UW-Madison-WSLH PFAS INITIATIVES

WDNR PFAS Technical Advisory Group
Water Quality Subgroup
September 06, 2019 Meeting

Martin Shafer PhD, UW-Madison, SMPH-WSLH

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Presentation Outline

- PFAS-relevant activities/research at the WSLH
  - ❖Method development/validation/accreditation
  - ❖WSLH directed research
  - ❖Research collaborations
  - ❖Grant proposals
- POTW-focused effort

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Grant (Methods) Proposals: Submitted

To **Wisconsin Sea Grant** – Special Call for Proposals 2018 – Healthy Coastal Ecosystems

- **Title: Enhancing Capability & Capacity for Per- and Polyfluoroalkyl Substances (PFAS) Characterization at the UW-Madison Wisconsin State Laboratory of Hygiene**
- PI: Shafer
- Submitted: September 07, 2018
- Budget: $35K
- Status: **Funded**
- Funds were used to develop new PFAS methods and obtain new data on the environmental presence of PFAS

WSLH PFAS METHOD IMPLEMENTATION TIMELINE

- EPA 537.1 (drinking water)
  - ✓ Established, accredited and currently being applied
  - ✓ 18 compounds
- Non-Potable Waters
  - ✓ Established and currently begin applied
  - ✓ ISO 21675 (30) + "DNR Target List" (6). 36 compounds total
- Tissue (Fish) Samples
  - ✓ Established and soon to be applied
  - ✓ ISO 21675 (30) + "DNR List" (6). 36 compounds total
- Soil/Sediments/Biosolids
  - ✓ Validation completed, August 2019
  - ✓ ISO 21675 (**30**) + "DNR List" (**6**). 31 compounds total

Note: the WSLH also maintains a serum PFAS method (with fewer compounds).

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WSLH PFAS METHOD ACCREDITATION SCHEDULE

- 537.1 Drinking Water
  - ✓ NELAP Accredited
- Non-Potable Waters, Tissue, Solids
  - ✓ Scheduled for NELAP audit in Fall 2019
- DoD ELAP Accreditation
  - ✓ DoD QSM 5.2 compliance
  - ✓ If DoD proposal is funded
- WDNR Accreditation
  - ✓ When WDNR finalizes its PFAS certification program

Internal WSLH Resources: PFAS Project

- **Title: Atmospheric Deposition of PFAS via Precipitation at Selected Locations Across the United States**
- **Title: Evaluation of the National Atmospheric Deposition Program (NADP) Infrastructure and Protocols for Monitoring PFAS Deposition in Precipitation**
- PI: Shafer
- Approved: February 2019
- Budget: $32K
- Status: Scope of Work completed (March – August 2019)
- Deliverables: SETAC Presentation, Draft Manuscript, SOP
- Follow-up: Additional Method Development and Precipitation Sampling

