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Webinar

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NEBRA PFAS Literature Review

nebra
North East Biosolids & Residuals Association

Topics to be Covered

- Background
- Research Concerns & Considerations
- PFAS and Wastewater Treatment
- PFAS in Sewage Sludge
- Land Application of Wastewater Residuals and Soil Impacts
- PFAS Mobility in the Soil and Risk to Groundwater
- Human PFAS Exposure Resulting from Plant and Animal Uptake from Soils Amended with Wastewater Residuals
- Conclusions and Research Priorities

Background (Why we're talking about PFAS)

- Mobile and ubiquitous (arctic, human blood & serum) (Rankin et al. 2016, Vedagiri et al. 2018)
- Detected in groundwater and drinking water in numerous states (Boone et al. 2018)
- Found in groundwater near land application sites
- Legislatures and state environmental agencies expressing increased concern about PFAS
  - Establishing regulatory limits
  - Attempting to identify sources other than industry (landfills and wastewater residuals)
- PFAS have been found in residuals and land applied soils **not** impacted by industrial sources. (Sepulvado et al. 2011, Gottschall et al. 2016)

Reactions of State Regulatory Agencies to PFAS Contamination of Groundwater

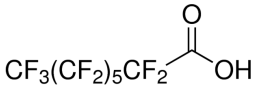
- State environmental agencies are under public and legislative pressure to adopt regulations to protect groundwater
- Adopting widely variable groundwater/drinking water PFAS standards based on still evolving understanding of PFAS toxicology.
  - Confusion over precursors and degradation pathways
  - Some are summing PFAS − may not be appropriate
- Proposals to adopt stringent PFAS regulations on other media
  - Hazardous waste determinations
  - Soil screening standards to protection groundwater
  - Screening standards in biosolids/residual to protect groundwater
- Proposed standards based on questionable modeling
  - Overly conservative assumptions (loading rates, aquifer size, dilution/attenuation, etc.)
  - Modeling based on lab studies/testing, limited field verification
  - Poor understanding of PFAS-soil equilibria and soil organic matter partitioning

Background

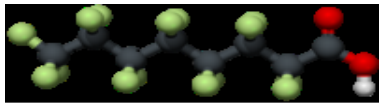
"Does land application of wastewater residuals (paper mill solids, municipal biosolids, etc.) at fertilizer rates with current common regulatory requirements and proper industrial source controls represent a risk to public health from PFAS contamination of groundwater via leaching and/or surface water via runoff?"

Research Concerns and Considerations

- Per- and polyfluoroalkyl substances (PFAS)



Perfluorooctanoic Acid (PFOA)


PFOA

- Large group of chemicals with many subgroups
- Man-made highly fluorinated alkyl (C2-C16) chemicals with unique properties
- Hydrophobic and Lipophobic
- High affinity for proteins
- No natural counterparts

Research Concerns and Considerations

- Lowers surface tension and enhances spreading
- High chemical and thermal stability (C-F bonds)
- Very useful compounds
  - Stain-resistant carpets and fabrics
  - Food cartons, containers, wrappers
  - Surfactants and lubricants
  - Aqueous film-forming foams (AFFFs)
  - Flame retardants

Research Concerns and Considerations

- Two production methods that yield different products:
  - Electro-chemical fluorination (ECF)
    - Electrolysis of organic compound in HF
    - Breaking and branching of C-chain
    - ~70% linear/30% branched in PFOA/PFOS synthesis
  - Telomerization
    - Multiple step reaction
    - PFEI – PFAI – FTI – FTOH – variety of PFAS products
    - Linear reactants yield linear alkyl chain products
- Perfluoroalkyl acids (PFAAs) are the metabolites of many PFAS precursors
- PFAS-based products can be complex mixtures containing the intended end-product, unreacted raw materials or intermediate chemicals, and unintended byproducts.

