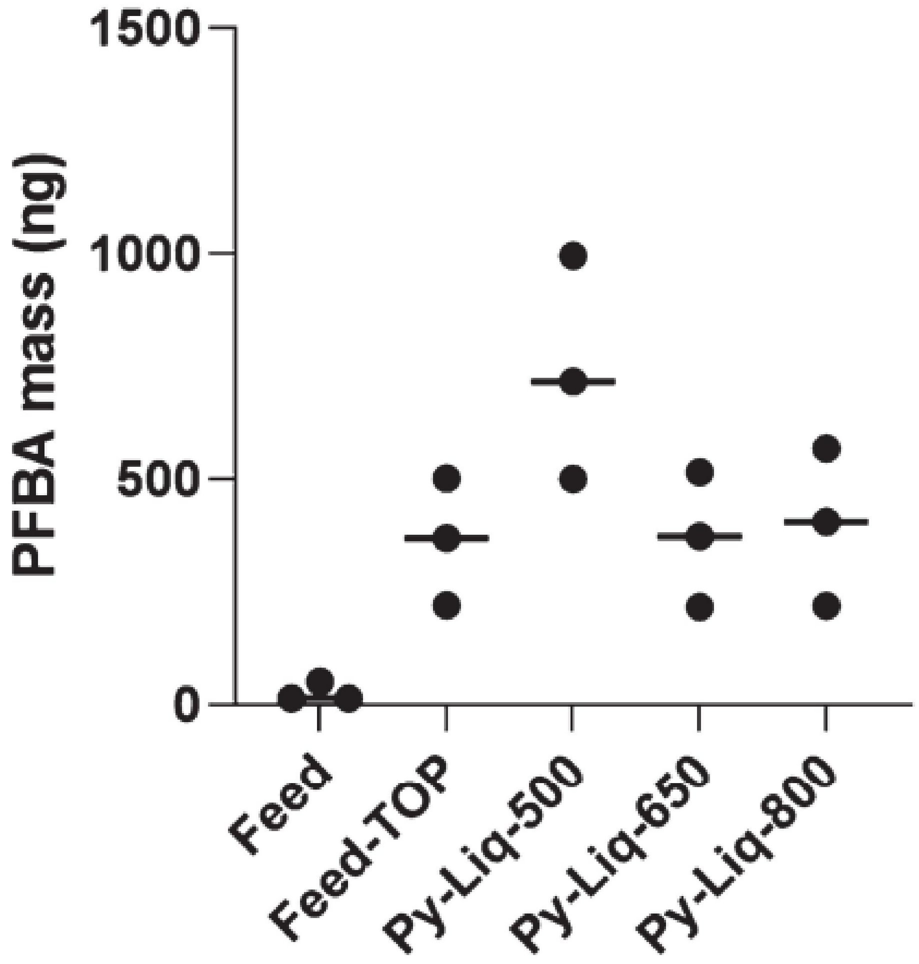
- Total Oxidizable Precursor (TOP) assay measures all the precursor compounds that could transform to PFBA



McNamara, P.J., et al., 2023. *Env. Sci: Wat. Res & Tech.(9) 336.*

PFBA Precursors are in Biosolids

- Total Oxidizable Precursor (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



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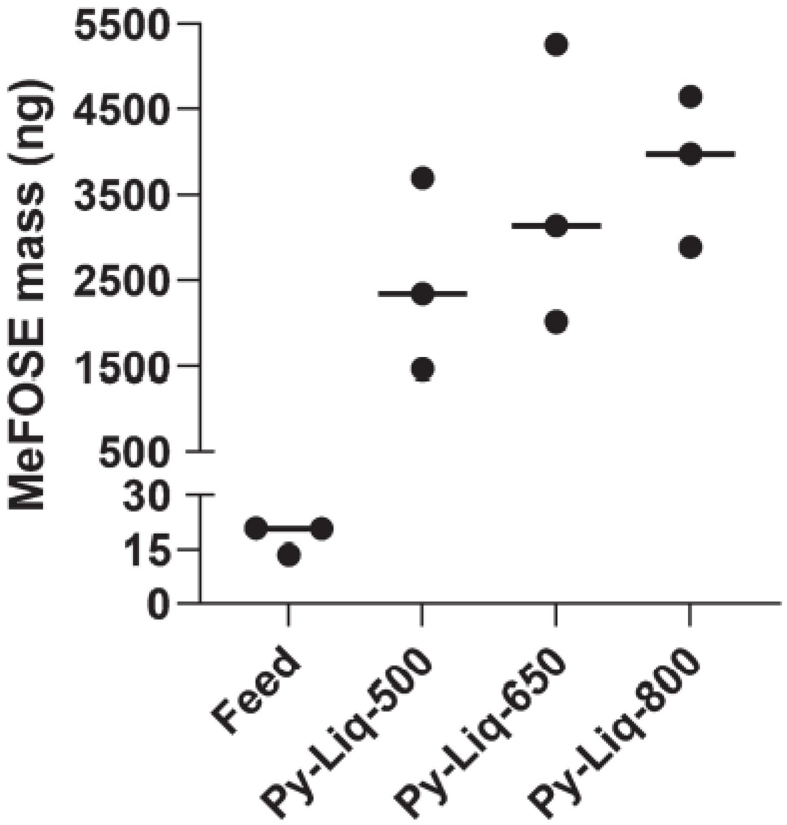
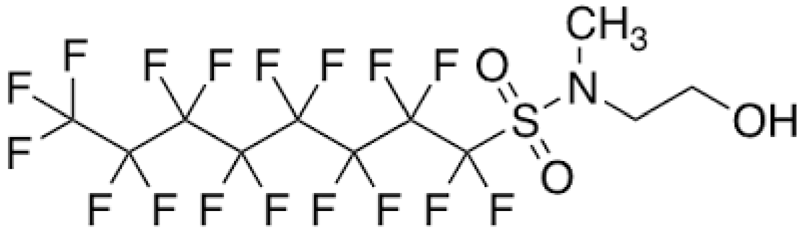
Pyrolysis Forms MeFOSE (via Transformation)





