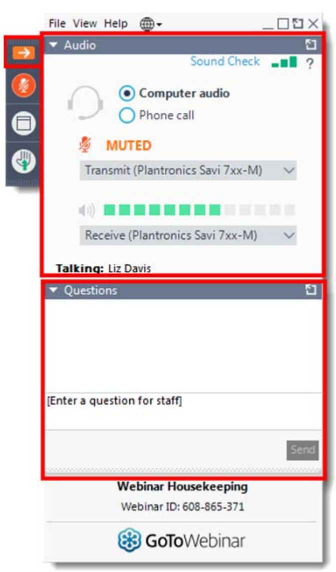
Relating PFAS Leaching from Sewage Sludge and Biosolids to Water and Sludge Quality

Thursday, February 27, 2020

1:00 – 2:00 pm ET

1

GoToWebinar Housekeeping: Attendee Participation



Your Participation

Open and close your control panel

Join audio:

- Choose **Mic & Speakers** to use VoIP
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Submit questions and comments via the Questions panel

Note: Today's presentation is being recorded and will be available within 48 hours.

2

Welcome and Introduction

Walt Marlowe
Executive Director, WEF

Peter Grevatt
CEO, WRF

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Today's Moderator

Lola Olabode
Program Director, WRF

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Today's Agenda

1:00 - 1:03p	Welcome – Walter Marlowe, WEF Executive Director
1:03 - 1:05p	Introduction – Peter Grevatt, WRF Chief Executive Officer
1:05 - 1:20p	Water Research Foundation's PFAS Research, WRF
1:20 - 1:50p	**Relating PFAS Leaching from Sewage Sludge and Biosolids** – Dr. Erica McKenzie, Temple University
1:50 – 2:00p	Q & A – Lola Olabode, WRF Moderator
2:00p	Adjourn

5

The Water Research Foundation PFAS Research

6

Summary

Completed Work addressing PFAS:

1. WRF 4322: Treatment Mitigation Strategies of Poly & Perfluorinated Chemicals, (http://www.waterrf.org/Pages/Projects.aspx?PID=4322)
2. WRF 4344: Removal of Perfluoralkyl Substances by PAC Adsorption and Ion Exchange, (http://www.waterrf.org/Pages/Projects.aspx?PID=4344)
3. Webcast: "Per- and Polyfluoroalkyl Substances (PFAS) in Water: Background, Treatment and Utility Perspective," provides overview of the issues, https://www.waterrf.org/resource/and-polyfluoroalkyl-substances-pfas-water-background-treatment-and-utility-perspective
4. State of the Science paper on PFAS, provides a great overview, https://www.waterrf.org/sites/default/files/file/2019-09/PFCs_StateOfTheScience.pdf
5. Formation of Nitrosamines and Perfluoroalkyl Acids During Ozonation in Water Reuse Applications (WRF 1693/Reuse 11-08), https://www.waterrf.org/research/projects/formation-nitrosamines-and-perfluorochemicals-during-ozonation-water-reuse

Ongoing Projects

1. PFAS Research Area, established 2018. https://www.waterrf.org/news/management-analysis-removal-fate-and-transport-and-polyfluoroalkyl-substances-pfass-water
2. WRF 4877: Concept Development of Chemical Treatment Strategy for PFOS-Contaminated Water, https://www.waterrf.org/research/projects/concept-development-chemical-treatment-strategy-pfos-contaminated-water
3. WRF 4913: Investigation of Treatment Alternatives for Short-Chain Per- Polyfluoroalkyl Substances, https://www.waterrf.org/research/projects/investigation-treatment-alternatives-short-chain-pfas
4. WRF 5011: Evaluation and Life Cycle Comparison of Ex-Situ Treatment Technologies for Per-and Polyfluoroalkyl Substances (PFASs) in Groundwater.
5. WRF 5042: Assessing Poly- and Perfluoroalkyl Substance Release from Finished Biosolids
6. WRF 5002: Determining the Role of Organic Matter Quality on PFAS Leaching from Sewage Sludge and Biosolids (NSF Project)

Funded Projects, Commencing 2020

1. WRF 5031: Occurrence of PFAS Compounds in U.S. Wastewater Treatment Plants

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Completed Work Addressing PFAS

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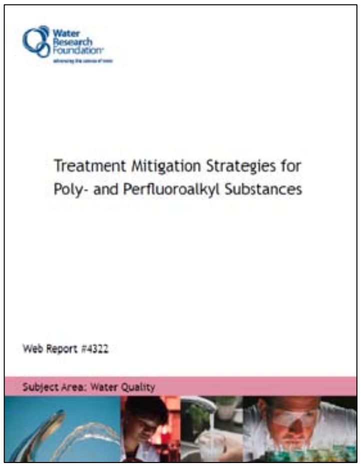
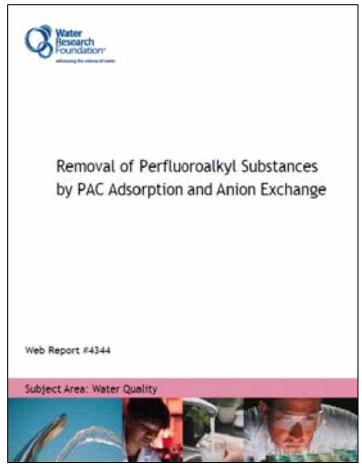
WRF PFAS Research