Research Concerns and Considerations

- As acids and esters, PFAS compounds susceptible to ionization/dissociation and increased mobility
- Ionized forms likely to predominate in the environment and biota (including humans)
- Some PFAS compounds may degrade in the environment or biota, but will ultimately transform to very stable and persistent perfluoroalkyl acids (PFAAs)
- The yield rate of PFAAs from biotic and abiotic degradation depends on the precursors and degradation conditions
- Increasing C-chain length reduces leachability and increases bioaccumulation
- Increasing use and production of alternatives to PFOA and PFOS

Research Concerns and Considerations

Buck et al. 2011. *Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins*.

Large number of chemical groups and individual chemicals (>3000 used on the global market)

- Similar properties valuable in commerce
- Variable behavior in the environment

PFAS products may contain multiple isomers of the intended ingredients, residual intermediary compounds, byproducts, and – after release –degradation products.

PFAS and Wastewater Treatment

- Pervasiveness and persistence of PFAS in commerce and the environment ensure PFAS loading to WWTFs over the long-term
- Across facilities, influent PFAS loading can be variable both in composition and concentration.
- Historically PFOA and PFOS the most abundant, typically 5-50 ng/L (Margot et al. 2015, Hamid and Li 2016)
- Total concentrations for common PFAS typically 30-150 ng/L (Margot et al. 2015)
- A survey of 19 Australian WWTFs, the average total PFAS concentration found in wastewater for 21 chemicals from four different classes of PFAS compounds was 110 ng/L (Coggan et al. 2019)
- One study involving an industrial user found influent concentrations of 470 ng/L, 640 ng/L and 61,205 ng/L for PFOS, PFOA, and Perfluorooctanesulfonamide (PFOSA), respectively (Koch, 2015)

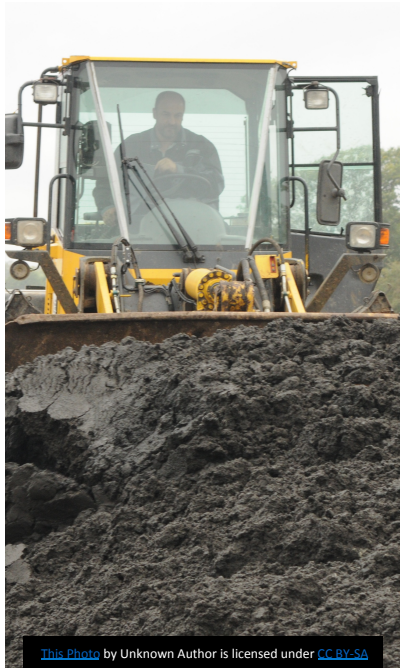
PFAS and Wastewater Treatment

- Negligible treatment by conventional wastewater treatment, <5% removal (Hamid and Li 2016, Koch, 2015)
- Most removal via sorption to wastewater solids
- Organic matter partitioning process (Zareitalabad et al. 2013)
- Longer carbon-chain (>6 C) tend to adsorb to solids and are removed in the sludge (Koch, 2015)
- Effluent PFAS concentrations slightly lower than influent

Study	PFOA (ng/L)	PFOS (ng/L)
Margot et al. 2015	13	12
Zareitalabad et al. 2013	24	13

- Precursor degradation can increase effluent PFAA concentrations over influent levels (Clarke and Smith 2011, Hamid and Li 2016, Coggan et al. 2019)

PFAS in Sewage Sludge



- PFAS is present in residuals
  - Variable compounds
  - Variable concentrations
- Highest concentrations are found in residuals with direct industrial input (Lindstrom et al., 2011):

	4 WWTF	Decatur, AL
• PFOA (ng/g):	<17	244
• PFOS (ng/g):	58-159	3000
• PFOSA (ng/g):	<44	244

- PFAS are also found in residuals without industrial input, but at lower concentrations.

