Linking PFAS partitioning behavior in sewage solids to the solid characteristics, solution chemistry, and treatment processes

Temple University

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Drexel University

- Asa Lewis and Dr. Christopher Sales

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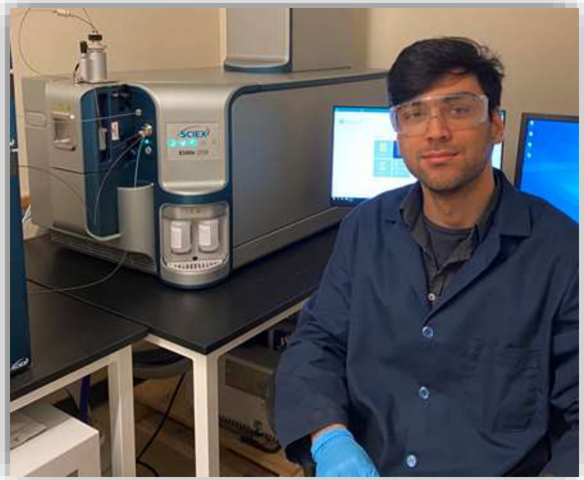

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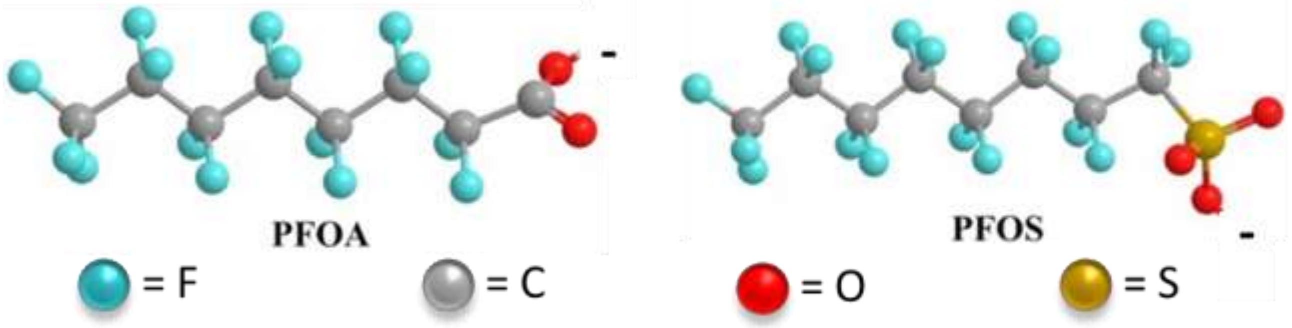
Introduction

Poly- and perfluoroalkyl substances (PFAS)

- Synthetic compounds
- Used in various consumer goods for over 50 years
- Highly fluorinated alkyl chain
    - Persistent
        - Will not easily degrade
    - Bioaccumulative
        - Partition into biotic tissue
    - Toxic
        - Negatively affect biological health
        - Potential link to cancer

Modified from PubChem



- Ubiquitous
    - Detected both in human & animals
    - Wastewater, surface water, and oceans
    - Globally transported

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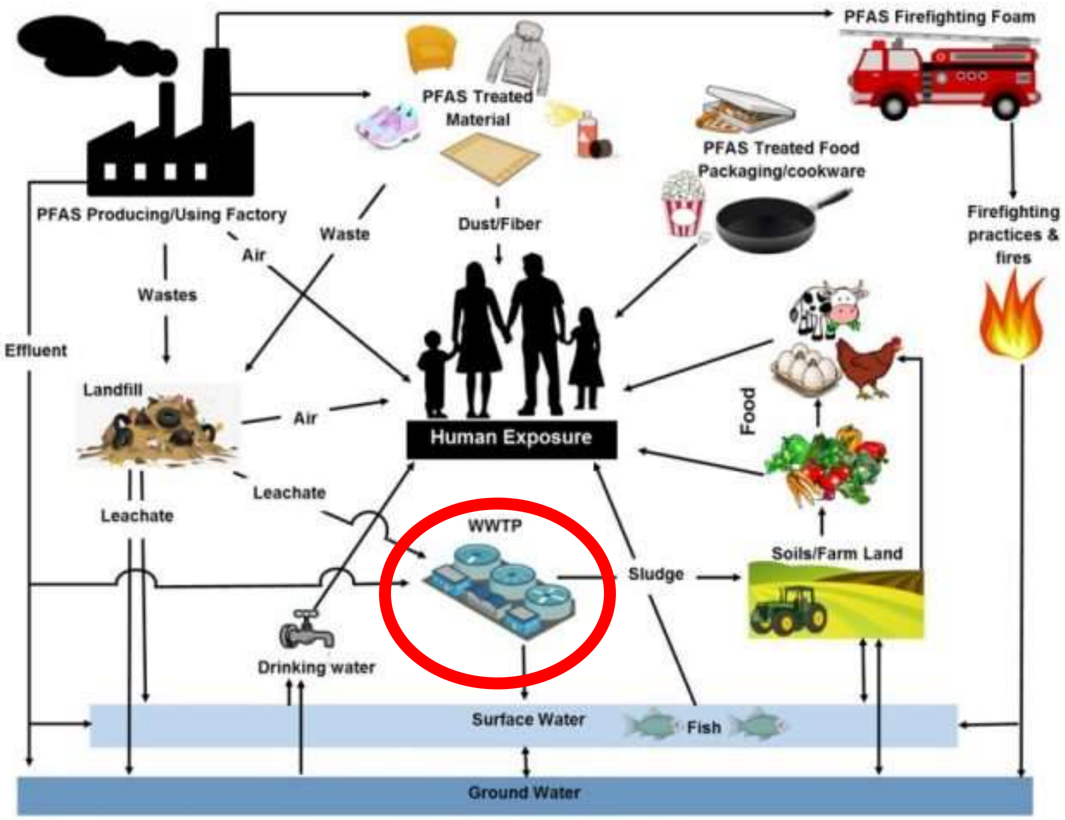
Introduction

- > 4000 compounds
- Usually present in charged form (primarily anions)
- Surfactant behavior
- Ability to partitioning into solids such as soil, sediment, sludge, and biosolids

SOURCES: TOXIC-FREE FUTURE; EPA



Human Exposure and sources of PFAS
Image: DWP, adapted from Oliaei et al. 2013.

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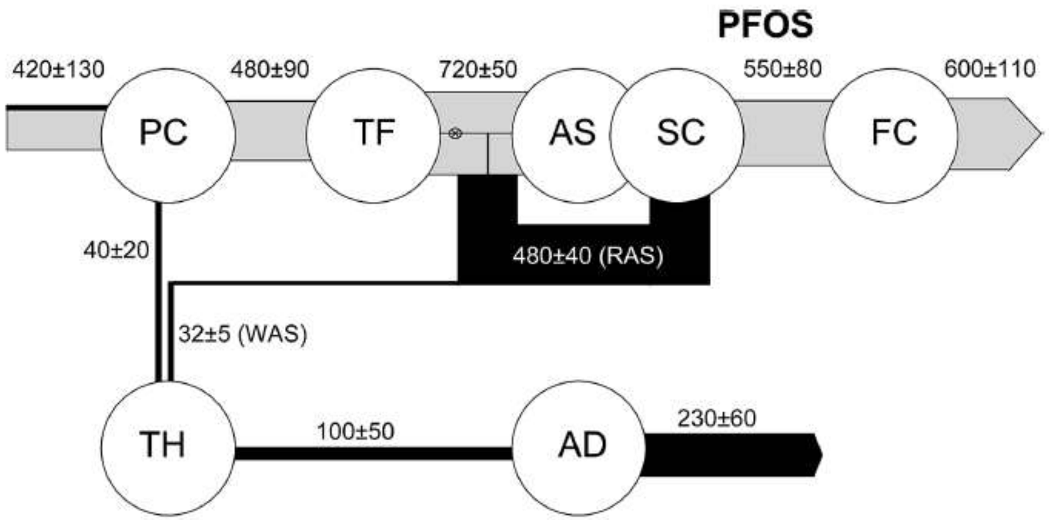
Introduction

- > 7 million tons of biosolids are either directly applied to agricultural land (~60%) or disposed (~40%) (Northeast Biosolid and Residual Association, 2004)
- > 3,000 kg PFAS/yr released (Venkatesan and Halden, 2013)
- PFOA and PFOS concentrations: up to 68 ng/g and 219 ng/g in activated sludge (Venkatesan and Halden, 2013)



PFOS mass flowrate (mg/day within WWTP)

Environ. Sci. Technol. **2006**, *40*, 7350–7357

Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility†

MELISSA M. SCHULTZ,‡ CHRISTOPHER P. HIGGINS,§ CARIN A. HUSET,‡ RICHARD G. LUTHY,§ DOUGLAS F. BAROFSKY,‡ AND JENNIFER A. FIELD*,†,‖

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The first phase of the project:

Looking at a variety of potentially effective parameters

Chemosphere 271 (2021) 129530

Contents lists available at ScienceDirect

Chemosphere

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

ELSEVIER

Linking PFAS partitioning behavior in sewage solids to the solid characteristics, solution chemistry, and treatment processes

