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PER- AND POLYFLUOROALKYL SUBSTANCES IN AGRICULTURE AND WASTEWATER TREATMENT

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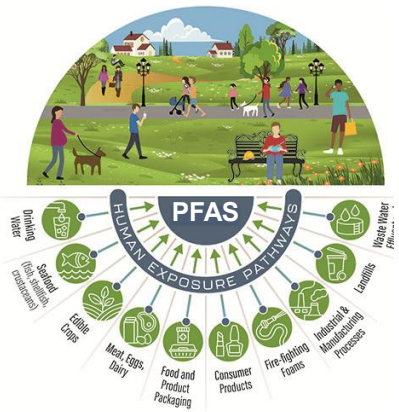
PA Citizens Advisory Council

Per- and Polyfluoroalkyl Substances in Agriculture and Wastewater Treatment



- A few PFAS Basics to Understand Fate
- PFAS flow in WWTFs
- Fate with land application examples
- Key Take-Aways
- Perspectives

Graphic Design Contracted by Purdue University Institute for a Sustainable Future

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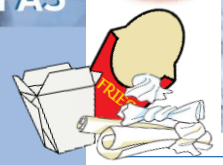
PFAS ARE PERVASIVE IN OUR PROCESSES AND PRODUCTS

Used in numerous products & processes due to their unique properties

PFAS BRAND NAMES
- Teflon
- Scotchguard
- Stainmaster
- Stainsafe
- Silverstone
- Polartec
- Texapore
- Gore-Tex

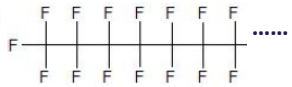
PFAS WORDS to AVOID
"nonstick"
"water-repellent"
"weather-protective"
"stain-resistant"
"fluoro" or "perfluoro"



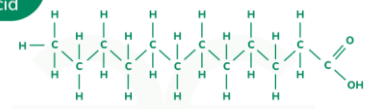
Industries & Infrastructures	Products
• Municipal water and waste treatment	• Water, oil, and stain-resistant textile
• Industrial manufacturing of PFAS	• Floor coatings and cleaners
• Oil and gas operations	• Food wrappers
• Metal plating and coating	• Pharmaceuticals & Personal care products
• Aviation and transportation fire extinguishing	• Aqueous Film-Forming Foams (AFFFs)

PFAS: PER- & POLYFLUOROALKYL SUBSTANCES – A LARGE SYNTHETIC DIVERSE CHEMICAL FAMILY

> 15,000 PFAS produced



Fatty Acid



- Fluorine-saturated chain of varying length
- Numerous subclasses
  - Each has a unique differentiating characteristic
  - Each with several different perfluoroalkyl chain lengths
- An individual PFAS like PFOS may be multiple molecules (isomers, same atoms but different arrangements)

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Units in the PFAS World

Water (ng/L) ppt

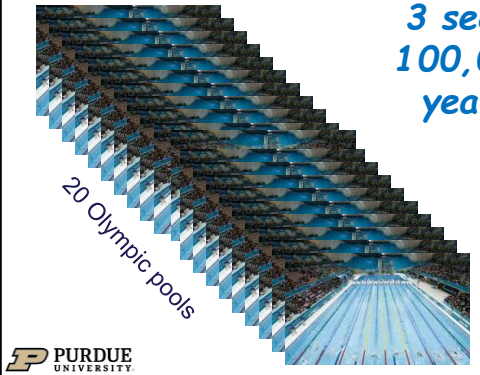
Bioaccumulation, Sorption

X 1000

versus

Blood, Biota, Plants, Soil, Biosolids (ng/g) ppt

3 sec in 100,000 years



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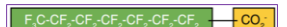
Short vs Long Chain vs Precursors/Intermediates

Perfluoroalkylcarboxylic acids (PFCAs, *like PFOA*)



Perfluoroalkyl sulfonic acids (PFSAs, *like PFOS*)