PFAS in Sewage Sludge

- In the 2000s, PFAS were found in typical biosolids in concentrations of tens of parts per billion (ppb), with a U. S. average of 34 ppb for PFOA and 403 ppb for PFOS (Venkatesan and Halden, 2013).
- Studies over time seem to show decreasing concentrations of PFOA and PFOS in residuals while increasing concentrations of alternative PFAS compounds
- Other studies have concluded that, at least for the time frame from 2001 to 2007, there was no statistically significant changes in PFOS or overall PFAS concentrations in sludge (Venkatesan & Halden, 2013; Sepulvado et al. 2011)
- Degradation and transformation of more complex molecules may explain the continued presence and stable concentrations of PFOA, PFOS, and other PFAA in wastewater residuals and other environmental media even as the use of PFOA, PFOS, and other PFAA is discontinued (Hamid and Li, 2016)

PFAS in Sewage Sludge: PFOA and PFOS Concentrations Over Time

Study	Year(s) of Testing	PFOA (ng/g)	PFOS (ng/g)	Data Type
Lindstrom et al. 2011	1999-2001	244	3000	single data point
Venkatesan & Halden 2013	2001	34	403	average
Clarke & Smith 2011	2001-2008	37	196	median
Sepulvado et al. 2011	2004-2007	8-68	80-219	range
Gottschall et al. 2016	2009	1.6	7.2	single data point
Zareitalabad et al. 2013	2013	37	69	median
NEBRA/DES Data	2017	6.7	34	average
Coggan et al. 2019	2017	2.6	14	average

PFAS in Sewage Sludge: PFAS Concentrations Changes Over Time

Compound	Venkatesan & Halden 2013 ng/g (2001 averages)	Gottschall et al. 2016 ng/g (2009 data point)	NEBRA/DES Data ng/g (2017 averages)
PFBA	2	<0.4	34.6
PFPeA	3.5	1.2	22.5
PFHxA	6.2	1.5	11.0
PFHpA	3.4	<0.4	1.1
PFOA	34	1.6	6.7
PFNA	9.2	19	2.6
PFBS	3.4	22	5.7
PFHxS	5.9	<0.7	13.3
PFOS	403	7.2	34

PFAS in Sewage Sludge

2017 PFAS data compiled by NHDES and NEBRA,

22 facilities from NH and Northeast, 27 data points

Chemical	% detection	Conc. Range (ug/Kg)	Ave. Conc. (ug/Kg)
PFBA	20	0.54 – 140	34.6
PFPeA	8	18 – 27	22.5
PFHxA	84	0.21 – 75	11.0
PFHpA	26	0.077 – 2.8	1.1
PFOA	32	1.1 – 15	6.7
PFNA	30	1 – 3.6	2.6
PFBS	7	5.2 – 6.2	5.7
PFHxS	22	0.24 – 73	13.3
PFOS	62	0.59 - 390	34

Land Application of Residuals and Soil Impacts

- Land application of PFAS contaminated residuals results in detectable PFAS concentrations in the soil.
- Soil concentrations following land application reported in the literature:

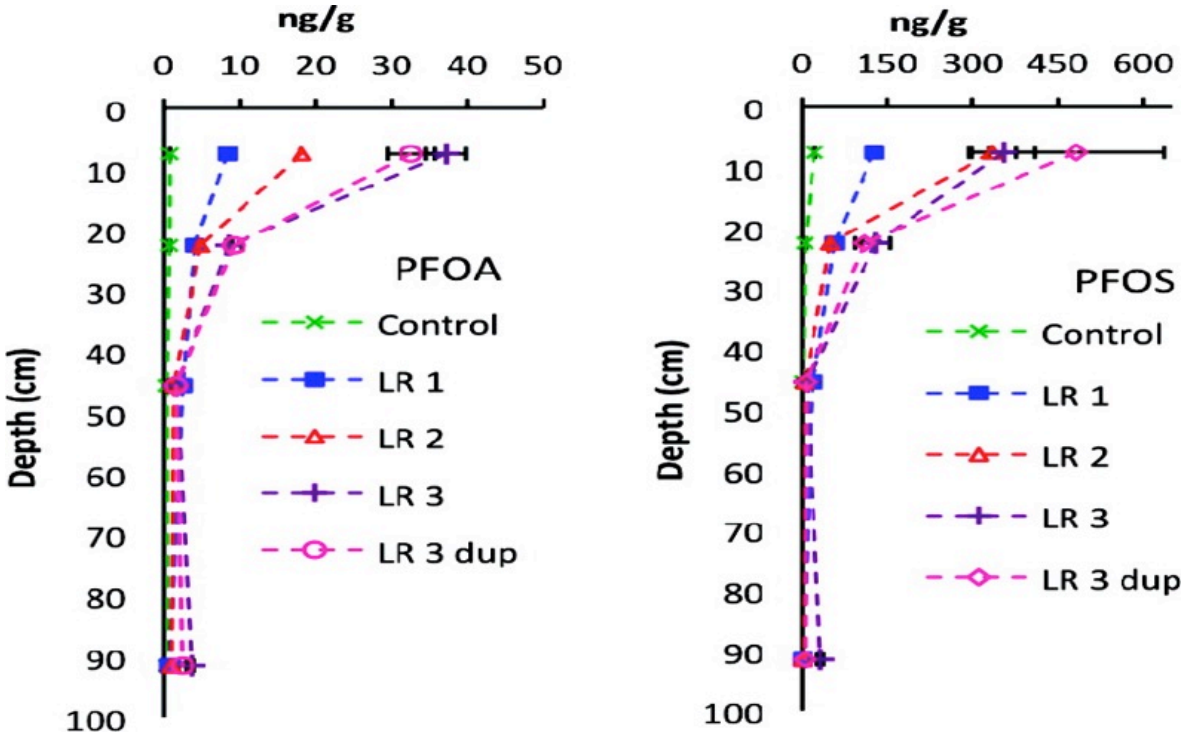
Source	Type of loading	PFOS (ug/Kg)	PFOA (ug/Kg)
Washington et al., 2009	High PFAS	30 – 410	50 – 320
Sepulvado et al., 2011	Short-term Long-term	2 – 11 5.5 – 483	No data
Gottschall et al., 2017	One-time	0.2 – 0.4	0.1 – 0.8
Zareitalabad et al., 2013	Background Conc.	0.124	0.472
Rankin et al. 2016	High Background	2.67	3.1

Land Application of Residuals and Soil Impacts

- PFAS soil concentrations can be correlated to residuals loading rate (Sepulvado et al. 2011; Lindstrom et al. 2011)
- Correlation is especially strong for longer chain (>C8) PFCA.
- For short chain PFCA, soil concentration may correlate better with time from last application.
- PFAS concentrations in well water and surface water can be correlated to loading rate of short chain PFAS.
- Soil PFAS concentrations at depth may increase over time.
- Soil PFAS concentration can change as a result of precursor degradation.