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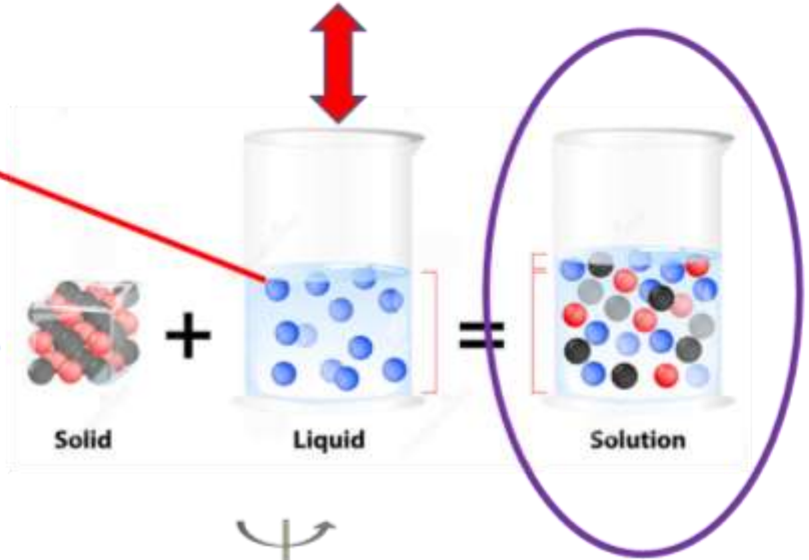
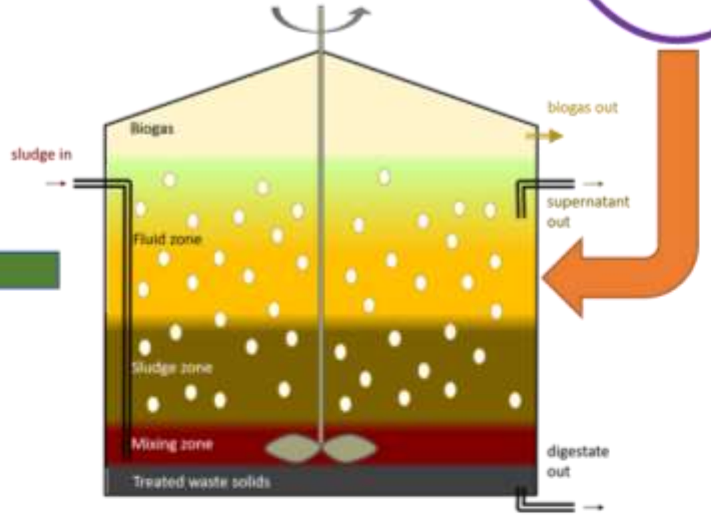
Looking at a variety of potentially effective parameters:

- *pH*
- *Mono-valent cation*
- *Di-valent Cation*

- *PFAS headgroup*
- *PFAS chain length*
- *C-F VS C-H bonds*

- *Protein*
- *Lipid*
- *Aromaticity*
- *Hydrophobicity*
- *Size*



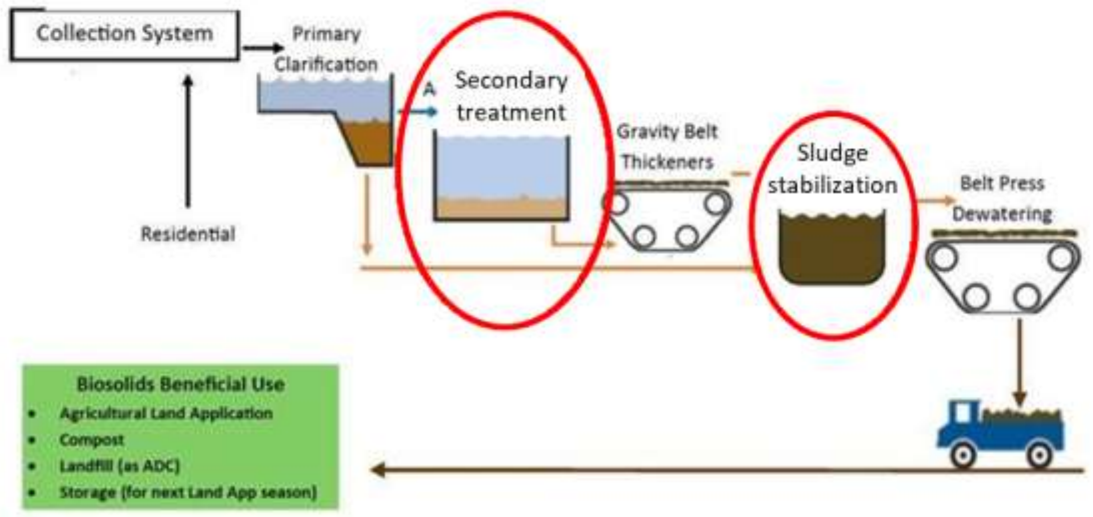


Anaerobic Digester

Photos: https://www.sludgeprocessing.com/

Experimental Design and methods

- 14 PFAS evaluated –head group, chain length, and fluorinated regions
- Solution chemistry – pH, ionic strength, calcium concentration
- Treatment process – secondary treatment (4) and stabilization (3)



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 Digestion_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

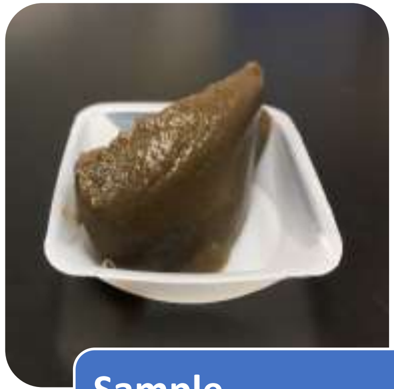
Experimental design

Isotherm- Equilibrium study

- Intensive – 7 concentrations
- Limited – 1 concentration

Edge- Testing solution parameters

- 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

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

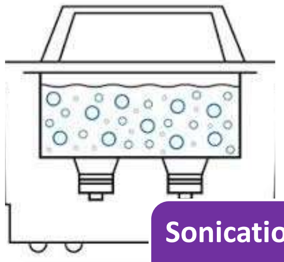
Centrifugation
- 12000 rpm for 20 mins

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

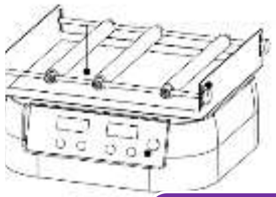
QTOF
- SCIEX x500r QTOF

SOLIDS*

Collection
- Decant supernatant
- Basic methanol for extraction



Sonication
- 1 hr at 60 º 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

* **Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge**

CHRISTOPHER P. HIGGINS, JENNIFER A. FIELD, CRAIG S. CRIDDLE, AND RICHARD G. LUTHY

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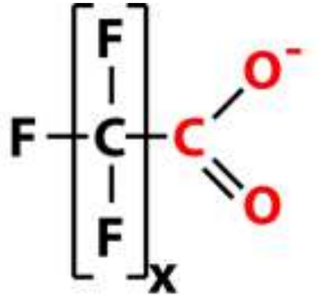
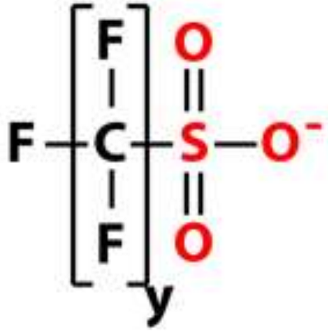
PFAS quantification using LC-QTOF/MS