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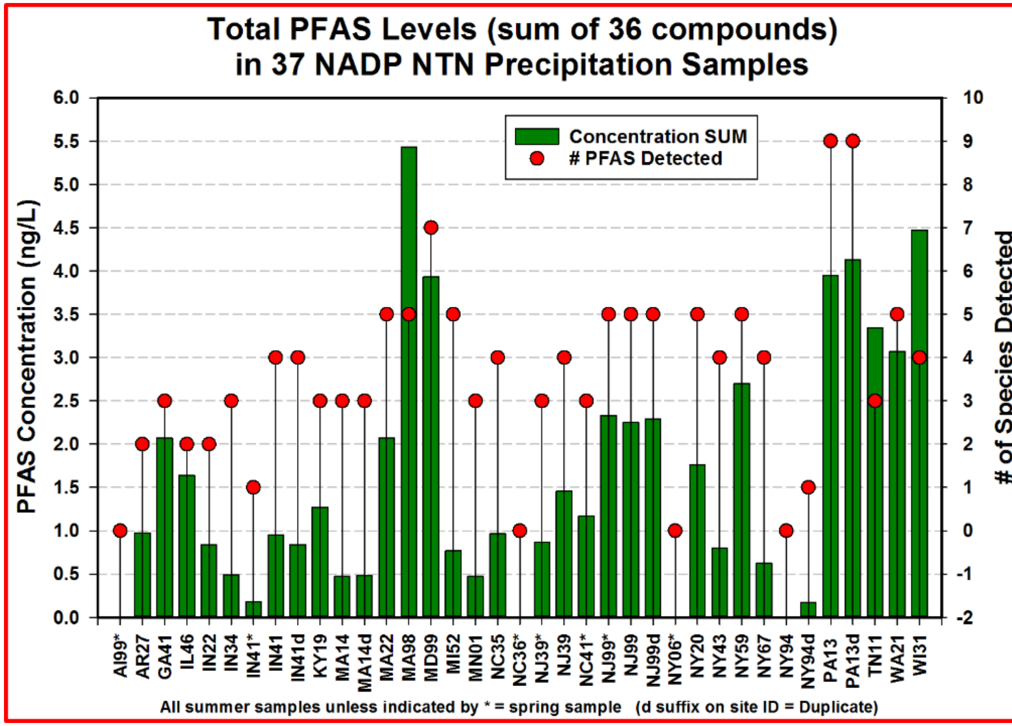
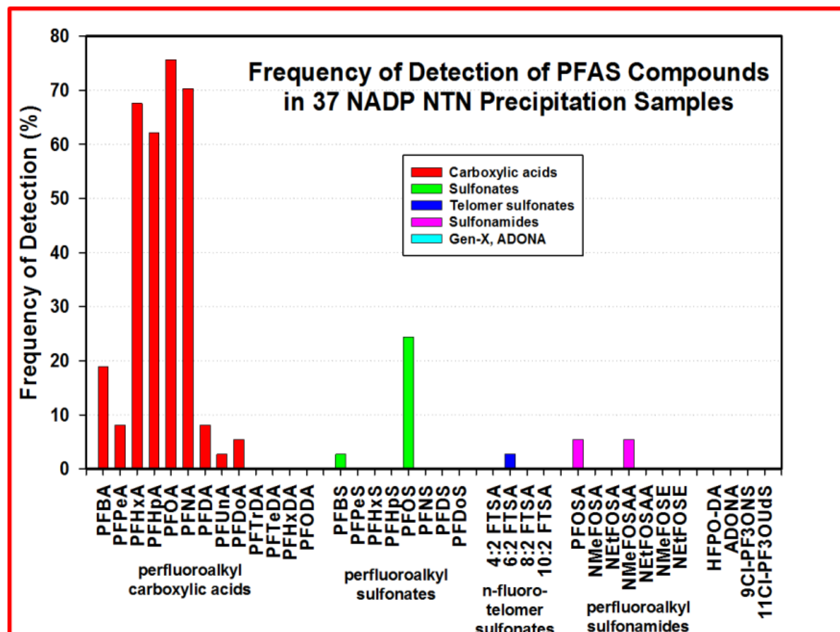
PFAS in Precipitation





Grant (Research) Proposals: Submitted

To the **US Environmental Protection Agency** – ORD/NCER Call for PFAS Proposals – Funding Opportunity: EPA-G2018-ORD-A1

- **Title: Per- and Polyfluoroalkyl Substances (PFAS): The Role of Atmospheric Cycling in Environmental Dispersal and Human Contaminant Burdens. Budget: $2.5M**
- PIs: Shafer, Remucal, Malecki, Edwards, submitted June 18, 2018
- Components: Deposition (precip./dry/vapor), surface waters, biomonitoring, historic deposition, transformations (lab), LMW
- Status: **passed scientific and technical merit review as well as past performance review**. Not funded at programmatic review. (two projects were funded nationally)

To the **US Department of Defense – SERDP**, Environmental Restoration 2020 Call for Proposals – ER20-C3-1378

- **Title: Development of Robust Batch Extraction Protocols with Soil-Column-Experiment Grounding for Assessment of PFAS Leaching Potential from DoD Relevant Matrices. Budget: $1.1M**
- PI: Shafer, Full Proposal Submitted: March 11th, 2019
- Components: Soil column mobility experiments, batch extraction development (TCLP-like), toxicology grounding
- Status: **Passed the Pre-Proposal stage with good reviews. Full proposal submitted on March 11th 2019**. Not funded at final review stage.

