PFAS in biosolids:
Partitioning during wastewater treatment and leaching from Florida biosolids

PFAS in e-waste:
Occurrence, types, and estimated quantities of PFAS in e-waste and appropriate management strategies for PFAS containing e-waste components

WELCOME

TAG Meeting 2 – February 2, 2024

Agenda

1. Introductions – PIs and Attendees
2. Project overview
3. Completed tasks
4. Results
5. Open discussion

FIU FLORIDA INTERNATIONAL UNIVERSITY

Hinkley Center for Solid and Hazardous Waste Management

PFAS in biosolids:

Partitioning during wastewater treatment and leaching from Florida biosolids

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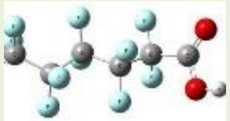
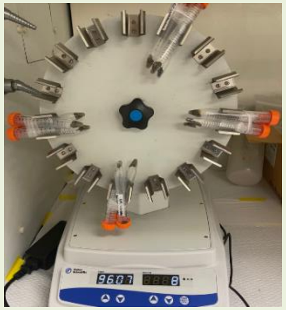
Objectives

1. Conduct **sampling of biosolids** after dewatering and drying processes at two Miami-Dade wastewater treatment plants (South District and Central District Wastewater Treatment Plants).
2. Analyze biosolids samples for **PFAS content and component profile**; determine the prevalent PFAS compounds.
3. Conduct **leaching experiments** to evaluate the release of PFAS from biosolids under site-specific conditions.
4. Estimate **time dependent solubilization and the release** characteristics of the PFAS homologues from biosolids.
5. Further scientific understanding of **PFAS originating from biosolids as a source in the environment**, potential exposure pathways for human health and ecological effects.
6. Provide **recommendations** for appropriate testing and land application practices of biosolids in Florida.





Technical Approach

Tasks
Task 1. Biosolids sampling (Tansel)
Task 2. Chemical analyses of PFAS content in biosolids and leachates (Quinete)
Task 3. PFAS leaching experiments (Katsenovich)
Task 4. Estimation of PFAS release characteristics from biosolids (all)
Task 5. PFAS exposure from land application of biosolids and biosolids amended products (Tansel)
Task 6. Final report (guidance document) (all)
TAG Meetings

Technical Approach

Task 1. Biosolids sampling

1. Sampling at two (2) wastewater treatment plants,
    - Central WWTP and South WWTP (receives leachate from landfill).
2. Characterization and PFAS dissolution experiments:
    - after thickening,
    - after anaerobic digestion, and
    - after dewatering and final biosolids product

Technical Approach

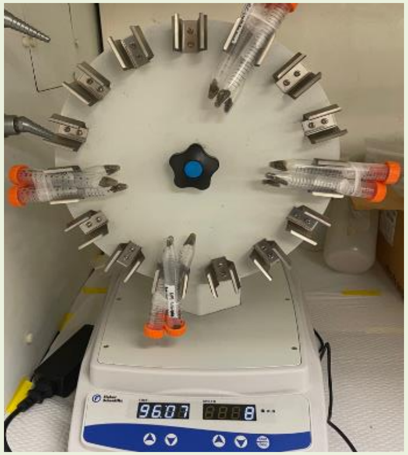
Task 3. PFAS leaching experiments

Leaching experiments: laboratory batch experiments at biosolids/water ratio as 1:1 using a sacrificial approach. Homogenized and air dried biosolids

Centrifuge tubes were placed on an end-over-end tube revolver at 10 rpm.

To ensure a constant biosolids: water ratio, all samples were sacrificed at certain times to evaluate for the release of PFAS after

1 day, 3 days, 7 days, 14 days, and 30 days.



FIU end-over-end tube revolver with PP tubes.

Technical Approach

Task 2. Chemical analyses of PFAS content in biosolids and leachates

Identification of appropriate analytical techniques and methods for PFAS

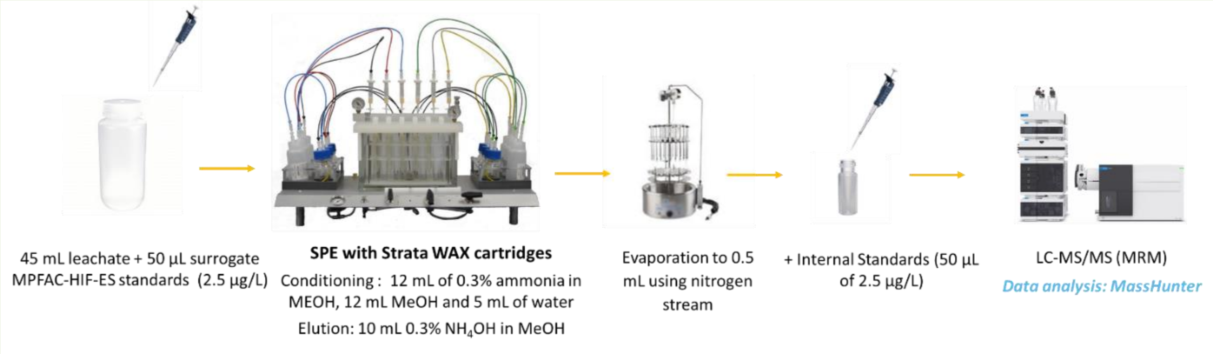
- Establishment of appropriate PFAS sampling protocols and best practices.

Analyses

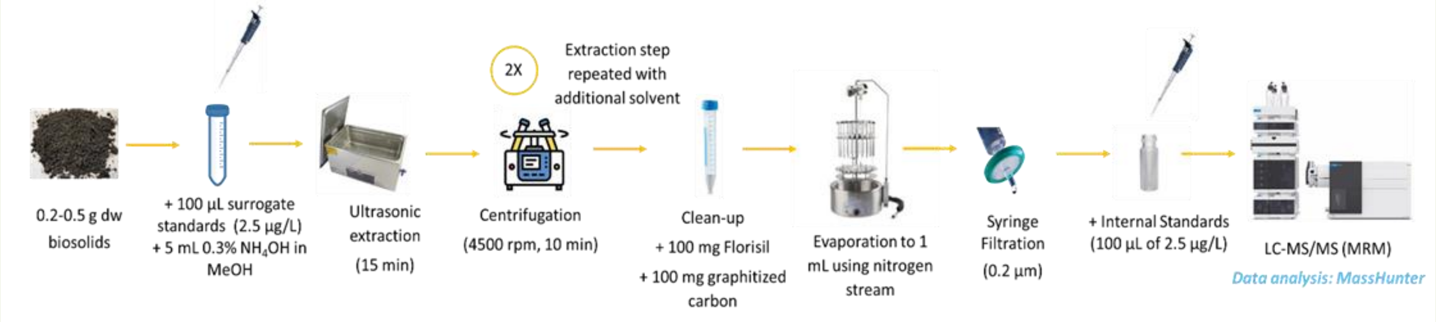
- Total and volatile solids
- Protein
- Metals
- **40 - PFAS** for leachate and solids samples (by high-performance liquid chromatography).

Technical Approach

Task 2. Chemical analyses of PFAS content in biosolids and leachates



Sample preparation workflow for PFAS analysis in Biosolid Leachate



Sample preparation workflow for PFAS analysis in Biosolid (solid part)

Technical Approach

Task 6. Results (guidance document)

Results include:

1. PFAS type and levels in biosolids,
2. PFAS release mechanisms from biosolids,
3. Data results from leaching tests,
4. Release rates,
5. PFAS fate released from biosolids, and
6. Relevant data and analyses.

