IS LAND APPLICATION OF BIOSOLIDS A SIGNIFICANT SOURCE OF HUMAN PFAS EXPOSURE VIA GROUNDWATER CONTAMINATION?

A nationwide research project

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BLOOM WEBINAR

LAND APPLICATION IN THE U.S.

- Regulated via 40 CFR Part 503 Federal Regs (1993)
- Biosolids designated as Class A or Class B
- 7 million dry metric tons produced annually
- Land application accounts for 60% of the biosolids
  - 28% Class A
  - 29% Class B
  - 43% unknown
- Major current issue = PFAS

POLY- AND PERFLUORINATED COMPOUNDS (PFAS)

- Formerly called "perfluorinated compounds" ("PFCs")
- Family of anthropogenic chemicals used for decades to make products resistant to heat, oil stains, grease and water
- Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) most prevalent PFCs in the U.S.
- Regarded by EPA as "emerging contaminants"

Household Exposure to PFCs

- Textiles
- Carpets
- Cleaning agents
- Leather

- Baking and sandwich papers
- Ski waxes
- Gloves
- Household dust

PFOS voluntarily phased out of production in the U.S. between 2000 and 2002

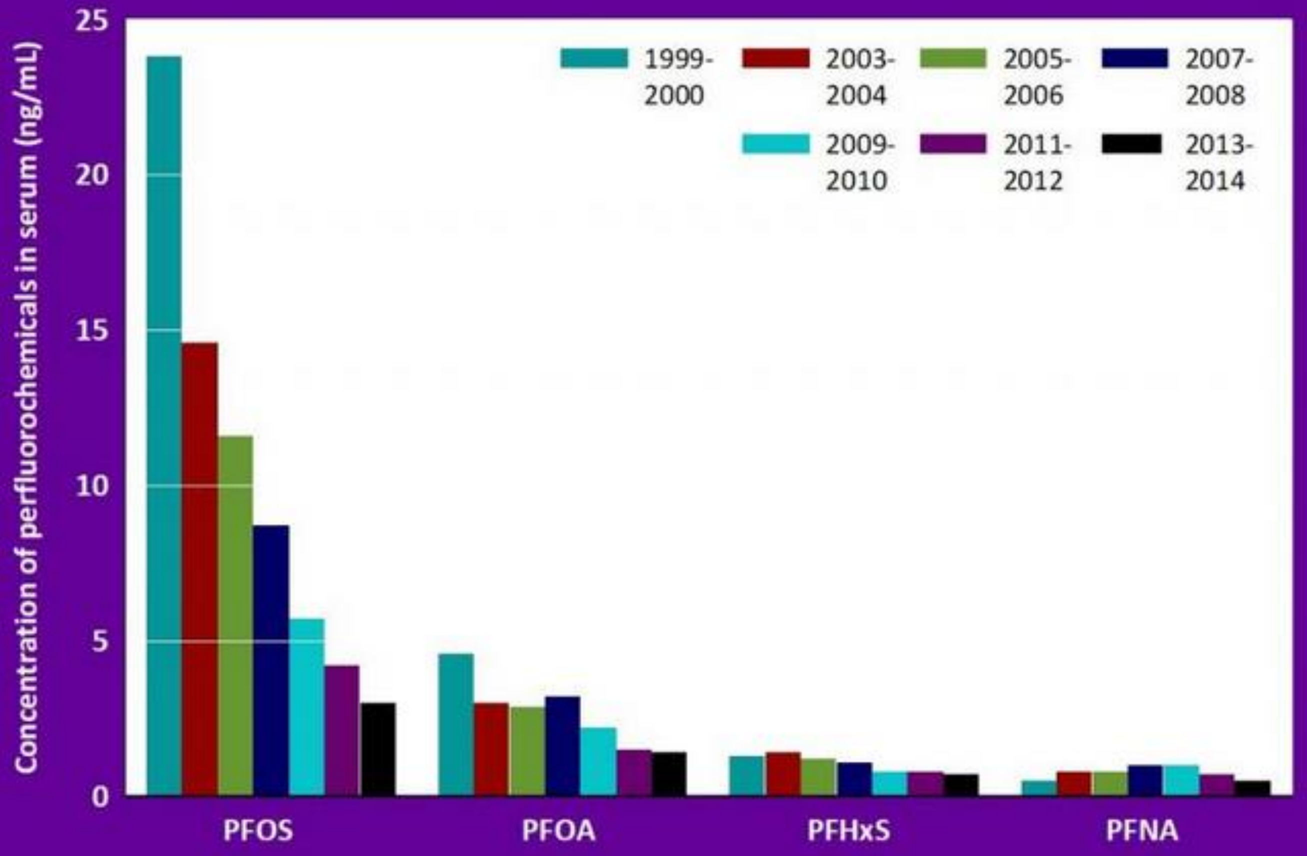
PFOA phased out by 8 major companies in the U.S. in 2006