Grant Proposals: In-Preparation

To **Water Research Foundation** – RFP_5031. Occurrence of PFAS Compounds in U.S. Wastewater Treatment Plants

- **Title: Presence, Processing and Retention of PFAS within Prototypical Municipal Wastewater Treatment Facilities**

- PI: Shafer
- To Be Submitted: September 12, 2019
- Budget: $330K, 2-years (01/01/2020 – 12/31/2021)
- Status: Working to meet the submission deadline

RECENT / SCHEDULED PFAS ENVIRONMENTAL MONITORING COLLABORATIONS at the WSLH

- Fish Tissue
  - ✓ WDNR
  - ✓ 100-150 Samples
  - ✓ Summer 2019
- Surface Waters
  - ✓ WDNR
  - ✓ 60-70 Samples
  - ✓ Summer/Fall 2019
- Runoff Waters
  - ✓ USGS
  - ✓ 20 Samples
  - ✓ Spring 2019
- Ground Waters
  - ✓ Madison Drinking (Well) Water
  - ✓ 12 Samples, 537.1
  - ✓ Spring 2019
- Fish/Water
  - ✓ Great Lakes Protection Fund
  - ✓ 12 Water Samples
  - ✓ 45 Fish Tissue

Grants/Projects Working to Secure

- UW-Madison Biological Systems Engineering – Soil Mobility and Crop Uptake of PFAS in Agro-ecosystems. Proposal in Preparation.
- Vermont Department of Environmental Conservation. Potable water analysis for PFAS – some fraction of 650 samples.

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WDNR – WI Sea Grant Project: Goals

Assessment of the Impacts of PFAS in Municipal Wastewater Effluents and Land-Spread Biosolids on Wisconsin Ground- and Surface Waters

Study Component A: Determine the TYPE and QUANTITIES of PFAS Associated with POTWs and Streams Receiving POTW Effluents

(a) **Quantify PFAS within the POTW** – dual emphasis **(a) retention** (influent – effluent); **(b) cycling**/**processing** of PFAS within the facility. Samples of influent and effluent streams as well as selected locations within the treatment facility, including sludges and biosolids slurries

(b) **Quantify PFAS in the Stream Receiving the POTW Effluent**. **Stream water** and **sediment** samples upstream of discharge, in the mixing zone, and downstream of mixing zone

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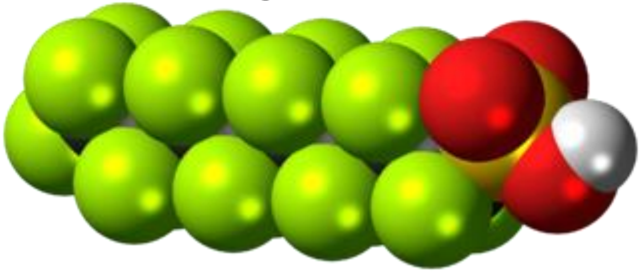


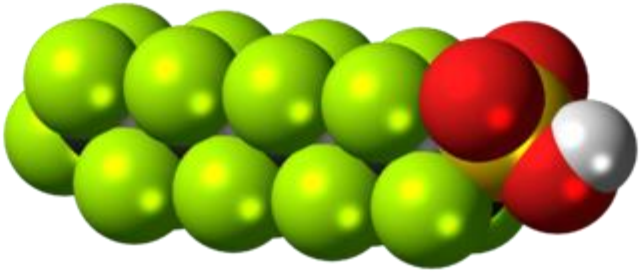
WDNR – WI Sea Grant Project: Goals

Assessment of the Impacts of PFAS in Municipal Wastewater Effluents and Land-Spread Biosolids on Wisconsin Ground- and Surface Waters