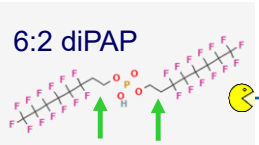
PFCAs + PFSAs = Perfluoroalkyl acids (PFAAs), that are persistent

- **Shorter chain PFAS**
  - More mobile (rapidly leach through soil)
  - Less bioaccumulative
  - Higher transpiration into plants
- **Longer chain (e.g., PFOS, PFOA)**
  - Not very mobile
  - More bioaccumulative
  - Biomagnify
  - Longer half-lives in humans

Transformation: Precursors/Intermediates → PFAAs

Fluorotelomer-based example

6:2 diPAP



→ **Multiple PFCAs**

Electrochemically-derived (ECF) example

EtFOSA (C8)

→ **C8 PFSA (PFOS)**

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THE CHALLENGE: MANAGING PFAS IN WASTEWATER AND BIOSOLIDS MANAGEMENT

Multiple PFAS sources – industry, AFFFs, landfills, domestic

Conduit of our wastes

Wastewater Influent → Sorption to Sludge → Effluent discharged to streams or used for irrigation

Treatment process with type and treatment stage

Biosolids → Land-applied as a soil amendment

PFAS enter our wastewater treatment plants and then exit via effluent or sludge (or air) unaffected or transformed to other PFAS

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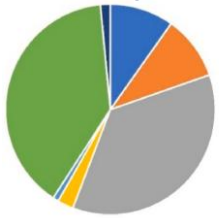
PFAS Transformation in Solids Processing: Example for Anaerobic Digestion (AD)

Before Digestion



After Digestion

- Bulk of the PFAS are precursors (**green**) and intermediates (**gray**) and most not measured in the current USEPA 40 targets list in the USA
- Digestion to remove pathogens, etc. leads to PFAS conversion to PFAAs (**orange** and **blue**)
- Aerobic >> anaerobic transformation rates

Alukkal, Lee et al., 2024a,b
https://doi.org/10.1016/j.chemosphere.2024.143406
https://doi.org/10.1016/j.chemosphere.2024.143357

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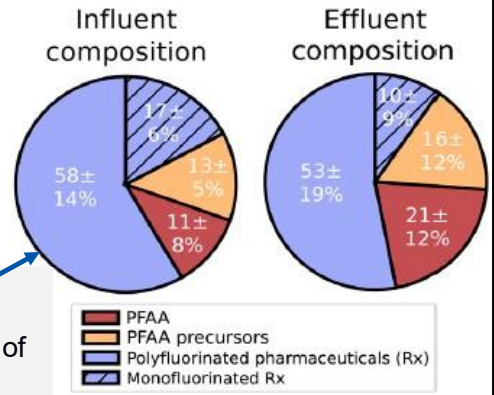
% PFAS IN EFFLUENT VS BIOSOLIDS

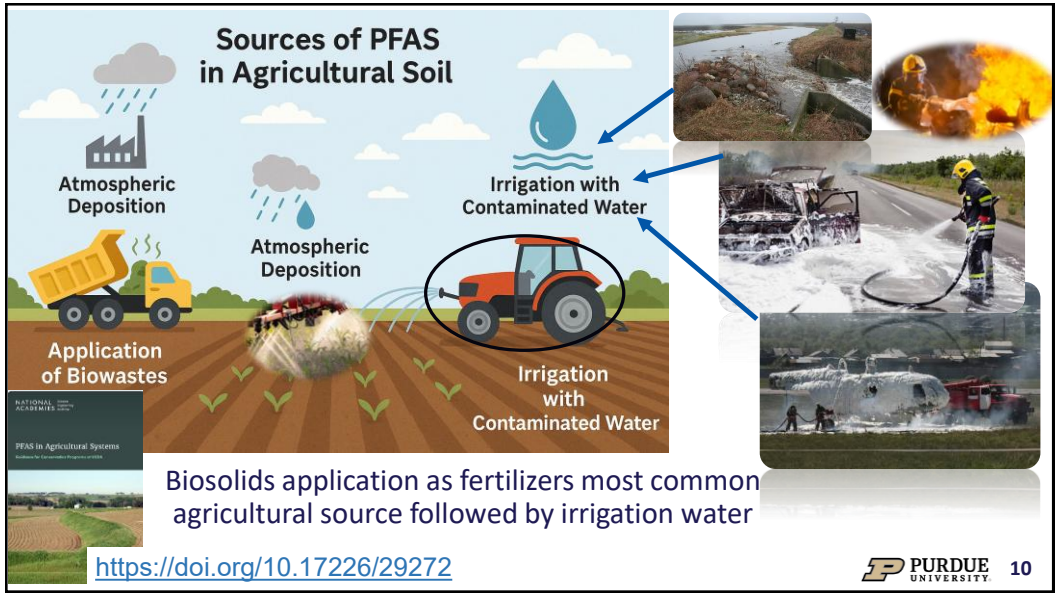
- Sanitation district-specific
- 40-90% of the total PFAS load leaving WWTPs
- Variation in the PFAS analyte list affects trends

