INCIDENCE AND MIGRATION OF PFAS FOLLOWING LONG-TERM LAND APPLICATION OF CLASS B BIOSOLIDS

Ian Pepper, Regents Professor

The University of Arizona

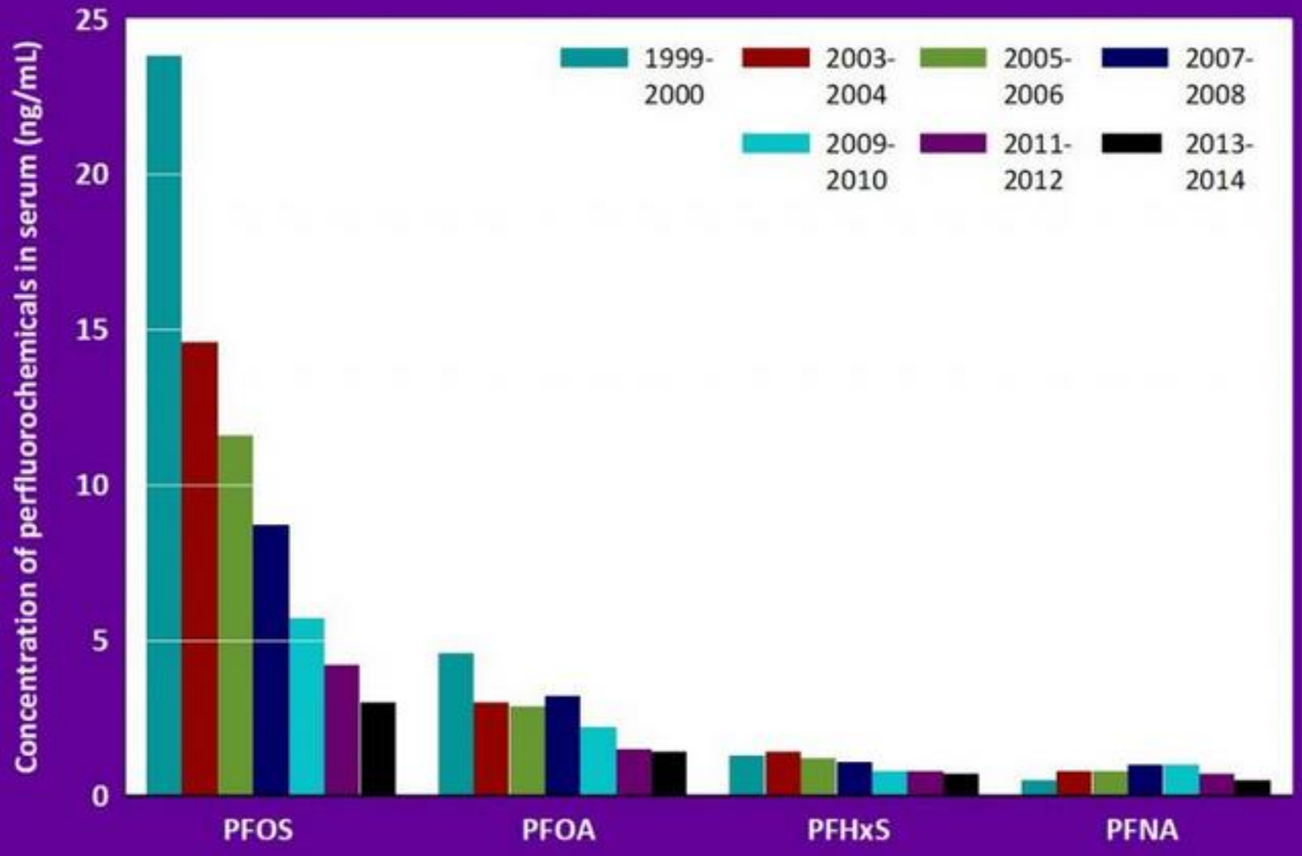
BIOFEST

September 20, 2021

Characteristics of PFOS and PFOA

- Persistent in the environment, resistant to most microbial degradation processes
- Found in soil, sediments, and water
- Soluble and can migrate through soils
- All people in the U.S. thought to have PFCs in their blood
- Can stay within human body for many years