Study Component B: Determine the Impacts to Soils, Surface- and Ground Waters of PFAS-Containing Municipal Biosolids Spread on Agricultural Fields

(a) **Quantify PFAS within the fields receiving biosolids.** Samples of **soils** and **soil-water**

(b) **Quantify PFAS in groundwater samples** near the agricultural field study sites and in regional deeper groundwater



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WDNR – WI Sea Grant Project: Overview

The overall study plan (Components A and B) incorporates:

(A) State-of-the-art analytical protocols across the targeted matrices that will enable quantification of 36 (31) PFAS compounds

(B) PFAS-appropriate field methods

(C) Sampling carried-out by UW-Madison/WSLH staff (and a graduate student) experienced in POTW and stream sampling

We will work closely and collaboratively with the POTW operators to identify the specific sampling locations with the treatment facilities and arrange for mutually acceptable sampling logistics

Close collaboration with the Wisconsin Department of Natural Resources (DNR) staff to help identify facilities and environments that are adequately representative so that effective strategies and policy decisions on wastewater impacts of PFAS to ground and surface waters can be made

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Study Component A: Objectives

1) Provide a comprehensive assessment of PFAS levels in municipal wastewater streams/solids – key information that is currently lacking
2) Provide a basic mass-balance of PFAS species within POTW facilities, and assess PFAS retention at specific points in the treatment process
3) Determine whether there are substantive differences in the behavior of specific PFAS compounds throughout the treatment processes and whether these differences can be reliably predicted/modeled
4) Quantify the partitioning of PFAS between solids and "dissolved" phases within the treatment facilities
5) Provide an assessment of the relative efficacy of treatment plant type on PFAS removal from municipal waste streams

Study Component A: Objectives

6) Provide "fingerprints" of PFAS entering the facilities; and working in collaboration with DNR staffers assess whether these fingerprints can be associated with certain industrial/commercial loadings to the waste stream
7) Provide new information on the proximal impacts of PFAS-containing POTW effluents on receiving streams
8) Determine the phase distribution (particulate, dissolved) of PFAS species in the receiving stream and develop particle partition coefficients for each of the measurable PFAS compounds
9) Using measured in-stream and bed sediment-associated quantities of PFAS, estimate the retention/loss of PFAS within the near-effluent reach of the receiving stream

