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In collaboration with



**Project Name**

National Collaborative Land Application Study

Scope of Work

**Prepared by**

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In addition, a post-doc will be hired specifically for this project.

PROJECT DESCRIPTION

**Project Goals**

Overall Goal:

Evaluate whether or not land application of municipal biosolids is a significant route of human exposure to PFAS.

**Specific Objectives**

Year 1

1. From field studies, evaluate incidence of soil borne PFAS derived from biosolids, following long and short term land application.
2. Evaluate mobility of soil borne PFAS through soil and vadose zone.
3. Evaluate PFAS concentrations in groundwater located beneath land application plots.

Year 2

1. Evaluate crop uptake of PFAS from land applied plots.

**Scope of Project, Year 1**

The project will be national in scope through evaluation of 25-30 different sites across broad geographic regions, with differing climates, soils, and depths to groundwater, including irrigated and non-irrigated soils. The depth of the obtained data set will inform USEPA risk assessment to determine whether long term land application of typical municipal biosolids increase soil concentrations of PFAS to levels that threaten groundwater contamination or excessive crop uptake.

Additionally, the project will provide robust field data to calibrate modeling that predicts the distribution of PFAS in soil and groundwater associated with land applied biosolids and other means of entry.

**Major Project Outcomes**

1. Provide credible and validated data to inform USEPA’s screening level risk assessment model that predicts whether land application sites are a significant public health route of exposure to PFAS via contamination of groundwater or crop uptake.
2. Documentation of the sustainability of land application at sites where the risk of human PFAS exposure is low.
3. Site specific data on soil, groundwater and biosolids PFAS concentrations.
4. Outreach and education on the benefits of land application via national and international meetings.
5. Interaction and collaboration with EPA.

**Unique Aspects of National Collaborative Project**

There are three aspects of this project that are critically unique:

1. This is a national project evaluating soil and water PFAS concentrations at land application sites across the nation.
2. The proposed research methods and analyses for each site will be identical, allowing for a direct comparison of data nation-wide.
3. Quantitative field data will allow for testing of models used for screening and risk assessments.

**Site Selection**

There will be 25-30 sites selected across broad geographic regions with different climate zones, soils, and depths to groundwater. Sites will include irrigated and non-irrigated agricultural plots.

Necessary criteria to be eligible for the project include:

* Long-term (>5 years) land application
* Known application rate of biosolids
* Control sites with no biosolids applied
* If possible, multiple application rates (two different rates)
* Any soil PFAS data from prior years
* Rainfall or irrigation data, if possible
* Soil characterization data
* Depth to groundwater
* PFAS analytical data from biosolids, if available

Of these, the first three criteria are essential.

**Soil Sampling at Unique Sites**

One-time soil samples from each site will be collected by site personnel pro bono. Site personnel will include farmers, biosolids managers, and academic researchers with long-term land application plots.

* Plots to be sampled:
  + Control (no biosolids)
  + Land applied plots with two different loading rates
* Soil depths: 1 ft, 3 ft, 6 ft (perhaps surface sample if no-till management is employed)

If depth to groundwater is less than six feet, a surface (1 ft) sample will be collected plus a sample at a depth halfway to the groundwater depth.

* For all soil samples, the top one inch of soil will be discarded to avoid PFAS contamination from atmospheric deposition.
* Soil sample size = one pound (1 lb) per sample
* Number of replicates = 3
* Controls: A field blank will also be included for analysis.
* Total number of soil cores per site: 3 replicates x 3 different plots = 9
* Total number of samples per site: 9 soil cores x 3 soil depths = 27 soil samples.
* Time of sampling
  + Soil must be dry or field moist, but not saturated.
  + Sites in the northern sections of the US will be sampled in the spring, summer, or fall (not winter when soils may be frozen).

**Water Sampling at Unique Sites**

For irrigated sites, irrigation water will be collected during an irrigation event or from wells, if available.