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

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

Health Effects of PFOS and PFOA

- No consistent evidence of adverse human health effects
- BUT, potential adverse health effects cannot be excluded due to laboratory studies on rats and mice showing changes in liver and thyroid activity and reproductive problems
- International Agency for Cancer Research (IACR) has classified PFOA as a possible carcinogen, but not PFOS
- Is there a link between PFAS blood levels and susceptibility to COVID-19?

CONCLUSION: health effects unclear

Health Effects of PFOS and PFOA

- EPA Health Advisory Levels

  - January 2009

    PFOS = 200 ng/L (ppt)

    PFOA = 400 ng/L (ppt

  - November 2016

    Combined PFOS + PFOA not to exceed 70 ng/L (ppt)

PFCs and BIOSOLIDS

PFC Exposure from Biosolids

- Direct exposure (minimal)
- Indirect exposure
  - drinking water
  - plant/animal uptake
- Bioaccumulation

BIAS AGAINST BIOSOLIDS

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

- Land application in Decatur, Alabama, 1995-2008
- Biosolids contaminated by effluent from industries producing PFC materials, e.g., 3M Company
- 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 PFCs in biosolids

BIAS AGAINST BIOSOLIDS

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

- Lab study
- Soil contaminated with PFCs
  - Nalgene 1 L bottles
- 5 worms added to each bottle
  - Industrially contaminated biosolids
  - PFOS in soil = 243 ng/g (ppb)
- Incubated for 28 days

RESULT

- Bioaccumulation of PFCs

QUESTION: Is this realistic?

BIAS AGAINST BIOSOLIDS

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

Greenhouse studies

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

Field Studies

- Municipal and industrial biosolids applied up to 10x agronomic rate

  - maximum PFOS soil concentrations ≃ 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

NEW STATE REGULATIONS FOR DRINKING WATER

Massachusetts	20 ppt PFAS
California	5.1 and 6.5 ppt respectively for PFOA and PFOS

- **CONCERN OVER PFAS LED TO PIMA COUNTY BOARD OF SUPERVISORS (IN TUCSON) IMPOSING A MORATORIUM ON LAND APPLICATION OF BIOSOLIDS IN PIMA COUNTY IN JANUARY 2020**
- Biosolids subsequently landfilled since then, resulting in cost increase of $1.3m to $3.3m annually


PFAS THREAT TO BIOSOLIDS AND LAND
APPLICATION

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 2020

- Surface and depth soil samples collected from agricultural plots that had received known loadings of biosolids since 1984 and assayed 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

TRES RIOS CLASS B BIOSOLID PFAS CONCENTRATIONS

Location	TRES RIOS WRF			
Sample Date	7/16/2020	7/16/2020	7/27/2020	7/27/2020
PFAS	Units = ug/kg (ppb)			
PFBS	1.9	1.4	6.5	ND
PFHxS	3.7	3.5	15	ND
PFHxA	4.2	4	4.1	2
PFHpA	ND	ND	ND	0.15
NEtFOSAA	ND	ND	ND	11
NMeFOSAA	21	22	23	18
PFOS	34	36	27	14
PFOA	ND	ND	ND	1.2
PFNA	ND	2	2	1.1
PFDA	12	13	12	12
PFUnA	2.3	2.1	2.4	1.8
PFDoA	8	7.3	7.4	6.5
PFTriA	ND	ND	ND	ND
PFTeA	3.2	3.3	ND	ND