- Only about 25% may be PFAS
- Fluorinated pharmaceuticals are the bulk of organo-fluorine in WW (8 facilities)
- Total organo-fluorine does not change much between influent and effluent

PFAS RELATIVE TO TOTAL ORGANO-FLUORINE SOURCES



https://doi.org/10.1073/pnas.2417156122



Biosolids application as fertilizers most common agricultural source followed by irrigation water

https://doi.org/10.17226/29272

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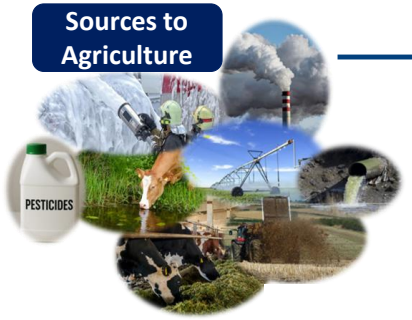
PFAS Fate after Discharge/Application to Land



PFAS Fate

Individual PFAS Properties

Soil Properties

Air-water interface accumulation (PFAS)

Solid Phase adsorption

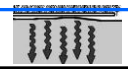
Biotransformation

Plant Uptake

Leaching

Runoff

Tile-drain discharge



Peter, L. & Lee, L.S. 2025. PFAS as contaminants in agricultural soils, Chapter 3 IN: Contaminants in agricultural soils: Challenges and solutions (ed. Laureate Prof. Ravi Naidu), burleigh dodds Science Publishing, http://dx.doi.org/10.19103/AS.2025.0151.03

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40-Y SURFACE DISPOSAL SCENARIO (CA SITE 1 USA)

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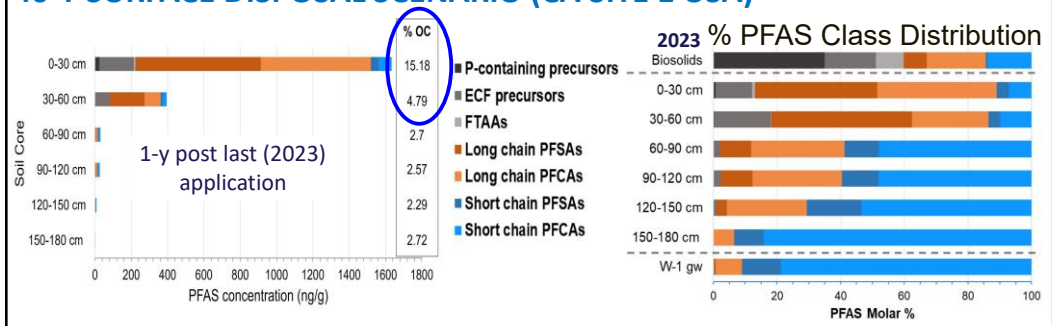
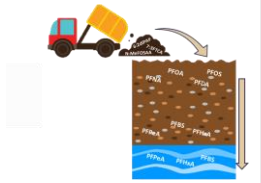