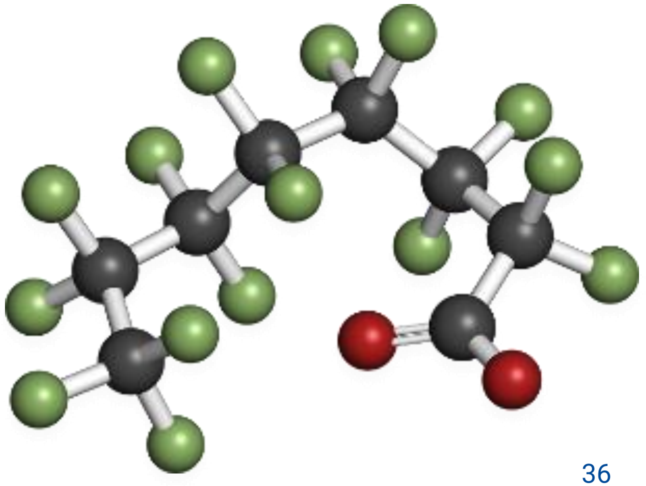
MeFOSE

WRF 5211: Answers to Research Questions

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

Does pyrolysis **transform** PFAS? ***Yes***

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



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Drying temperatures are too low to affect PFAS, right?

Experimental Approach

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

Precursor Transformation

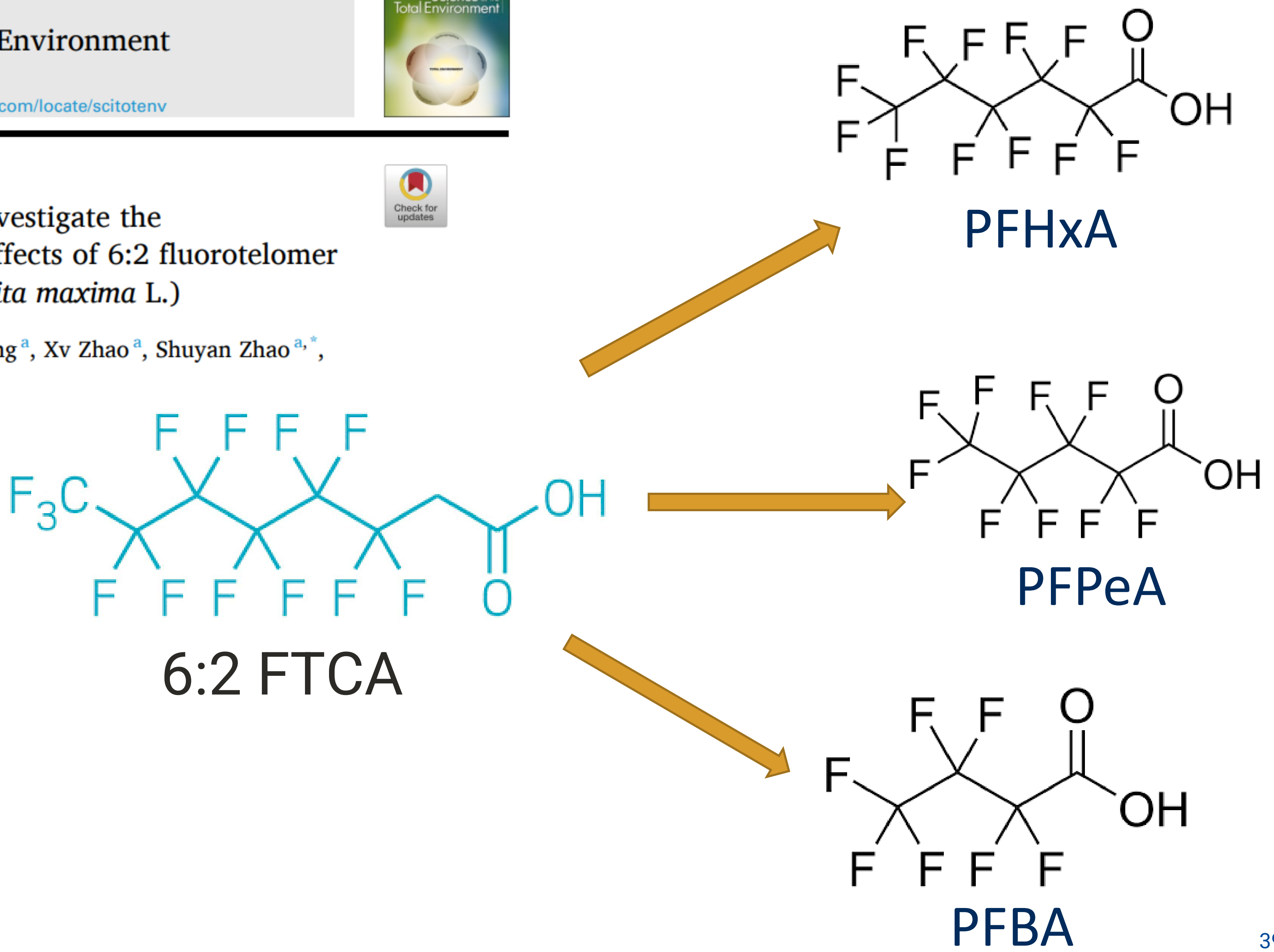