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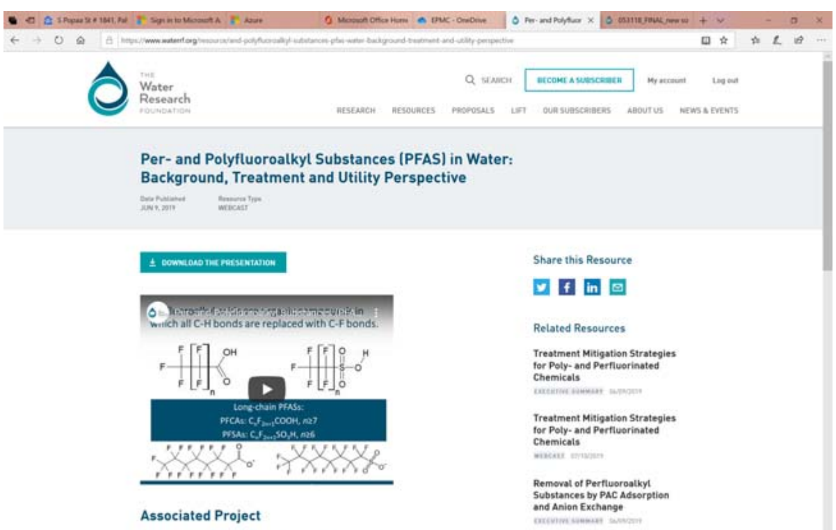
PFAS Webcast



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State of the Science Paper on PFAS

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Formation of Nitrosamines and Perfluoroalkyl Acids During Ozonation in Water Reuse Applications (Reuse 11-08/WRF 1693)

Objectives:

- Assess the formation of nitrosamines (e.g., NDMA) upon ozonation of treated wastewaters.
- Assess the formation of perfluoroalkyl acids (PFAAs; e.g., PFOA and PFOS) upon ozonation of treated wastewaters.
- Evaluate the factors responsible for the formation of these ozone byproducts;
- Recommend potential mitigation strategies.

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Ongoing PFAS Efforts

13

WRF PFAS Research Area

Research Priority Program

- Management, analysis, removal, fate and transport of per- and polyfluoroalkyl substances (PFAS) in water.
- Objectives
  - Assess effectiveness of analytical methods.
  - Evaluate vulnerability of waters to PFAS and identify sources and hotspots.
  - Understand behavior, fate, and transport of PFAS in treatment and environment.
  - Evaluate treatment for removing PFAS and reliability of technologies.
  - Develop risk communication strategies.

14

Multi-Year Research Agenda

- Treatment, Disposal and Management Options of Residuals Containing PFAS (spent GAC and resins)
- Development of an Analytical Procedure for Total PFAS Measurement and Determining it Usefulness for Management Decisions
- Evaluation of Analytical Methods for PFAS via Inter-laboratory Comparison
- Qualitative Structure Activity Relationships For Predicting Removal of New and Emerging PFAS
- Investigation of Alternative Management Strategies to Prevent PFAS from Entering Drinking Water Supplies and Wastewater (e.g., Policies, Pre-treatment of point-sources)

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Project 4877 - Concept Development of Chemical Treatment Strategy for PFO-Contaminated Water

Objectives

- The primary goal of this research was to develop a practical high-efficiency chemical treatment strategy for PFOS in water. This research investigated advanced oxidation integrated with chemical reduction.

Status

- Draft Final Report

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Project 4913 - Investigation of Treatment Alternatives for Short-Chain PFAS

Objectives

- Systematically investigate short-chain PFAS removal by readily implementable treatment processes - and to a more limited extent, innovative techniques - in a wide range of background water matrices (groundwater, surface water, treated wastewater) at multiple scales (bench, pilot, full).

Status

- Started on March 1, 2019

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WRF 5002 - Determining the Role of Organic Matter Quality on PFAS Leaching from Sewage Sludge and Biosolids

Objectives

- Understand how solid characteristics and water quality affect PFAS desorption from sewage-derived solids.

Status

- Funded by NSF. Started on February 2019. Expected completion early 2022.

WRF 5042 - Assessing PFAS Release from Finished Biosolids

Objectives

- Assess PFAS release from finished biosolids as a function of PFAS loading, post-digestion processing, and age of the biosolids.

Status

- Started Fall 2019. Expected completion early 2021.