Technical Approach

Task 2. Chemical analyses of PFAS content in biosolids and leachates

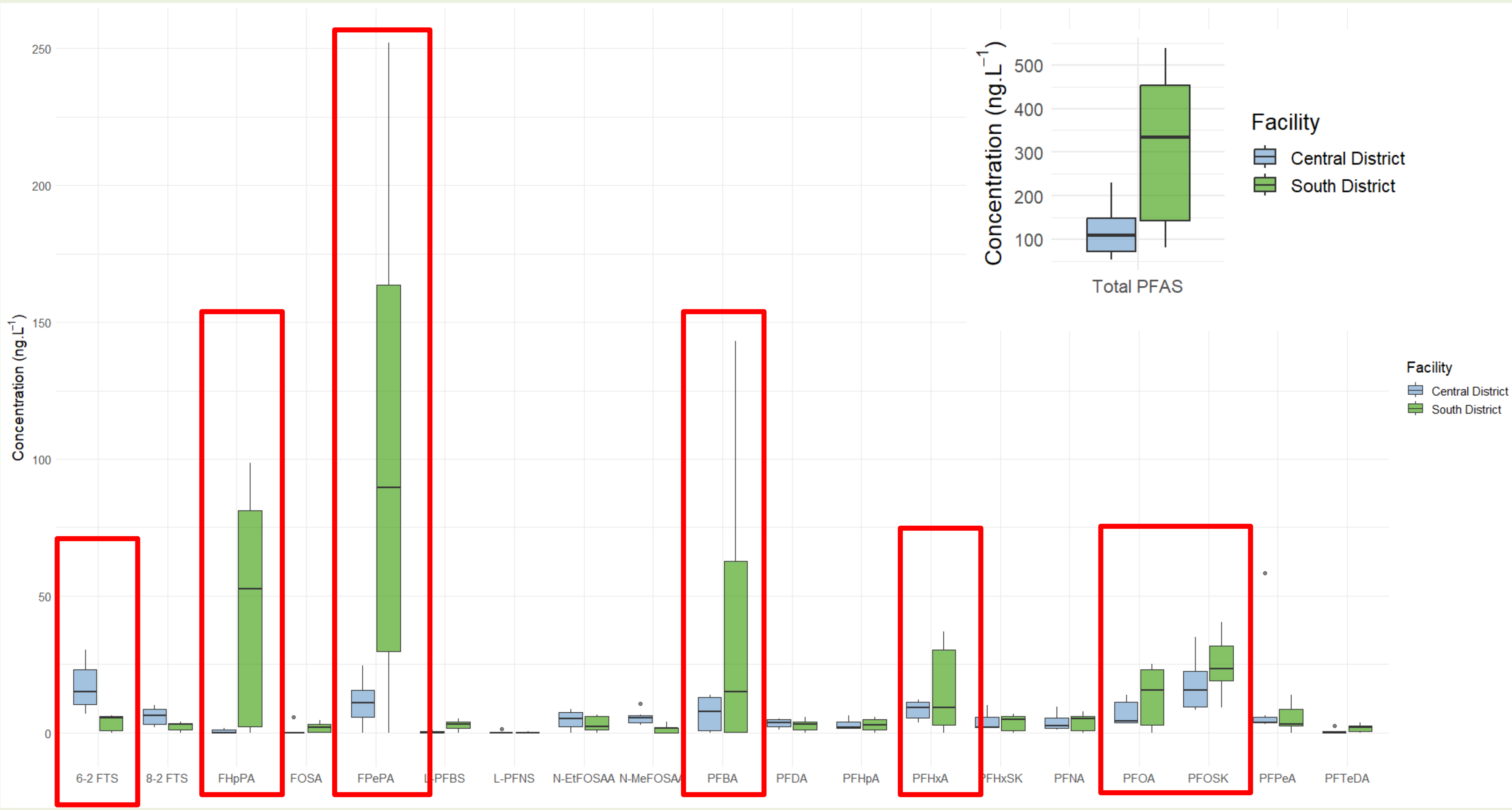
40 PFAS analyzed

Abbreviation	**Compound Name**	Formula	Mol Weight
Perfluoroalkyl carboxylic acids			
PFBA	Perfluorobutanoic acid	$C_4HF_7O_2$	214.04
PFPeA	Perfluoropentanoic acid	$C_5HF_9O_2$	264.05
PFHxA	Perfluorohexanoic acid	$C_6HF_{11}O_2$	314.05
PFHpA	Perfluoroheptanoic acid	$C_7HF_{13}O_2$	364.06
PFOA	Perfluorooctanoic acid	$C_8HF_{15}O_2$	414.07
PFNA	Perfluorononanoic acid	$C_9HF_{17}O_2$	464.08
PFDA	Perfluorodecanoic acid	$C_{10}HF_{19}O_2$	514.08
PFUdA	Perfluoroundecanoic acid	$C_{11}HF_{21}O_2$	564.09
PFDoA	Perfluorododecanoic acid	$C_{12}HF_{23}O_2$	614.10
PFTrDA	Perfluorotridecanoic acid	$C_{13}HF_{25}O_2$	664.11
PFTeDA	Perfluorotetradecanoic acid	$C_{14}HF_{27}O_2$	714.11
Perfluoroalkyl sulfonic acids			
PFBS	Perfluorobutanesulfonate	$C_4HF_9O_3S$	300.10
PFPeS	Perfluoropentanesulfonate	$C_5HF_{11}O_3S$	350.11
PFHxS	Perfluorohexanesulfonate	$C_6HF_{13}O_3S$	400.11
PFHpS	Perfluoroheptanesulfonate	$C_7HF_{15}O_3S$	450.12
PFOS	Perfluorooctanesulfonate	$C_8HF_{17}O_3S$	500.13
PFNS	Perfluorononanesulfonate	$C_9HF_{19}O_3S$	550.14
PFDS	Perfluorodecanesulfonate	$C_{10}HF_{21}O_3S$	600.14
PFDoS	Perfluorododecanesulfonate	$C_{12}HF_5O_3S$	700.16
Fluorotelomer sulfonic acids			
4-2 FTS	1H,1H,2H,2H-perfluorohexanesulfonate	$C_6H_5F_9O_3S$	328.15
6-2FTS	1H,1H,2H,2H-perfluorooctanesulfonate	$C_8H_5F_{13}O_3S$	428.17
8-2 FTS	1H,1H,2H,2H-perfluorodecanesulfonate	$C_{10}H_5F_{17}O_3S$	528.18
Perfluorooctane sulfonamides			
FOSA	Perfluorooctanesulfonamide	$C_8H_2F_{17}NO_2S$	499.15
NMeFOSA	N-methyl perfluorooctanesulfonamide	$C_9H_4F_{17}NO_2S$	513.17
NEtFOSA	N-ethyl perfluorooctanesulfonamide	$C_{12}H_{10}F_{17}NO_3S$	571.25
Perfluorooctane sulfonamidoacetic acids			
N-MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	$C_{11}H_6F_{17}NO_4S$	571.21
N-EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	$C_{12}H_8F_{17}NO_4S$	585.23
Perfluorooctane sulfonamide ethanols			
NMeFOSE	N-methyl perfluorooctanesulfonamidoethanol	$C_{11}H_4F_{21}NO_3S$	629.19
NEtFOSE	N-ethyl perfluorooctanesulfonamidoethanol	$C_{12}H_6F_{21}NO_3S$	643.21
Per- and Polyfluoroether carboxylic acids			
HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid	$C_6HF_{11}O_3$	330.05
ADONA	4,8-Dioxa-3H-perfluorononanoic acid	$C_{10}H_{11}N_4NaO_5S$	322.27
PFMPA	Perfluoro-3-methoxypropanoic acid	$C_4HF_7O_3$	230.04
PFMBA	Perfluoro-4-methoxybutanoic acid	$C_5HF_9O_3$	280.04
NFDHA	Nonafluoro-3,6-dioxaheptanoic acid	$C_5HF_9O_4$	296.04
Ether sulfonic acids			
9Cl-PF3ONS	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	$C_8HClF_{16}O_4S$	532.58
11Cl-PF3OUdS	11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	$C_{10}HClF_{20}O_4S$	632.60
PFEESA	Perfluoro(2-ethoxyethane)sulfonic acid	$C_4HF_9O_4S$	316.10
Fluorotelomer carboxylic acids			
FPrPA or 3:3FTCA	3-Perfluoropropyl propanoic acid	$C_6H_5F_7O_2$	242.09
FPePA or 5:3FTCA	3-Perfluoropentyl propanoic acid	$C_8H_5F_{11}O_2$	342.11
FHpPA or 7:3FTCA	3-Perfluoroheptyl propanoic acid	$C_{10}H_3F_{17}O_2$	478.10

Results

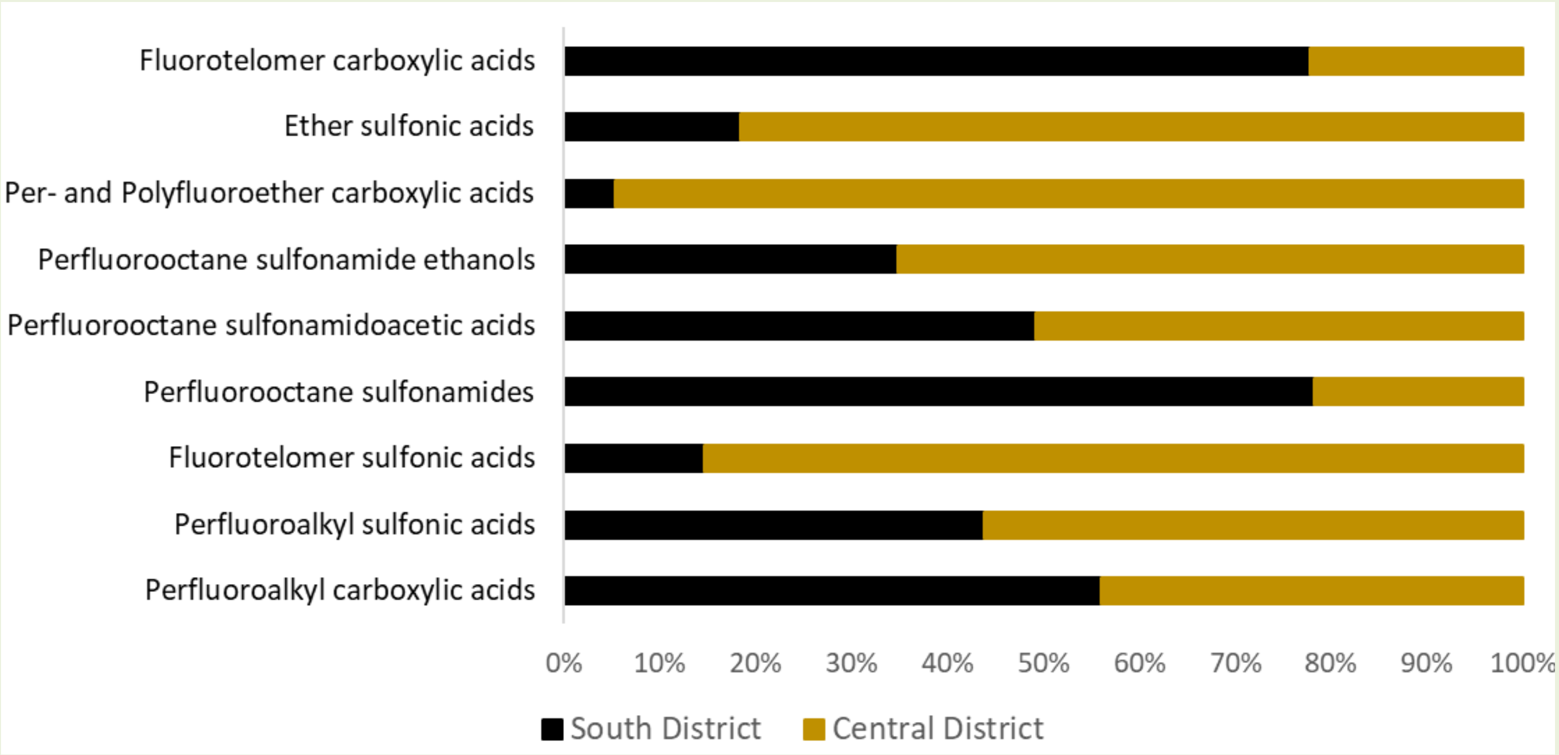
Compound	MDL (ng/L)	Variation %RSD	Recovery (%)	Linearity (R^2)
PFBA	0.09	16.09	123.6	0.998 - 0.999
PFPeA	0.04	12.99	122.2	0.997 - 0.998
L-PFBS	0.02	12.59	117.8	0.988 - 0.999
PFHxA	0.06	15.84	125.67	0.986 - 0.999
PFHxSK	0.06	10.62	128.02	0.963 - 0.997
PFHpA	0.02	14.87	132.14	0.988 - 0.998
6-2 FTS	0.22	17.07	124.63	0.981 - 0.995
PFOA	0.06	21.69	124.44	0.985 - 0.997
FPePA	0.44	8.26	98.45	0.989 - 0.999
PFNA	0.11	13.87	87.22	0.888 - 0.995
PFOSK	0.06	28.71	64.20	0.986 - 0.997
8-2 FTS	0.22	37.94	61.47	0.977 - 0.998
FHpPA	1.11	42.17	67.39	0.932 - 0.986
N-MeFOSAA	0.11	24.90	33.28	0.911 - 0.964
L-PFHpS	0.11	45.59	100.38	0.989- 0.995
N-EtFOSAA	0.06	15.55	34.39	0.925 - 0.979
FOSA	0.06	19.23	49.52	0.888 - 0.967
PFDA	0.11	28.24	58.28	0.931 - 0.995