Contents lists available at ScienceDirect

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.)

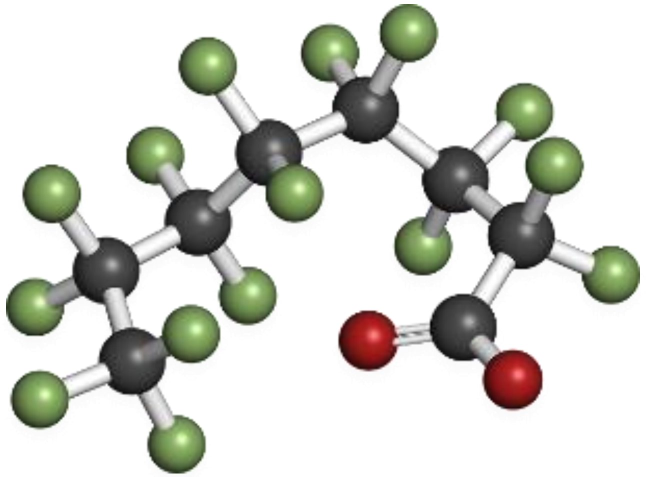
Fanghui Chi [a,1], Jingyan Zhao [a,1], Liping Yang [b], Xiaojing Yang [a], Xv Zhao [a], Shuyan Zhao [a,*], Jingjing Zhan [a]



WRF 5211: Answers to Research Questions

Can drying also impact PFAS profiles?

Yes, *drying can also lead to transformation reactions*



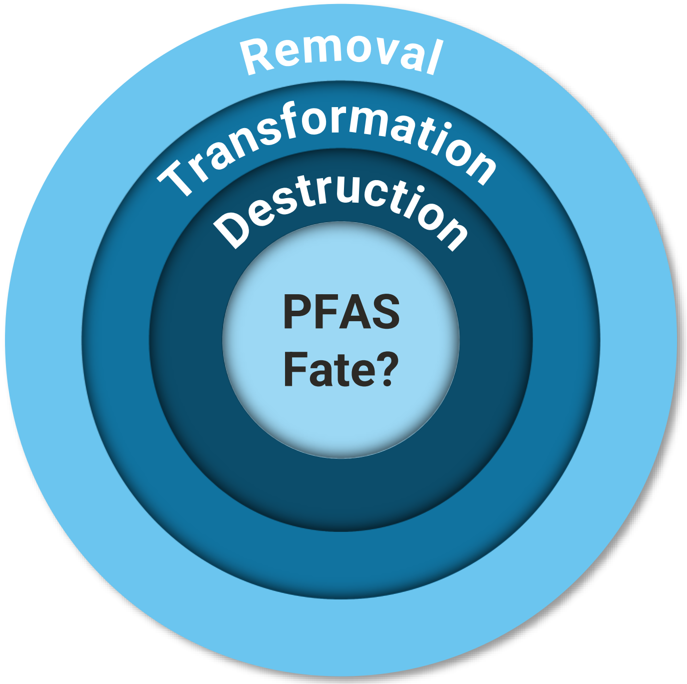
WRF 5211: Working on Answers to More Questions