Non-detects on all dates: DONA; F-53B (Major); F-53B (Minor); GenX

PFAS IN GROUNDWATER USED FOR IRRIGATION

	Agriculture Only Irrigation Sources			Biosolids Amended <20 tons/acre		Biosolids Amended 21-30 tons/acre		Biosolids Amended > 30 tons/acre	
	ng/L			ng/L		ng/L		ng/L	
PFBS	**10**	ND	**3.8**	ND	**1.4**	ND	**0.68**	**0.68**	**3.6**
PFHxS	**34**	ND	**20**	ND	**7.7**	ND	**0.76**	**0.52**	**7.0**
PFHxA	**14**	ND	**8.6**	ND	**1.9**	ND	ND	**2.2**	**6.9**
PFHpA	**5.3**	ND	**3.2**	ND	**0.98**	ND	ND	ND	**1.9**
PFOS	**80**	ND	**26**	ND	**11**	0.53	ND	ND	**16**
PFOA	**20**	ND	**0.91**	ND	**3.1**	ND	**0.81**	ND	**5.0**
PFNA	**3.4**	ND	**0.57**	ND	ND	ND	ND	ND	**0.63**
PFDA	**1.9**	ND	ND	ND	ND	ND	ND	ND	**0.57**

Multiple irrigation sources are depicted for each soil group.
ND indicates not-detected.
Non-detects for all irrigation waters: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTeA; PFTriA; PFDoA; PFUnA.

PFAS SOIL CONCENTRATIONS IRRIGATED AGRICULTURAL SOILS WITHOUT LAND APPLICATION OF BIOSOLIDS.

Depth	1 foot	3 feet	6 feet	Irrigation source presence
Contaminant	**µg/kg (ppb)**			
PFBS	**0.03**	ND	ND	√
PFDA	**0.05**	ND	ND	√
PFHpA	**0.05**	**0.03**	**0.04**	√
PFHxS	**0.07**	**0.06**	**0.09**	√
PFHxA	**0.09**	**0.06**	**0.05**	√
PFNA	**0.08**	ND	ND	√
PFOS	**1.9 ± 1.2**	**0.59 ± 0.36**	**0.25 ± 0.16**	√
PFOA	**0.26 ± 0.14**	**0.18 ± 0.12**	**0.22 ± 0.09**	√
PFOS Attenuation	N/A	69%	87%	

PFAS SOIL CONCENTRATIONS IN IRRIGATED AGRICULTURAL SOILS THAT RECEIVED <20 TONS OF BIOSOLIDS/ACRE.