Land Application of Residuals and Soil Impacts

Sepulvado et al; *Environ. Sci. Technol.* 2011, 45, 8106-8112

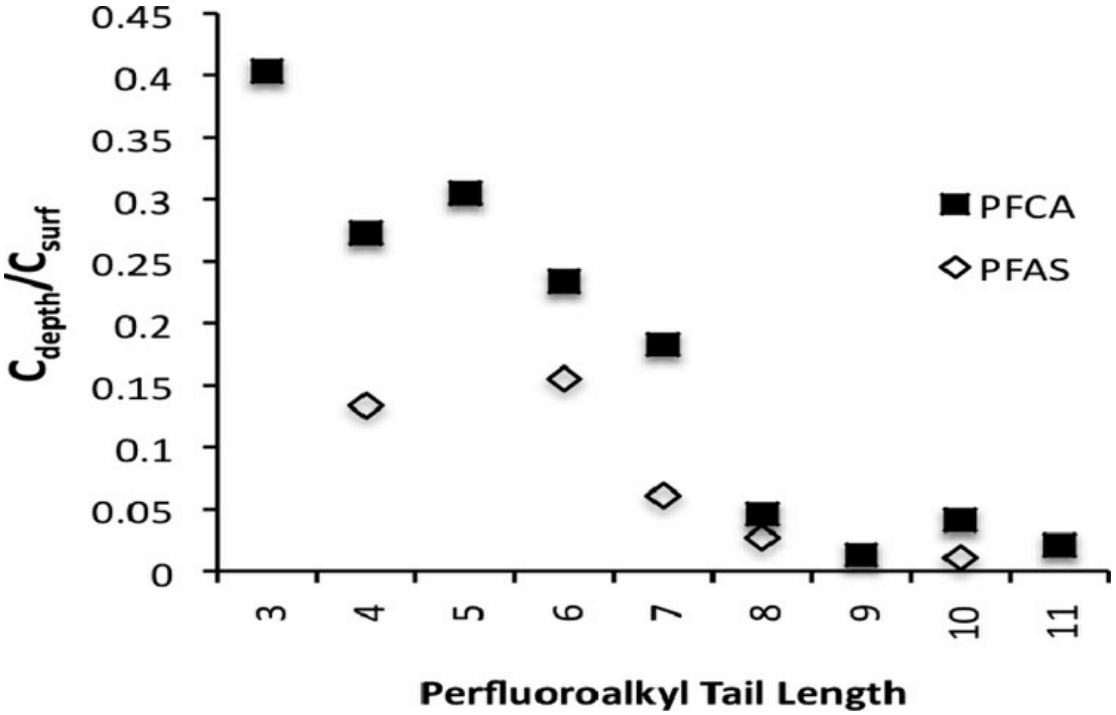


Concentrations of PFOA and PFOS with depth in the long-term plots at various loading rates.

Control = 0 Mg/ha
LR1 = 553 Mg/ha
LR 2 = 1109 Mg/ha
LR 3 and LR 3 dup = 2218 Mg/ha (dry weight basis).

Mobility varies with chemical structure

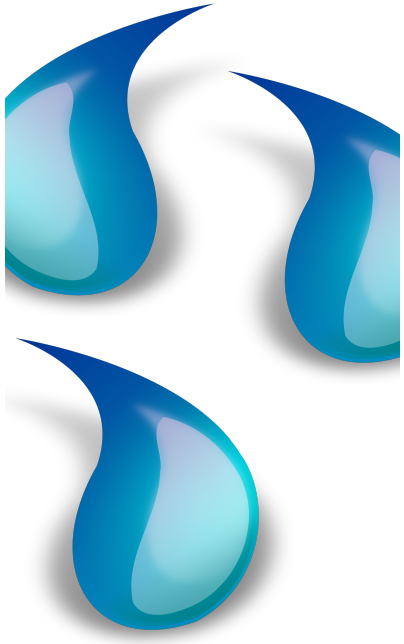
Sepulvado et al; *Environ. Sci. Technol.* 2011, 45, 8106-8112



Ratios of surface concentration (*C*surf) to concentration in the bottom soil core depth interval (60—120 cm, *C*depth).

Ratios represent an average of the ratios calculated for the long-term plots for each biosolids loading rate.

PFAS Risk and Wastewater Residuals (Mobility/Leaching)



- Little direct evidence that residuals without obvious industrial PFAS contributions are a risk to public health via groundwater contamination following land application
- A determination of public health risk is influenced by several factors:
  - Type and quality of wastewater residuals,
  - PFAS compounds to be considered,
  - Field conditions (OM content, climate, soil type, depth to groundwater, etc.), and
  - Regulatory requirements (loading limits, land application restriction, drinking water standards, required setback, application rates).
- Differences in these factors from state to state can lead to different conclusions regarding public health risk

