Incidence and Mobility of PFAS in Soil from Land Application Sites Across the United States

A nationwide research project

Assessing the risk of PFAS from land applied biosolids as other common exposure pathways

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Ian Pepper, Regents Professor

GLOBAL DISTRIBUTIONS OF PFAS: PRESENCE IN SOILS AND WATERS

Two important papers:

– Johnson et al., 2022, *Sci., Tot. Environ.,* 841(2022)156602

Global distributions, source type dependencies, and concentration ranges of per and polyfluoroalkyl substances in groundwater

– Brusseau, et al., 2020, *Sci. Tot. Environ.,* 740(2020) 140017

PFAS concentrations in soils: Background levels versus contaminated sites

DATA COLLECTION FROM THREE TYPES OF SITES

- –**Primary PFAS source sites**: fire training areas, manufacturing plants
- –**Secondary source sites:** biosolid land application, contaminated irrigation water use, landfills
- –**No-known-source (background)** sites

SOILS: 30,000 samples from throughout the world

GROUNDWATERS: 21,000 data points from 20 counties around the world

GROUNDWATER PFAS CONCENTRATIONS

	(Median values of maximum groundwater concentrations, ppt)		
	Type of Site		
	Primary (Industrial)	Secondary (Land Application)	No-known-source (Background)
PFOS	45,700	95	30
PFOA	7,400	96	15

- Highest primary site concentrations associated with aqueous film-forming foams (AFFF sites)
- Highest no-known-source concentrations generally associated with metropolitan areas

SOIL PFAS CONCENTRATIONS

	(Median values of maximum soil concentrations, ppb)		
	Type of Site		
	Primary (Industrial)	Secondary (Land Application)	No-known-source (Background)
PFOS	4,000	350	2.7
PFOA	58	38	3.1

SUMMARY OF GLOBAL PFAS DISTRIBUTIONS

- PFAS detected in almost every soil tested and is a significant reservoir of PFAS
- Soil concentrations generally greater than groundwater concentrations
- Soil PFAS detected in ‘remote’ areas far from potential PFAS sources, i.e., ‘Background’ levels
- Primary, e.g. AFFF and industrial sources of PFAS orders of magnitude greater than secondary, e.g., land application sites

HEALTH ADVISORIES FOR PFOS AND PFOA

- **EPA Health Advisory Levels for Drinking Water**
  - January 2009
    PFOS = 200 ng/L (ppt)
    PFOA = 400 ng/L (ppt
  - May 2016 Health Advisory Level for Drinking Water
    Combined PFOS + PFOA not to exceed 70
    ng/L (ppt)
  - June 2022 Health Advisory Levels for Drinking Water
    PFOS =0.02 ppt PFOA = 0.004 ppt
- **Proposed New EPA Drinking Water Regulation: 4 ppt**
  - Even 1 ppt is equivalent to 1 second in 31,700 years

PFAS AND BIOSOLIDS

PFAS Potential Exposure from Biosolids

–Direct exposure (minimal risk)

–Indirect exposure

  -drinking water

  -plant/animal uptake

–Bioaccumulation

PFAS THREAT TO LAND APPLICATION

A nationwide research project

National Collaborative Project Overall

To evaluate whether or not land application of biosolids is a significant public health route of exposure to per- and polyfluoroalkyl substances (PFAS)

SPECIFIC OBJECTIVES

- At land application sites nationwide, measure:
  - **Incidence of PFAS in soil** following long-term land application of biosolids and at various soil depths
  - **Assess Mobility** (leaching) of PFAS analytes through soil and vadose zone
  - **Evaluate PFAS in groundwater** to create paired data sets of soil and water PFAS concentrations
  - **Crop uptake of PFAS analytes**, utilizing paired data sets of soil PFAS concentrations versus plant uptake

UNIQUE ASPECTS OF THE NATIONAL COLLABORATIVE PROJECT:
How is it different from EPA-funded research on PFAS?