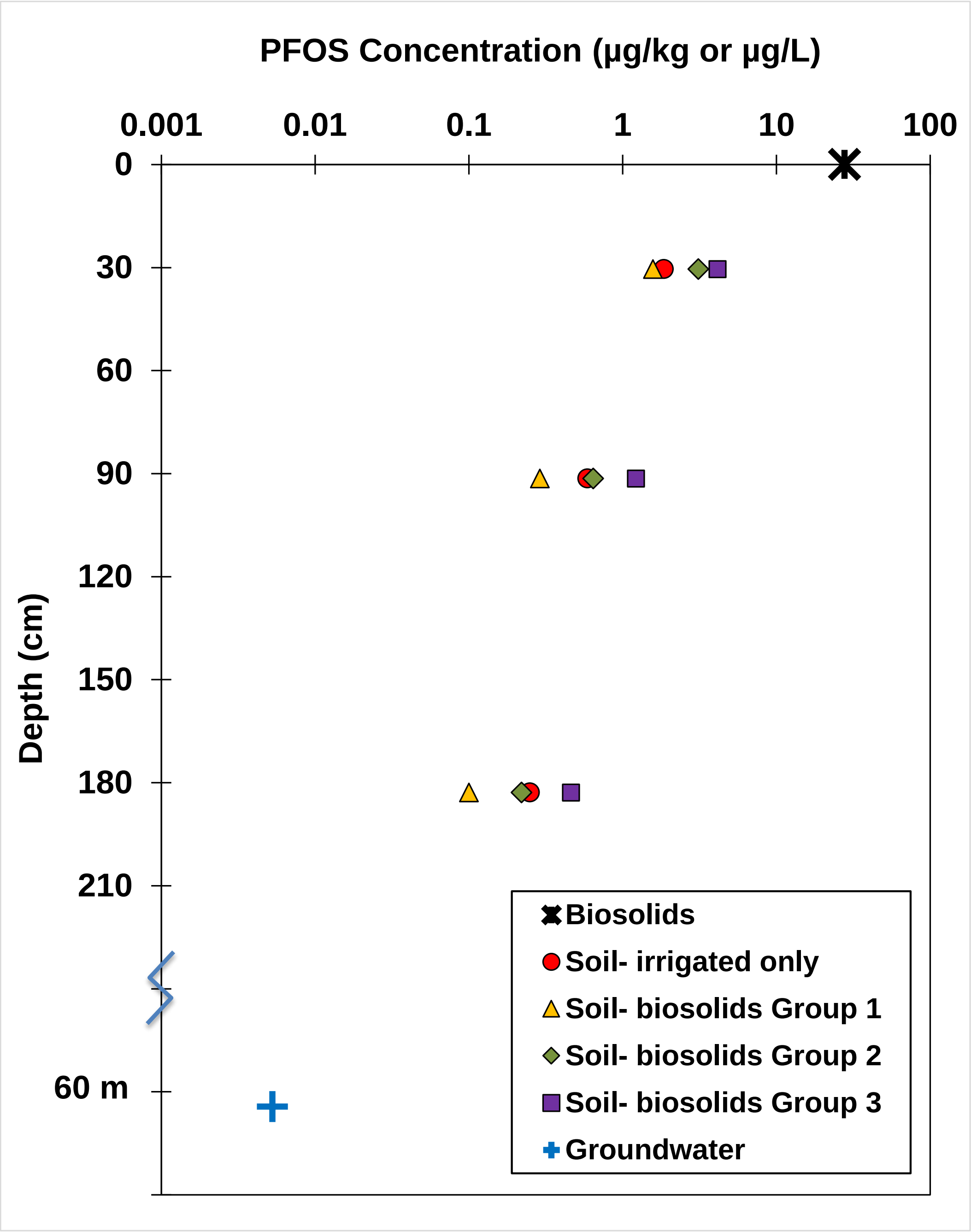
Depth	1 foot	3 feet	6 feet	PFAS present	
PFAS	**µg/kg (ppb)**			**Biosolids**	**Irrigation Source**
PFBS	ND	**0.08**	**0.04**	√	√
PFDA	**0.10**	ND	ND	√	
PFHpA	**0.08**	**0.06**	ND	√	√
PFHxS	**0.10**	**0.17**	**0.04**	√	√
PFHxA	**0.14**	**0.11**	ND	√	√
PFNA	**0.06**	ND	ND	√	√
PFOS	**1.6 ± 1.7**	**0.29 ±0.20**	ND	√	√
PFOA	**0.32 ± 0.33**	**0.26 ± 0.25**	ND	√	√
PFOS Attenuation	**N/A**	**82%**	**93%**		

Non-detects at all depths: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTeA; PFTriA; PFDoA; PFUnA.