Results



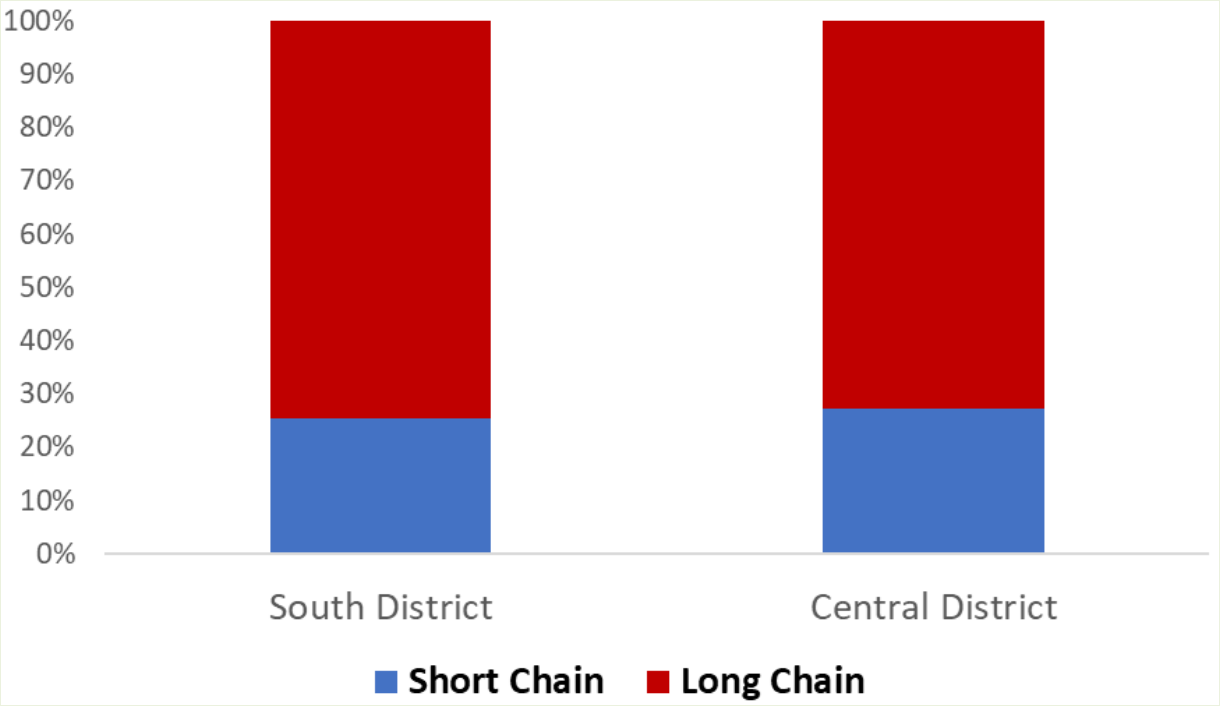
Predominant PFAS composition in Biosolids Leachate

Results



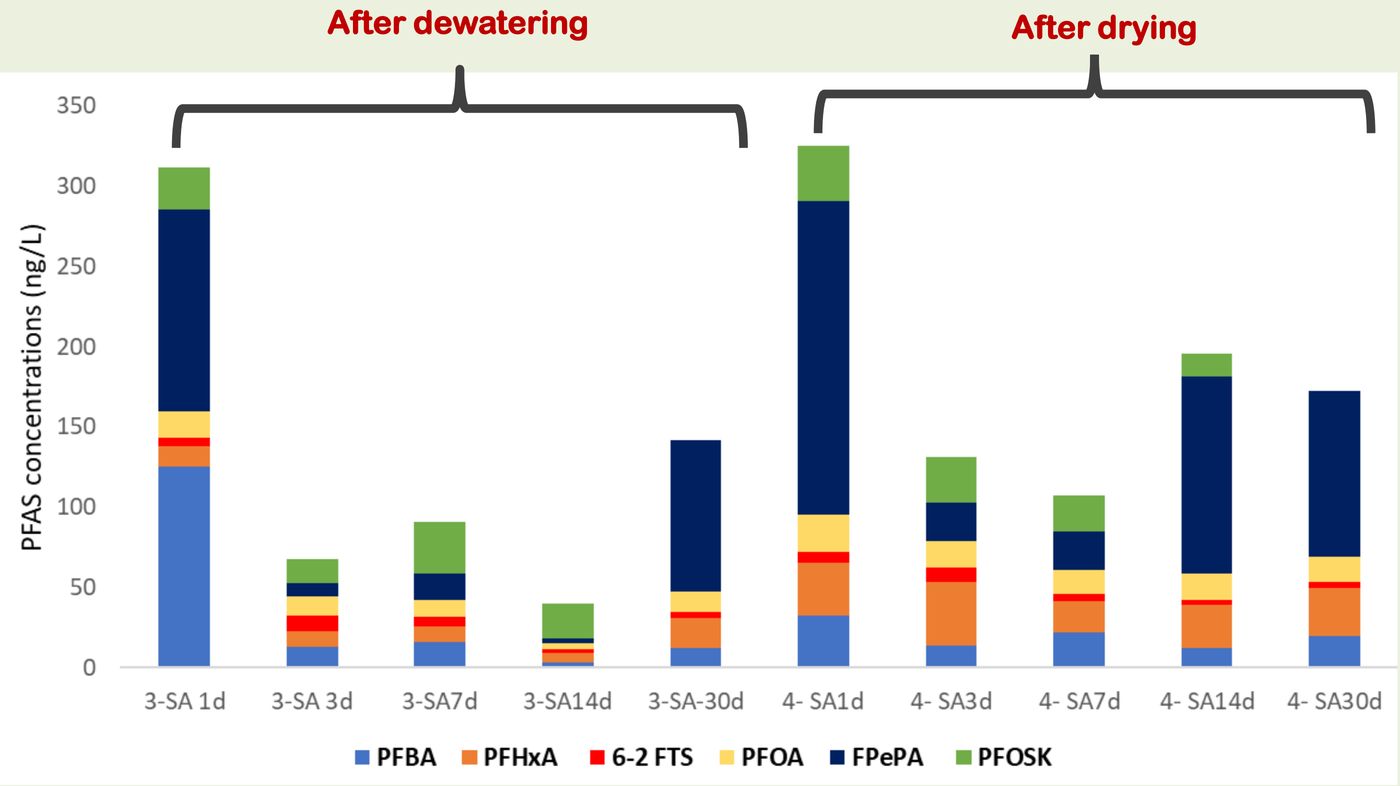
PFAS Average Composition in Biosolids Leachate by class

