Perfluorinated Alkyl Substance (PFAS) Concerns Related to Wastewater & Residuals

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- Brandon Kernen, NH DES
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Waste Management

Topics to Be Covered

- Brief Background
- PFAS in Wastewater & Residuals (Presence)
- PFAS in Soils, Leaching, Risks (Fate & Impacts)
- Northeast Recent Examples: Some impacts
- Reactions Can Impact Recycling

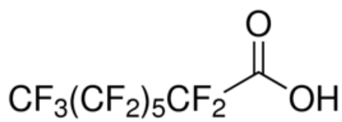
Why is this a hot topic for you now?

(the elevator talk on PFAS & wastewater & residuals)

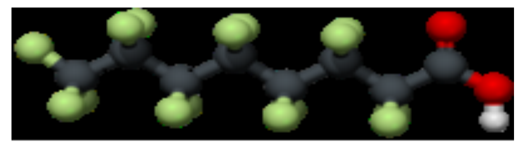
- 2010s: Increasing focus on PFOA & PFOS in the environment worldwide, because of correlations to health impacts. PFOA & PFOS voluntary phase-out by 2015.
- Focus on drinking water and potential public health impacts → EPA public health advisory (PHA) - May 2016 - 70 ng/L (ppt) for PFOA & PFOS combined.
- Agencies look around → literature points to wastewater & residuals.
- PFOA and PFOS have been in ubiquitous use for decades. Wastewater, biosolids, & other residuals (e.g. from recycle paper mills) typically today contain low microgram/L (ppb) concentrations.
- PFOA & PFOS chemistry and persistence → some leaching to groundwater possible at levels approaching the EPA PHA concentration → Regulators concerned.
- States' cursory screening sampling & analysis supports some concern. More study needed.
- Meanwhile, pressure to take action is driving the benchmark lower (EPA PHA of 70 ppt). This is what threatens wastewater & residuals use right now.

Background (general info)

- Per- and polyfluoroalkyl substances (PFAS)