Experiments on Thermal Processes:

- ✓ Drying
- ✓ Pyrolysis
- ✓ Gasification

PFAS Analysis in Products

- ✓ Solids
- ✓ Liquids
- ✓ Gas



Full-Scale Gasification System – PFAS Study

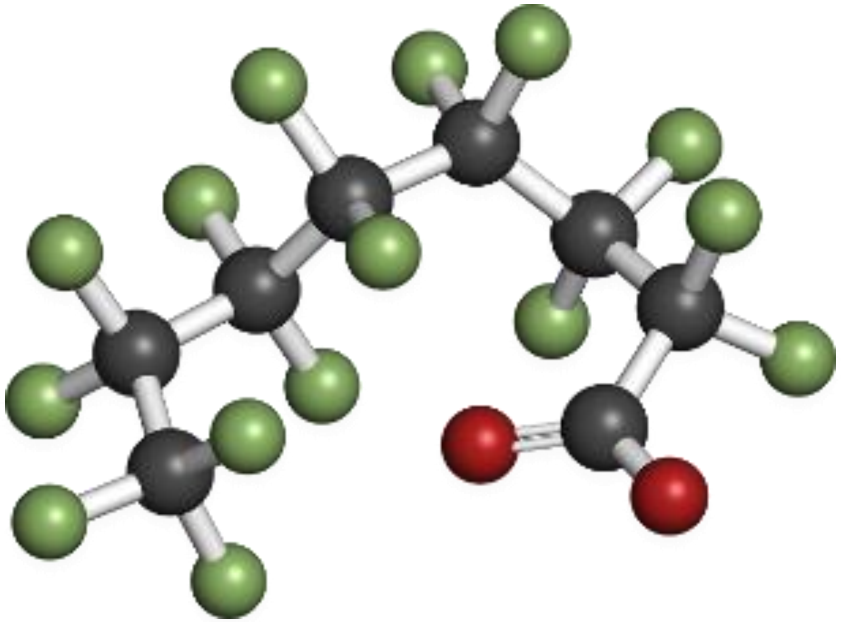
Goal of WRF 5211: Provide Tools to Support Biosolids Planning

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.

Final Thoughts

Biochar

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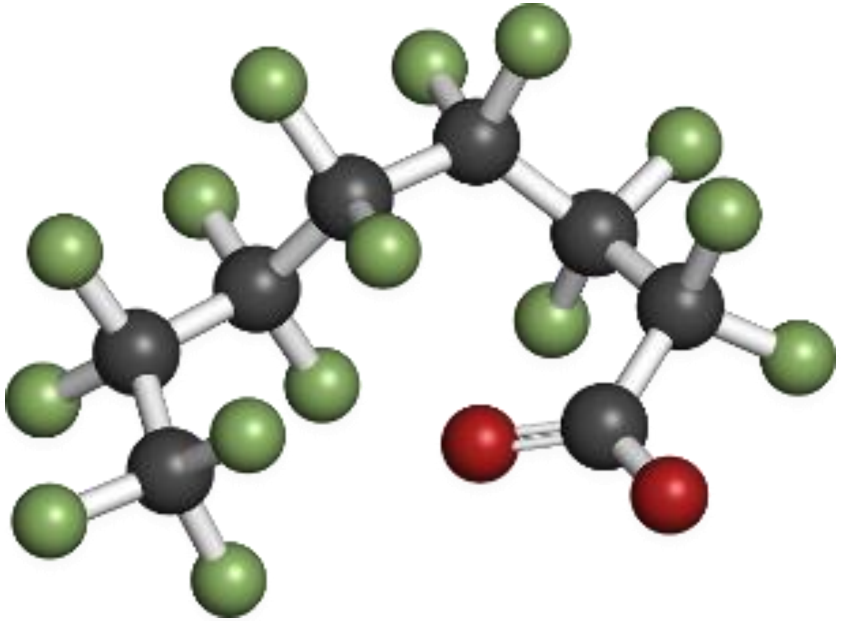

Acknowledgements

WRF Project 5211

- BV (Lynne Moss)
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BV – PFAS Research

- Research & Innovation Platform BV
- Pace® Analytical Services
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  - 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!

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Lynne Moss mosslh@bv.com

Potential Challenges

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