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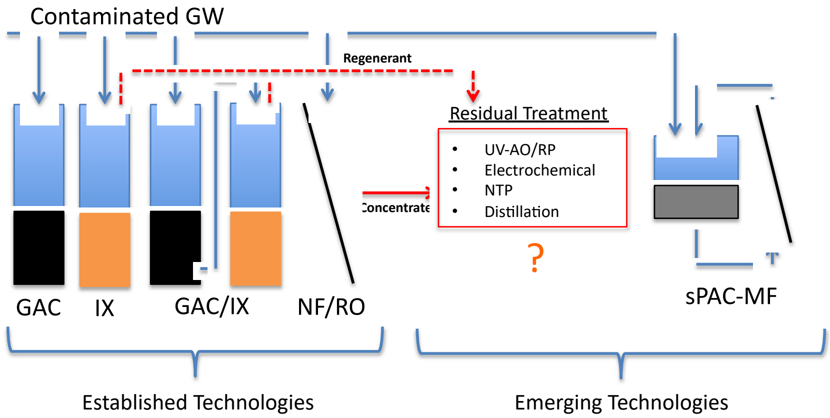
Project 5011 - Evaluation and Life Cycle Comparison of Ex-Situ Treatment Technologies for PFASs in Groundwater



Status – Started October 1, 2018

19

Upcoming PFAS Efforts

20

WRF 5031 - Occurrence of PFAS Compounds in U.S. Wastewater Treatment Plants

Objectives

- Evaluate PFAS occurrence in US wastewater treatment plants and determine the fate of PFAS compounds during wastewater treatment.

Status

- Selection is made. Project will start in March.

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THANK YOU!!!

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WRF Funding Mechanism Timelines for 2020

Research Priority Program		Tailored Collaboration Program		Unsolicited Program		Emerging Opportunities		Facilitated Research
8/14/2020	RFPs posted: 15 Priority Research Areas	4/24/2020	2020 Program Launch	1/14/2020	2020 Program Launch	2/4/2020	2020 Program Launch: first due date for proposals	Open all year
	RFPs due ~ 6-8 weeks after posting	6/8/2020	Deadline for pre-proposals	3/30/2020	Preproposal Deadline	Monthly Review	Coordinate with Staff	Coordinate with Staff

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Today’s Speaker

Erica R. McKenzie, Ph.D.
Assistant Professor
Civil and Environmental Engineering
Temple University

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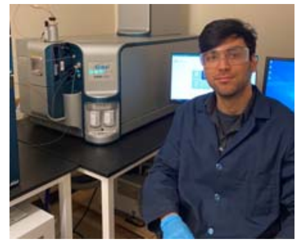
24

Acknowledgements

Temple University
- Farshad Ebrahimi, graduate student
- Dr. Rominder Suri, Dr. Erica R. McKenzie

Drexel University
- Asa Lewis and Dr. Christopher Sales



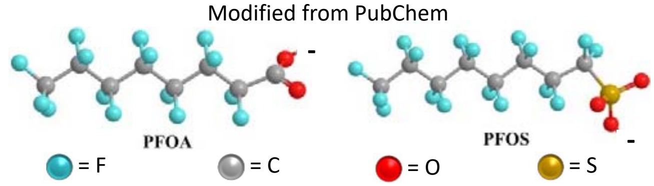
Financial Support
- Water Research Foundation (award #5002)
- National Science Foundation (award #CBET-1805588)
- Army Research Office DURIP (award #W911NF1910131)

25

Per- and Polyfluoroalkyl Substances (PFAS)

- Synthetic compounds
- Used in various consumer goods for more than 50 years
- Highly fluorinated alkyl region
- Ubiquitous
  - Human (99% detected), animals
  - Wastewater, surface water, oceans
  - Globally transported

Modified from PubChem

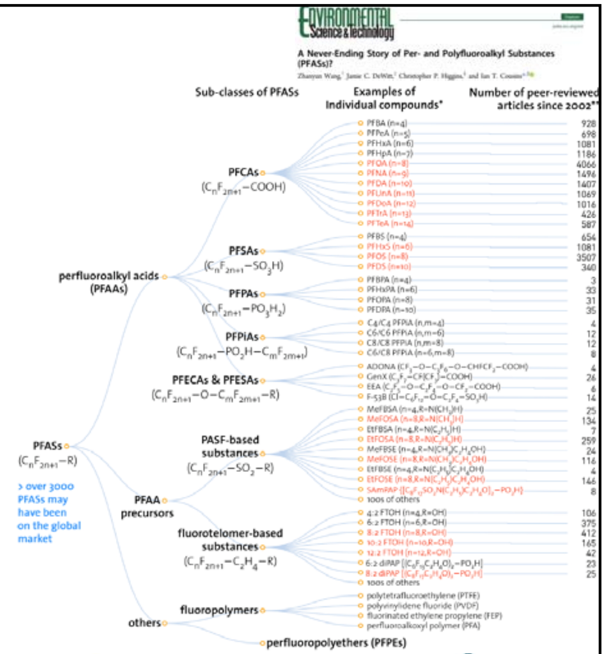


- **P**ersistent
  - Does not easily degrade
- **B**ioaccumulative
  - Transfers into biotic tissue
- **T**oxic
  - Negatively affect biological health
  - Probable link to cancer

26

PFAS Compounds

- Thousands of compounds
- Often charged
- Surfactant behavior
  - Hydrophobic and hydrophilic
- Highly stable end products
- Known to sorb to solids
  - Organic carbon
  - Protein
- More info: ITRC PFAS fact sheets