Results



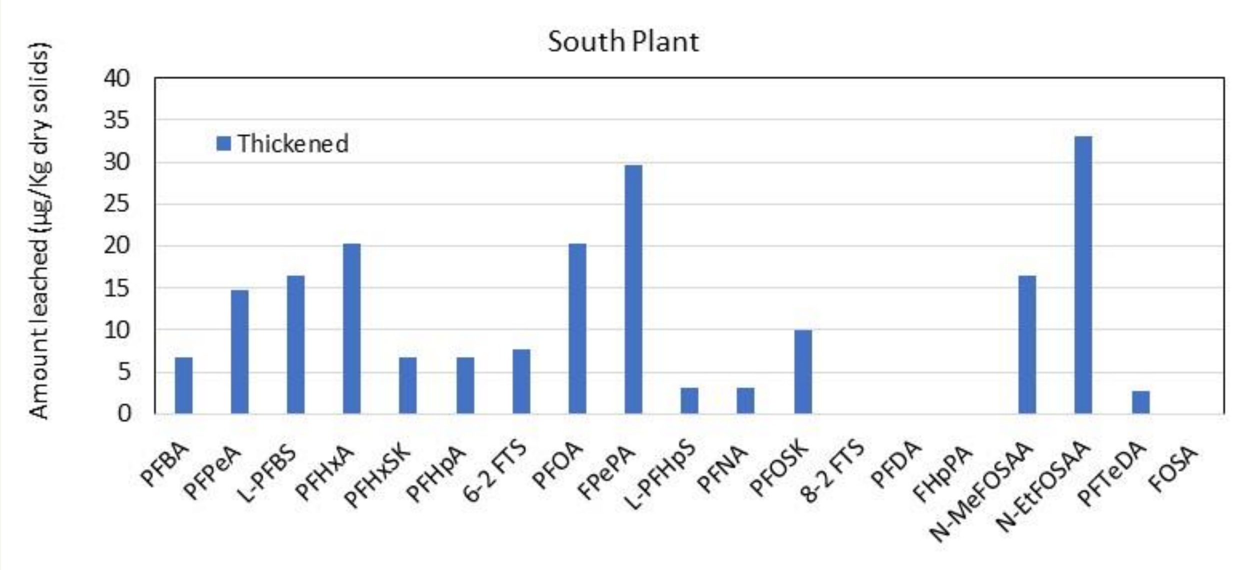
PFAS composition in biosolid leachate in terms of chain length

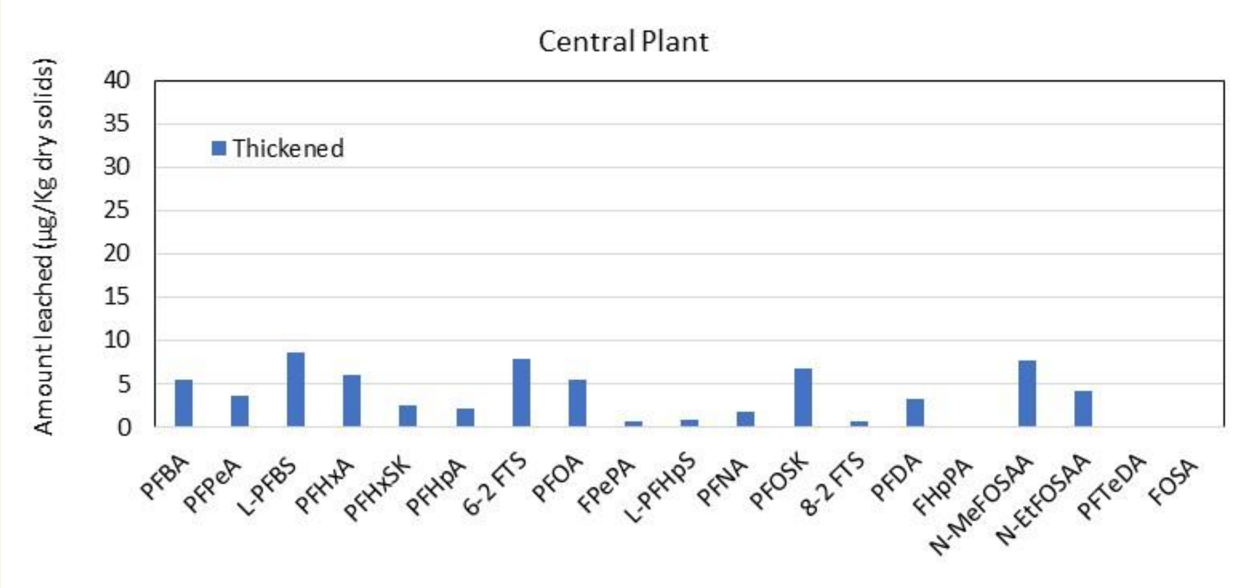
Results



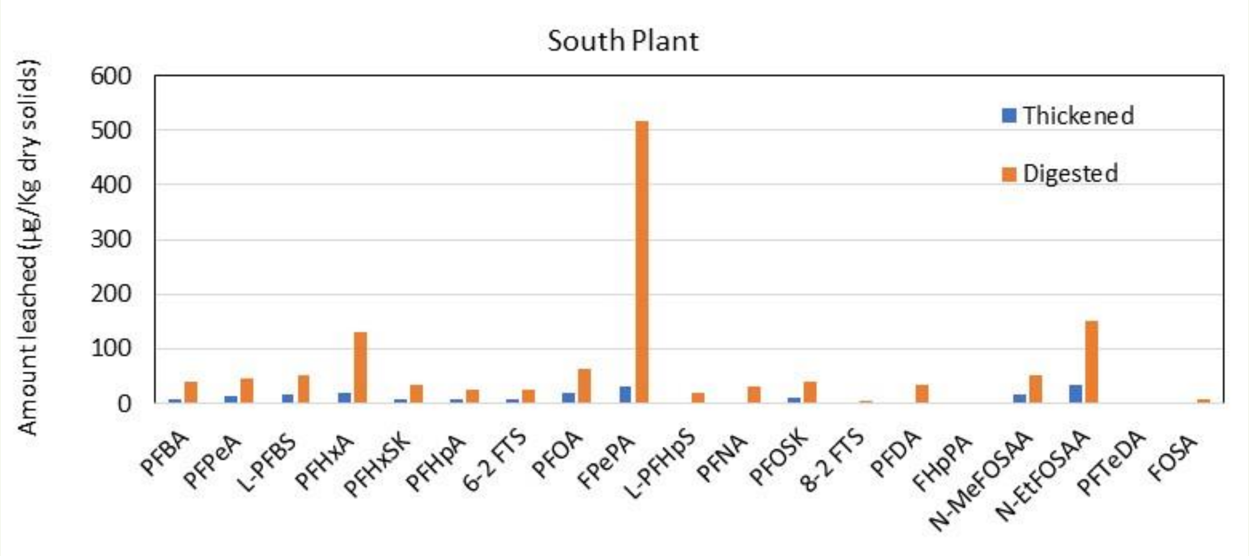
Predominant PFAS leaching from biosolids after dewatering and drying processes from South District plant (1 day to up to 1 month)