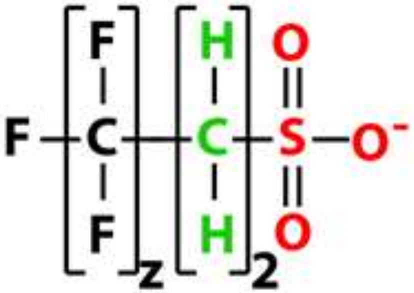
8 × PFCA

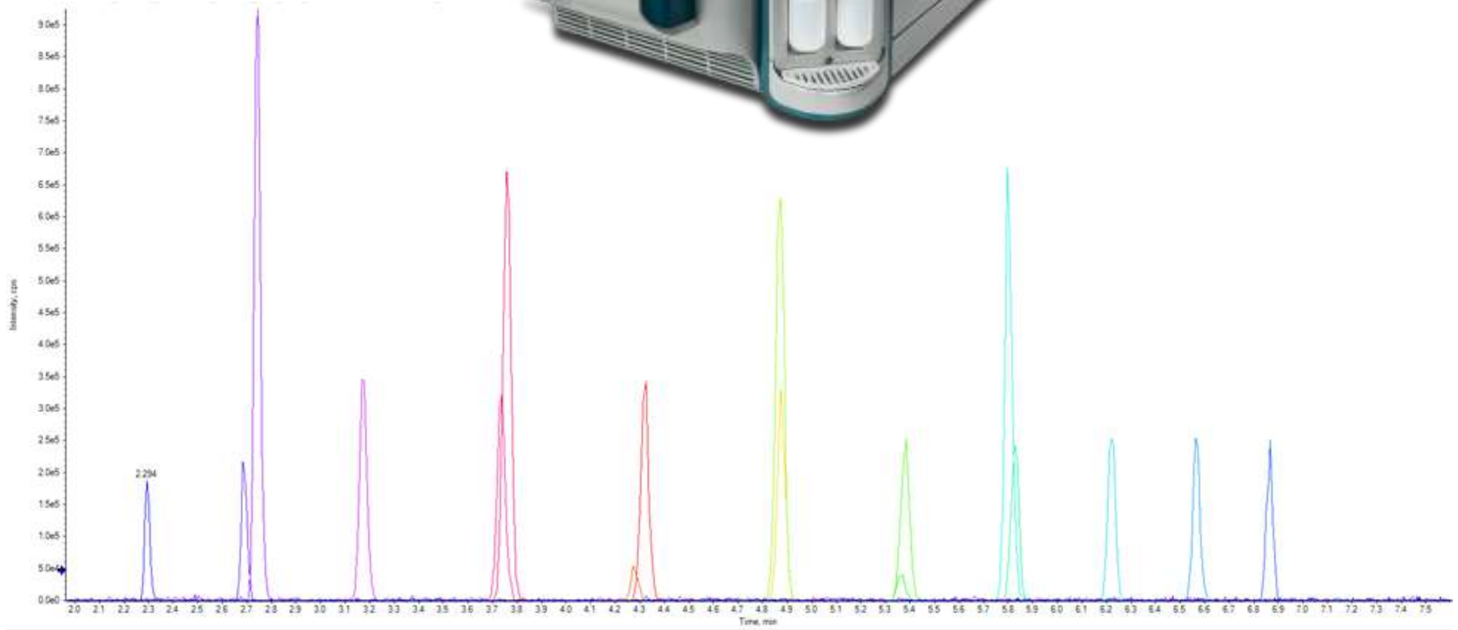


4 × PFSA



2 × FtS





A chromatogram of the standards achieved in the lab

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PFAS partitioning behavior in sludge/biosolid

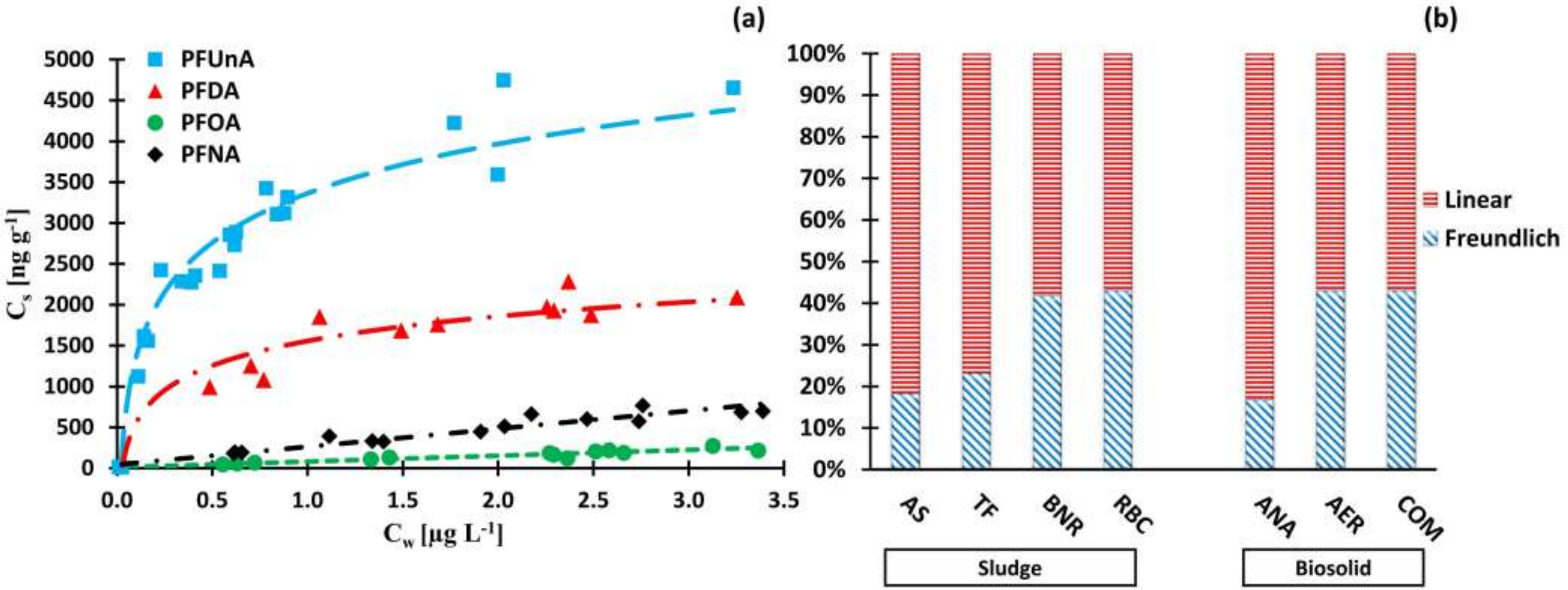
The linear model prevailed

This can occur as a result of:

- *Substantially porous texture*
- *No concentration effects*

$C_s = AC_w$ Linear

$C_s = K_f C_w^n$ Freundlich model



a. Examples of isotherm model fittings (linear and Freundlich) in RBC_J sludge sample;
b. Distribution of best-fit isotherm models across sludge and biosolid samples

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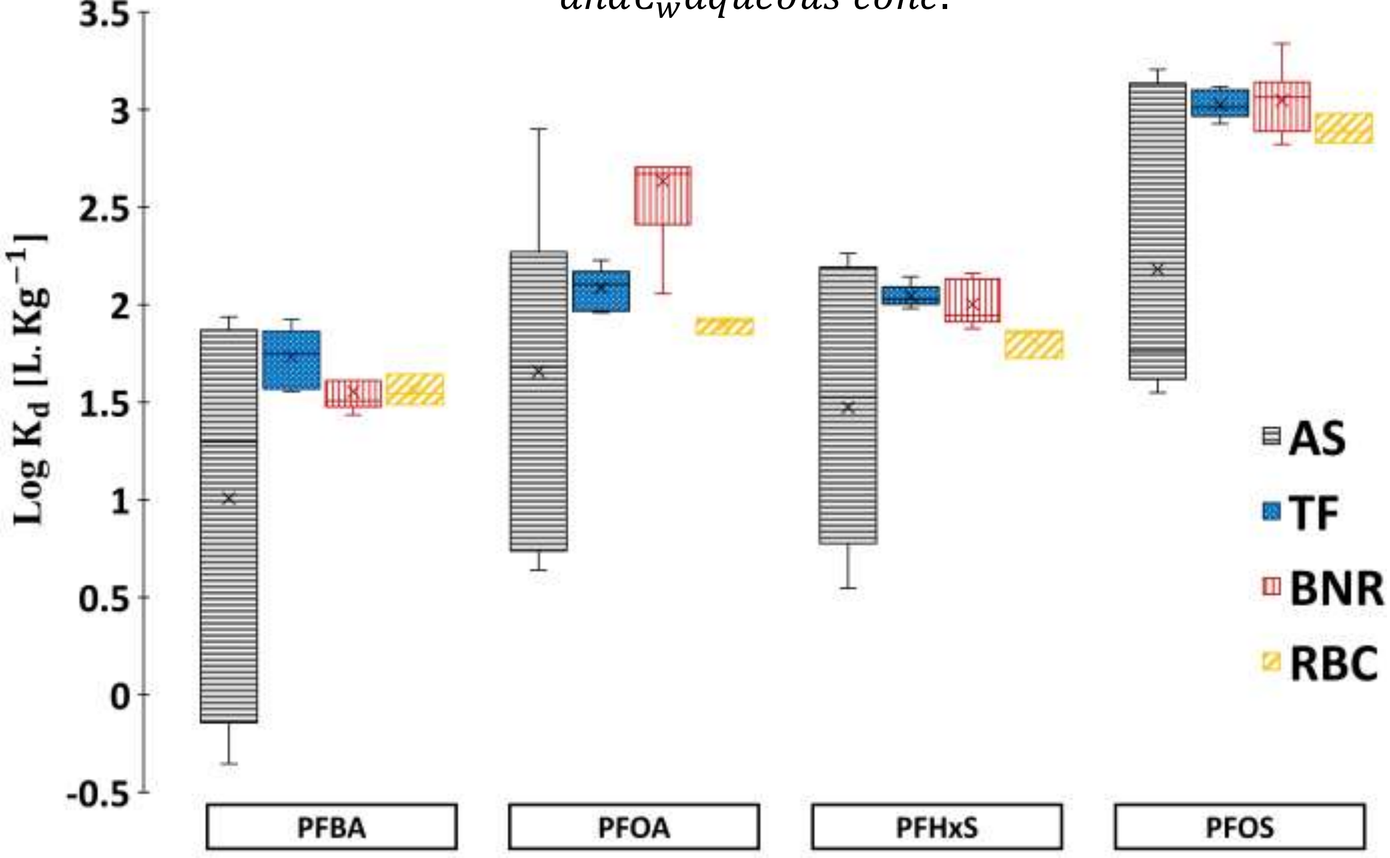
Partitioning behavior in secondary sludge

$$K_d = \frac{C_s}{C_w}\text{ ; where } C_s \text{ is the solid conc. and } C_w \text{ aqueous conc.}$$

- ***No significant effects on PFAS K_d***
- ***Effects may be canceled out by:***
  - ***Variable influent source***
  - ***Sludge compositions***



PFBA, PFOA, PFHxS, and PFOS partitioning coefficients across different secondary treatments (10 sludge samples with isotherm experiments conducted in reference solution)