CHARACTERISTICS OF PFOS AND PFOA (PFAS)

- Persistent in the environment, resistant to microbial degradation processes
- Found worldwide in soil, sediments, and water
- Soluble and can migrate through soils
- Almost all people in the U.S. have PFAS in their blood in parts per billion (ppb)

Indicator B6

Perfluorochemicals in women ages 16 to 49 years: Median concentrations in blood serum, 1999-2014



Data: Centers for Disease Control and Prevention, National Center for Health Statistics and National Center for Environmental Health, National Health and Nutrition Examination Survey

Note: To reflect exposures to women who are pregnant or may become pregnant, the estimates are adjusted for the probability (by age and race/ethnicity) that a woman gives birth.

America's Children and the Environment, Third Edition, Updated August 2017

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

- 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

FOCUS ON PFAS IN BIOSOLIDS

Industrially Contaminated Biosolids Used for Land Application (Lindstrom, 2011)

- Land application in Decatur, Alabama, 1995-2008
- Biosolids contaminated by effluent from industries producing PFAS, e.g., manufacturer
- 34,000 dry metric tons applied to $\simeq$ 2000 ha of agricultural fields (17 metric ton/ha)
- Surface and ground waters contaminated with PFOA at levels above EPA Health Advisory Levels

This led to scrutiny of PFAS in biosolids.

FOCUS ON PFAS IN **BIOSOLIDS**

Bioaccumulation of PFCs by Earthworms (Rich et al., 2015)

- Lab study
- Soil contaminated with PFAS
  - Nalgene 1 L bottles
- 5 worms added to each bottle
  - Industrially contaminated biosolids
  - PFOS in soil = 243 ng/g (ppb)

    – high level found only where industrial contamination has happened
- Incubated for 28 days

RESULT

- Bioaccumulation of PFAS

QUESTION: Is this realistic?

FOCUS ON PFAS IN BIOSOLIDS

Uptake of PFAS into Edible Crops (Blaine et al., 2013)

Greenhouse studies

- Soil contaminated with PFAS
  - Industrially contaminated biosolids
  - Biosolids applied at 10x agronomic rate
- Pot study!!
  - Lettuce grown and shown to take up PFCs
  - PFOS levels in soil ≃ 100 ng/g (ppb)

- Spiked (unrealistic) studies show uptake of PFAS

Field Studies

- Municipal and industrial biosolids applied up to 10x agronomic rate
  - maximum PFOS soil level ≃ 14 ng/g (ppb)
  - PFOS in corn grain below the level of detection

Author quote:
"… crops grown on soils amended with municipal biosolids (not impacted by PFAA industries) are unlikely to be a primary source of PFC exposure."

CLASSIC RESEARCH MISTAKES

Research Mistake #1:

Pot studies instead of field studies

Research Mistake #2:

10x agronomic rate is not the same as 10 years at 1x rate

Research Mistake #3:

Spiked chemicals not the same as chemicals within biosolids

CONCERN OVER PFAS IN BIOSOLIDS AND LAND APPLICATION

- IN JANUARY 2020 CONCERN OVER PFAS LED TO PIMA COUNTY ARIZONA BOARD OF SUPERVISORS (IN TUCSON) IMPOSING A MORATORIUM ON LAND APPLICATION OF BIOSOLIDS IN PIMA COUNTY
- Biosolids subsequently landfilled, resulting in cost increase of $1.3m to $3.3m annually
- Land application recently banned in Maine, USA

IS LAND APPLICATION A MAJOR SOURCE OF PFAS?