For non-irrigated sites with shallow water tables, groundwater itself will be sampled. These water samples plus corresponding soil samples allow for paired data sets.

**Biosolids Samples**

Municipal biosolid samples (Class A or B) will be collected after undergoing full wastewater treatment. The samples will be taken from material that is going to be land applied. Since PFAS concentrations in biosolids are typically at the ppb level, contamination is not a major issue for biosolid sampling. Generally, cake biosolids will be obtained for samples.

**Sampling Procedures**

Per- and polyfluoroalkyl substances (PFAS) are a group of anthropogenic chemicals that includes PFOA, PFOS, GenX, and many other chemicals. These chemicals are extensively used in a variety of industrial, commercial, and consumer products. Some of these products are used during routine sampling events such as plastic bottles, bags, sampling equipment, waterproof clothing, detergents, and sunscreen and insect repellent.

The potential for many sources of cross-contamination, combined with laboratory detection limits in the parts per trillion demonstrates the level of care that must be taken to collect representative samples and avoid contamination.

The objective of this protocol is to give guidance for the collection of soil samples for PFAS analysis. The sampling procedures used should be consistent with sampling guidelines and techniques found in the following documents.

The sampling team has adapted their sampling procedures by referencing the following protocols:

Michigan Department of Environmental Quality General PFAS Sampling Guidance (10/2018)

<https://www.michigan.gov/documents/pfasresponse/General_PFAS_Sampling_Guidance_634597_7.pdf>

Michigan Department of Environmental Quality Soil PFAS Sampling Guidance (11/2018)

<https://www.michigan.gov/documents/pfasresponse/Soil_PFAS_Sampling_Guidance_639407_7.pdf>

Michigan Department of Environmental Quality Groundwater PFAS Sampling Guidance (10/2018)

<https://www.michigan.gov/documents/pfasresponse/Groundwater_PFAS_Sampling_Guidance_637871_7.pdf>

Michigan Department of Environment, Great Lakes, and Energy Biosolids and Sludge PFAS Sampling (10/2019)

<https://www.michigan.gov/documents/pfasresponse/Biosolids_and_Sludge_PFAS_Sampling_Guidance_+_Quick_Reference_Field_Guide_679307_7.pdf>

**Soil Sampling Techniques**

Soil samples will be collected from a single borehole at depths below surface at one, three, and six feet. Boring methods include the use of general purpose and sand barrel augers or power flight augers. Method selection will depend on the soil type.

Soil samples will be collected directly from the barrel auger. The auger is rotated to advance the barrel into the ground. When the barrel is filled, the unit is withdrawn from the soil cavity and a sample may be collected from the barrel. Because the sample is retained inside the barrel, there is less of a chance of mixing it with soil from a shallower interval during insertion or withdrawal of the sampler.

Soil from the barrel will be released into a stainless steel mixing bowl and then transferred into a one liter high-density polyethylene (HDPE) bottle for transport to the laboratory. Soil samples will be weighed, sieved, weighed again, and reduced by riffle splitter before analysis.

Dewatered Cake Biosolids samples will be collected from appropriate wastewater reclamation facilities (WRF). Dewatered Cake Bio-solids samples will be collected directly from the dewatering unit sampling port into HDPE sample containers.

Irrigation well water samples adjacent to the soil sampling sites will be collected directly from the discharging well. Groundwater samples will be taken directly when depth to groundwater is shallow (<6ft).

**Field Equipment, Clothing, and PPE**

Prevention of Contamination: Potential sources of PFAS cross-contamination are extensive and prolific. As such, field and equipment blanks will be collected and submitted to the laboratory for analysis.

Potential sources of PFAS cross-contamination in this sampling environment include, field clothing and PPE, sunscreen and insect repellent, personal hygiene and personal care products, food packaging, and the surrounding environment. Field and equipment blanks will be collected and submitted to the laboratory for analysis.