NSF

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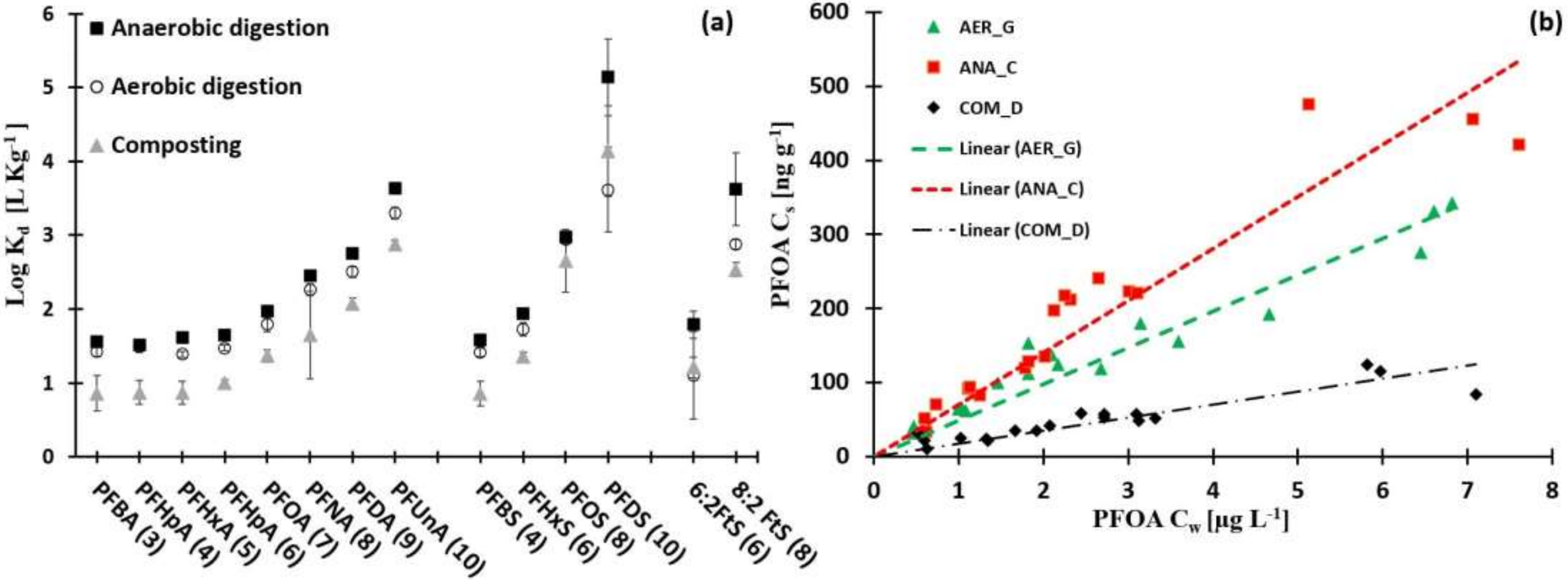
Partitioning behavior in biosolid

- ➢ *K_d order: anaerobic digestion > aerobic digestion > composting*



PFAS partitioning coefficients across different sludge stabilization methods

NSF

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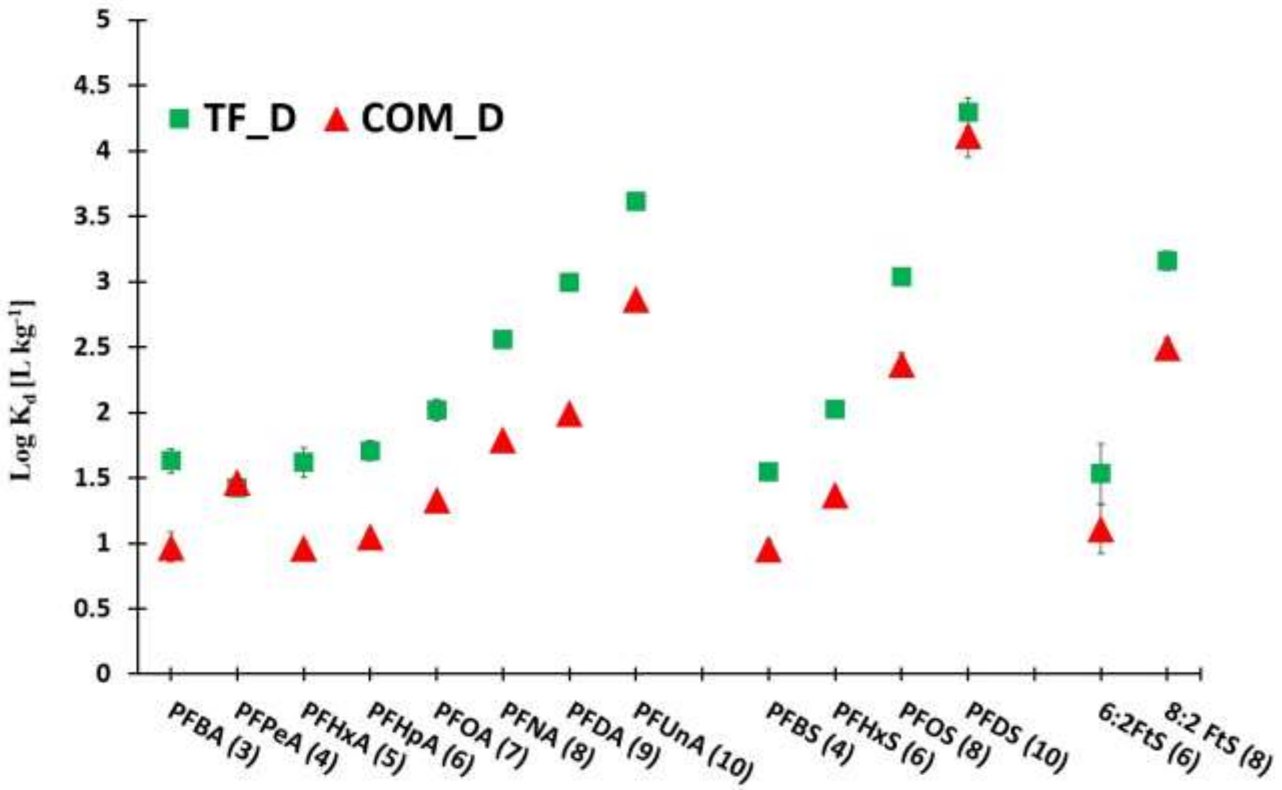
Sludge stabilization effects on partitioning behavior

- Stabilization decreases the PFAS sorption capacity significantly



K_d comparison among paired-biosolid sludge samples in plant D. Partitioning experiments conducted in reference solution (200 ng spiking of suite of PFAS).

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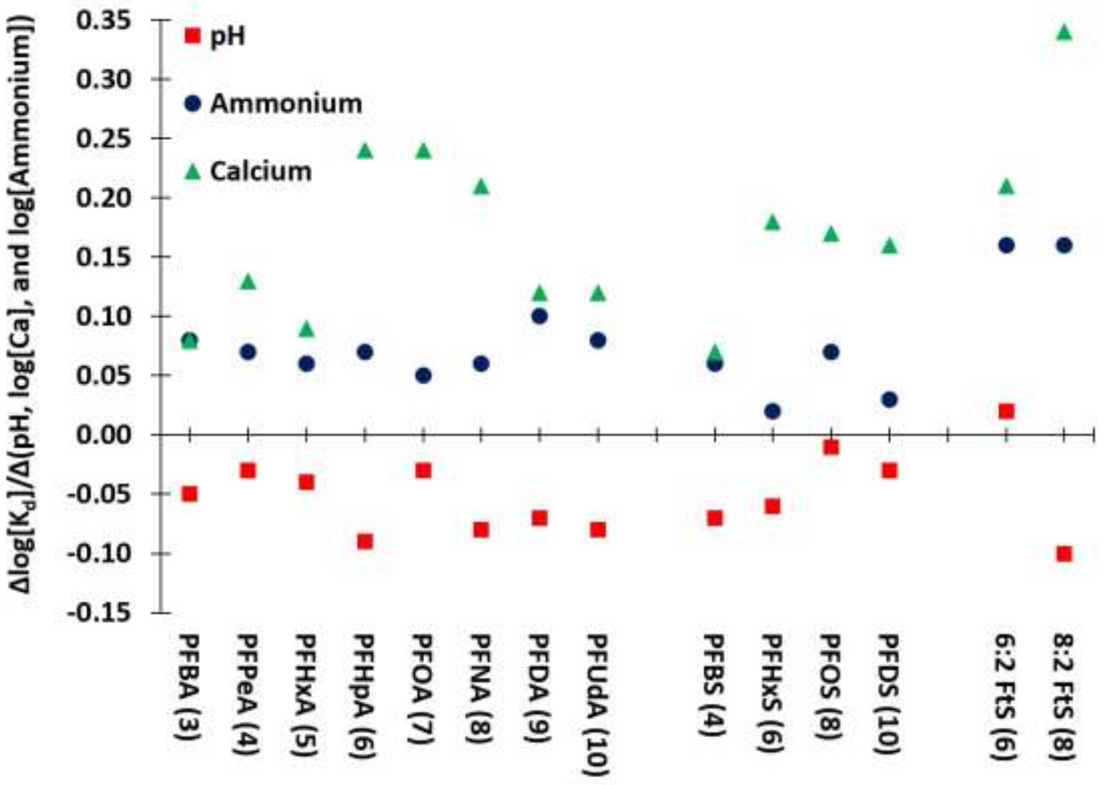
Solution and solid-specific effects on PFAS K_d

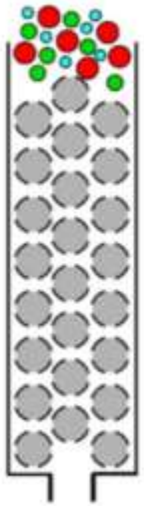
- Elevated mono- and divalent cations increased PFAS K_d
- High pH decreased PFAS K_d
- Protein was stronger predictor of PFAS K_d than organic matter or lipid fraction.