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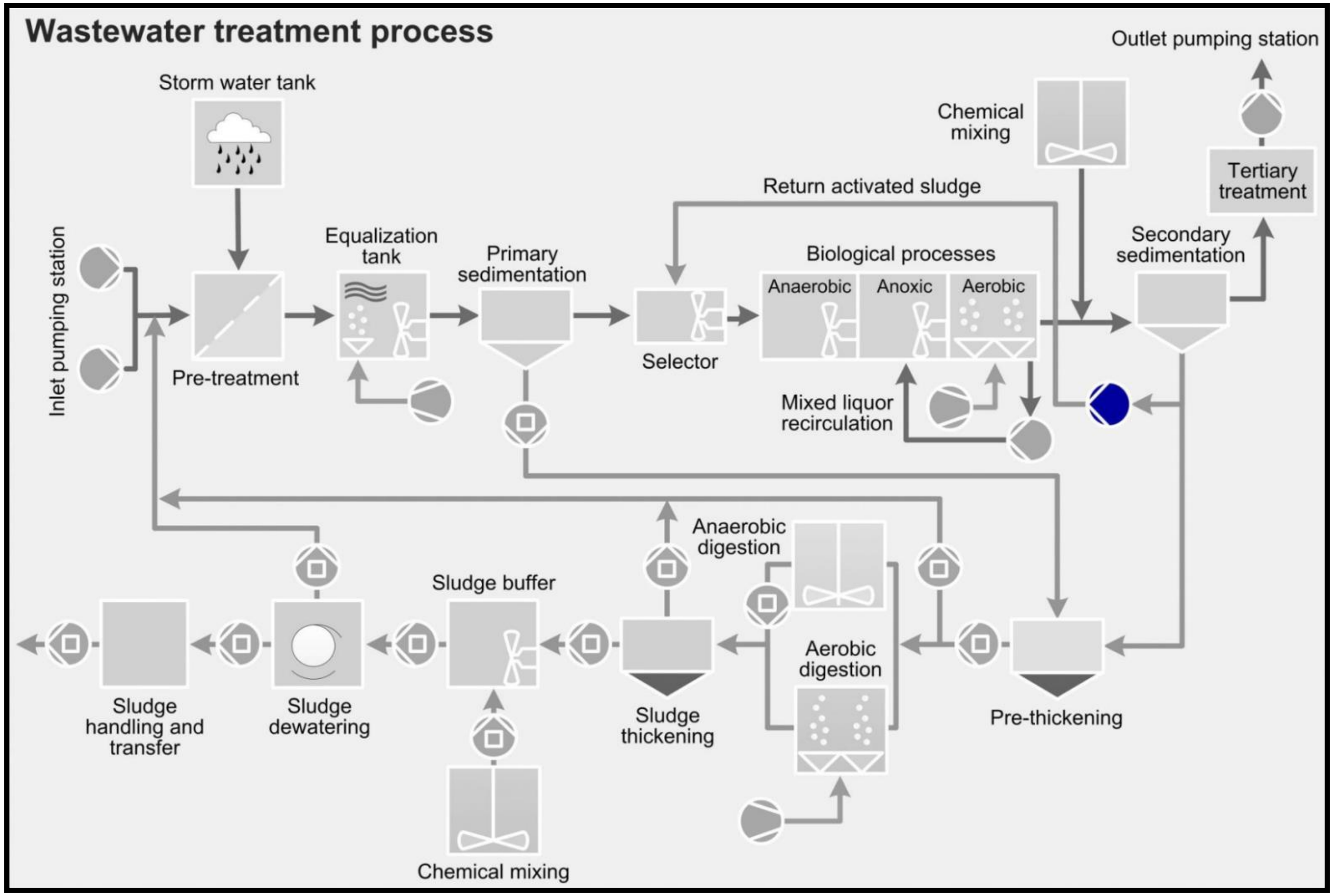
Study Component A: Structure

- 12 POTWs in WI (likely to be receiving significant loads of PFAS), PFAS screened before final selection
- Focus on activated sludge treatment facilities
- Focus on small-medium scale (0.5-10 MGD) facilities
- Encourage several of the states larger POTWs to also participate and emphasize within-plant PFAS cycling studies
- Include several facilities that discharge to a stream where robust in-stream/sediment sampling is feasible

Study Component A: POTW Sampling

In addition to Influent and Effluent:



Aqueous Samples

1. After grit removal
2. After primary clarifier
3. After aeration tank
4. After secondary clarifier
5. After tertiary treatment

Sludge Samples

1. From primary clarifier
2. Activated sludge
3. From secondary clarifier
4. After digestion
5. Biosolids slurry as prepared for land-spreading

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Study Component A: Receiving Stream Sampling

Sampling Locations

1. Upstream of the effluent discharge
2. Within the immediate mixing zone of the stream and effluent
3. Downstream of the primary mixing zone

Sample Types

1. Water
   - ✓ Flow proportional composite, or composite of discrete grabs
   - ✓ Phase separation in the lab if necessary
2. Bed Sediment
   - ✓ Composite of multiple cores
   - ✓ Wet-sieved in the lab
   - ✓ De-watered by centrifugation

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Study Component A: Supporting Info

Collected On-Site
1. Influent and Effluent Discharges
2. Receiving Stream Flow/Discharge
3. pH, SpCond, T, DO (within plant and in the stream)
4. Records of treatment chemicals added to process streams
5. Records of sludge generated or pumped