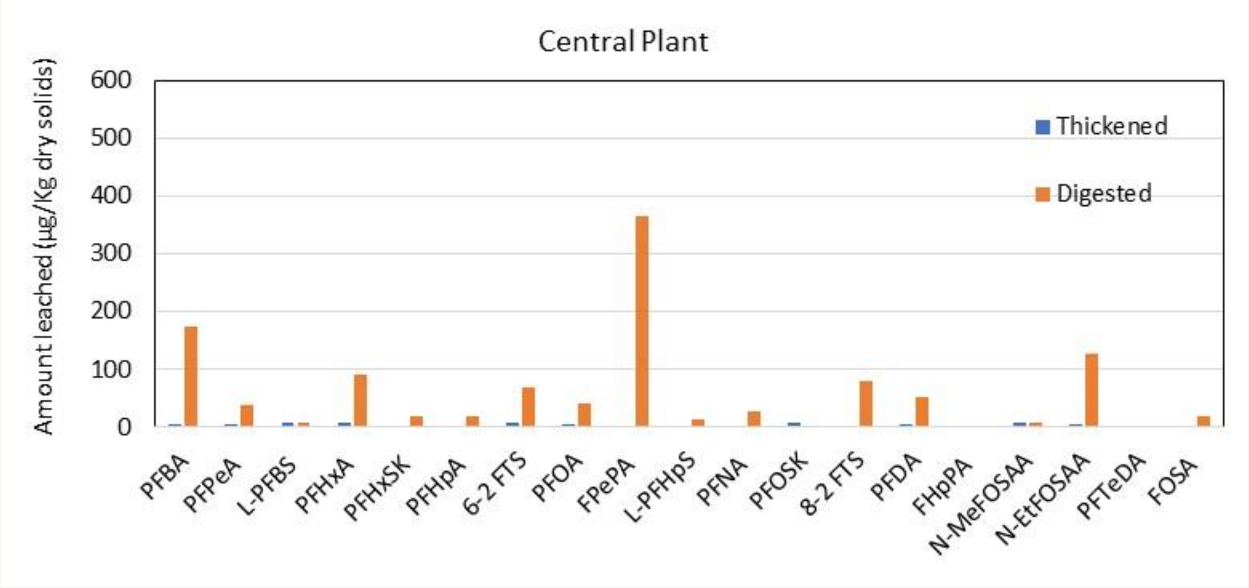
Thickened sludge - 30-day leaching data



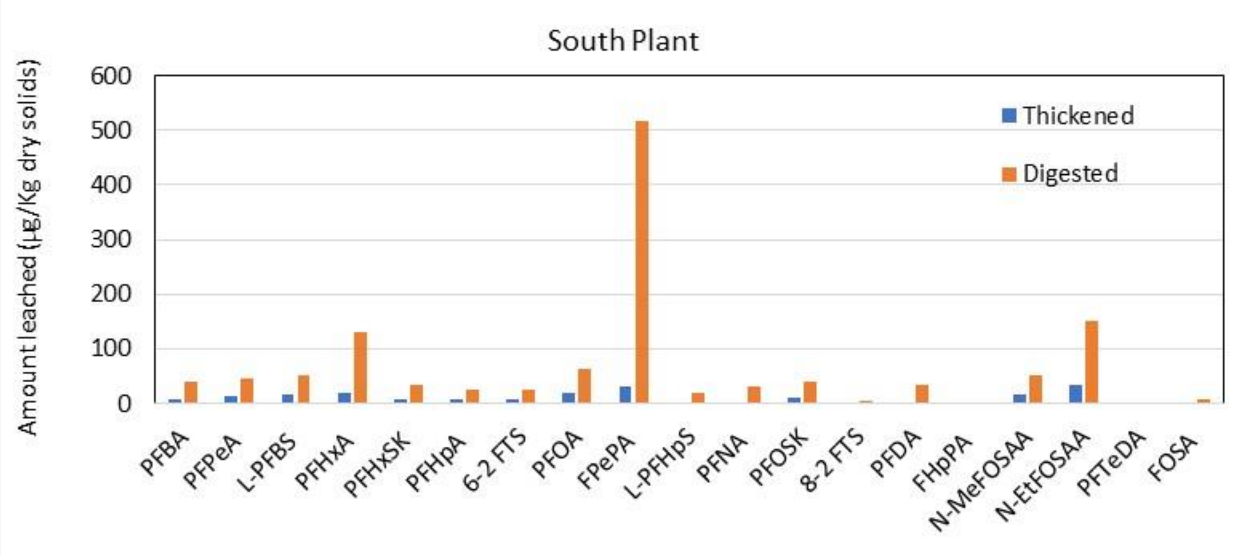


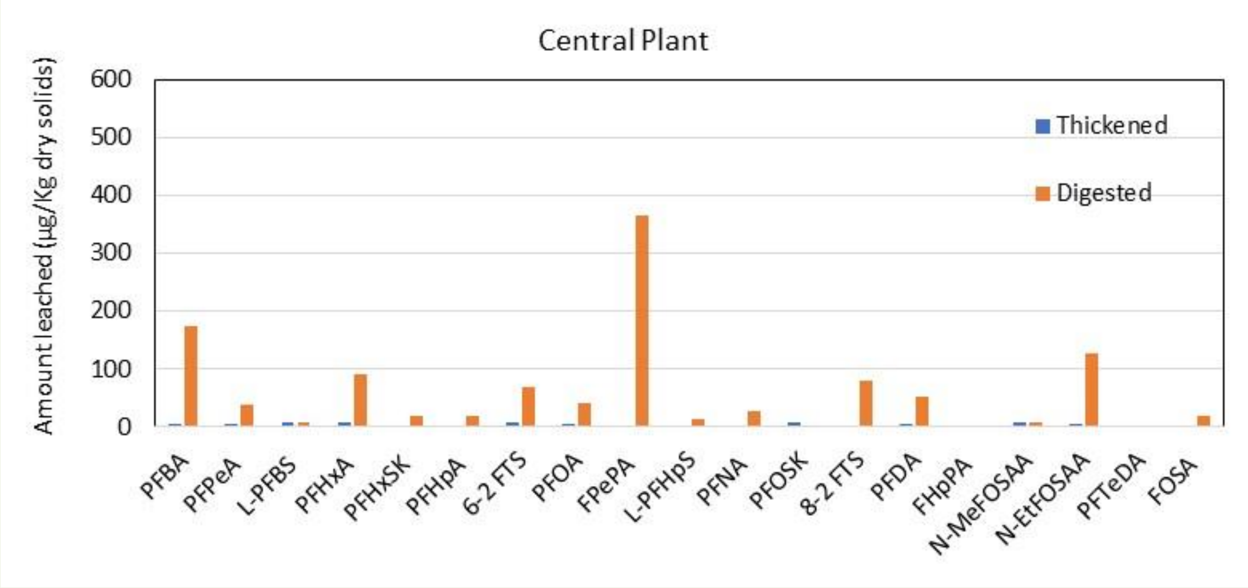
Change from thickened to digested



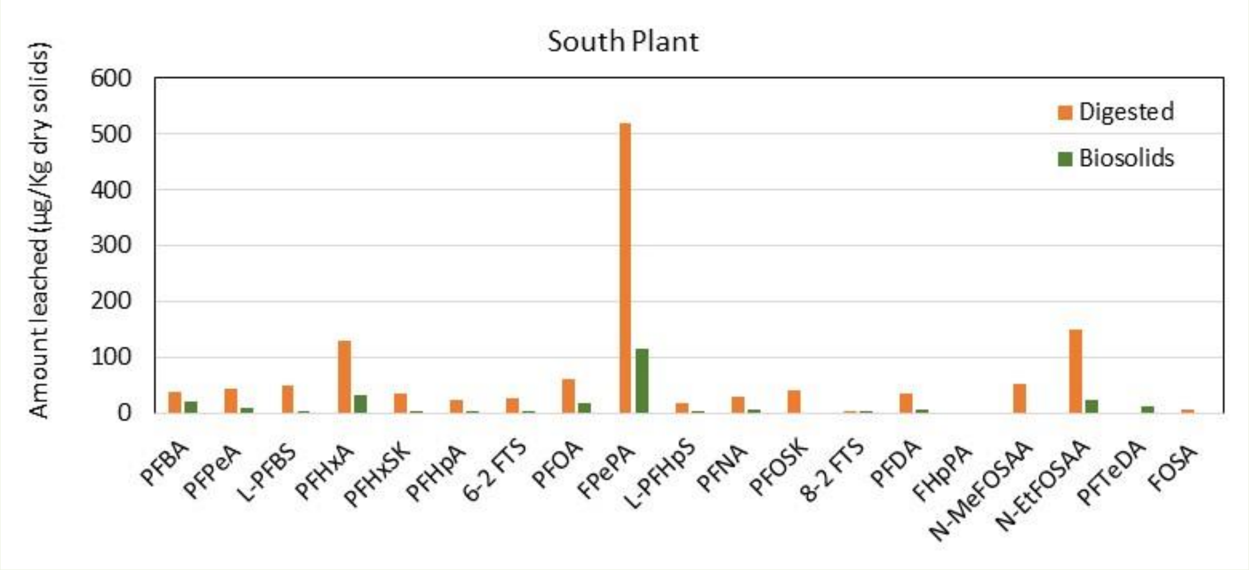


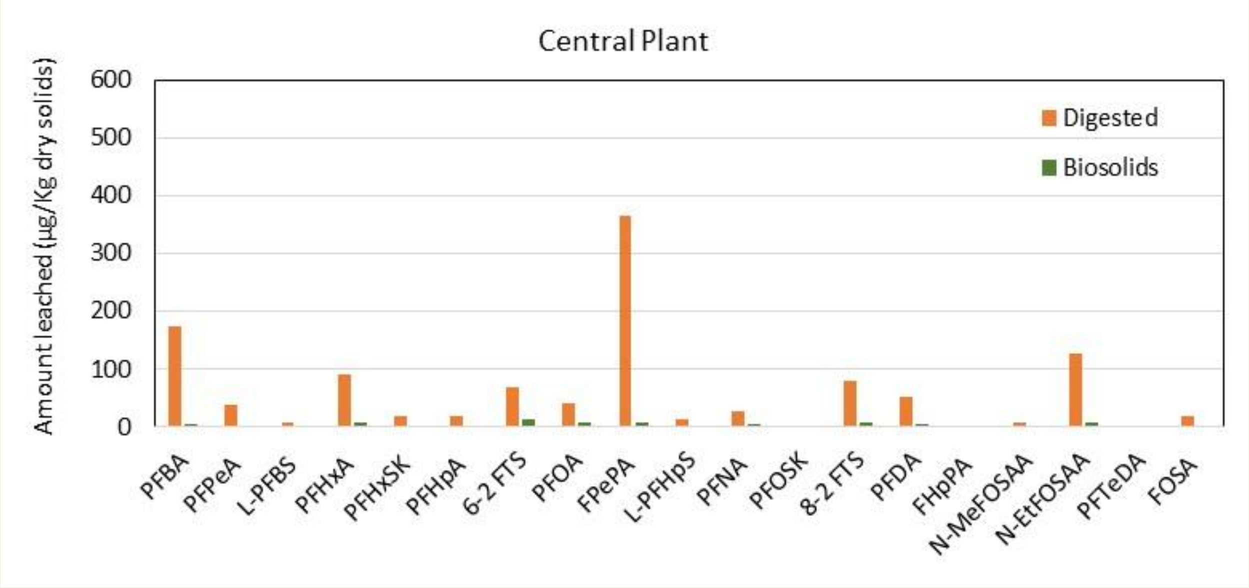
Change from thickened to digested



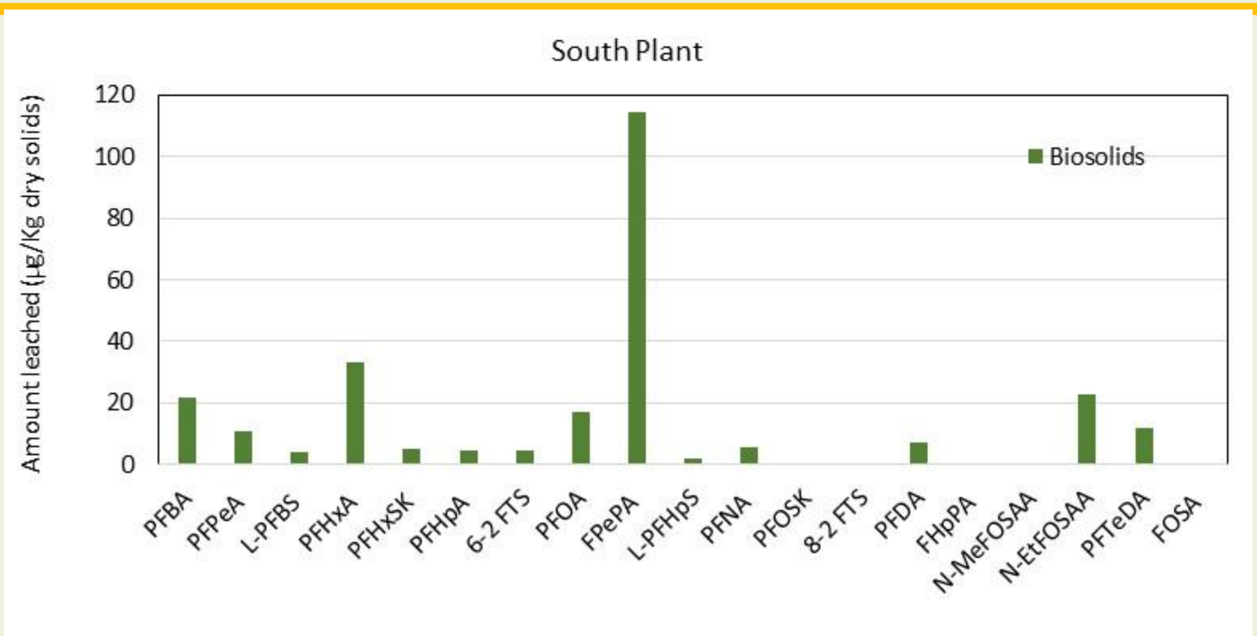


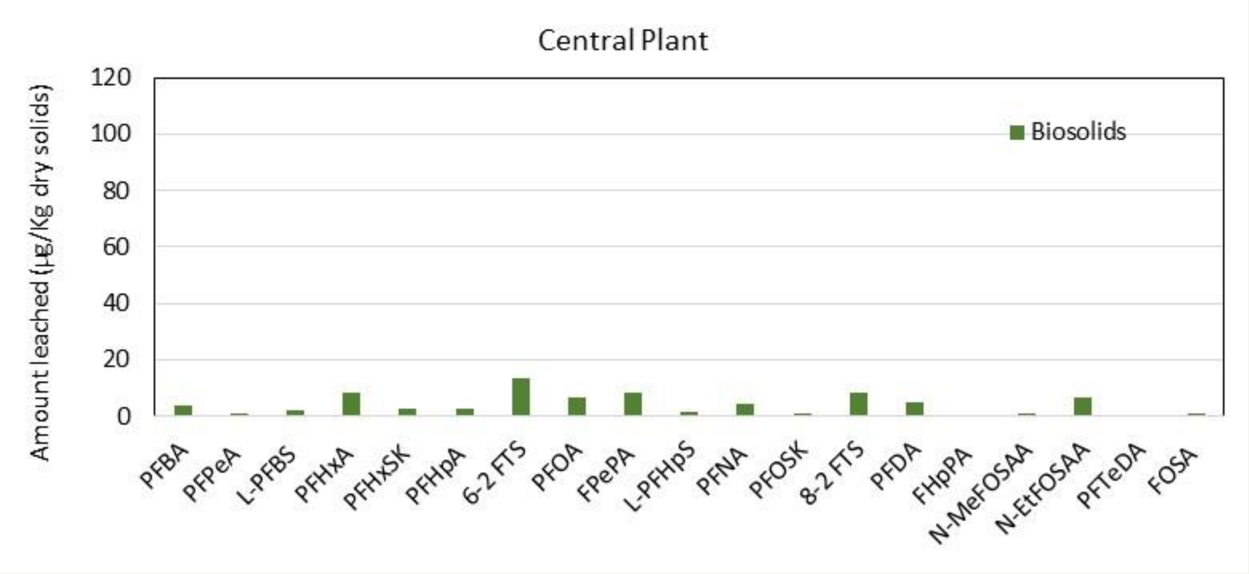
Change from thickened to dewatered





Dewatered biosolids - 30-day leaching data





PFAS fate during biosolids handling

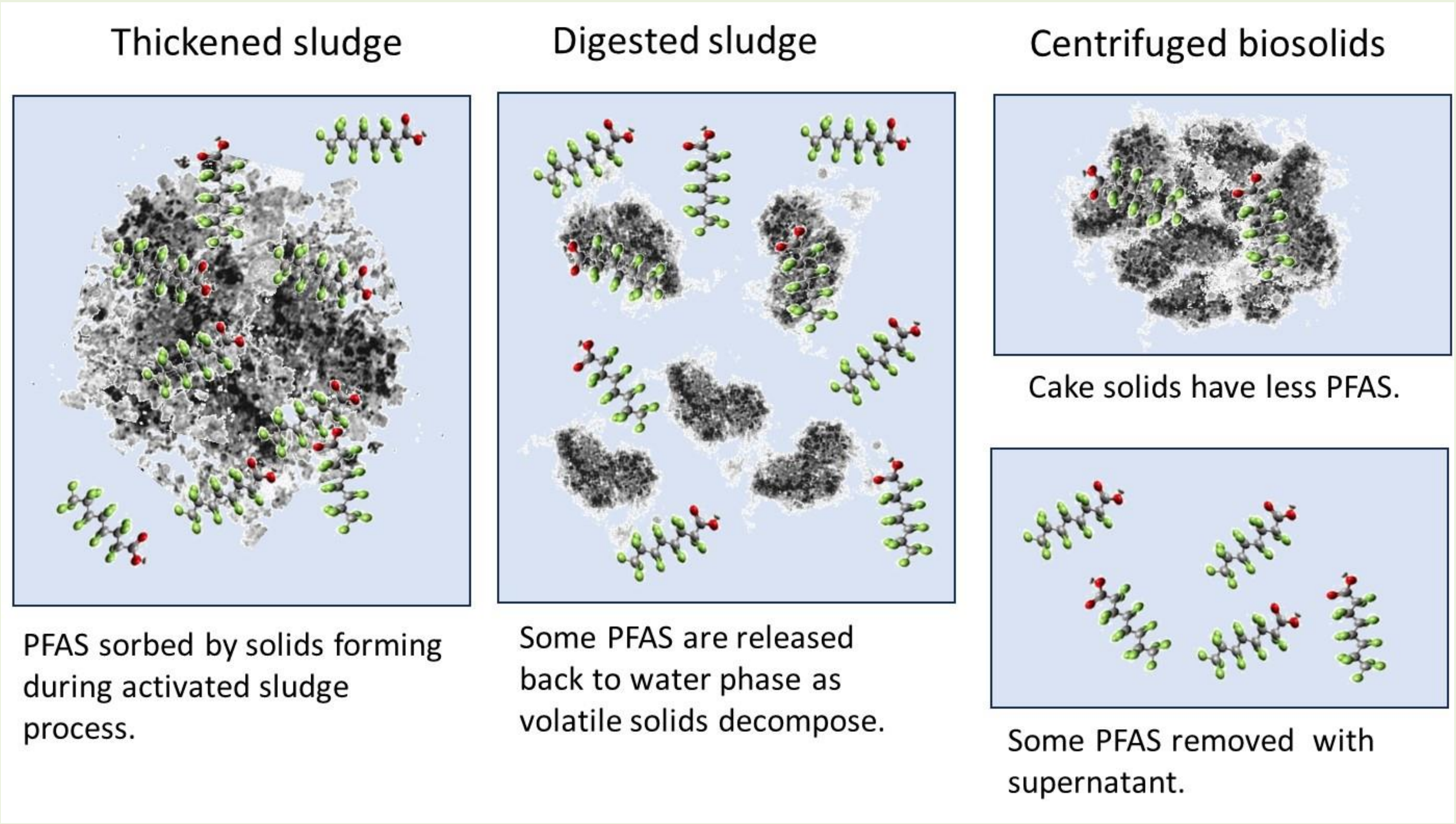


Image: B Tansel

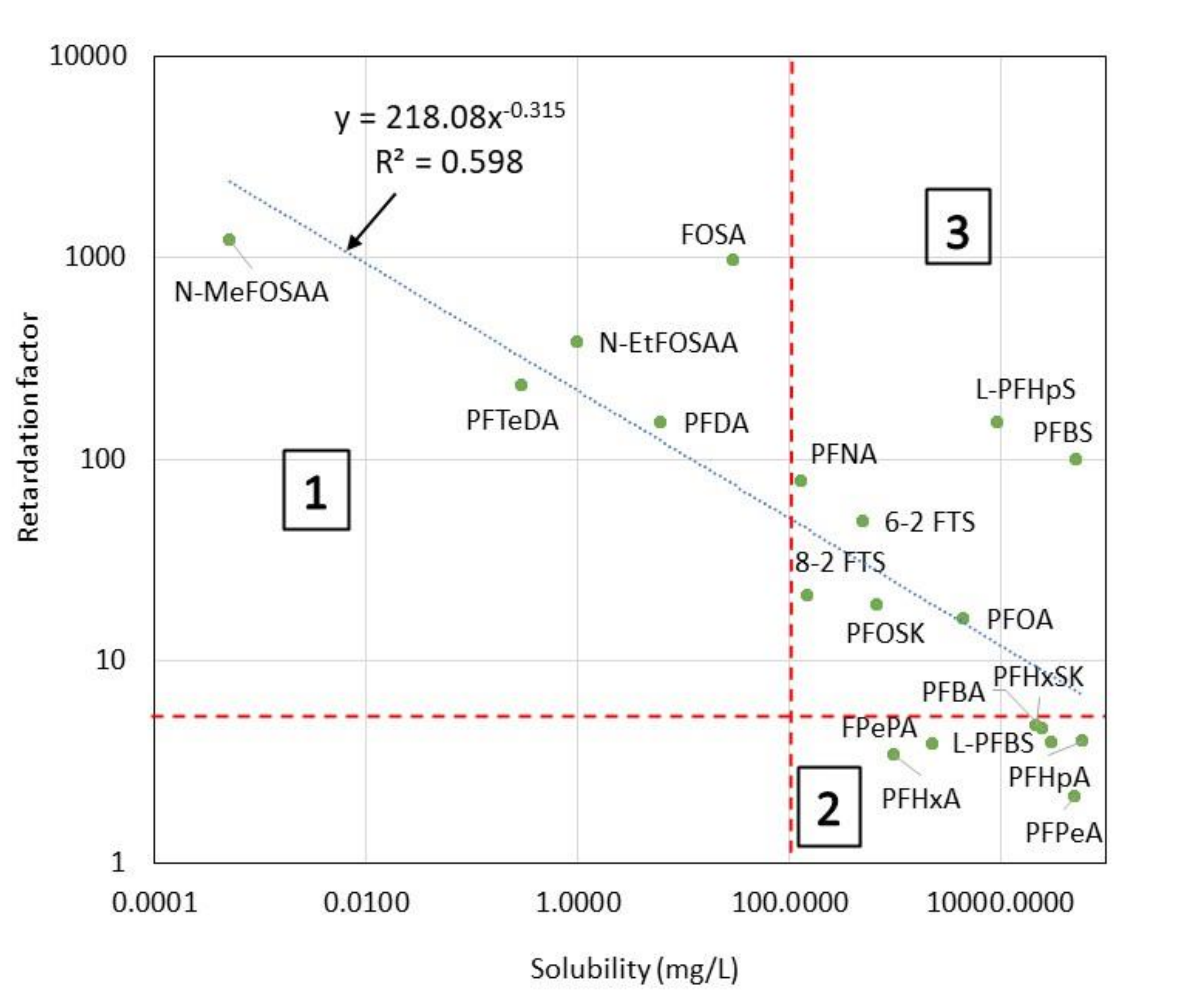
Concentration in dewatered biosolids

	PFAS in dewatered biosolids concentration > 10 µg/Kg		Concentration in dewatered biosolids (µg/Kg)	
	South Plant	Central Plant	South Plant	Central Plant
PFBA	x		**21.53**	3.59
PFPeA	x		**10.90**	2.07
L-PFBS			4.07	1.95