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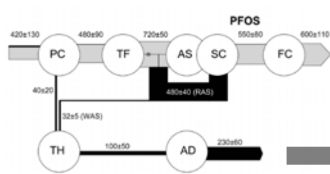
PFAS in Wastewater Treatment Process

Sources

Everypixel.com

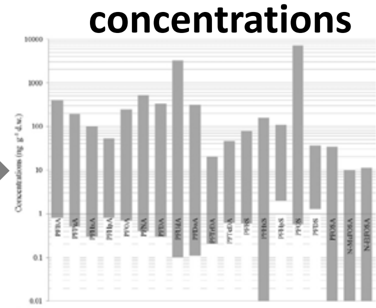
Unsplash.com

WWTP mass flows

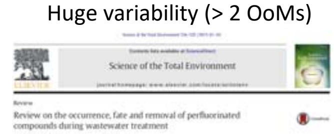


Mass flow are compound dependent

Worldwide sludge concentrations



Huge variability (> 2 OoMs)



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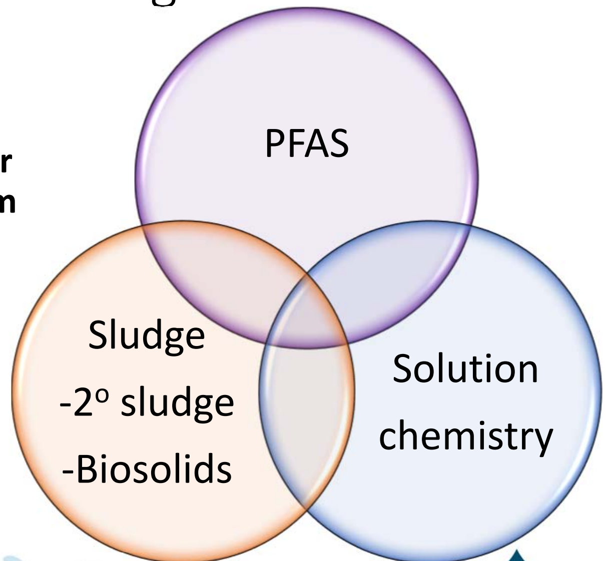
Project Scope – PFAS Leaching from Sewage Sludges

Overarching goal: To understand how solid characteristics and water quality affect PFAS desorption from sewage-derived solids.

- Solids characteristics
- PFAS characteristics
- Solution chemistry



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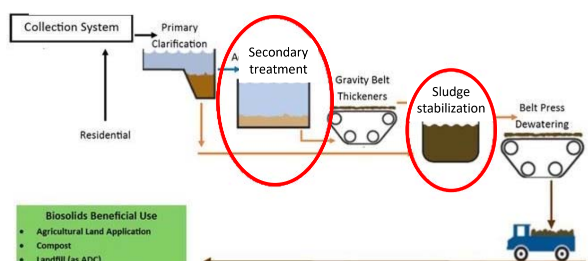
Sewage-Derived Solids

- "Sludge" – from secondary treatment
- Biosolids
  - Stabilized
  - Class A or B

How is PFAS partitioning affected by:
- PFAS characteristics
- Concentration
- Solution chemistry
- Treatment or stabilization process



*City of Santa Rosa, CA, water

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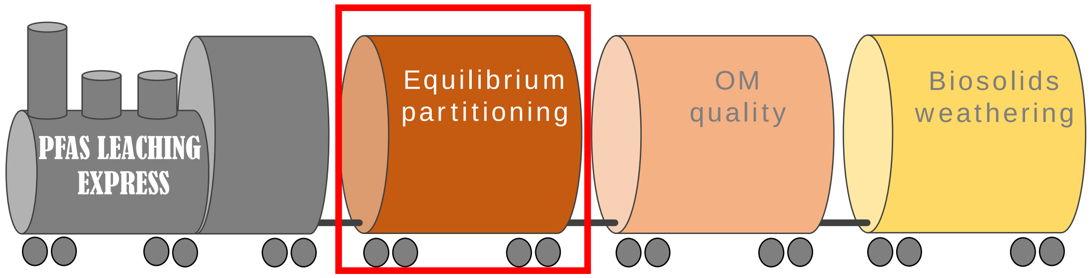
Three-Year Project Research Objectives



- 14 PFAS evaluated –head group, chain length, and unfluorinated regions
- Solution chemistry – pH, ionic strength, calcium concentration
- Solids quality – organic carbon, protein, lipids
- Treatment process – secondary treatment (4) and stabilization (3)

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WWTP Recruitment

Sludge sample	Biosolid sample	Size
Activated Sludge_A	NA	Small
Activated Sludge_B	NA	Medium
Activated Sludge_C	Class B anaerobic digestion_C	Small
Trickling filter_D	Class A composting_D	Small
Trickling filter_E	NA	Medium
BNR_F	Class A composting_F	Small
BNR_G	Aerobic Didgestion_G	Large
BNR_H	Class A composting_H	Small
BNR_I	Aerobic Digestion_I	Medium
Rotating biological contactors_J	NA	Small