COLLABORATIVE STUDY BETWEEN UNIVERSITY OF ARIZONA AND PIMA COUNTY WASTEWATER

Field study implemented in Pima County in March 2020

- Surface and depth soil samples collected from agricultural plots that had received **known loadings of biosolids since 1984**
- Analyzed for PFAS
- Biosolids and groundwater samples also assayed
- Appropriate controls also utilized

PROJECT SAMPLE PLAN CRITERIA

Field Type	Agriculture	Irrigated with groundwater	Cumulative biosolids applied	Duration of application (years)
Undisturbed	No	No	None	--
Agricultural	Yes	Yes	None	--
Group 1	Yes	Yes	≤20 (tons/acre)	4-9
Group 2	Yes	Yes	21-30 (tons/acre)	12-20
Group 3	Yes	Yes	>30 (tons/acre)	6-9

PREVENTING CONTAMINATION

Field Clothing and PPE	
Prohibited Items	**Acceptable Items**
• New clothing that is waterproof, water resistant, or stain-treated • Clothing or footwear containing Gore-Tex™, Scotch Gard™, RUCO®, etc. • Clothing laundered with fabric softener • Latex gloves • Cosmetics, moisturizers, or other personal hygiene/care products on the morning of sampling that are not PFAS free • Plastic water bottles and food wrappers	• Boots made with polyurethane and PVC for wet conditions, or rubber overboots (“chicken boots”) • Reflective safety vests, Tyvek®, Cotton clothing, synthetic under clothing, medical braces • Banana Boat Sport performance Coolzone Broad Spectrum SPF 30 Sunscreen • PFAS-free deionized (DI) water

PREVENTING CONTAMINATION

Sampling Equipment	
Prohibited Items	**Acceptable Items**
• Teflon® containing materials (tubing, aluminum foil) • Low density polyethylene (LDPE) • Waterproof field books/plastic clipboards or binders. • Water resistant sample bottle labels. • Tyvek® material • Sample containers made of LDPE materials • Post-It Notes • Chemical (blue) ice packs • Excel Purity Paste, TFW Multipurpose Thread Sealant, Vibra-Tite Thread Sealant • Equipment with Viton Components (need to be evaluated on a case by case basis)	• Stainless steel • High density polyethylene (HDPE) • Polyvinyl chloride (PVC) • Silicone • Acetate • Polyurethane and Polypropylene • Loose paper (non-waterproof). Clear packing tape, or lab-applied labels. • Aluminum or Masonite field clipboards • Sharpies®, pens • Regular ice • Gasoils NT Non-PTFE Thread Sealant Bentonite

PREVENTING CONTAMINATION

Required blanks to check for contamination

1) Travel Blank

- In lab, fill 500 ml HDPE container with PFAS-free di-water and CAP
- Take out into field, do not open
- Return container to lab for PFAS analysis

2) Field Blank

- In lab, fill 500 ml HDPE container with PFAS-free di-water and CAP
- In field during soil sampling, transfer the di-water into an empty HDPE container and CAP
- Return container to lab for PFAS analysis

3) Equipment Blank

- Decontaminate soil auger in the field
- Rinse clean auger with PFAS-free di-water and collect the rinsate in HDPE container
- Return container to lab for PFAS analysis

PFAS in groundwater used for irrigation - *continued*

	AGRICULTURAL SITES (no biosolids)			GROUP 1		GROUP 2		GROUP 3	
Contaminant	ng/L (ppt)			ng/L (ppt)		ng/L (ppt)		ng/L (ppt)	
PFNA	3.4	ND	0.57	ND	0.28	ND	ND	ND	0.63
PFOS	80	ND	26	ND	11	0.53	ND	ND	16
PFOA	20	ND	9.1	ND	3.1	ND	0.81	ND	5.0
PFTeA	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFTriA	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFUnA	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND indicates not-detected