- Annual and high biosolids application rates led to PFAS and organic carbon (% OC) accumulation in soil over time
- Long-chain PFAS retained in the upper soil profile
- Most precursors degrade to PFAAs within 1 year
- Short-chain PFAAs dominate what is getting to groundwater



The Water Research Foundation

EPA United States Environmental Protection Agency

Alvarez, Lee et al. 2024 https://doi.org/10.1016/j.scitotenv.2024.176540

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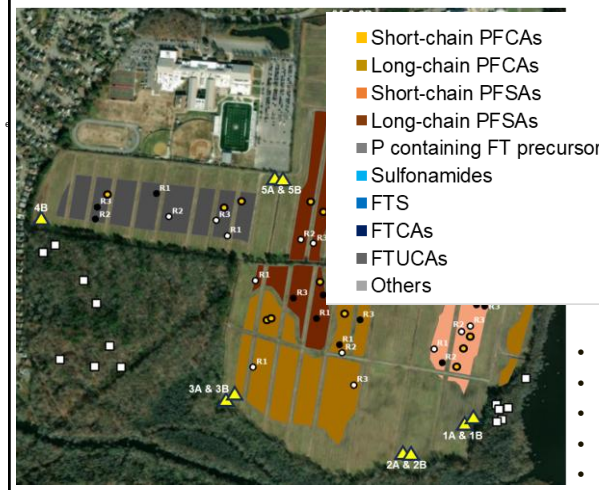
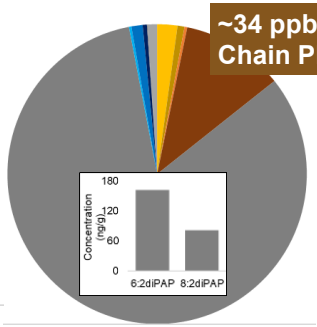
38-Y AGRONOMIC BIOSOLIDS APPLICATION HRSD, VA, USA STUDY SITE



- Short-chain PFCAs
- Long-chain PFCAs
- Short-chain PFSAs
- Long-chain PFSAs
- P containing FT precursors
- Sulfonamides
- FTS
- FTCAs
- FTUCAs
- Others



- 3 soil types – low to high permeability
- Class B biosolids application 1986 – 2014
- Mostly Corn/soybean rotations – animal feed
- Switch to Class A in 2023 (after a 9-y pause)
- PFAS in 2023 biosolids mostly diPAPs

Peter, Lee et al. 2025, https://doi.org/10.1016/j.jenvman.2025.128137

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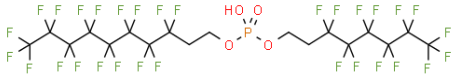
PFAS RANGES IN 2018-2025 USA BIOSOLIDS (PPB DRY WT)

	PFAS	~Min	~Max
Perfluoroalkyl acids (PFAAs) - terminal metabolites	PFOS	< LOD	130
	PFHxS	< LOD	50
	PFOA	< LOD	30
	PFHxA	< LOD	30
Precursors/ intermediates	6:2 FTS	< LOD	15
	8:2 FTS	< LOD	30
	MeFOSAA	< LOD	100
	EtFOSAA	< LOD	50
PFAA intermediates	7:3 FTCA	< LOD	100
	5:3 FTCA	< LOD	220
	3:3 FTCA	< LOD	220

Some Additional Common Precursors

PFAS	~Min	~Max
6:2 diPAP	10	400
8:2 diPAP	0	200
6:2 PAP	20	350
6:6 PFPI	0	10
6:8 PFPI	0	10



- For most utilities, identified precursors are typically at least 75% of the quantifiable PFAS fluorine mole balance