PFHxA	x		**33.27**	8.40
PFHxSK			4.86	2.80
PFHpA			4.61	2.39
6-2 FTS		x	4.38	**13.29**
PFOA	x		**17.29**	6.77
FPePA	x		**114.25**	8.51
L-PFHpS			2.14	1.74
PFNA			5.67	4.15
PFOSK			0.00	0.68
8-2 FTS			0.46	8.36
PFDA			7.32	4.83
PFBS			0.00	0.00
N-MeFOSAA			0.00	1.16
N-EtFOSAA	x		**22.97**	6.81
PFTeDA	x		**11.66**	0.00
FOSA			0.00	1.09
TOTAL			**265.38**	**78.59**

Likely PFAS fate after land application

	PFAS in dewatered biosolids detected over 10 µg/Kg		Concentration in dewatered biosolids (µg/Kg)		Characteristics that affect fate			Fate	
	South Plant	Central Plant	South Plant	Central Plant	Solubility (mg/L)	log Koc	Retardation factor	Tendency to accumulate in soil	Tendency to be transported with water
PFBA	x		**21.53**	3.59	25000	1.88	4.64		xx
PFPeA	x		**10.90**	2.07	50000	1.37	2.13		xx
L-PFBS			4.07	1.95	30000	1.79	3.96		xx
PFHxA	x		**33.27**	8.40	1000	1.70	3.41		xx
PFHxSK			4.86	2.80	22000	1.90	4.81		xx