PFAS IN IRRIGATED AGRICULTURAL SITES WITH NO BIOSOLIDS

Depth	1’	3’	6’	PFAS present in irrigation wells
Contaminant	µg/kg (ppb)			
PFHxA	0.09	0.06	0.05	√
PFNA	0.08	ND	ND	√
PFOS	1.85 ± 1.2	0.59 ± 0.37	0.25 ± 0.17	√
PFOA	0.26 ± 0.14	0.18 ± 0.12	0.22 ± 0.09	√
PFTeA	ND	ND	ND	
PFTriA	ND	ND	ND	
PFUnA	ND	ND	ND	
Attenuation	**N/A**	**63%**	**84%**	

N/A: Not applicable.
ND indicates not detected at the MDL.

PFAS IN IRRIGATED AGRICULTURAL SITES WITH BIOSOLIDS (<20 tons/acre)

Depth	1'	3'	6'	PFAS present	
Contaminant	µg/kg (ppb)			Biosolids	Irrigation Wells
PFHxA	0.14	0.11	ND	√	√
PFNA	0.06	ND	ND	√	√
PFOS	1.58 ± 1.76	0.29 ± 0.20	ND	√	√
PFOA	0.32 ± 0.33	0.26 ± 0.26	ND	√	√
PFTeA	ND	ND	ND	√	
PFTriA	ND	ND	ND		
PFUnA	ND	ND	ND	√	
Moisture	7.8%	9.5%	9.9%		
Attenuation	**N/A**	**82%**	**100%**		

ND indicates not detected at the MDL

PFAS IN IRRIGATED AGRICULTURAL SITES WITH BIOSOLIDS (21-30 tons/acre)

Depth	1'	3'	6'	PFAS present	
Contaminant	μg/kg (ppb)			Biosolids	Irrigation Wells
PFHxA	0.13	0.09	0.09	√	
PFNA	0.43	0.12	ND	√	
PFOS	3.11 ± 2.06	0.64 ± 0.31	0.22 ± 0.09	√	√
PFOA	0.47 ± 0.29	0.49 ± 0.18	1.65 ± 2.38	√	√
PFTeA	ND	ND	ND	√	
PFTriA	ND	ND	ND		
PFUnA	ND	ND	ND	√	
Moisture	5.3%	10.5%	10.2%		
Attenuation	**N/A**	**79%**	**93%**		