- **Nationwide scope will include a variety of different soils, depths to groundwater, and climates, by studying land application plots across the entire United States, including irrigated and non-irrigated soils.**
- **Research methodology at each site will be identical, allowing for direct comparison of data and a national set of real-world field data**
- Study will provide for robust, calibrated model development
- Quantitative data will allow for risk assessments on specific sites
- Municipal biosolids not industrially contaminated

STANDARDIZATION OF RESEARCH

- All PFAS analyses conducted by the same lab
- Strict sampling & analysis protocol followed at all sites.
- Soil, groundwater, and plant samples collected from long-term land application sites with known biosolids loadings
- All soil samples sent to University of Arizona prior to being sent to University of Arizona Laboratory for Emerging Contaminants for PFAS analysis (ALEC)

OUTLINE OF WORK FOR YEAR 1

Soil Sample Collection at Select Sites

- Soil samples taken at 1, 3 and 6 feet depths from the surface

- Groundwater samples taken allowing for data pairing soil PFAS levels with groundwater PFAS levels

- Samples collected from across the U.S.
  - Farmers with long-term land application plots, with records of biosolid loading rates
  - Academic researchers with established long-term land application plots with known biosolids applications at different loading rates
  - We anticipate at least 30 sample sites across broad geographic regions

27 Total Soil Samples

3 plots/site x 3 cores/plot x 3 samples/core

Control agricultural plot

Lower biosolids rate plot

Higher biosolids rate plot

Proposed PFAS Analytes

PFAS ANALYSIS

- Analysis at ALEC ($187/sample)

Source: Target and Nontarget Screening of PFAS in Biosolids, Composts, and Other Organic Waste Products for Land Application in France. 2022. *Environ. Sci. Technol.* 56, 10, 6056-6068.

EPA Draft Method 1633

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 RESOURCES

- Dr. Brusseau (University of Arizona) will evaluate PFAS transport through pristine soils
- Research will be at the University of Arizona WEST center via a $1.3m Department of Defense grant.
- Data will allow for an evaluation of the effects of biosolids on mobility, relative to non-biosolid PFAS transport and will aid in model development

SCOPE OF WORK IN YEAR 2: CROP UPTAKE STUDIES

- Evaluation of crop uptake.
- At harvest, various edible portions of plants will be analyzed for PFAS.
- Allow for paired data sets of soil and plant PFAS concentrations

MODELLING THE DATA

- Guo Bo and Mark Brusseau have developed a “Screening Level Model” for PFAS leaching (Advances in Water Resources 160 (2022) 104102)
- Lab evaluation of model already conducted
- Field evaluation will utilize paired data sets from the national project
- Data from land application used to predict extent of leaching e.g., biosolid loading rate and PFAS concentration, soil texture
- Site specific evaluation of risk for groundwater contamination

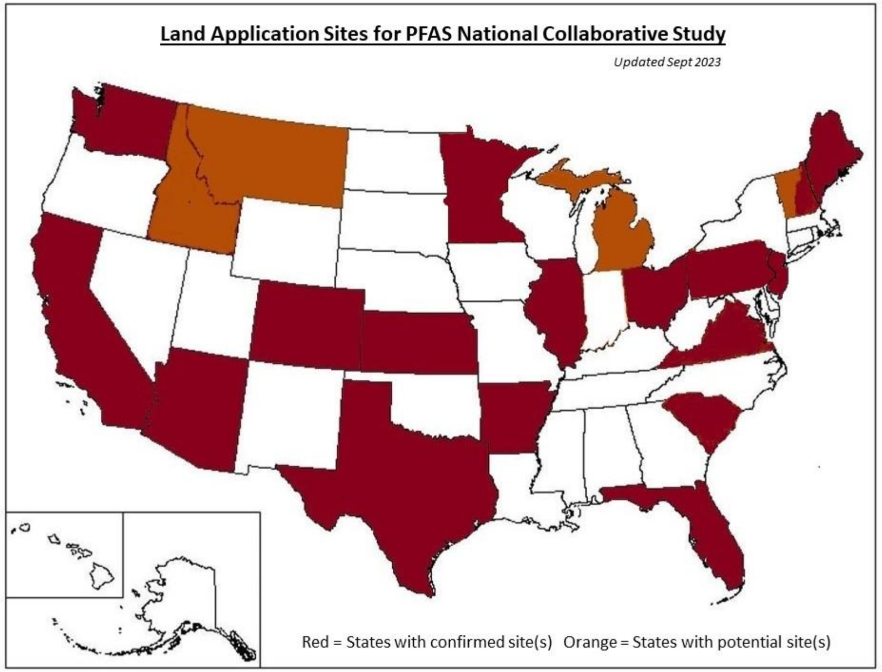
SPECIAL SOIL ANALYSES NEEDED FOR MODELLING

- Texture
- Solid surface area
- Organic carbon content
- Metal-oxide content
- Clay mineralogy
- Soil pH
- Soil-water characteristic

POTENTIAL SITES TO BE SAMPLED (to date)

- We already have potential sites identified in 10 states nationally and anticipate many more.