Mobility in the Soil and Risk to Groundwater

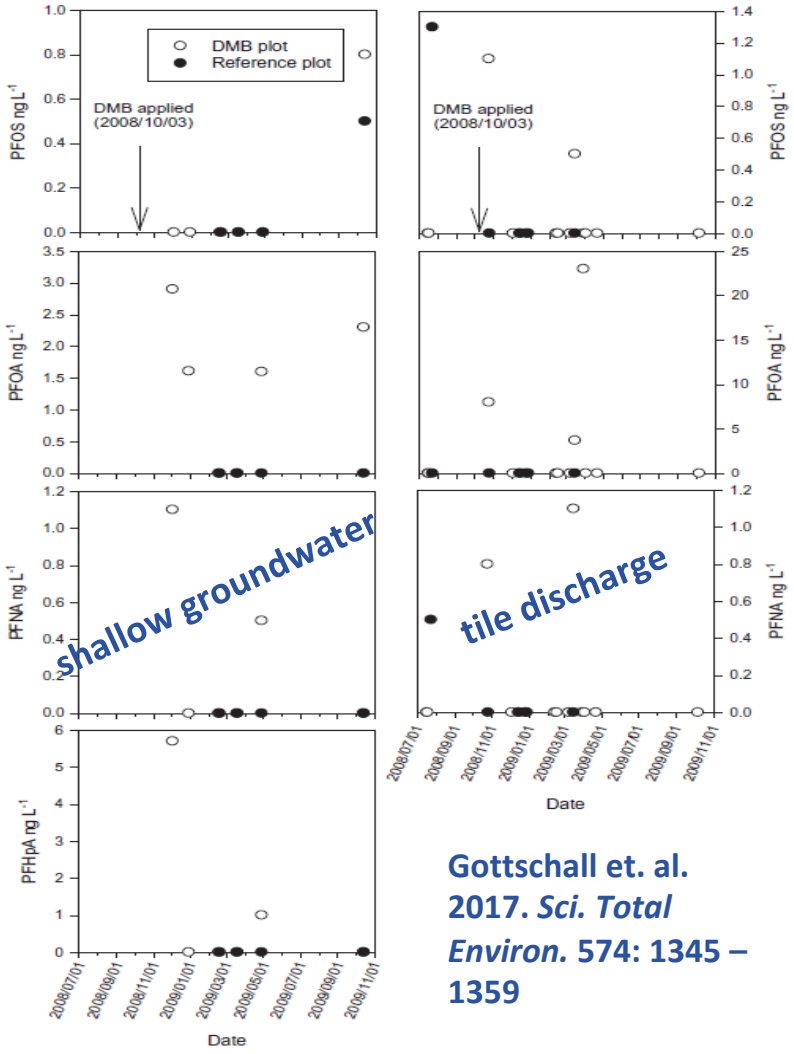
Study site in Ontario:

- Humid continental climate
- Corn, wheat, soy rotations
- Very light tillage
- Systematic tiling, 15m spacing, about 1m depth
- Ottawa biosolids (mixed residential, industrial, commercial):
- 1.6 *u*g/kg PFOA, 7.2 *u*g/kg PFOS
- Treated by AD, centrifugation
- 22 Mg dw/ha (9.8 tons dw/ac)
- Moldboard plow to ~ 20cm
- Planted to winter wheat

Gottschall et. al. 2017. *Sci. Total Environ.* 574: 1345 – 1359

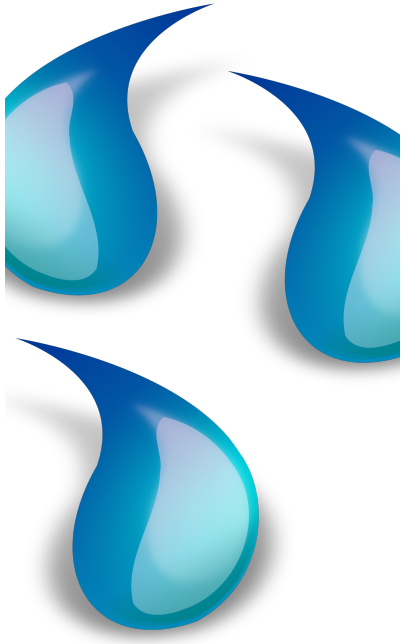
Conclusions (Gottschall et al. 2017)

- Perfluorinated chemicals detected in both groundwater and tile discharge after a single large biosolids application.
- For groundwater concentrations, there was no statistically significant difference between control and treatment plots.
- Highest 2m groundwater concentrations:
  - PFOA: bd - 3 ng/L
  - PFOS: bd – 0.8 ng/L
- Chemicals detected for months after the application.
- Relative contributions of leaching through soil matrix, and preferential flow through macropores are unknown.
- No groundwater standards or guidelines exceeded
- No PFAS in wheat grain samples