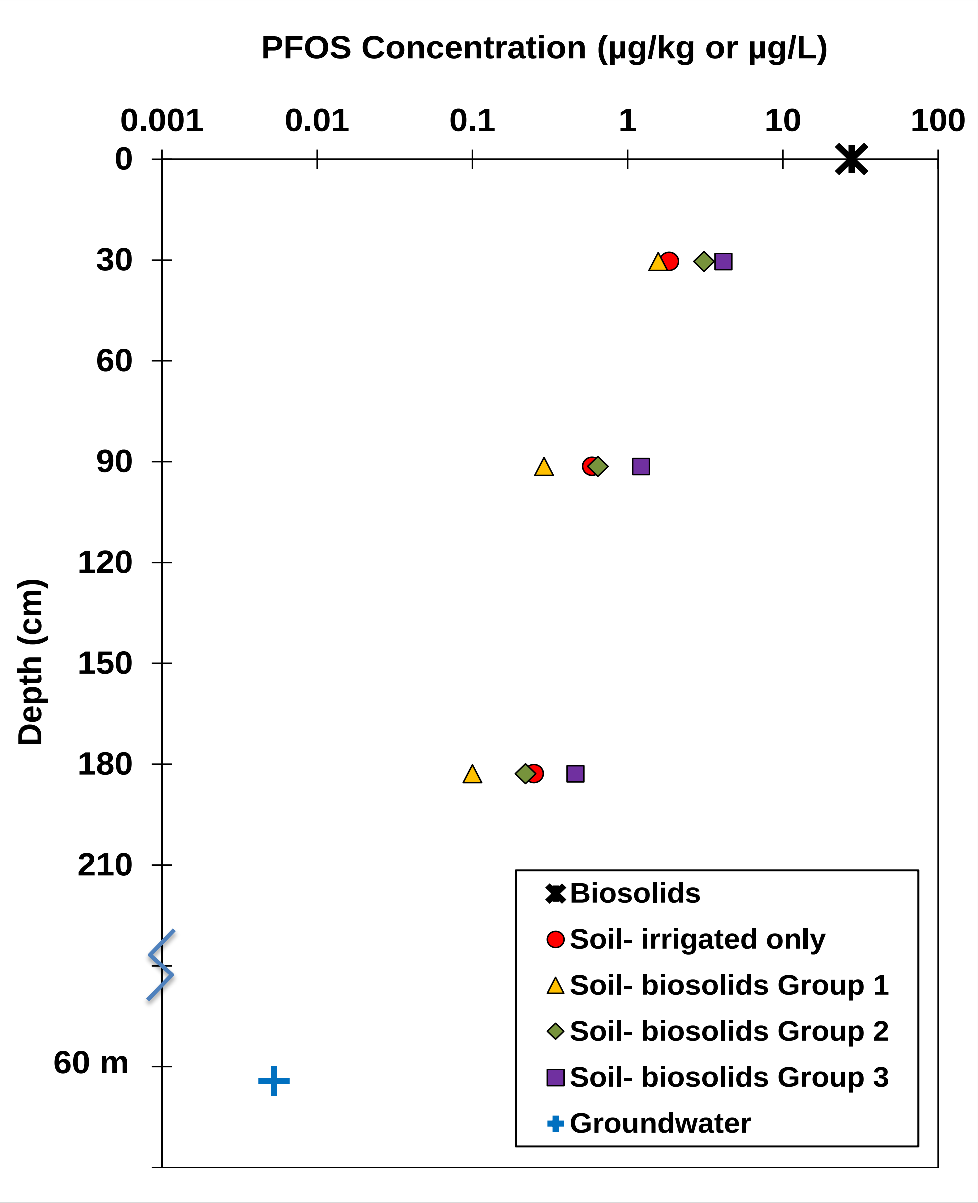
ND indicates not detected at the MDL.

PFAS IN IRRIGATED AGRICULTURAL SITES WITH BIOSOLIDS (>30 tons/acre)

Depth	1'	3'	6'	PFAS present	
Contaminant	µg/kg (ppb)			Biosolids	Irrigation Wells
PFHxS	0.12	0.15	0.16	√	√
PFHxA	0.51	0.22	0.13	√	√
PFNA	0.43	0.15	0.05	√	√
PFOS	4.13 ± 1.86	1.22 ± 1.36	0.46 ± 0.46	√	√
PFOA	0.84 ± 0.48	1.32 ± 1.43	0.51 ± 0.61	√	√
PFTeA	0.09	ND	ND	√	
PFTriA	ND	ND	ND		
PFUnA	0.10	ND	ND	√	
Moisture	9.5%	8.9%	10%		
Attenuation	**N/A**	**84%**	**90%**		

ND indicates not detected at the MDL.

Mobility OF PFOS



Mean concentrations of PFOS in biosolids, soil, and groundwater (log scale).

HIGHLIGHTS

- Low incidence of PFAS analytes in soils with long-term land application of biosolids
- PFAS soil concentrations in irrigated agricultural plots were fairly similar with or without land application of biosolids
- Biosolids and irrigation water were both sources of PFAS
- 72% attenuation of PFAS occurred within the surface 6 feet of soil

MORATORIUM ON LAND APPLICATION RESCINDED IN NOVEMBER 2020

PIMA COUNTY RESEARCH: LOCAL PROBLEM SOLVED BY LOCAL STUDY

- Study focused on incidence and mobility (where PFAS shows up after land application of biosolids)

Peer-review publication:

- *Science of the Total Environment*: 793 (2021) 148449

FOR A NATIONAL PROBLEM WE NEED A NATIONAL STUDY

THE ISSUE

- PFAS identified as causing adverse human health effects
- PFAS known to be present in wastewater and ultimately in biosolids

THE QUESTION

- Does land application of biosolids result in significantly increased human exposure to PFAS?
- Will it lead to national or state bans or severe restrictions?