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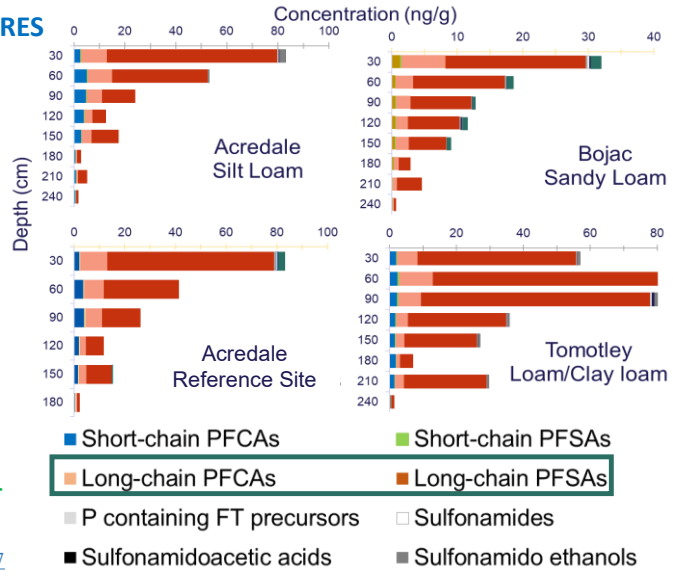
HRSD VA STUDY SITE: SOIL CORES

- Soil cores after a 9-y pause in land application prior to the 2023 application
- Long-chain PFAS (**oranges**) persist, mobility limited
- Textural driven processes evident
- Trends post-2023 application no different than Acredale reference not receiving 2023 application



EPA United States Environmental Protection Agency HRSD PURDUE UNIVERSITY

Peter, Lee et al. 2025, https://doi.org/10.1016/j.jenvman.2025.128137

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West Coast Site: 5-year Biosolids Application Cycle PFAS snapshot

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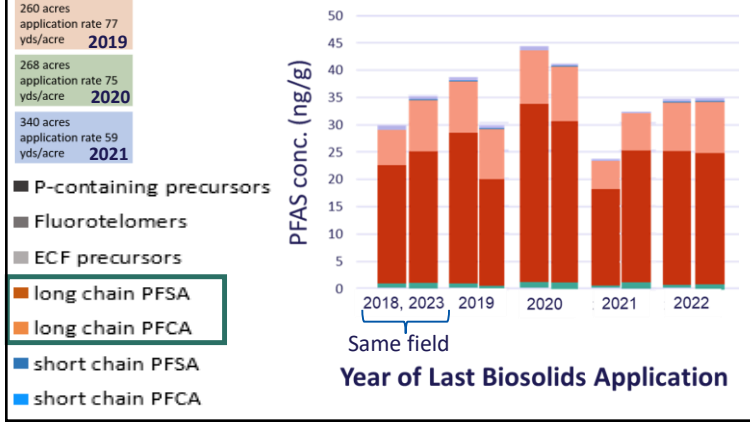
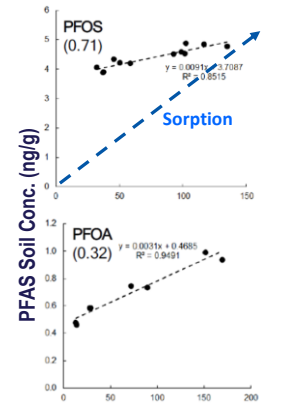
274 acres application rate 73 yds/acre **2022**
275 acres application rate 73 yds/acre **2018** *
260 acres application rate 77 yds/acre **2019**
268 acres application rate 75 yds/acre **2020**
340 acres application rate 59 yds/acre **2021**

Surface Soil Sampling Times twice:
- Pre-2023 biosolids application
- In 2024, post 2023 application





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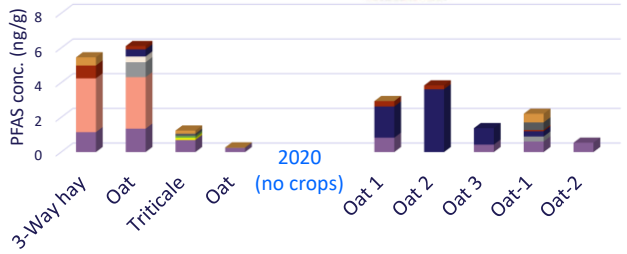
FEED CROP UPTAKE EXAMPLE: 5-Y CYCLE BIOSOLIDS-APPLIED SITE IN CA