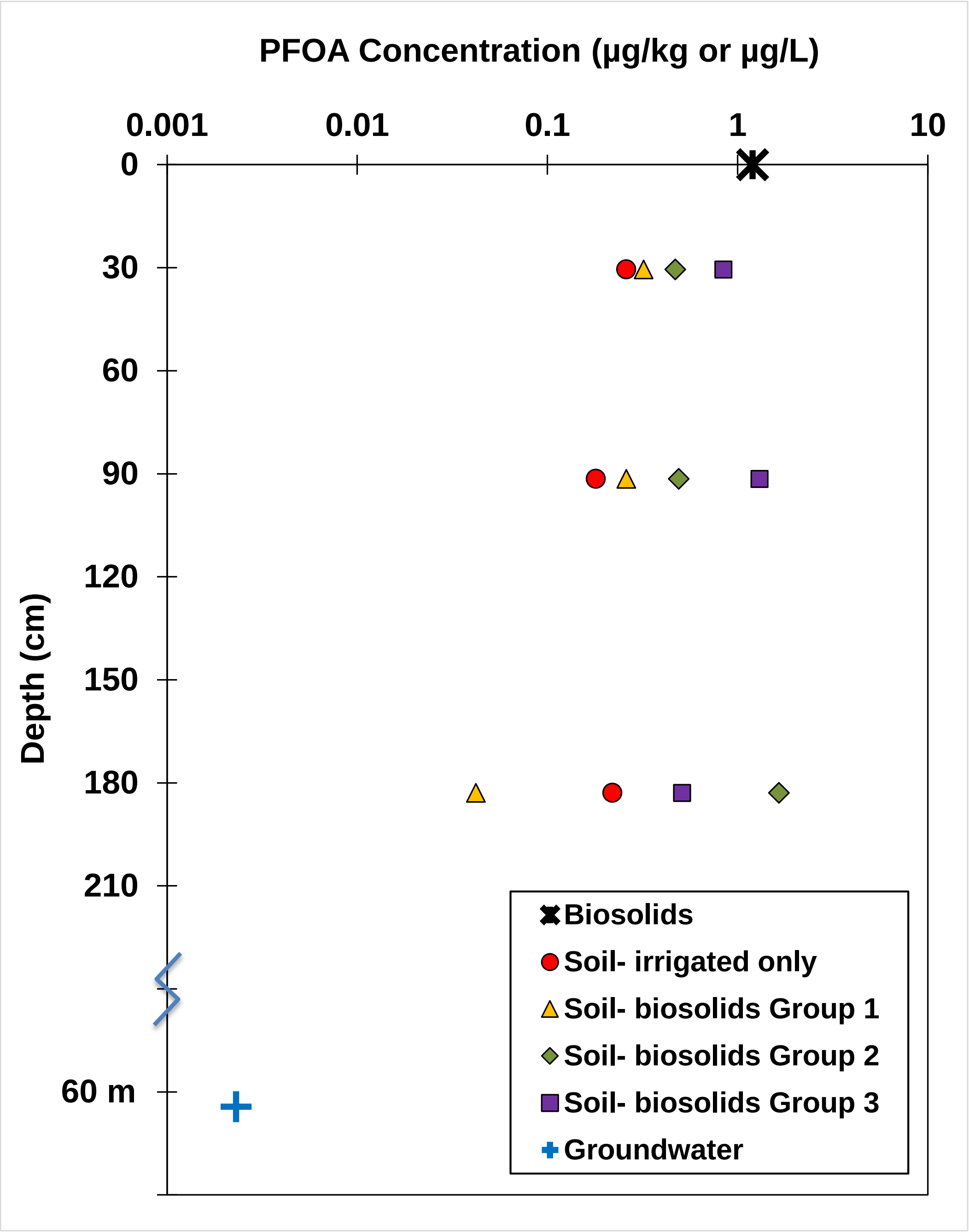
PFAS SOIL CONCENTRATIONS IN IRRIGATED AGRICULTURAL SOILS THAT RECEIVED >30 TONS OF BIOSOLIDS/ACRE.