- Small: < 10 MGD
- Medium: 10 – 20 MGD
- Large: > 20 MGD

Participants from Mid-Atlantic region

Sewage solids
- Sludge and biosolids
- Collected by WWTP -> shipped to Temple U.
- Collections: Fall 2019, Winter 2020

Solids management at Temple University
- Dewatered via centrifugation
- Sludge experiments started promptly
- Biosolids stored in fridge

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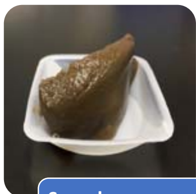
Experimental Design – Environmental Relevance

- Total concentrations
- Isotherm (concentration)
  - Intensive – 7 concentrations
  - Summary – 1 concentration

Edge

- pH: 6, 7, and 8
- Ionic strength: 1, 10, 100 mM $NaNO_3$
- Ca^{2+}: 0.33, 3.3, 33 mM $Ca(NO_3)_2$



Sample
- 200 mg wet weight solids

Solution
- 50 mL solution
- PFAS amended

Vials
- 50 mL PP vials

Equilibrium
- Mixed for 7 days

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Sample processing

AQUEOUS

Collection
- Mixed sample

Centrifugation
- Centrifuge 50 ml vials at 2000 G for 20 mins

Subsampling
- Subsample for metals, pH and conductivity analysis

IS

PFAS liquid processing
- Subsample 300 µL and add 300 µL MeOH with IS

Centrifugation
- 12000 rpm for 20 mins

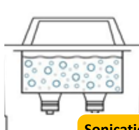
Analysis prep
- Transfer 100 µL to LC vials
- Archive rest

QTOF
- SCIEX x500r QTOF

SOLIDS

IS

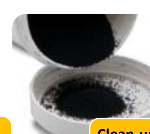
Collection
- Decant supernatant
- Basic methanol for extraction



Sonication
- 1 hr at 30 ° Celsius

Mix
- Shake for 2 hrs
- Repeat x2

Nitrogen Evaporator
- To dryness



Clean-up
- Reconstitute with acidic methanol
- EnviCarb

Analysis prep
- 300 µL extract + 300 µL dilution water

QTOF
- SCIEX x500r QTOF

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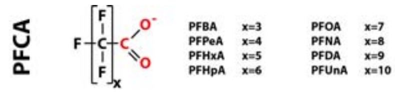
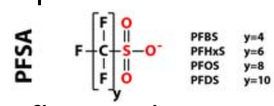
34

PFAS Quantification

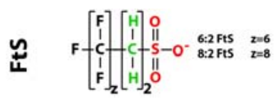
- LC-QTOF-MS (accurate mass, MRM)
- Eight perfluorocarboxylates

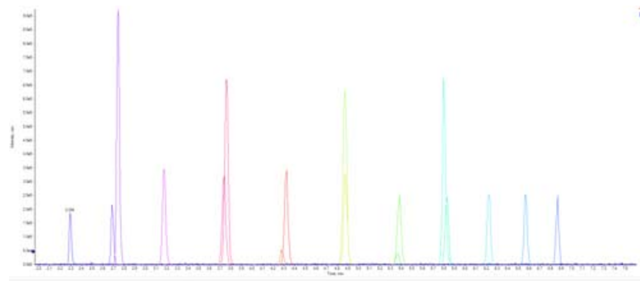


- Four perfluorosulfonates



- Two fluorotelomersulfonates





- Quantifiable (commercial standards)
- Range of PFAS properties
- Future – accurate mass suspect screening

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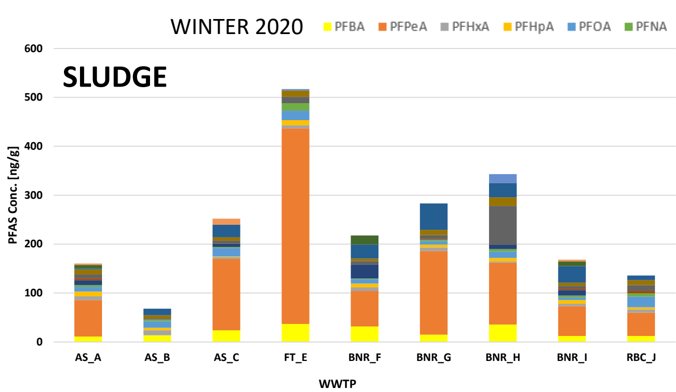
35

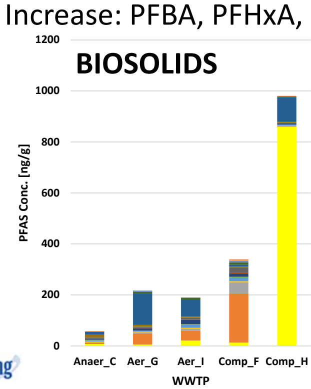
What Are the Solids-PFAS Concentrations?