**Table 1: Field Equipment, Clothing and PPE**

|  |  |
| --- | --- |
| **Prohibited Items** | **Equipment Used** |
| * New clothing that is waterproof, water resistant, or stain-treated * Clothing containing Gore-Tex™, Scotchgard™, RUCO®, etc. * Clothing laundered with fabric softener * Tyvek® material * Latex gloves * Cosmetics, moisturizers, or other personal hygiene/care products on the morning of sampling that are not PFAS free * Plastic water bottles and all food wrappers | * Cotton uniform pants and shirts. Well laundered without fabric softener * Dura wear PVC knee boots * Powder free nitrile gloves * Banana Boat Sport performance Coolzone Broad Spectrum SPF 30 Suncreen * Water to be brought and consumed away from sample area |

**Containers, preservation methods, holding times**

**Table 2: Containers, Preservation Methods, Holding Times**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Parameter** | **Matrix** | **Sample Volume** | **Container** | **Preservation** | **Holding Time** |
| PFAS | Soil | 100 g | 4 oz HDPE | 0 - 4°C | 28 days |
| Percent Solids | Soil | 100 g | 8 oz HDPE | 0 - 4°C | 7 days |
| PFAS | iosolids | 250 g | 8 oz HDPE | 0 - 4°C | 28 days |
| PFAS | Water | 250 ml | 8 oz HDPE | 0 - 4°C | 28 days |
| Soil Characterization & Soil Textural Analysis | Soil | 300 g | 8 oz HDPE | None | N/A |

**Equipment Decontamination**

Soil sampling equipment will be decontaminated between sampling locations with non-phosphate LiquinoxTM detergent, PFAS-free deionized water, and methanol.

**Sample Preparation**

All soil and water samples will be sent to the University of Arizona. Soil samples will be dried and sieved (2mm). All samples will subsequently be sent to the University of Arizona Laboratory for Emerging Contaminants.

**PFAS Analysis**

The Arizona Laboratory for Emerging Contaminants will perform LC-MS/MS analysis for 25 PFAS analytes (Table 3). EPA Draft Method 1633 will be utilized for all soil, water, and biosolid samples.

**Table 3: PFAS Analytes (will be updated as methods become available)**

|  |  |  |
| --- | --- | --- |
| **CAS ID** | **PFAS Analyte** | **Acronym** |
| 375-22-4 | Perfluorobutanoic acid | PFBA |
| 2706-90-3 | Perfluoropentanoic acid | PFPeA |
| 307-24-4 | Perfluorohexanoic cid | PFHxA |
| 375-85-9 | Perfluoroheptanoic acid | PFHpA |
| 335-67-1 | Perfluorooctanoic acid | PFOA |
| 375-95-1 | Perfluorononanoic acid | PFNA |
| 335-76-2 | Perfluorodecanoic acid | PFDA |
| 2058-94-8 | Perfluoroundecanoic acid | PFUnA |
| 307-55-1 | Perfluorododecanoic acid | PFDoA |
| 72629-94-8 | Perfluorotridecanoic acid | PFTriDA |
| 376-06-7 | Perfluorotetradecanoic acid | PFTreA |
| 375-73-5 | Perfluorobutanesulfonic acid | PFBS |
| 2706-91-4 | Perfluoropentanesulfonic acid | PFPeS |
| 355-46-4 | Perfluorohexanesulfonic acid | PFHxS |
| 375-92-8 | Perfluoroheptanesulfonic acid | PFHpS |
| 1763-23-1 | Perfluorooctanesulfonic acid | PFOS |
| 68259-12-1 | Perfluorononanesulfonic acid | PFNS |
| 335-77-3 | Perfluorodecanesulfonic acid | PFDS |
| 757124-72-4 | Fluorotelomer sulphonic acid 4:2 | 4:2 FTS |
| 27619-97-2 | Fluorotelomer sulphonic acid 6:2 | 6:2FTS |
| 39108-34-4 | Fluorotelomer sulphonic acid 8:2 | 8:2FTS |
| 754-91-6 | Perfluorooctanesulfonamide | FOSA |
| 31506-32-8 | N-methylperfluorooctanesulfonamide | N-MeFOSA |
| 2355-31-9 | 2- (N-Methylperfluorooctanesulfonamido) acetic acid | NMeFOSAA |
| 2991-50-6 | 2-(N-Ethylperfluorooctanesulfonamido) acetic acid | NEtFOSAA |