Depth	1 foot	3 feet	6 feet	PFAS present	
PFAS	**µg/kg (ppb)**			**Biosolids**	**Irrigation Wells**
PFBS	**0.37 ± 0.47**	**0.20**	**0.14**	√	√
PFDA	**0.98 ± 0.41**	**0.11**	**0.15**	√	
PFDoA	**0.24 ± 0.17**	ND	**0.08**	√	
PFHpA	**0.19**	**0.16**	**0.24 ± 0.29**	√	√
PFHxS	**0.12**	**0.15**	**0.16**	√	√
PFHxA	**0.51 ± 0.51**	**0.22 ± 0.21**	**0.13**	√	√
PFNA	**0.43 ± 0.17**	**0.15**	**0.05**	√	√
PFOS	**4.1 ± 1.9**	**1.2 ± 1.4**	**0.46 ± 0.46**	√	√
PFOA	**0.84 ± 0.48**	**1.3 ± 1.4**	**0.51 ± 0.61**	√	√
PFTeA	**0.09**	ND	ND	√	
PFUnA	**0.10**	ND	ND	√	
PFOS Attenuation	**N/A**	**71%**	**89%**		

Bold values indicate values above the method reporting limit (MRL J values).
Non-detects at all depths: DONA; F-53B (Major); F-53B (Minor); GenX; NEtFOSAA; NMeFOSAA; PFTriA



Mean concentrations of PFOS in biosolids, soil, and groundwater. Note that the geometric mean concentration for all field types is used for groundwater.



Mean concentrations of PFOA in biosolids, soil, and groundwater. Note that the geometric mean concentration for all field types is used for groundwater.

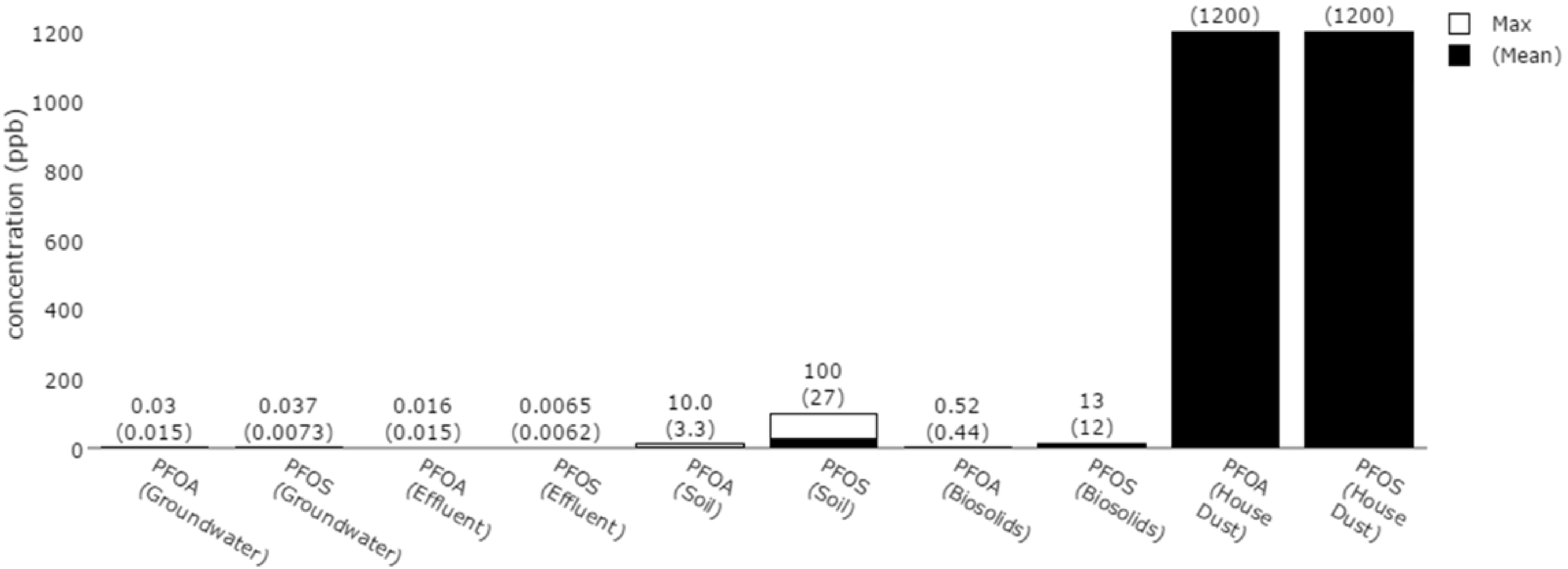
HIGHLIGHTS

- 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
- 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 20