- Uptake is variable
- Mostly short chain PFAS
- Of the long chain, PFOA uptake dominates and dependent on time since last application and soil PFAS levels



Last Biosolids Application→ 2018 2019 2021 2022

Confidential, unpublished data
Manuscript in preparation

L-PFBS PFPeA PFHxA PFHpA L-PFHxS
L+BrPFHxS PFOA PFNA L-PFOS L+Br-PFOS

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HRSD: MAXIMUM TOTAL PFAS CONCENTRATIONS IN SHALLOW AND DEEP MONITORING WELLS (38-y agronomic biosolids application

Total PFAS (ng/L)
- 0 – 20
- 21 – 100
- 101 – 200
- 201 – 620

Soil Type
- Acredale
- Bojac
- Tomotley

- Most wells had < 20 ppt TOTAL PFAS
- Major exceptions are well complexes 2 located in the sandy soil and bordering a multiple PFAS-impacted lake
- Sources to lake: Naval base, old WWTP discharged directly into the lake, airport

Noteworthy, non-PFAS chemicals (e.g., PPCPs) were not elevated in these wells by the lake. PPCPs were only elevated in well 7B (deep well) near a housing development).

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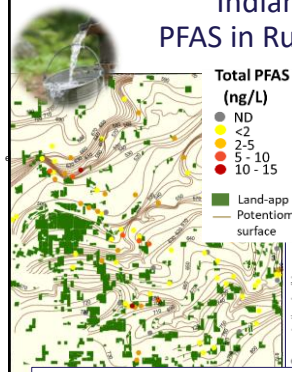
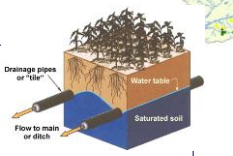
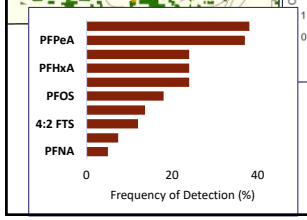
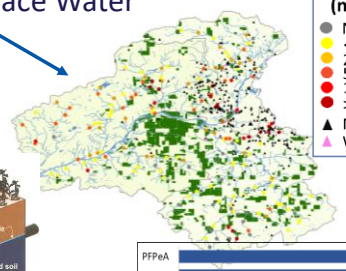
Indiana: Greater Tippecanoe County: PFAS in Rural Water Supplies & Surface Water

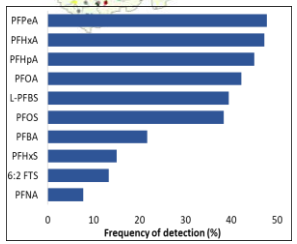


- Major sources: agricultural, industrial and WTTP discharges
- Most agriculture fields are tile-drained









- PFAS detected in 88% of surface water samples.
- 20 PFAS detected in surface water with highest for PFBS @ 85 ng/L

Peter, Lee, 2024 https://doi.org/10.1021/acs.est.4c09490

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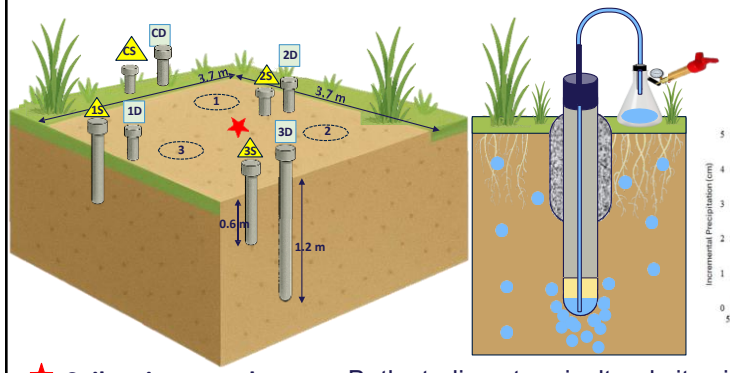
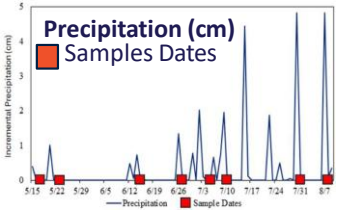
LEACHATE MONITORING: FIRST TIME APP VERSUS HISTORIC SITE