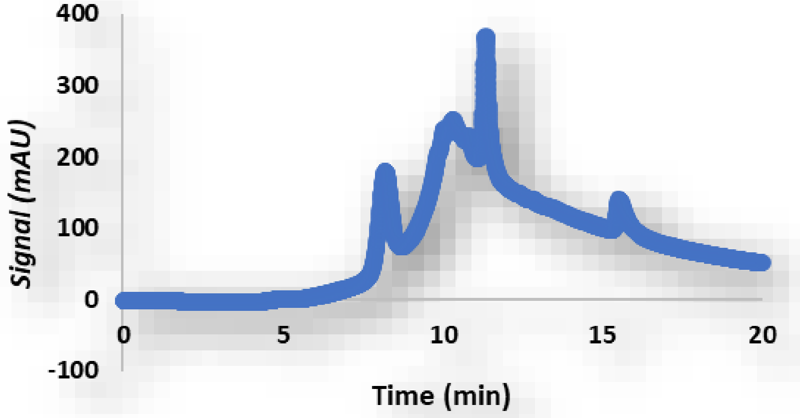


Coefficient of analyte-specific linear regression to assess the effects of pH, mono-valent cation (ammonium), and di-valent cation (calcium) on PFAS sorption.

The second phase of the project:

Why we saw differences in biosolids partitioning behavior?





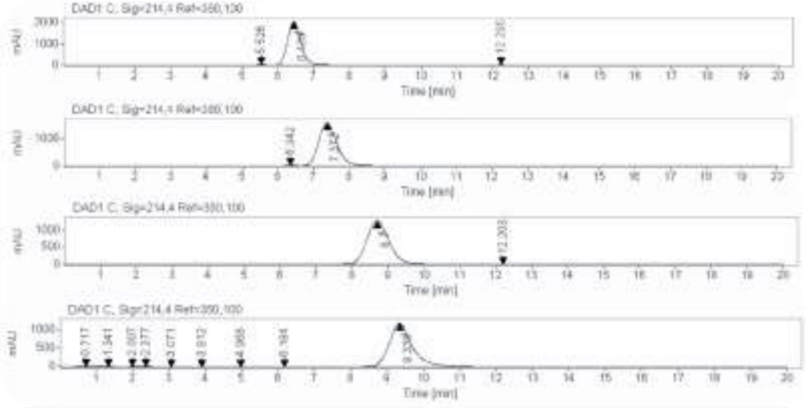
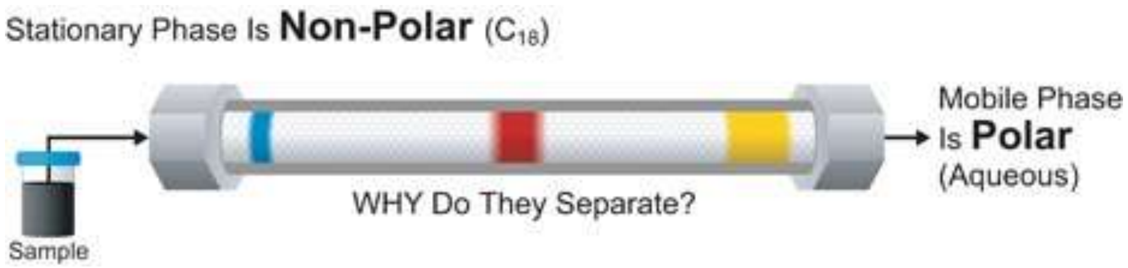


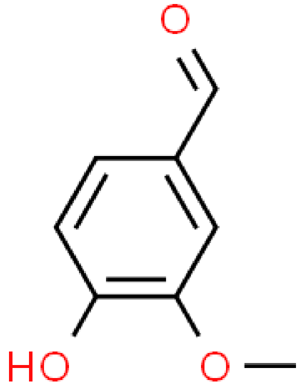
Photo: https://www.wbdg.org/

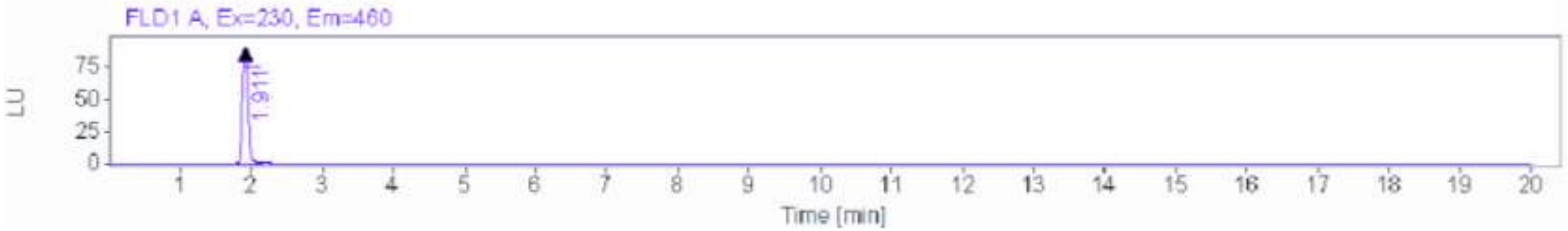
Looking deeper at the organic matter characteristics

Reverse-phase analysis in HPLC

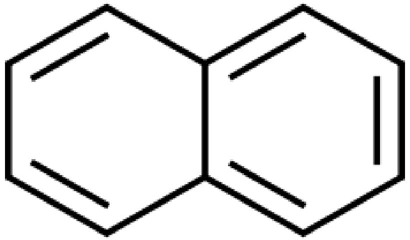


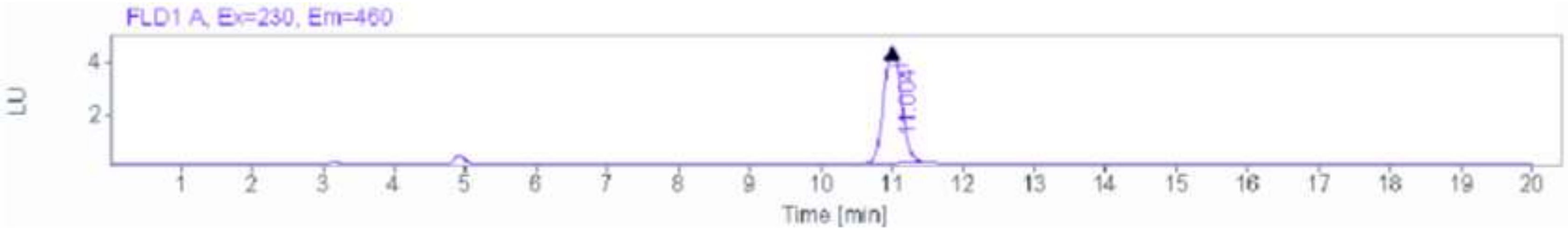
Vanillin





Naphthalene





Naphthalene's hydrophobicity > Vanillin's hydrophobicity

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Figure credits reserved for Waters Inc.