KERN COUNTY CASE

PFOA and PFOS in effluent, soil, and biosolids measured at Green Acres Farm, 2015, compared with PFOA and PFOS concentrations in household dust*



*Household dust measurements from Trudel et al. *Risk Analysis, Vol. 28, No. 2, 2008*

NEW PROPOSED STUDY:

EVALUATION OF FATE AND TRANSPORT OF PFAS FOLLOWING LONG-TERM LAND APPLICATION: A COLLABORATIVE NATIONAL STUDY

Principal Investigator: Ian Pepper
University of Arizona

Co-Principal Investigators: Mark Brusseau
University of Arizona

Greg Kester
California Association of Sanitation Agencies

Jeff Prevatt
Pima County Wastewater

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?

MECHANISM

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

GROUNDWATER CONTAMINATION

- EPA Drinking Water Health Advisory Level = 70 ppt
- Some STATE levels = 20 ppt or less
- Biosolids known to contain PFAS
- Can biosolids be a source of PFAS contamination of groundwater?
- Will this lead to a national ban on land application?

LOCAL PROBLEM SOLVED BY LOCAL STUDY

- January 2020 – Pima County Board of Supervisors impose moratorium on land application in Pima County (Tucson, AZ)
- March – October 2020 – University of Arizona Water and Environmental Technology Center (WET) in collaboration with Pima County Wastewater evaluate incidence and transport of PFAS following long-term land application
- Data showed low incidence of soil PFAS and limited mobility of PFAS through soil and vadose zone
- Data presented to Pima County Administrator and Board of Supervisors
- December 2020, moratorium rescinded

FOR A NATIONAL PROBLEM WE NEED A NATIONAL STUDY

THE UNIVERSITY OF ARIZONA

CASA

PIMA COUNTY WASTEWATER RECLAMATION

NATIONAL COLLABORATIVE PROJECT OVERALL PROJECT GOAL

- To evaluate whether or not land application of biosolids is a significant public health route of exposure to perfluorinated compounds (PFAS)

Specific Objectives:

Evaluate

- Incidence of PFAS analytes in soil following long-term land application of biosolids
- Mobility (leaching) of PFAS analytes through soil and vadose zone under the influence of rainfall and/or irrigation
- Crop uptake of PFAS analytes

THE UNIVERSITY OF ARIZONA

CASA

PIMA COUNTY WASTEWATER RECLAMATION

These specific objectives should be evaluated over a variety of different soils, depth to groundwater, and climates, by studying land application plots nationally, across the entire United States, including irrigated and non-irrigated soils.

Depth and breadth of dataset should be sufficient to allow future predictions of potential groundwater contamination events and crop uptake of PFAS.

PROJECTED STUDY TIMELINE

Year 1 – Focus on exposure to PFAS in groundwater
(leaching through soil)

Year 2 – Focus on exposure to PFAS in crops
(plant uptake)

THE UNIVERSITY OF ARIZONA

CASA

PIMA COUNTY
WASTEWATER RECLAMATION

SCOPE OF WORK IN YEAR 1

GOAL: Evaluate the incidence and mobility of PFAS in soil following long-term land application of Class B and/or Class A biosolids

Soil Sample Collection at Select Sites

- Soil samples taken at 1, 3, and 6 feet depths from the surface
- 4 replicates
- Samples collected from across the U.S.
  - Farms 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

Groundwater Monitoring at Select Sites

- This will be done via sampling of monitoring wells

THE UNIVERSITY OF ARIZONA CASA PIMA COUNTY WASTEWATER RECLAMATION

PROCESSING SOIL SAMPLES

- Collection and processing of soil samples requires stringent precautions to avoid contamination
- University of Arizona / Pima County has all necessary protocols
- Soil samples will be sent to the University of Arizona
- Soil samples will be dried and sieved prior to sending to Eurofin, Los Angeles for PFAS analysis
- PFAS analysis will be for a suite of PFAS analytes