ROUTES OF EXPOSURE:

- Exposure to PFAS in groundwater (leaching through soil)
- Exposure to PFAS in crops (plant uptake)

PFAS THREAT TO LAND APPLICATION

A nationwide research project

National Collaborative Project Overall Objective

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

Depth and breadth of dataset should be sufficient to:

- Provide robust field data to calibrate modeling that predicts PFAS in groundwater & crops.
- Utilize the model for site specific evaluation of land application plots with respect to PFAS

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
- Soil samples all collected at the same depths
- 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

<u>Soil Sample Collection at Select Sites</u>

- 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: All sites will grow the same crop.
- At harvest, various edible portions of plants will be analyzed for PFAS.
- Allow for paired data sets of soil and plant PFAS concentrations

QUESTION:

How do we fund it?

ANSWER:

Donations from parties interested in land application

ALREADY ESTABLISHED PARTNERS

1. **Utilities:** major wastewater treatment plant that recycles its biosolids via land application
2. **Non-Profit Associations:** Groups such as CASA, NACWA, NEBRA, MABA, NW Biosolids, Arizona Business Council are all on board. These groups in turn are well connected with utilities.
3. **Private Sector:** Companies that manage biosolids for public agencies will be contacted. These include companies like Synagro, Denali Water.

SUGGESTED FUNDING

SUGGESTED CONTRIBUTIONS

Design flow greater than 50 MGD	$25,000
Design flow between 25 and 50 MGD	$20,000
Design flow between 5 and 25 MGD	$15,000
Design flow between 1 and 5 MGD	$5,000
All others	$1,000
Non-profit associations	$3,000
Consulting firms	$5,000
Biosolids private sector management firms	$10,000

PROGRESS TO DATE

- Advisory Committee formed
- Detailed Scope of Work created
- **$450,000 pledged to date**
- Enough funding for 25 - 30 sites
- Site selection underway: 23 sites already selected
- Video produced on how to sample soils for PFAS without contamination, 20 minutes long
- Video link

FUNDING ORGANIZATIONS

Bay Area Biosolids Coalition
Brown & Caldwell
Carollo Engineers
City of Boulder
City of Fort Collins
City of Greeley
City of Los Angeles
Colorado Wastewater Utility Council
Denali Water
Galesburg Sanitary District, IL
Gate 5
Great Lakes Water Authority
Illinois Association of WW Agencies
Inland Empire Utilities Agency
Ironhouse Sanitary District
Loudoun Water
Metropolitan Washington Council of Governments
New England Fertilizer Company
North Front Range Water Quality Planning Association
Northwest Biosolids/King County, WA
Orange County Sanitation District
Pima County Regional Water Reclamation Dept, AZ
Responsible Biosolids Management, Inc.
Sacramento Regional County Sanitation District
San Francisco Public Utilities Commission
Sanitation Districts of Los Angeles County, CA
Synagro
Trinity River Authority of Texas
Virginia Biosolids
Woodard Curran

PROPOSED SCHEDULE

- Fundraising: Ongoing
- Planning: Ongoing
- Site selection: Sept-Nov 2022
- **First two sites sampled – Tucson October 2022**
- **Soil sampling continues through 2023**

MODELLING THE DATA

- Guo Bo and Mark Brusseau have developed a “Screening Level Risk Assessment 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

RESPONSIBILITIES OF EACH SITE (Pro Bono)

- One time collection of soil samples
- If available, well water or groundwater samples: three samples?
- Send samples to University of Arizona
- Collect biosolid samples and send to University of Arizona
- Send any available relevant soil or biosolid data, already collected