PFHpA			4.61	2.39	60000	1.80	4.03		xx
6-2 FTS		x	4.38	**13.29**	500	3.0	49.00	x	s
PFOA	x		**17.29**	6.77	4500	2.50	16.18	x	s
FPePA	x		**114.25**	8.51	2300	1.78	3.89		xx
L-PFHpS			2.14	1.74	6.2	3.50	152.79	x	s
PFNA			5.67	4.15	131	3.20	77.07	x	s
PFOSK			0.00	0.68	680	2.57	18.83	x	s
8-2 FTS			0.46	8.36	150	2.62	21.01	x	s
PFDA			7.32	4.83	9500	3.50	152.79	xx	
PFBS			0.00	0.00	52600	2.00	100.00	x	s
N-MeFOSAA			0.00	1.16	0.00052	4.40	1206.73	xx	
N-EtFOSAA	x		**22.97**	6.81	1	3.90	382.28	xx	
PFTeDA	x		**11.66**	0.00	0.3	3.68	230.74	xx	
FOSA			0.00	1.09	30	4.30	958.73	xx	
TOTAL			**265.38**	**78.59**					

Likely PFAS fate after land application



Likely PFAS fate after land application

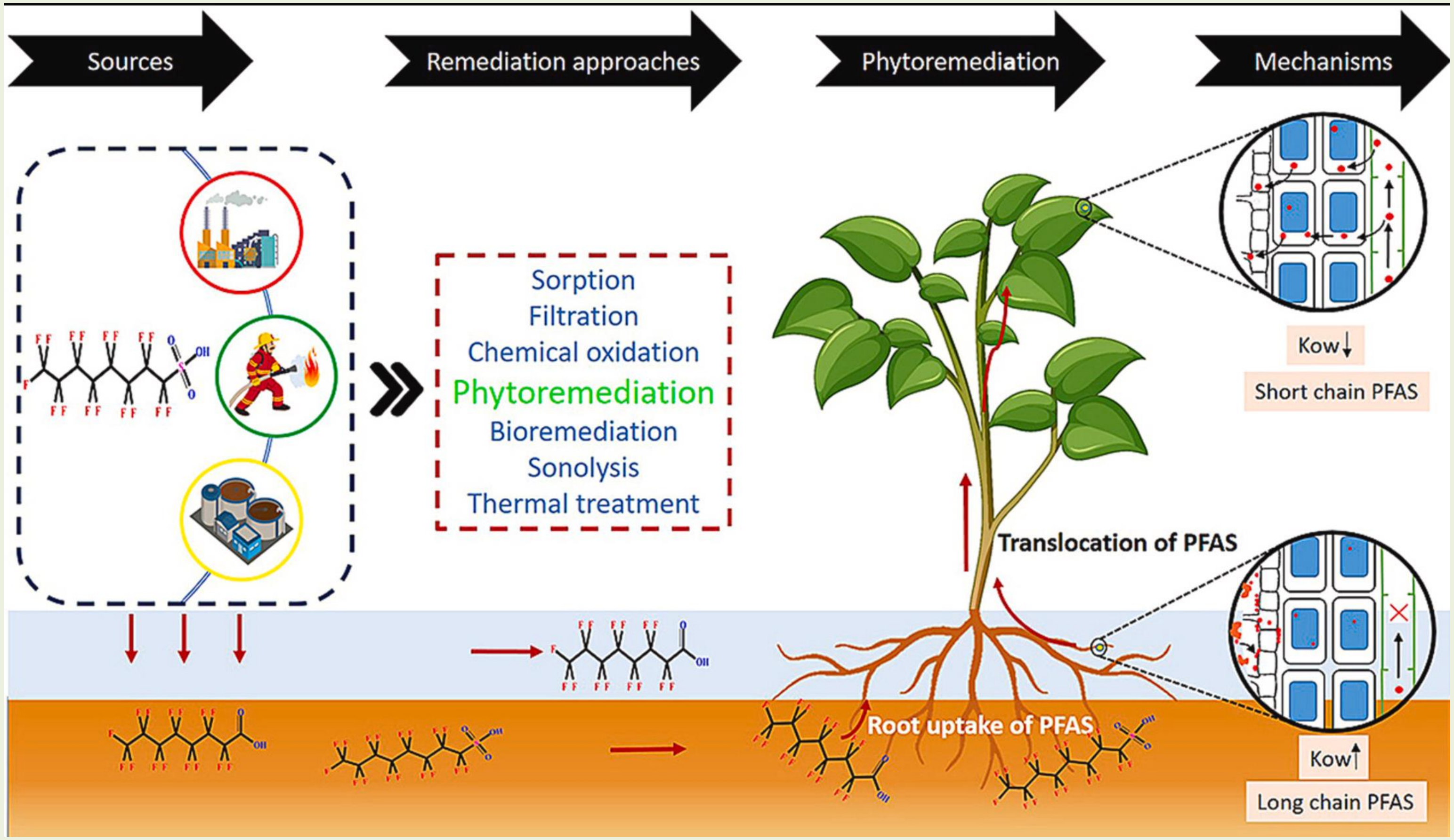


Image:
https://doi.org/10.1016/j.envres.2022.113311

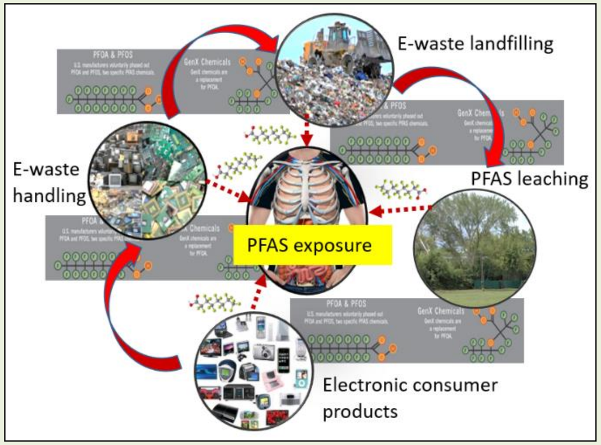
Conclusions - Next tasks -

Benefits for end users:

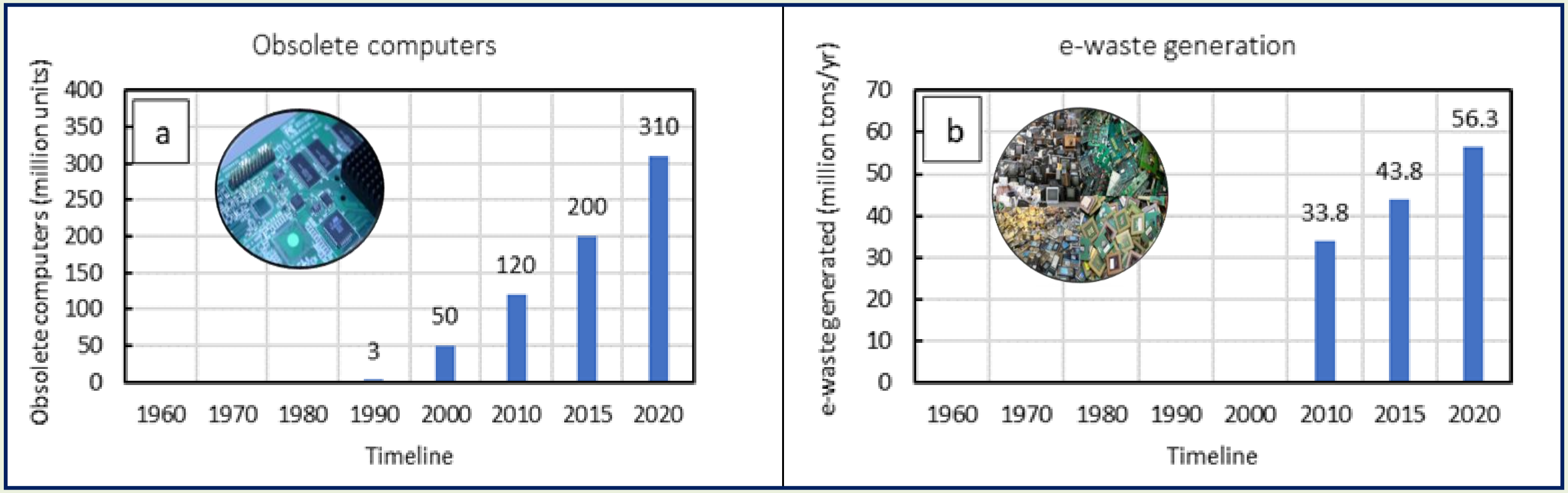
- What types of PFAS entering wastewater treatment plants partition to biosolids?
- Should we be concerned about PFAS in biosolids for land application?
- Do PFAS leach from biosolids over time?
- Is there any difference in PFAS content and composition in samples collected before and after thickening, digestion, and dewatering in leachate?
- Is there any effect on the PFAS dissolution behavior from biosolids in the presence of divalent metals like Ca^{2+} or Mg^{2+} that is potentially important to include in a fate and transport site evaluation?
- Which PFAS should be included in a database for biosolids that would affect biosolids management.

PFAS in e-waste:

Occurrence, types, and estimated quantities of PFAS in e-waste and appropriate management strategies for PFAS containing e-waste components



Quantities of e-waste



PFAS in e-waste

Product	Use in electronic system components and manufacturing processes	
Mobile devices	• Anti-smudge on touch panel	• Smoothness
Printed circuit boards	• Dielectric properties • Heat resistance	• Solder resistance • Low water absorption
Electric wire and cables	• Electric insulation • Dielectric properties	• Molding and processing
Foldable smartphones	• Transparency • Low dielectric constant	• Flexibility • Improving folding function
Electronic industry	• Testing electronic devices & equipment • Heat transfer fluids • Solvent systems and cleaning	• Carrier fluid/lubricant deposition • Etching piezoelectric ceramic filters
Semiconductor industry	• Photoresistance • Photosensitivity • Controlling diffusion of acid to unexposed regions • Reducing reflection on surface • Wetting agent • Non-stick coating on carrier wafers • Bonding agent	• Increasing stress tolerance • Separation of high voltage components (dielectric fluid) • Electrical signal for mechanical & thermal signals • Providing liquid crystal with dipole moment • Reducing static electricity build-up and dust attraction • Cleaning integrated circuit modules • Antireflective coating
Glass surface treatment & finishing	• Making glass hydrophobic and oleophobic • Preventing misting • Repelling dirt • Etching and polishing	• Improving fire or weather resistance • Increasing speed of etching, improving wetting • Solvent displacement drying
Metallic & ceramic surfaces	• Making surfaces hydrophobic and oleophobic	• Ease of cleaning
Wires and cables	• Increasing temperature endurance • Providing fire resistance	• Providing high stress crack resistance

Technical Approach

Tasks
Task 1. Visits to e-waste recycling centers and sampling of e-waste components
Task 2. Chemical analyses of PFAS content and type in e-waste
Task 3. Leaching experiments
Task 4. Modeling PFAS release and mobilization from discarded e-waste components
Task 5. PFAS exposure during e-waste handling
Task 6. Final report
TAG Meetings

Technical Approach

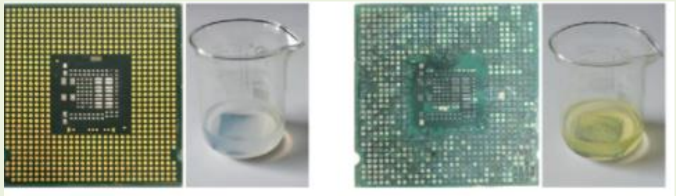
Task 3. Leaching experiments

Dissolution and leaching experiments

Release and leaching profiles of PFAS from selected e-waste components.

Specific samples tested include:

- Printed circuit brads
- Wires and cables
- Keyboard
- Flat panel displays or liquid crystal displays



Technical Approach

Task 5. PFAS: in leachate + exposure via e-waste handling

- ingestion (water solubility and organic carbon partition coefficient),
- inhalation (volatility in air),
- dermal (lipid solubility), or ocular (water solubility).

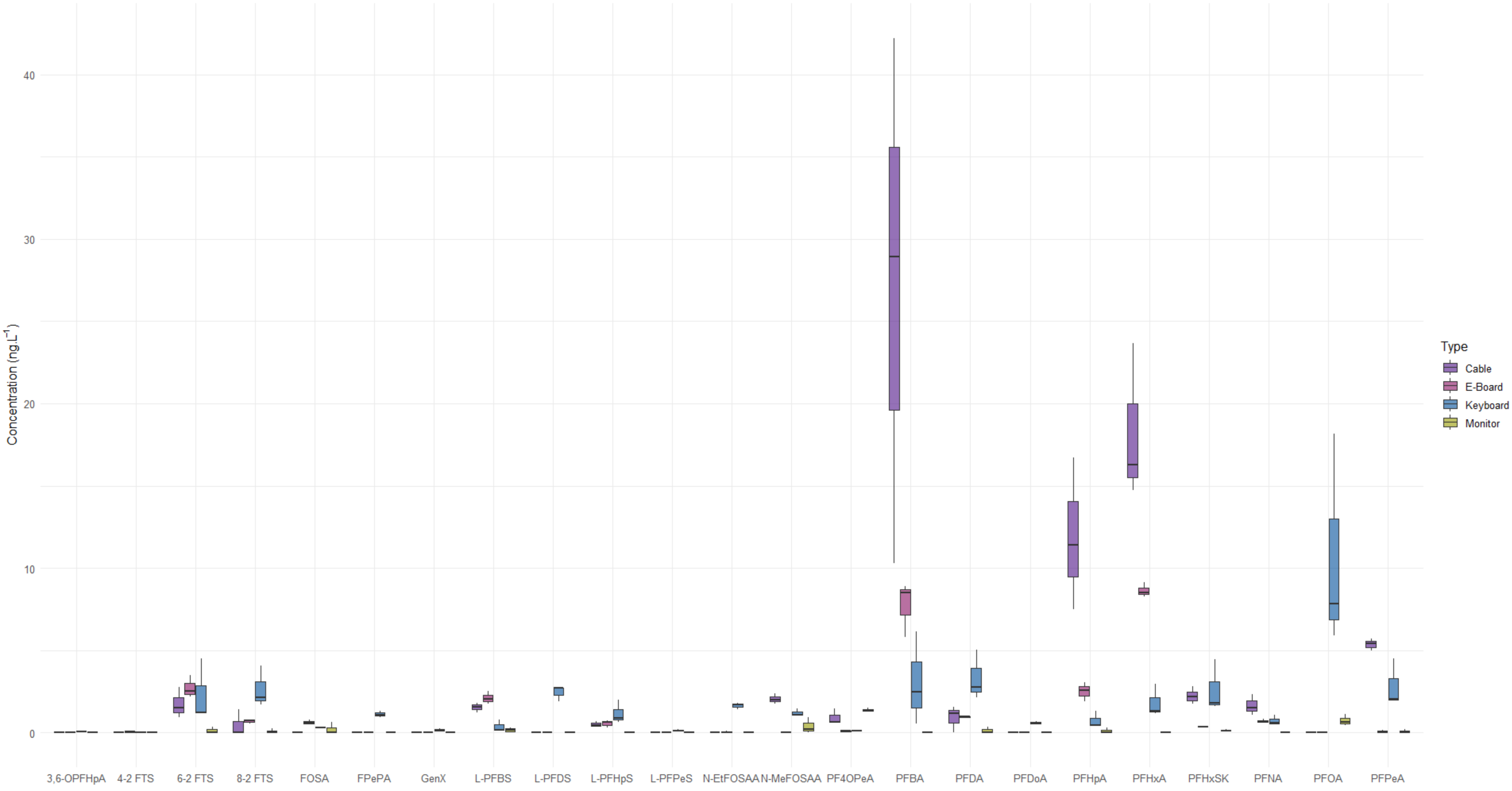









Preliminary Results



PFAS composition in e-waste Leachate

Thank you.