Measured in the Laboratory
1. Total suspended solids (influent and effluent)
2. Suspended particulate matter at in-stream locations
3. Dissolved organic carbon in effluent and at in-stream locations

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Study Component A: Deliverables

Concentrations

1. Levels (ng/L) of each PFAS compound in all aqueous phases, in-facility and in-stream
2. Levels (ng/g) of each PFAS compound in all particulate and solid phases, in-facility and in-stream

Fluxes

1. Discharges to POTW (influent) and from POTW (effluent) [mg/day) of each PFAS compound
2. Receiving stream discharges: upstream, in-mixing zone and downstream, of each PFAS compound

QA/QC Summary

1. Field Blanks
2. Field Duplicates
3. Field Spikes
4. Uncertainty metrics

"Mass Balances"

1. Total retention with the treatment facility (influent –effluent) for each PFAS compound
2. Losses/Gains of each PFAS compound at selected points in the treatment process
3. Comparison of total in-facility retention with sludge masses for each PFAS compound
4. In-stream retention of each PFAS compound at 2 sites
5. Comparison of in-stream retention with bed-sediment masses

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Study Component B: Objectives

(1) Provide a critically needed assessment of the ***presence and persistence*** of PFAS compounds in municipal biosolids-impacted agricultural fields – foundational information that is currently lacking

(2) Provide new information on the impacts of land-spreading of municipal biosolids on soil-water and shallow groundwater

(3) Provide information on “background” levels of PFAS in selected regional groundwaters

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Study Component B: Key Questions

1) What fractions of the biosolids applied PFAS can be accounted for within the soil horizons? Are significant export/loss processes indicated?
2) Are there substantive differences in the retention characteristics of specific PFAS compounds (i.e. does the "fingerprint" of applied PFAS look different that than measured in the fields), and how does this difference (if any) change over time?
3) What are the absolute and relative half-lives of specific PFAS compounds in an agricultural field environment? Can the differences be related to the chemical structure of the PFAS compounds?
4) Does the presence/magnitude of PFAS in soil water suggest that movement of PFAS through the soil column could be significant?
5) What are the partition coefficients of PFAS compounds between soil and soil-water?

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Study Component B: Key Questions

6) Is PFAS loss to the atmosphere (volatilization) a likely loss pathway?
7) If the two study systems have contrasting soil properties, how is relative PFAS retention in the soils related to these properties?
8) Does shallow groundwater in the proximity of the study fields exhibit PFAS levels elevated above that of regional groundwater, suggesting impacts from the fields? Which PFAS compounds appear to most mobile in this regard? Can this mobility be related to structural properties of the PFAS compounds?
9) How does the mobility of PFAS in the soil system compare to other species of concern, such as nitrogen and phosphorus species?

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Study Component B: Structure

- 2 agricultural systems that currently and/or historically have received land-spread municipal biosolids from POTW facilities with known high PFAS loading will be studied. PFAS levels in biosolids and fields will be screened before final selection.
- The specific field experimental design is subject to identification of appropriate systems of fields with well-documented provenance of biosolids application, but in general two designs are under consideration:

(a) Within one uniform geographical/geochemical landscape a range of treatment fields representing a gradient in total mass of biosolids applied over a generally similar timeframe. Best if the field applications were performed within the past few years. Active spreading not a pre-requisite.

(b) Within one uniform geographical/geochemical landscape a range of treatment fields representing generally similar total mass of biosolids applied, but over a gradient of time (years) within the past few years. Active spreading not a pre-requisite.