Looking deeper at the organic matter characteristics

Reverse-phase analysis in HPLC

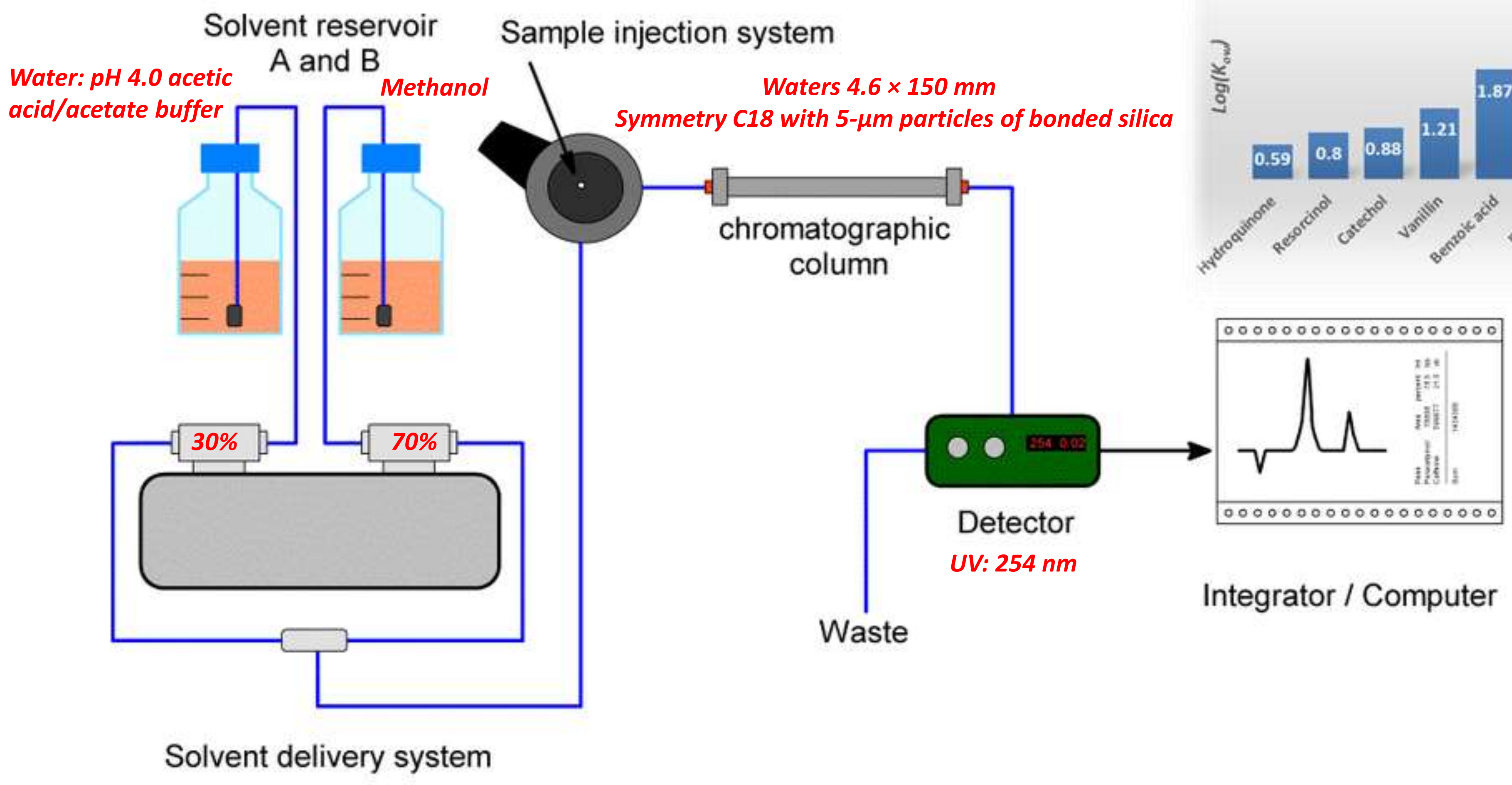

Photo credit: Oliver Scherf-Clavel

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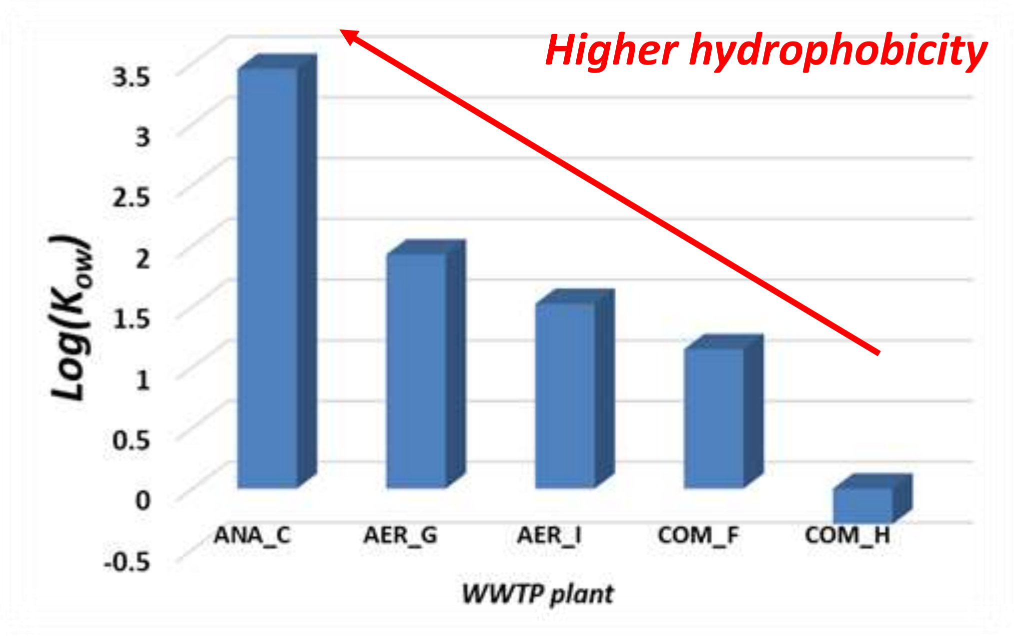
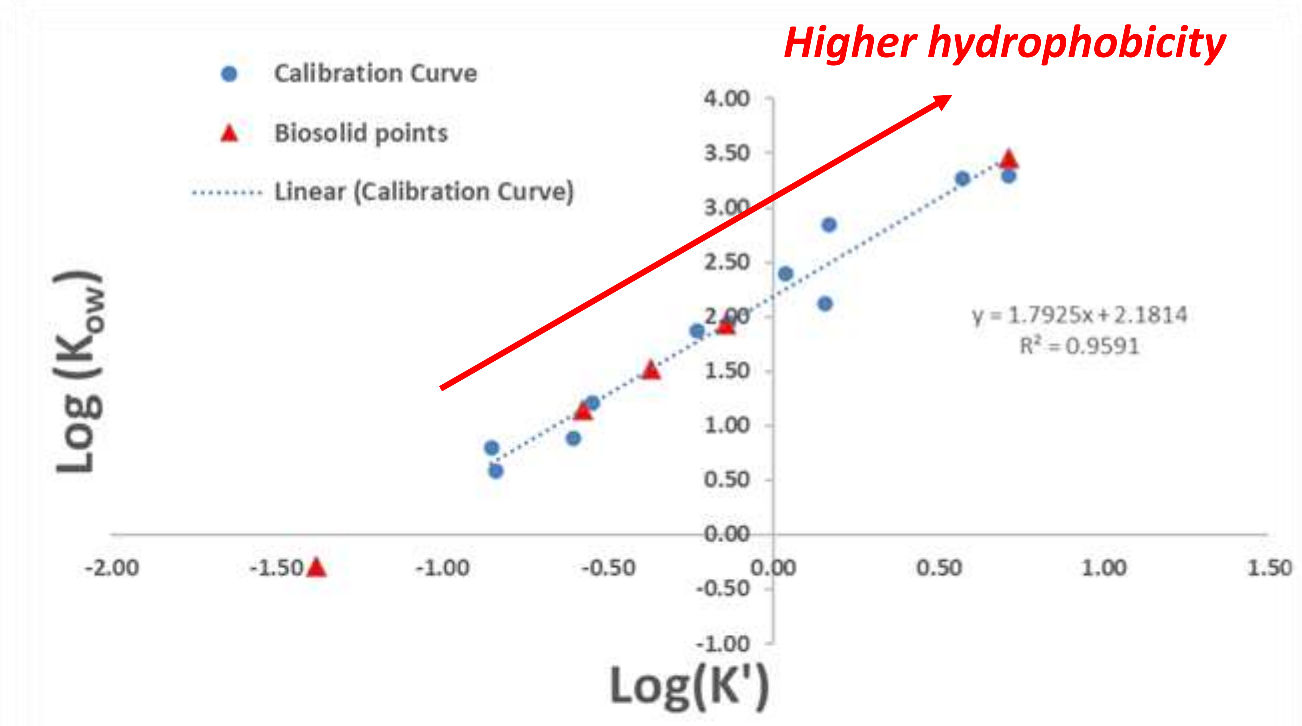
Figure credits reserved for Waters Inc.

Looking deeper at the organic matter characteristics

Reverse-phase analysis in HPLC

- **Organic matter extracted by sodium hydroxide and formaldehyde**
- **Hydrophobicity level order: anaerobically digested sludge> aerobically digested> composted sludge**





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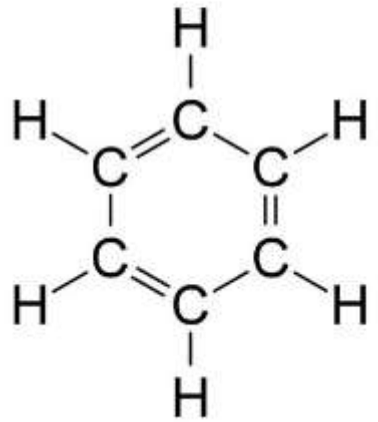
Looking deeper at the organic matter characteristics

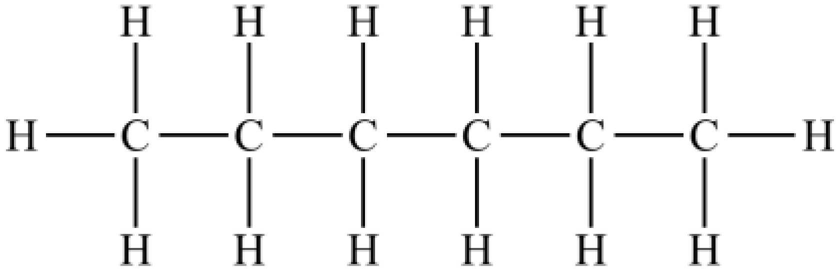
Elemental analysis of biosolids: Aromaticity