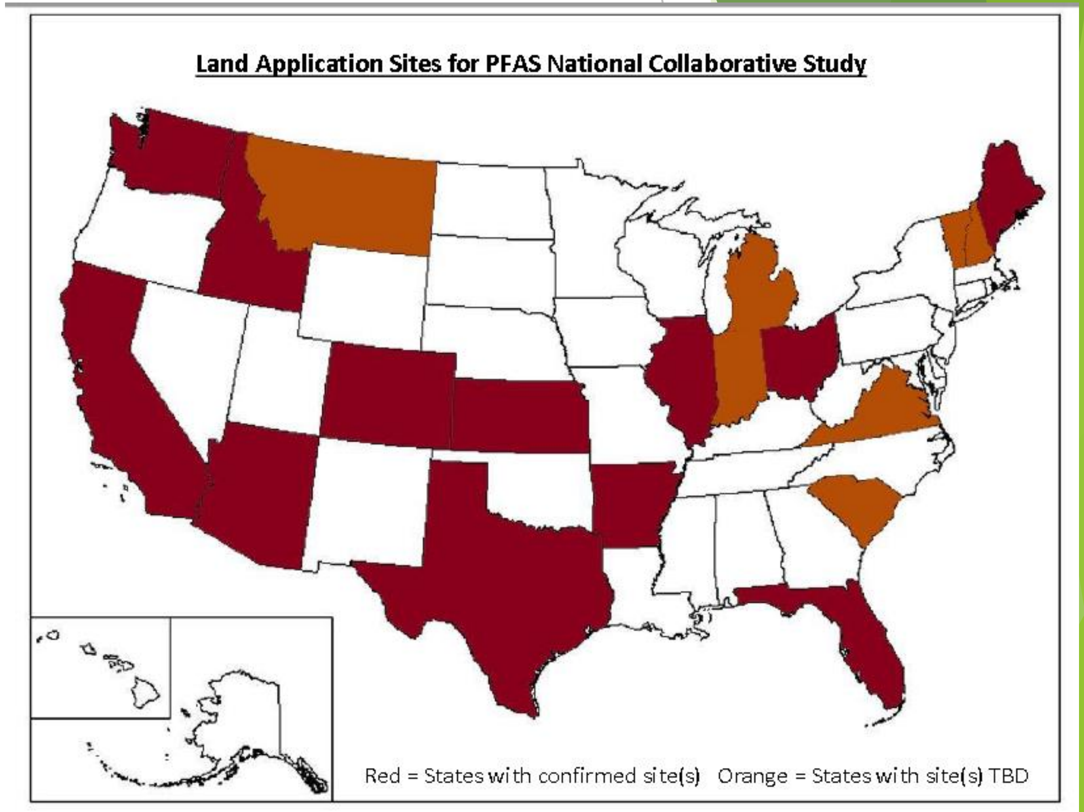
BENEFITS FOR EACH SITE

- Soil, water and biosolid PFAS data
- Co-authors of final report
- Participation in ensuring the future sustainability of land application of biosolids in the U.S.

POTENTIAL SITES TO BE SAMPLED (to date)