- Necessary criteria to be eligible for the project
  - Long-term (>10 years) land application
  - Known loading rate of biosolids
  - If possible, multiple loading rates (2 or 3 different rates) plus control (no biosolids)
  - Any soil PFAS data from prior years
  - Rainfall or irrigation data, if possible
  - Soil characterization data, if possible
  - Depth to groundwater
  - PFAS analytical data from biosolids, if available



SITES SAMPLED TO DATE

- Arizona (2 sites)
- South Carolina
- Florida
- Texas
- Illinois
- Arkansas
- New Jersey
- Southern California
- Northern California
- Washington
- Kansas (2 sites)
- Virginia
- Colorado
- Ohio (in progress)

APPROACH IN MODELING THE DATA

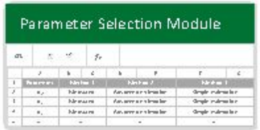
1) Collect and analyze all soil PFAS data
2) Identify which sites should have soils characterized
   - sites with paired datasets (soil and groundwater)
   - sites with measured>background or unique PFAS values
3) Input data per specific sites, run model
4) Compare predicted PFAS groundwater concentrations with actual concentrations

PFAS-LEACH – A Comprehensive Decision Support Platform for Predicting PFAS Leaching in Source Zones

Bo Guo & Mark Brusseau, University of Arizona

- i. Four models spanning a wide range of complexity
- ii. Comprehensive parameter selection module
- iii. Documentation and user manual

Utility Toolbox



Applications:

-Simulate retention & transport in multiphase systems

-Quantify mass discharge to groundwater

-Support risk assessments for soil-groundwater route

-Determine soil screening levels

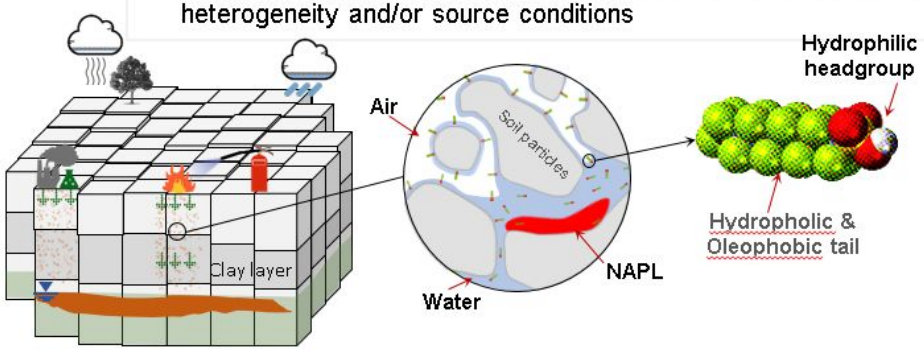
-Determine remedial action targets

-Evaluate remedial action performance

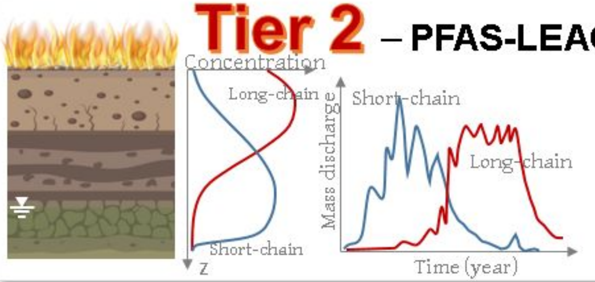
Tier 1 – PFAS-LEACH-COMP

Features: Full-process model in 3D

- *Anticipated application:* Sites with sufficient data; complex spatial heterogeneity and/or source conditions



Tier 2 – PFAS-LEACH-HYDRUS HYDRUS-1D GUI

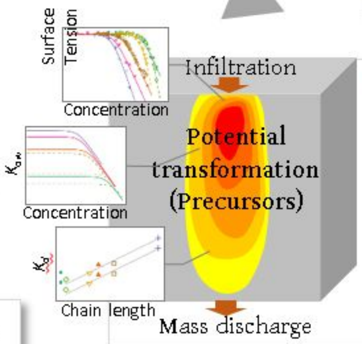


Features: Implemented in HYDRUS-1D GUI

- Mode 1: surfactant-induced flow neglected
- Mode 2: Assuming steady-state flow

Anticipated application: Insignificant lateral heterogeneity; uncertainty quantification

Tier 3 – PFAS-LEACH-Screening Excel

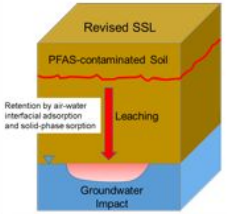


Features: Implemented in Excel

- Mode 1: Analytical solutions of linearized 1D transport equation
- Mode 2: Simple compartment model to compute source attenuation and mass discharge

Anticipated application: Limited data; early stage of site management; order-of-magnitude estimate.