Gottschall et. al. 2017. *Sci. Total Environ.* 574: 1345 – 1359

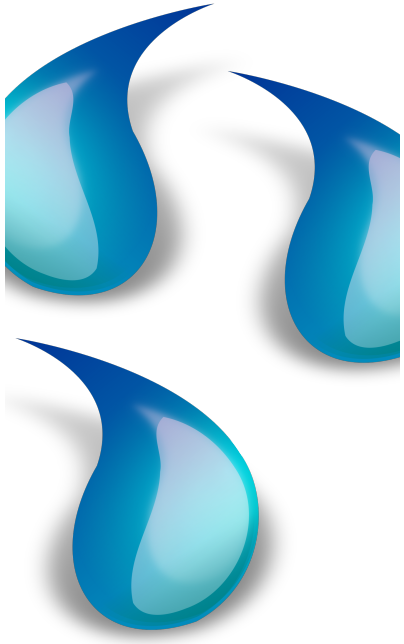
Mobility in the Soil and Risk to Groundwater



What does the scientific literature tell us about leachability of PFAS:

- PFAS can and does move through the vadose zone to groundwater
- Correlations between biosolids/PFAS loading and observed groundwater and surface water concentrations have been observed
- One potential set of conservative soil screening levels for protection of groundwater were calculated for PFOS (3 ug/kg) and PFOA (3 ug/kg) (Xiao et al. 2015)
- Observation in groundwater can follow release to surface soils by years if not decades, especially for longer chain PFAS (C8 and higher)

Mobility in the Soil and Risk to Groundwater



- Sorption in the soil does occur and is best described as a complex sorption equilibrium reaction
- PFAS sorption equilibria (log K_d)are influenced by:
  - **PFAS carbon chain length**
  - **Organic carbon content and type**
  - pH
  - Cation concentrations
  - Specific surface area/clay content
  - Types of soil minerals

Human PFAS Exposure Resulting from Plant and Animal Uptake from Soils Amended with Wastewater Residuals

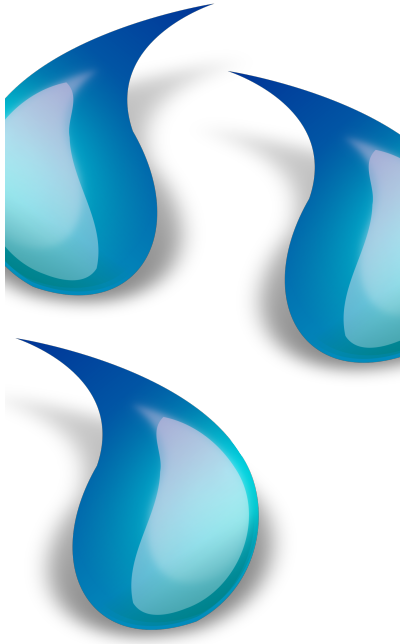
Controlling factors for plant uptake:

- PFAS concentrations in the soil,
- PFAS chain length and functional groups,
- Plant species/organ, and
- Soil organic matter content.

Human PFAS Exposure Resulting from Plant and Animal Uptake from Soils Amended with Wastewater Residuals

- Carbon-chain length and functional groups are significant factors controlling accumulation and elimination (route and rate) of PFAS from animal tissue
  - Longer C-chain and sulfonate functional groups favor retention
  - Shorter C-chain and carboxylate functional groups favor faster elimination
- Unlike other organic contaminants PFAS doesn't accumulate in fatty tissue
- Generally, liver, kidneys, and blood plasma tend to accumulate higher PFAS concentrations than muscle tissue
- Consumption of plant and animal products can be a source of PFAS in the human diet
- There is little evidence that PFAS in the human diet is a significant public health concern (Lupton et al. 2011; Kowalczyk et al. 2013; Blaine et al. 2014; Perez et al. 2017)
- Limited use of residuals and harvesting restriction make it unlikely land application will increase PFAS risk

Conclusions



Conclusions on PFAS risk:

- The ubiquitous presence of PFAS in plant, animal, and human tissue as well as air, soil, and water resources confirms the obvious mobility of these chemicals
- However, there is little information to answer our original question
- Need research on long-term land application sites to answer questions about PFAS risk
- A little perspective on PFAS risk from wastewater residuals:
  - PFAS are in residuals because they have been widely used for decades and persistent in the environment
  - Presence in residuals is not evidence of risk or even significant exposure in excess of current everyday exposure
  - Uncertainty on extent of public health risk

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QUESTIONS?

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