- Range for total and analytes
- Elevated: PFPeA, PFOS, PFOA, PFBS

Paired sludge-biosolids samples

- Increase: PFBA, PFHxA, PFOS



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Comparative Concentrations

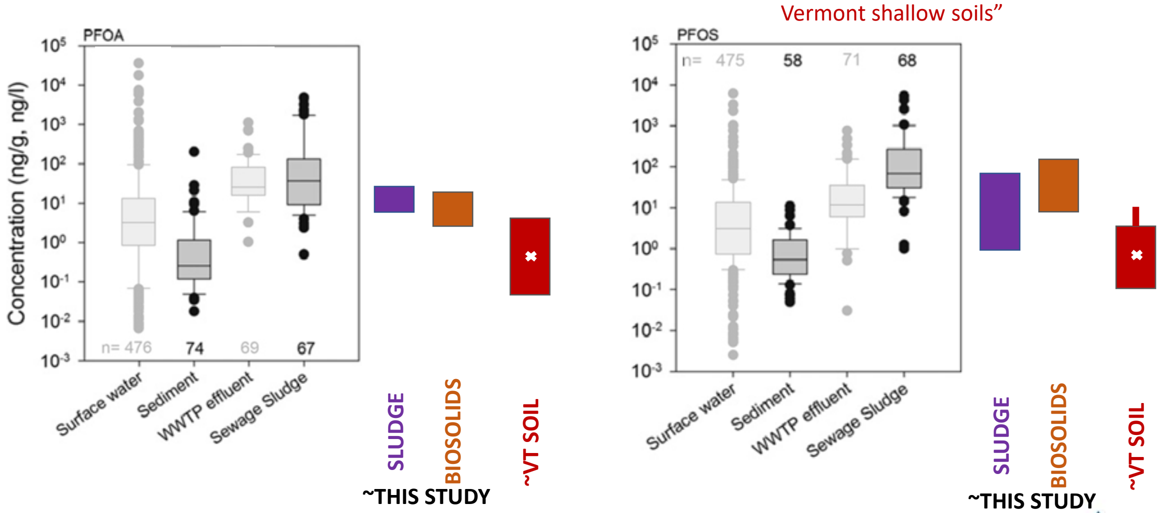
Chemosphere (2013)

Review

Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – A review on concentrations and distribution coefficients

P. Zareitalabad, J. Siemens, M. Hamer, W. Amelung

Zhu et al., (2019) "PFAS background in Vermont shallow soils"



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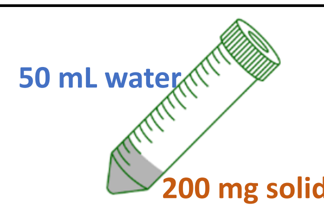
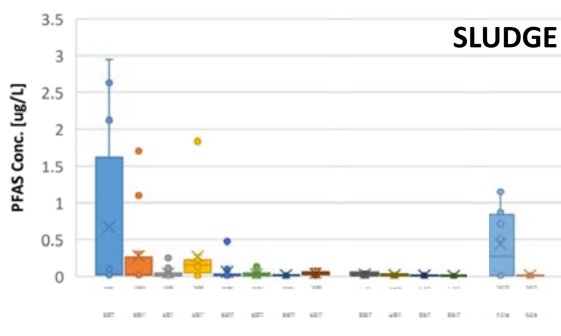
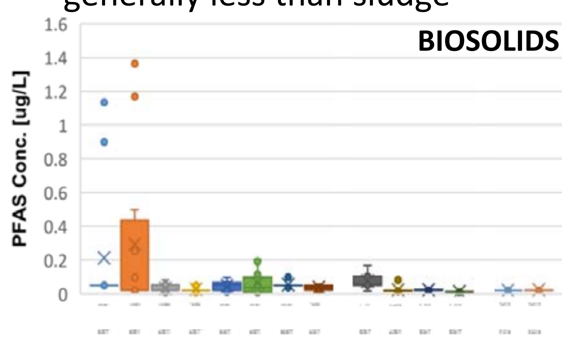
PFAS Leaching from Solids





- Biosolids leach concentration generally less than sludge



- Many non-detects or low concentration
- Higher leach concentrations for shorter chain length

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Solid-Water Distribution Coefficients to Better Understand Partitioning

- To go beyond leached concentration, we used solid-water distribution coefficients to evaluated equilibrated systems.

$$K_d = \frac{solid\ associated\ concentration}{liquid\ concentration} = \frac{C_s}{C_w}$$

wide range values → $logK_d$ OR present on log axis

- In an isotherm, we examine concentration effect on partitioning
- We can extend this to examine the role of specific solid components

$$K_{oc} = \frac{K_d}{f_{oc}} = \frac{C_s}{C_w \cdot f_{oc}} \qquad K_{lipid} = \frac{K_d}{f_{lipid}} = \frac{C_s}{C_w \cdot f_{lipid}} \qquad K_{protein} = \frac{K_d}{f_{protein}} = \frac{C_s}{C_w \cdot f_{protein}}$$