Tier 4 – PFAS-LEACH-DAF



Features: Revised EPA dilution-attenuation model

- Simplified mass-balance calculations

Anticipated application: Initial screening of sites

Computational Cost & Input Parameters

Model Complexity

Example Preliminary Data – Site 5 (PFAS soil concentrations, ppb)

	Control (no biosolids)			Low Rate Biosolids (6.6 tons/acre)			High Rate Biosolids (8.8 tons/acre)		
Plot Depth	**1’**	**3’**	**6’**	**1’**	**3’**	**6’**	**1’**	**3’**	**6’**
PFOS	ND	ND	ND	0.062	ND	ND	0.048	ND	ND
	ND	ND	ND	ND	ND	ND	0.034		
	ND	ND	ND	0.10	0.04	ND			
PFOA	0.014	0.026	0.016	0.044	ND	0.012	0.027	0.016	0.004
	0.018	0.011	0.009	0.062	ND	0.013	0.020		
	0.01	0.024	0.042	0.181	0.013	0.009			

Low Rate: 6.6 tons/acre (lifetime load), 2016-2022, 7 applications over 7 years
High Rate: 8.8 tons/acre (lifetime load), 2016-2022, 7 applications over 7 years

Example Preliminary Data – Site 1 (PFAS soil concentrations, ppb)

	Control (no biosolids)			Low Rate Biosolids (13 tons/acre)			High Rate Biosolids (40 tons/acre)		
Plot Depth	**1’**	**3’**	**6’**	**1’**	**3’**	**6’**	**1’**	**3’**	**6’**
PFOS	2.280	0.469	0.087	1.204	<0.002	<0.002	3.412	<0.002	<0.002
	2.131	<0.002	<0.002	2.270	0.041	<0.002	1.797	2.093	0.295
	2.214	0.467	0.420	0.533	<0.002	<0.002	2.700	<0.002	0.327
PFOA	0.326	0.169	0.083	0.576	0.058	0.038	0.395	0.080	0.095
	0.337	0.107	0.078	0.262	0.074	0.052	0.225	1.508	0.107
	0.296	0.174	0.226	0.155	0.063	0.021	0.380	0.093	0.116

Low Rate: 13 dry tons/acre (lifetime load), 1987-2019, 6 applications over 32 years
High Rate: 40 dry tons/acre (lifetime load), 2014-2019, 6 applications over 5 years

Example Preliminary Data – Site 3 (PFAS soil concentrations, ppb)

	Control (no biosolids)			Low Rate Biosolids (36.4 tons/acre)			High Rate Biosolids (52.6 tons/acre)		
Plot Depth	**1’**	**3’**	**6’**	**1’**	**3’**	**6’**	**1’**	**3’**	**6’**
PFOS	0.307	0.010	<0.006	6.11	5.32	6.56 R*	77.1 R*	26.9 R*	23.4 R*
	0.141	0.017	0.058	7.73 R*	5.146	4.22	48.4 R*	27.4 R*	13.9 R*
	0.637	<0.006	<0.006	24.2 R*	7.702	15.5 R*	102 R*	16.7 R*	2.95 R*
PFOA	0.242	0.044	0.077	1.07	1.15	1.88	9.90 R*	8.36	9.54 R*
	0.301	0.117	0.189	4.65	6.00	3.32	10.8 R*	12.1 R*	12.8 R*
	0.187	<0.006	0.092	4.83	9.93 R*	4.30	9.08 R*	10.2 R*	18.9 R*

R* = sample result exceeds calibration range

Low Rate: 36.4 dry tons/acre (lifetime load), 1996-2016, 76 applications over 20 years

High Rate: 52.6 dry tons/acre (lifetime load), 1997-2022, 38 applications over 25 years

QUESTIONS?

PROJECT IS SUCCESSFULLY UNDERWAY

CONTACTS:

- Ian Pepper (Univ. of AZ), PI
  - **ipepper@arizona.edu** or 520-307-4396
- Greg Kester (CASA)
  - **gkester@casaweb.org** or 916-844-5262