**Additional Soil Analyses Needed for Modelling**

**(To be conducted by the Post-Doc on the project)**

* Texture
* Solid surface area
* Organic carbon content
* Metal-oxide content
* Clay mineralogy
* Soil pH
* Cation Exchange Capacity

**Modelling PFAS Transport through Soil and Vadose Zone**

A screening level transport model for quantifying PFAS leaching in the vadose zone and mass discharge to groundwater will be utilized (Guo et al., 2022). Data from all sites will be modelled to validate the model and also assess the risk of groundwater contamination with PFAS. The results obtained from this modeling will be compared to results obtained using the standard EPA screening method.

**University of Arizona Preparation for Sample Collection from all Sites**

* Identify potential sites based on project criteria.
* For each selected site, discuss and identify which biosolid plots will be sampled plus a control plot.
* Send written SOWs to each site with instructions on:
  + How to collect soil and water samples including sample size
  + How to avoid contamination
* Conduct webinar with video on sample collection to all selected sites.
* Send pre-sampling kit to each site
  + Containers for soil, water, and biosolid samples
  + Mechanism for pre-paid return packaging to allow sample shipment back to University of Arizona
  + Materials for decontamination

**Project Schedule**

1. Prepare video and webinar on how to sample
   * August 2022
2. Soil sampling and analysis
   * September 2022 – November 2022: Northern sites
   * December 2022 – February 2023: Southwest and Southeast sites
   * March 2023 – May 2023: Midwest, Central, and Mid-Atlantic sites
3. Data review and modeling
   * January 2023 – June 2023
4. Final Report Preparation

* July/August 2023

1. Scope of Project: Year 2

* July/August 2023

**Budget**

Note: Income continues to increase due to new pledges. The budget described here is to show that we have sufficient income for Year 1 of the research, with carryover income for Year 2.

|  |  |
| --- | --- |
| **Income** |  |
| Pledged Donations | $ 365,000 |
| Indirect Costs | $ (25,000) |
| Income Subtotal | $ 340,000 |
|  |  |
| **Expenditures** |  |
| Personnel |  |
| Post-Doctoral Associate (0.5 FTE\*) |  |
| Stipend | $ 30,000 |
| Fringe Benefits | $ 10,000 |
| Technician (soil sieving) | $ 10,000 |
| Technician (data coordination) | $ 10,000 |
| Personnel Subtotal | $ 60,000 |
|  |  |
| Soil Analyses |  |
| PFAS analysis (27 samples x 30 sites) |  |
| $187/sample x 27 soil samples/site = $5,049 |  |
| $5,049/site x 30 sites = $151,470 | $ 151,470 |
|  |  |
| Groundwater Analyses |  |
| PFAS analysis (3 samples x 30 sites) |  |
| $187/sample x 3 samples/site = $561 |  |
| $561/site x 30 sites = $16,830 | $ 16,830 |
|  |  |
| Biosolid Analyses |  |
| PFAS analysis (3 samples x 30 sites) |  |
| $187/sample x 3 samples/site = $561 |  |
| $561/site x 30 sites = $16,830 | $ 16,830 |
|  |  |
| Shipping |  |
| Kits shipped to each site ($20/site) and soil samples shipped back to the University of Arizona ($20/site) |  |
| $40/site x 30 sites = $1,200 | $ 1,200 |
| Analyses Subtotal | $ 191,940 |
|  |  |
| Total Income | $ 340,000 |
| Total Direct Costs | $ 246,330 |
| Carryover for Year 2 | $ 93,670 |

\*The other 0.5 FTE will be covered by Dr. Mark Brusseau.