- Hexane has 6 carbon and 14 hydrogen, with a C/H ratio of 0.43
- Benzene has 6 carbon and 6 hydrogen with a C/H ratio of 1.
- Higher C/H implies higher level of aromaticity in organic molecules.
- **Bituminous coals** have a **C/H ratio** between 14 and 17 (highly aromatic)

Benzene (C_6H_6): C/H = 1



Hexane (C_6H_{14}): C/H = 0.43



C/H level

Bituminous coals

14-17

Sludge

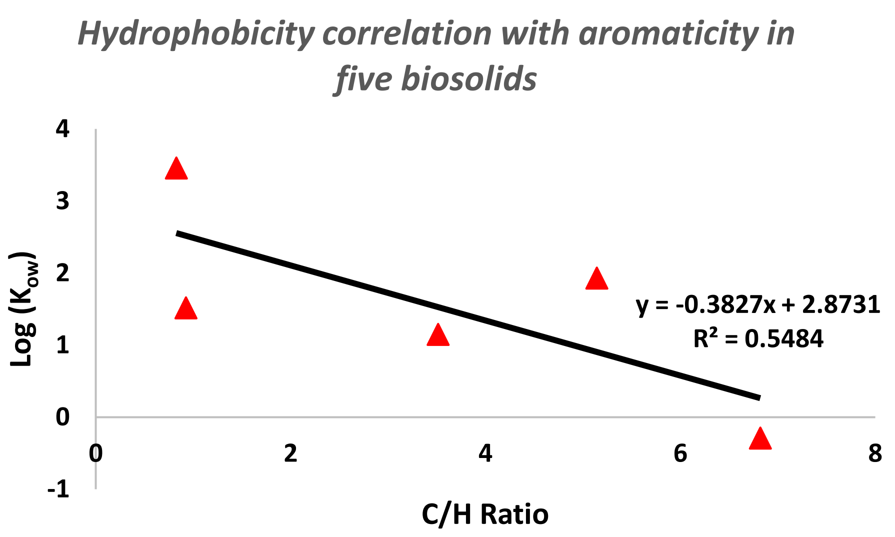
Biosolid

1-8

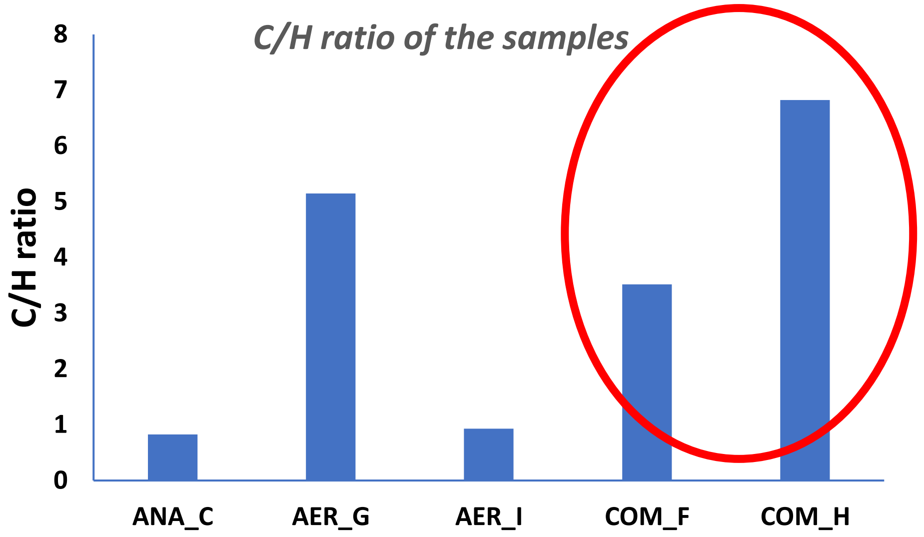
Looking deeper at the organic matter characteristics

Elemental analysis of biosolids: Aromaticity

- Higher level of C/H implies higher aromaticity level
- Higher aromaticity may result in higher polar molecules
- This is consistent with reverse phase analysis as the composting samples had the fastest elution times (lowest hydrophobicity)



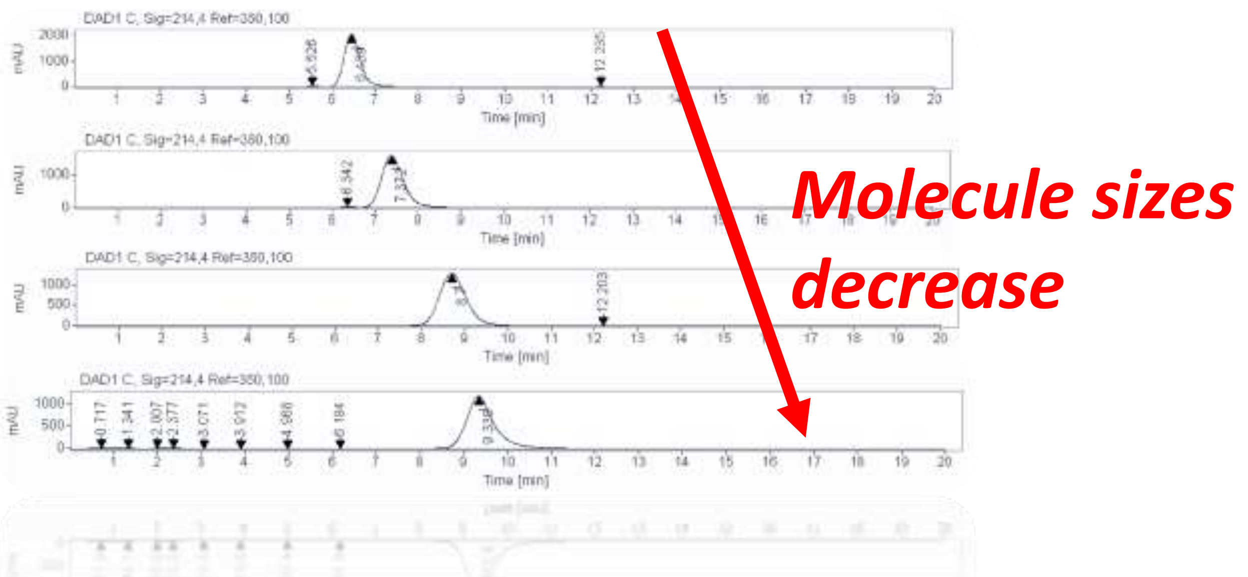
Composting with highest C/H ratio



Looking deeper at the organic matter characteristics

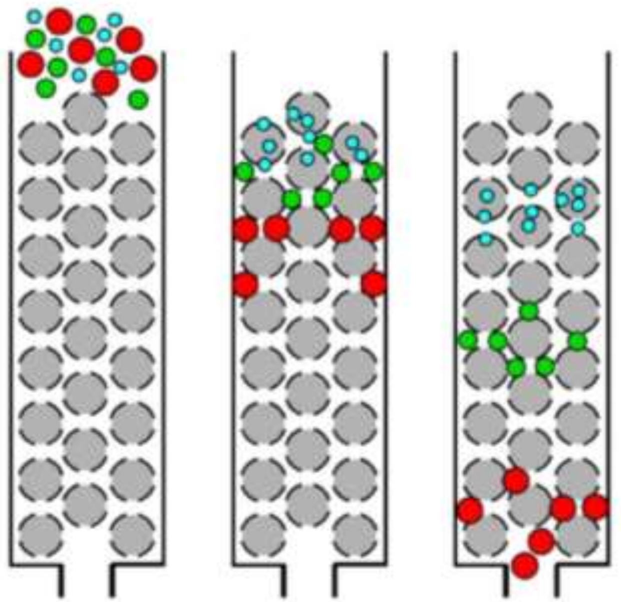
Size Exclusion Chromatography (SEC)

- **Characterize the organic matter content of 5 biosolids based on their size**



SEC standards (PSS: 33400, 16000, 7540, 5180 mw)

Standards eluting based on size



Wei et al., 2017; Aalto University

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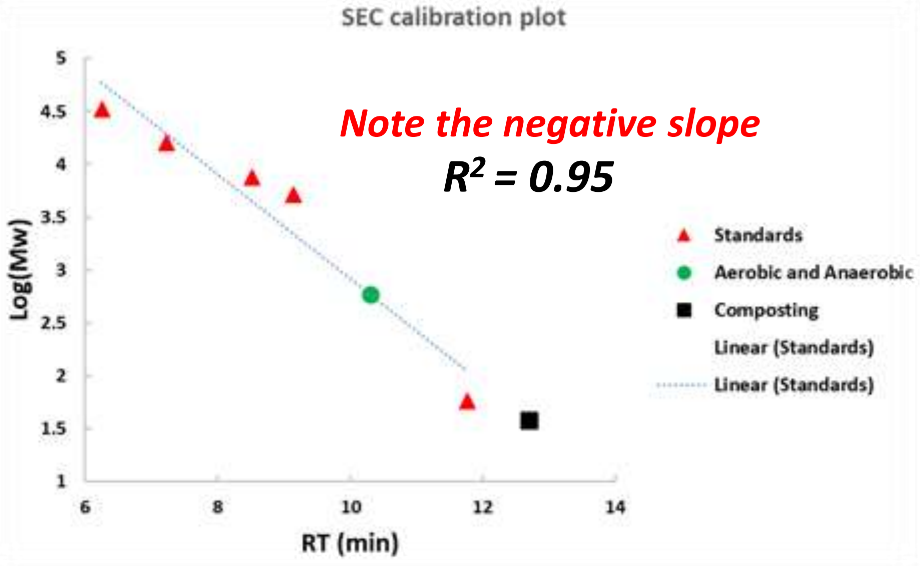
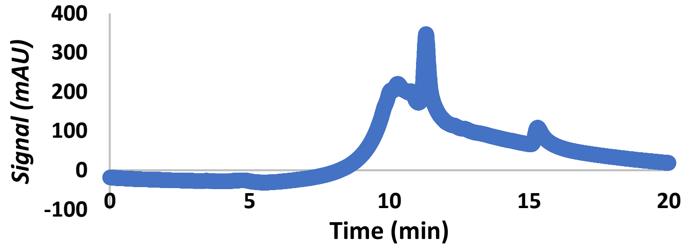
Looking deeper at the organic matter characteristics