- **Soil moisture probe**
- **Deep lysimeters**
- **Shallow lysimeters**
- **Soil cores**

- Both studies at agricultural sites in Indiana.
- First time biosolids plot on pastureland and historic site corn/soybean rotations
- Same biosolids source
- Plants removed in both case
- Subsurface injection

WRF5214

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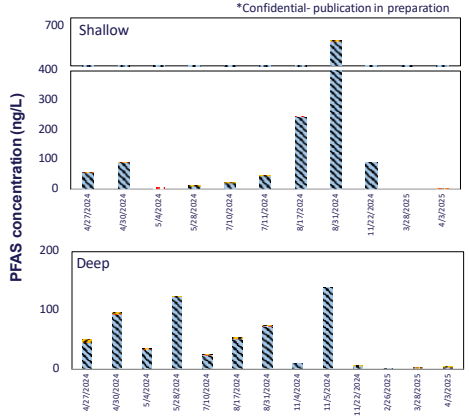
TEMPORAL POREWATER MONITORING

FIRST-TIME APPLICATION, Monitoring commenced with first rain event post application

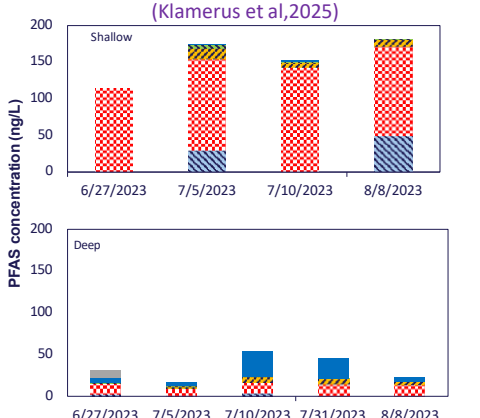
*Confidential- publication in preparation



~ Annual applications for ~ 40 y

Monitoring started on year after last application

(Klamerus et al,2025)



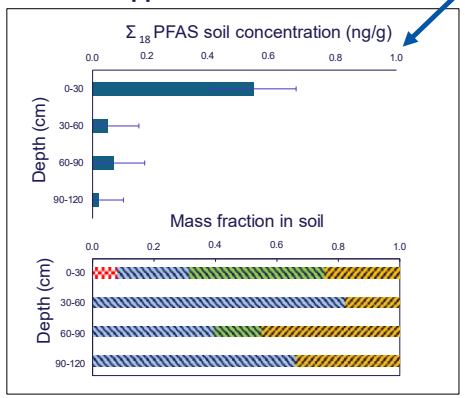
Short PFCAs | Short PFSAs | Long PFSAs | Long PFCAs | ECF | Intermediate | Other

Confidential, unpublished data

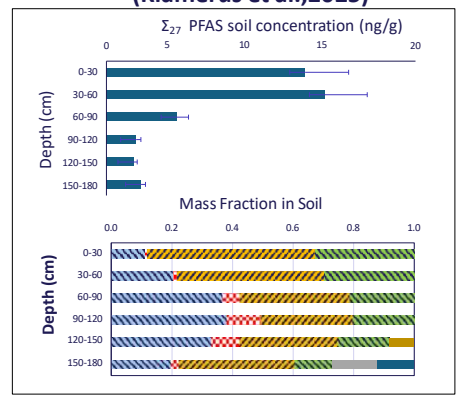
PFAS CONCENTRATIONS AND PROFILE WITH DEPTH IN SOIL CORES

First-Time application

Similar to background



Long-term (40 y annual) application (Klamerus et al.,2025)



Short PFCAs | Short PFSAs | Long PFSAs | Long PFCAs | Other | FTCAs | ECF | Intermediate

Confidential, unpublished data