THE UNIVERSITY OF ARIZONA

CASA

PIMA COUNTY
WASTEWATER RECLAMATION

FUNDING REQUIRED (YEAR 1)

Estimate

Cost Per Site:

3 soil depths x 4 replicates x 3 loading rates (hypothetical) = 36 samples

1) Soil Sampling Personnel = Cost covered by partners	
2) Shipping	TBD
3) Soil Processing	$800
4) PFAS Suite Analysis ($400/sample @ 36 samples)	$14,400
	$15,200 + shipping

Total Project Cost:

For 30 sites = $456,000 + shipping

THE UNIVERSITY OF ARIZONA

CASA

PIMA COUNTY WASTEWATER RECLAMATION

LIKELY PARTNERS

1. Utilities: Any wastewater treatment plant that recycles its biosolids via land application may be interested in funding the project (16,000 WWTPs nationally)
2. Non-Profit Associations: Groups such as CASA, NACWA, NEBRA, MABA, NW Biosolids, Arizona Business Council will be contacted. 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, Material Matters and others.

MECHANISM TO OBTAIN FUNDING

- Academic researchers (members of national research group W4170) who send soil samples from know land application plots should engage the appropriate utility to cover the costs of the research
- All utilities that recycle biosolids via land application should consider a contribution to the project. $ amount TBD
- Private sector companies that manage biosolids should consider a contribution to the project. $ amount TBD
- All funds will be sent to the University of Arizona Water and Environmental Technology Center (WET) Director, Ian Pepper, with a known research track record and low indirect cost rate of 10%
- Additional funds available from the WET Center

THE UNIVERSITY OF ARIZONA CASA PIMA COUNTY WASTEWATER RECLAMATION

CURRENT WET CENTER MEMBERS CONTRIBUTING TO THE PROJECT

Member	Project Contribution
Pima County Wastewater	$50,000
Los Angeles County Sanitation Districts	$15,000
Orange County Sanitation Districts	Contribution TBD
Northwest Biosolids	$10,000
CASA	Contribution TBD
Synagro	Contribution TBD

THE UNIVERSITY OF ARIZONA

CASA

PIMA COUNTY WASTEWATER RECLAMATION

PFAS TRANSPORT WITHOUT BIOSOLIDS

- Dr. Brusseau will evaluate PFAS transport through pristine soils via a $1.2m 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

DATA COLLECTION AND COORDINATION

- All data from Eurofin will be sent to the UA WET Center
- Focus will be to evaluate incidence and transport of PFAS
- UA personnel will run statistics on the data resulting from each site
- Project PI and Co-PIs will work with W4170 representatives to determine responsibility for reports and peer review publications
- A final report will be generated for distribution to EPA, contributing partners, and interested stakeholders
- Data and findings will be presented at local, state and national meetings

THE UNIVERSITY OF ARIZONA

CASA

PIMA COUNTY WASTEWATER RECLAMATION

LEVERAGING PRIOR EXPERIENCE

- Local problem was solved by local study
- For a national problem, we need a national study

- Locally, we learned how to do a successful PFAS study
  - ✓ Soil sampling
  - ✓ Soil processing
  - ✓ Avoiding contamination
  - ✓ PFAS analysis
  - ✓ Evaluation of incidence and mobility
- WET Center has the tools to effectively manage the project
- Project has national implications, universal response has been overwhelmingly supportive

IF YOU'RE INTERESTED IN THE PROJECT, CONTACT:

Ian Pepper
ipepper@email.arizona.edu or 520-626-2322

Greg Kester
gkester@casaweb.org or 916-446-0388

THE UNIVERSITY OF ARIZONA

CASA

PIMA COUNTY WASTEWATER RECLAMATION