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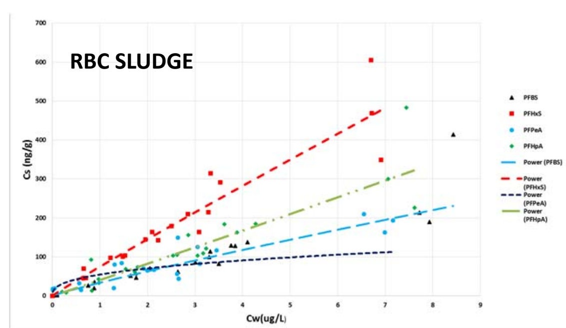
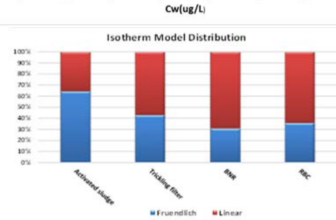
Isotherm Fit to Evaluate Concentration Effects

- Spiked PFAS to achieve concentration range
- Sludge generally fit with linear
  - Longer chain length trend toward Freundlich
- Biosolids mix of linear and Freundlich
- Concentration may be important for biosolids and for longer chain length





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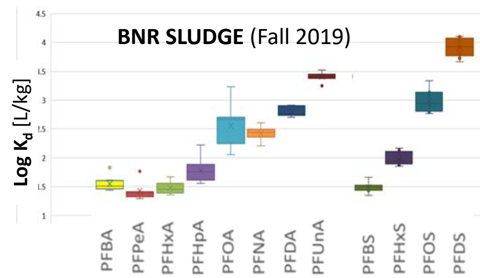
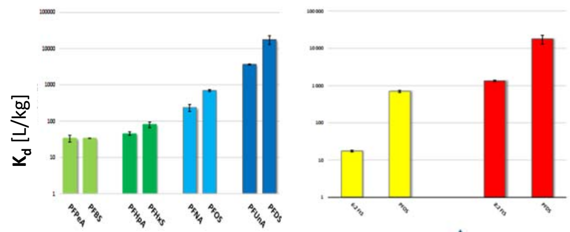
PFAS Compound Characteristic Effects

- ↑ K_d means greater sorption
- Sorption ↑ with chain length
- Head group effects (for equal chain length)
  - Sulfonates > carboxylates
- Unfluorinated region (for equal chain length)
  - Perfluorinated > polyfluorinated
- These trends observed across treatment
- These trends observed in many other matrices





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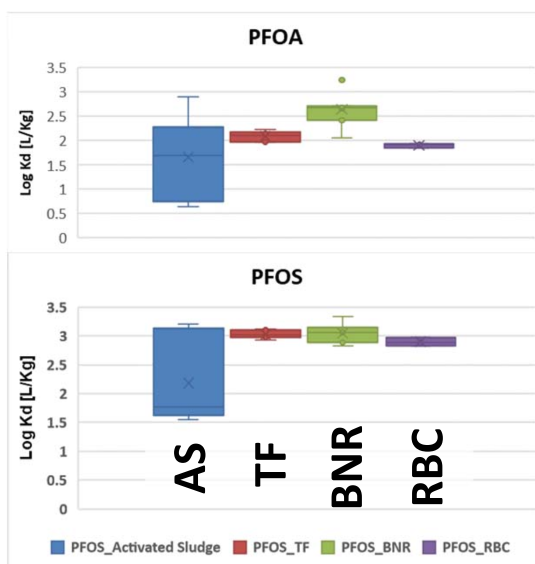
Treatment Effects

- Activated sludge more variable
  - Sample replicates – representative
  - Among WWTP samples
  - Need to look to sludge characteristics
- Generally similar K_d values among treatments
  - AS may be lower
  - Statistical analysis needed



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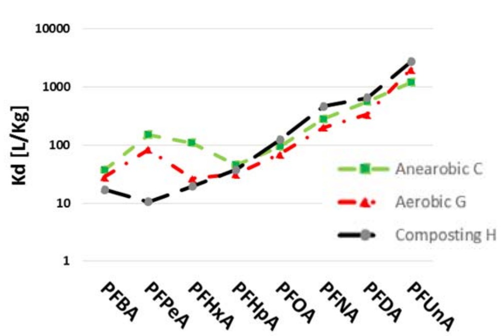
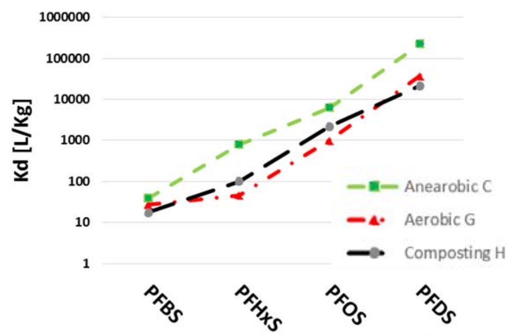
42

Biosolids Stabilization

- Anaerobic often highest K_d values (but only 1 plant)
- Limited biosolids samples – aim to include more plants in the future





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Solution Chemistry Effect

Calcium concentration

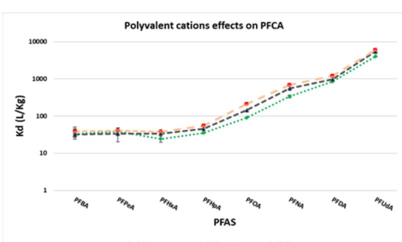
- ↑ K_d with ↑ [Ca]