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Sampling Plan for Biosolids-Impacted Fields

Quantify PFAS in the *fields that have received biosolids*

- ❑ **Soils**
  - ✓ **Within the tilled/rooted zone (upper 25 cm)**
  - ✓ **Below the tilled/rooted zone (25-50 cm)**
  - ✓ **Multiple samples (approx. 12) from a given zone within a given field will be composited (n=3)**
- ❑ **Mobile Soil-Water**
  - ✓ **Sampled with lysimeters**
  - ✓ **Installed two per field, sampled regularly and after significant rain events**
- ❑ **Source Biosolids**
- ❑ **The field design will incorporate 3-4 treatment fields (gradient of PFAS loading and/or time of biosolids application) and one control field**
- ❑ **Sampled on at least two dates over the 9-month study period of non-frozen soils**
- ❑ **The study team has experience in agricultural field sampling**

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Surface water runoff may be sampled if field-edge runoff monitoring infrastructure can be placed/funded.

Groundwater Sampling

Quantify PFAS in ***groundwater samples near the study sites:***

- ❑ **Shallow wells or monitoring wells** in the vicinity of the biosolid-impacted fields will be sampled
- ❑ **Regional deep groundwater** will be sampled from homes and public water supplies
- ❑ Samples collected every four months for a period of 9-12 months

We will pursue supplemental funding to enable Geoprobe sampling of shallow groundwater underlying the study fields.

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Study Component B: Supporting Info

Collected On-Site
1. Exact location of soil cores
2. Temperature of the soils
3. Physical classification of the soils
4. pH, SpCond, T, DO of the groundwaters

Measured in the Laboratory
1. pH and SpCond of the soil water
2. Major cations and anions in the soil water
3. Major cations and anions in the groundwaters
4. Dissolved organic carbon in the soil water and groundwaters
5. Organic carbon in the soils

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Study Component B: Deliverables

Concentrations

1. Levels (ng/L) of each PFAS compound in all **soil water** samples
2. Levels (ng/L) of each PFAS compound in all **ground water** samples
3. Levels (ng/g) of each PFAS compound in all **soil** samples
4. Levels (ng/L) of each PFAS compound in all field-adjacent **runoff** and/or **stream samples** (if collected)

Fluxes

1. Estimates of the flux of each PFAS compound via movement of soil water through the vadose zone [mg/day/ha]
2. Net transport/transformation fluxes (see mass-balance below) of each PFAS compound

QA/QC Summary

1. Field Blanks
2. Field Duplicates
3. Field Spikes
4. Uncertainty metrics

"Mass Balances"

1. Comparison of estimated PFAS loading from biosolids with PFAS quantities present in the soils and soil-water for each PFAS compound
2. Estimates of total losses/retention of each PFAS compound based upon "1".

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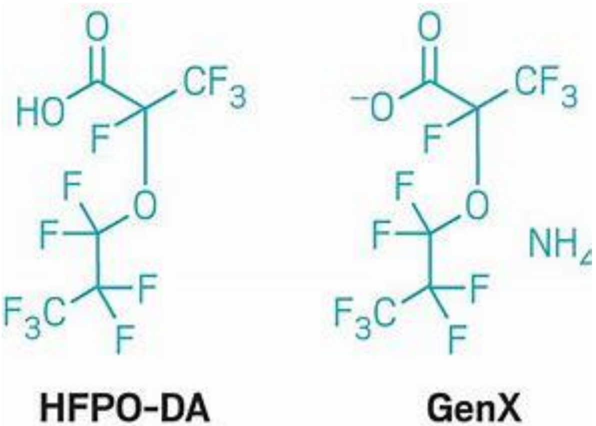
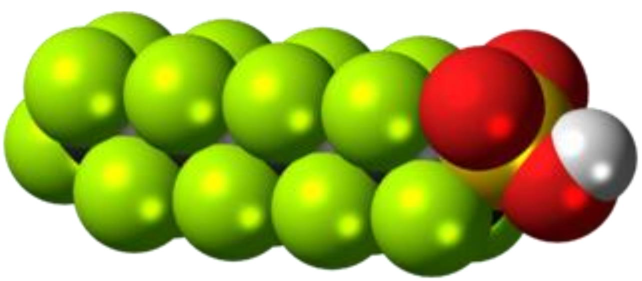
Questions …… Thank You





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