Size Exclusion Chromatography (SEC)

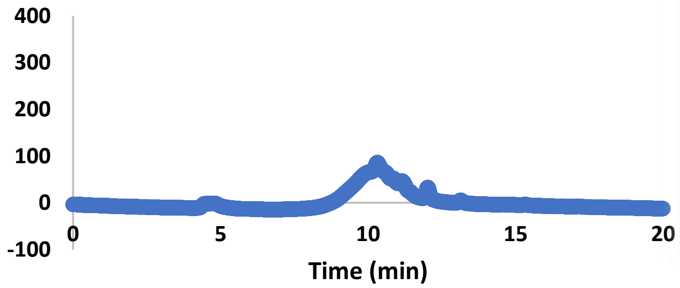
- **Characterize the organic matter content of 5 biosolids based on their size**
- **Hypothesis: Organic matter with higher molecular weight/size will show higher polarity**
- **Molecule size order: aerobic and anaerobic > composting**



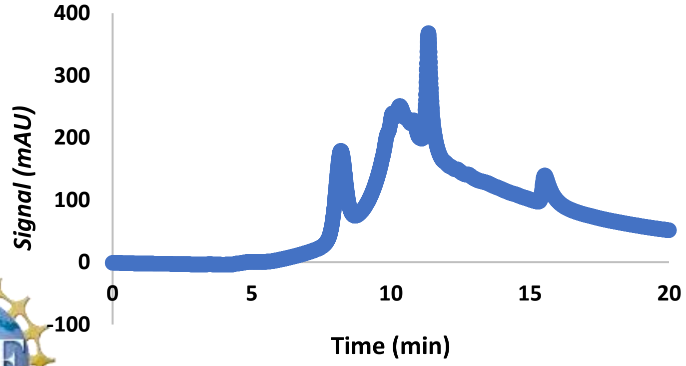
COM_F (Retention time 12.75 min)



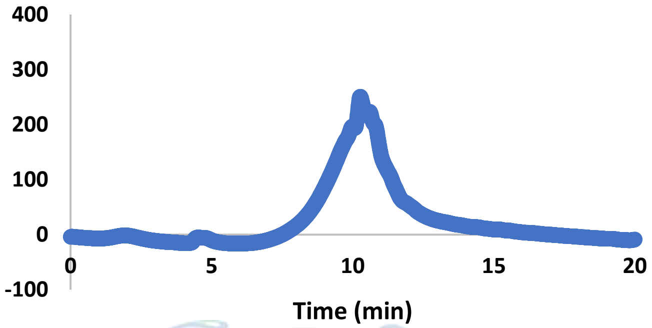
AER_G (Retention time 10.3 min)



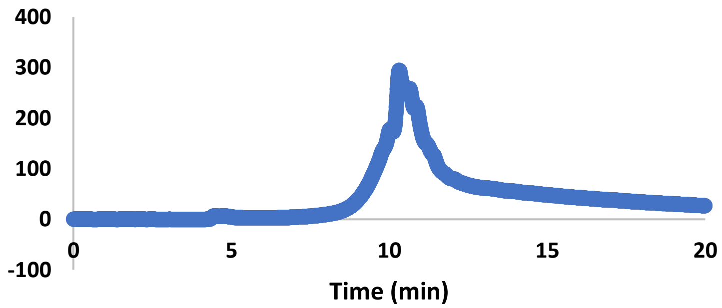
COM_H (Retention time 12.7 min)



AER_I (Retention time 10.3 min)



ANA_C (Retention time 10.3 min)



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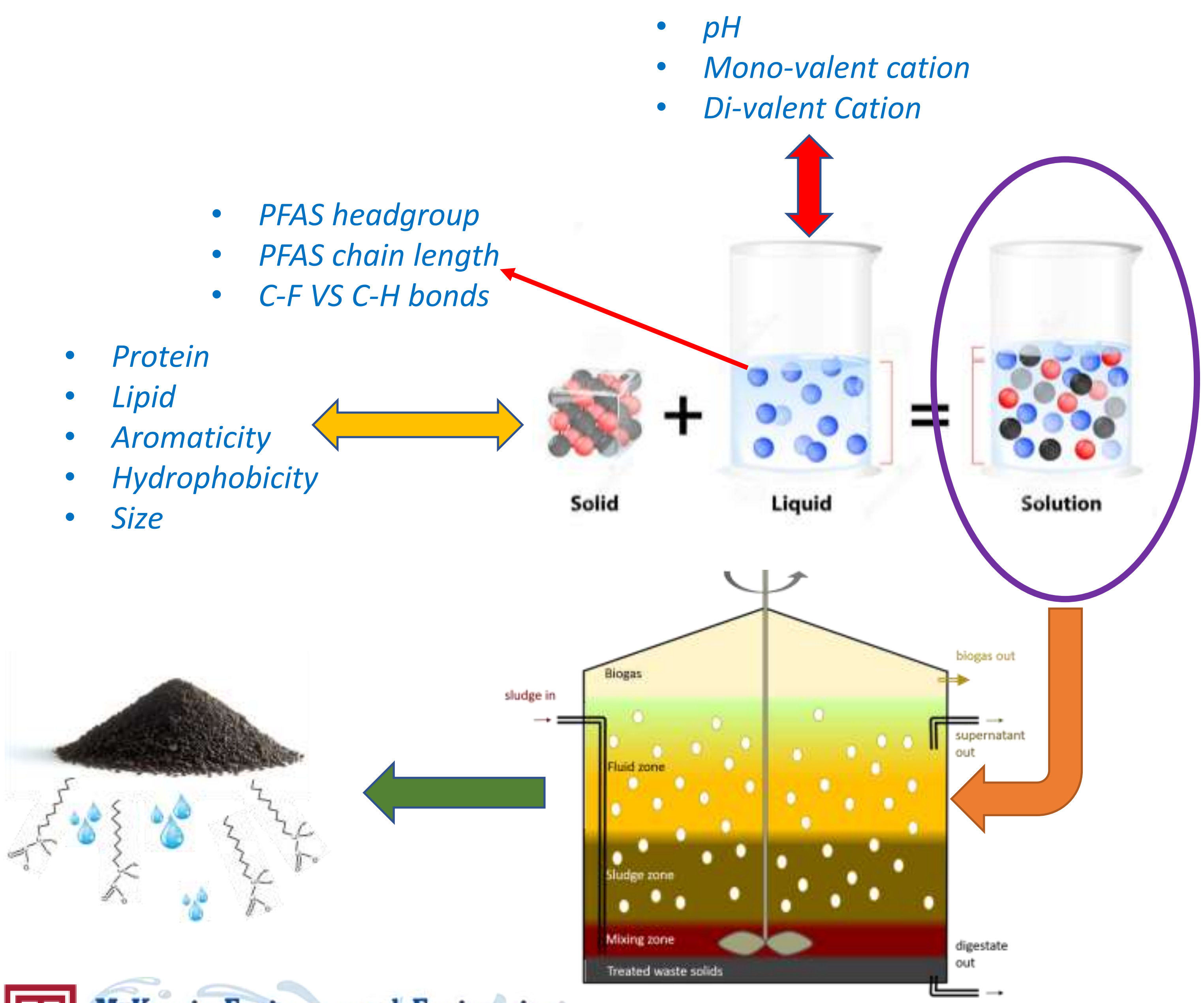
Conclusions

- PFAS-specific properties, solution chemistry, solid characteristics and stabilization methods can change the leaching potential of the sewage solids
- Sludge stabilization showed significant difference in PFAS partitioning behavior
- Higher hydrophobicity and bigger size of organic matter have resulted in higher partitioning coefficients, while higher aromatic fraction have resulted in lower partitioning coefficients in biosolid samples
- Source-derived PFAS loads, and influent composition are significant parameters in addition to the current factors



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Anaerobic Digester

Photos: https://www.sludgeprocessing.com/

Implications

- *Monitoring solution chemistry parameters proactively and maintaining a lower pH (<7) in wastewater would result in less PFAS leaching across sewage solids.*

- *Add di-valent cations may reduce PFAS leaching across sewage solids.*

- *Pretreatment efforts are of high importance, as secondary treatment and sludge stabilization are not able to remove PFAS.*

- *Sludge stabilization can potentially be optimized to reduce PFAS leaching.*

- *More research is needed to assess the effect of SRT, storage time, temperature, humidity, and solar radiation on the leaching potential of PFAS from biosolids.*

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