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

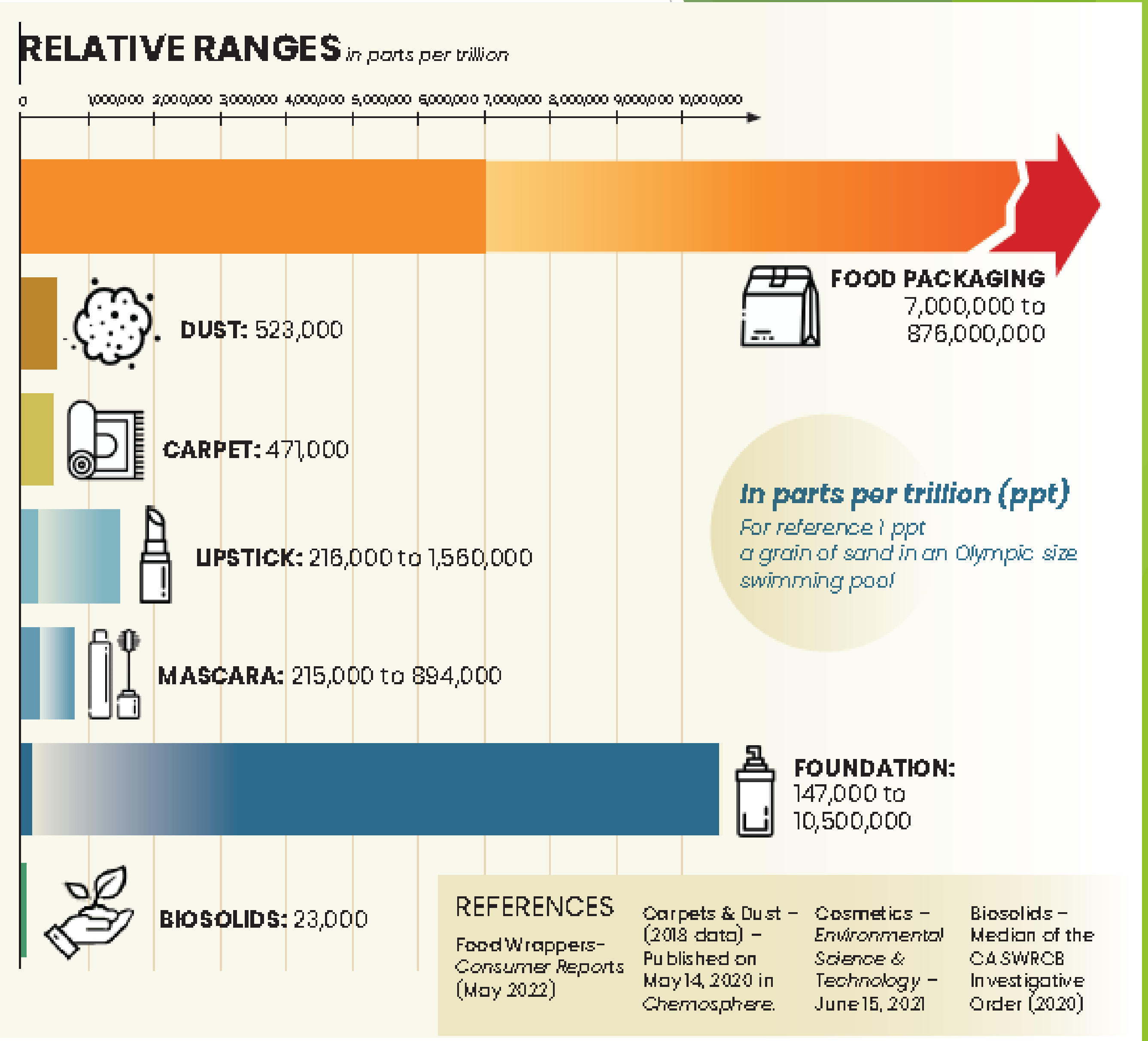
- Necessary criteria to be eligible for the project
  - Long-term (>10 years) land application
  - Known loading rate of biosolids
  - If possible, multiple loading rates (2 or 3 different rates) plus control (no biosolids)
  - Any soil PFAS data from prior years
  - Rainfall or irrigation data, if possible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



PFAS by the numbers

Per and polyfluoroalkyl substances (PFAS) are a group of manmade fluorinated compounds that have been in commercial use since the 1940's and are abundant in today's society. These chemicals are widely used for their resistance to heat, water and oil. PFAS are found in every American household, and in products as shown in the bar graph with typical concentrations. Entities providing essential public services such as safe drinking water, wastewater treatment, water recycling, biosolids recycling, and municipal solid waste management are not "users" or "producers" of PFAS but receive them as a function of their prevalent use in society.

Our collective essential public service mission is to ensure safe drinking water, wastewater treatment, and sanitation services. We embrace our role as environmental and public health stewards and our continued responsibility and commitment to providing a clean environment now and for future generations. To ensure successful achievement of our mission, we must transition away from use of PFAS in our society.



QUESTIONS?

PROJECT IS SUCCESSFULLY UNDERWAY

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