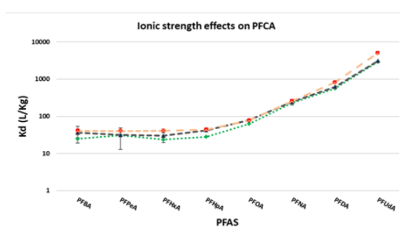
Ionic strength

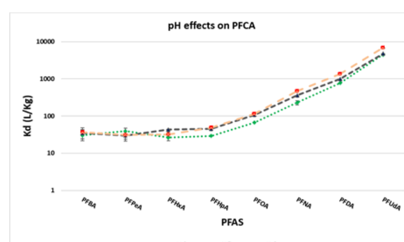
- ↑ K_d with ↑ IS

pH

- ↑ K_d with ↓ pH







- All modest impacts (e.g., 2x change K_d); longer chain length more impacted
  - Statistical analysis is a future activity

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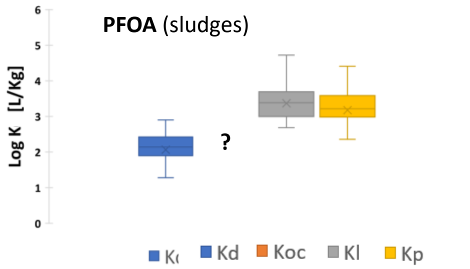
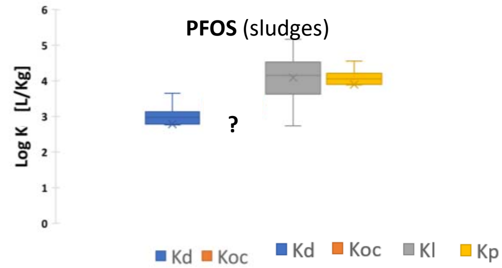
Comparison of partitioning constants





- Ongoing effort to compare normalized partitioning coefficients (e.g, K_{oc} outstanding)
- Lipid content does not appear to decrease variability; protein ~ un-normalized
- Statistical analysis required

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45

Conclusions

- Sludge and biosolids PFAS concentrations were similar to other reports, and greater than background concentrations
- PFAS isotherms
  - No concentration effect for shorter chain length PFAS, especially in sludge (i.e., linear)
  - Concentration effect for longer chain length PFAS, especially in biosolids (i.e., Freundlich)
- PFAS sorption capacity trends similar to some other solids
  - ↑ with chain length, ↑ for sulfonates, ↑ for perfluorinated
- Solution chemistry had modest effect - ↑ K_d with ↑ [Ca], ↑ IS, or ↓ pH
- Secondary treatment and stabilization had mixed effects
  - Activated sludge more variable
- No clear solid component clearly drives sorption capacity (protein or lipid)

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46

Closing Considerations

- These are "forever chemicals" – what comes into a WWTP leaves via either liquid effluent or solids
  - Source control and pre-treatment should be included to the extent possible
  - This is not easy – requires a multi-industry effort
- Biosolids stabilization process reduced leachable PFAS, compared to sludges, however biosolids-associated concentrations are above background
  - Application rates should be appropriately selected
- Our findings thus far do not indicate clear differences among secondary treatment or stabilization treatment methods.

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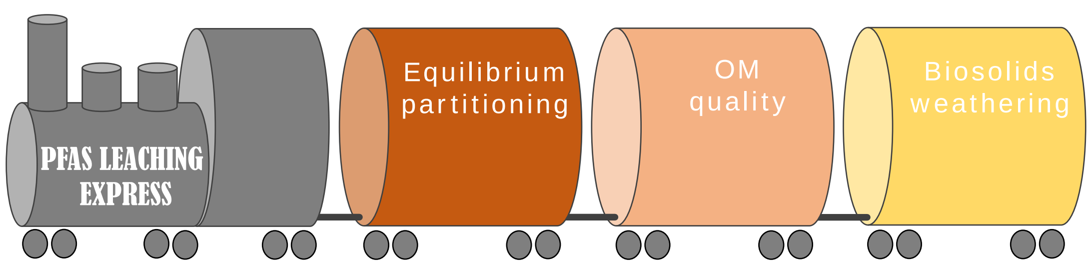
47



Questions?

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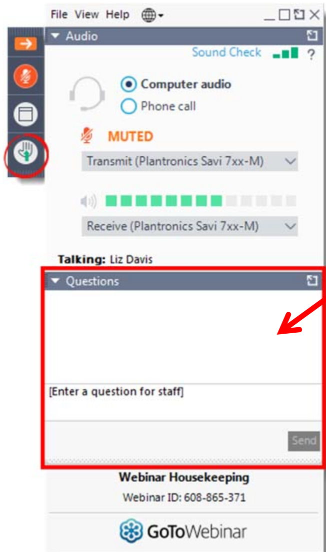
48

Time for Questions



Your Participation

- Please continue to submit your text questions and comments using the Questions panel.
- Please raise your hand to be unmuted for verbal questions. You must be called in on a phone and have entered your audio PIN.

Note: Today's presentation is being recorded and will be available shortly after today's webcast

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49

Thank You

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50