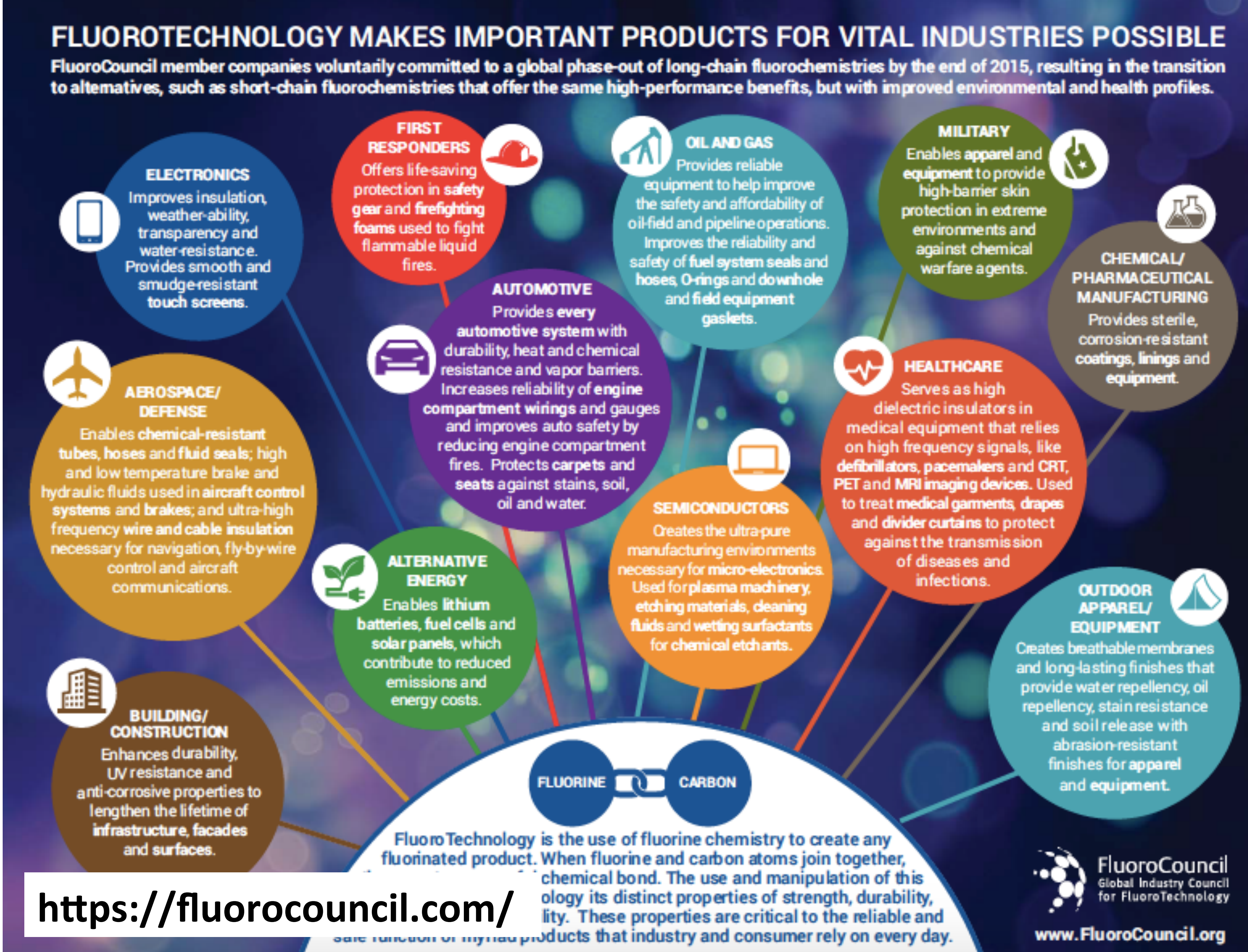


Perfluorooctanoic Acid (PFOA)



PFOA

- Large group of chemicals with many subgroups
- Man-made highly fluorinated <u>alkyl</u> (C2-C16) chemicals with unique properties
- Hydrophobic and lipophobic
- No natural counterparts



https://fluorocouncil.com/

Good new resource (more on this later in session)

http://pfas-1.itrcweb.org/

PFAS – Per- and Polyfluoroalkyl Substances

Why PFAS are used

- 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

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PFAS Chemistry/Fate

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 Chemistry/Fate

- 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 (PFAI)
- Perfluoroalkyl acids (PFAAs) are the metabolites of PFAS precursors

PFAS Chemistry/Fate

- 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

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PFAS in Wastewater (Presence 2017 data)

	PFBA	PFHPA	PFHXS	PFHXA	PFNA	PFOA	PFOS	PFPEA
	C4	C7	C6-S	C6	C9	C8	C8	C5
Small City Influent	13	<4	<4	7	<4	6	6	5
Small City Effluent	7	<4	<4	46	<4	6	7	21
Mid-size City Influent	<9.6	7	7	10	<4.8	15	22	29
Mid-size City Effluent	<9.6	5	8	20	<4.8	15	14	9
Municipality with industrial impacts Influent	56	8	<4	49	<4	50	4	36
Municipality with industrial impacts Effluent	73	19	<4	195	<4	49	<4	101

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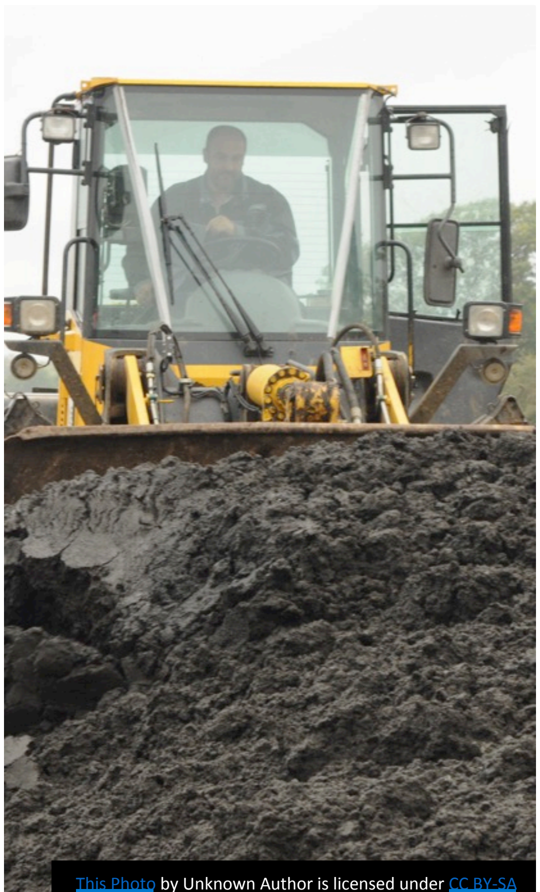
PFAS Risk and Wastewater Residuals (Presence)



- PFAS is present in residuals
  - Variable compounds (results for 19 tabulated)
  - Variable concentrations
- Highest concentrations are found in residuals with direct industrial input:

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

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

PFAS Risk and Wastewater Residuals (Presence)

- 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). Recent tests of land applied New England biosolids and residuals found average concentrations of 2.3 and 5.3 ppb.
- Recent studies including wastewater solids:

Study	PFOA (ug/Kg)	PFOS (ug/Kg)
Zareitalabad et al., 2013 (median)	37	69
Sepulvado et al., 2011 (range)	8 – 68	80 – 219

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PFAS Risk and Wastewater Residuals (Presence)

2017 PFAS screening data compiled by NHDES &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
PFHeA	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

PFAS Risk and Wastewater Residuals (PFAS in Soil)

- Land application of PFAS-contaminated residuals has resulted in detectable PFAS concentrations in 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

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PFAS Risk and Wastewater Residuals (PFAS in Soil)

Limited research shows:

- PFAS soil concentrations can be correlated to residuals loading rate
- 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 seem to be correlated to loading rate of short chain PFAS.
- Soil PFAS concentrations at depth may increase over time (slow leaching? degradation of precursors?)
- Soil PFAS concentration can change as a result of precursor degradation.

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 typical 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 (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

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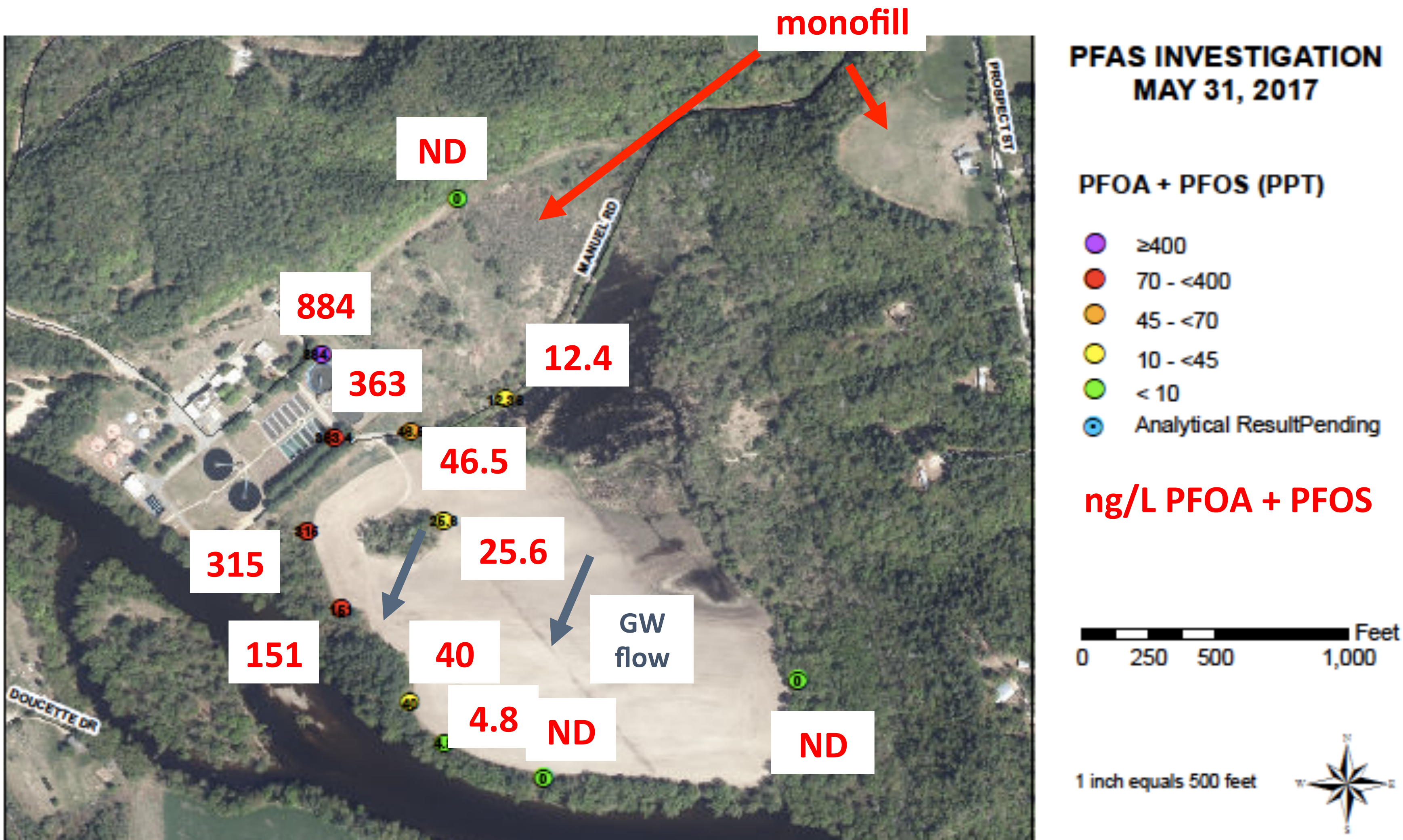
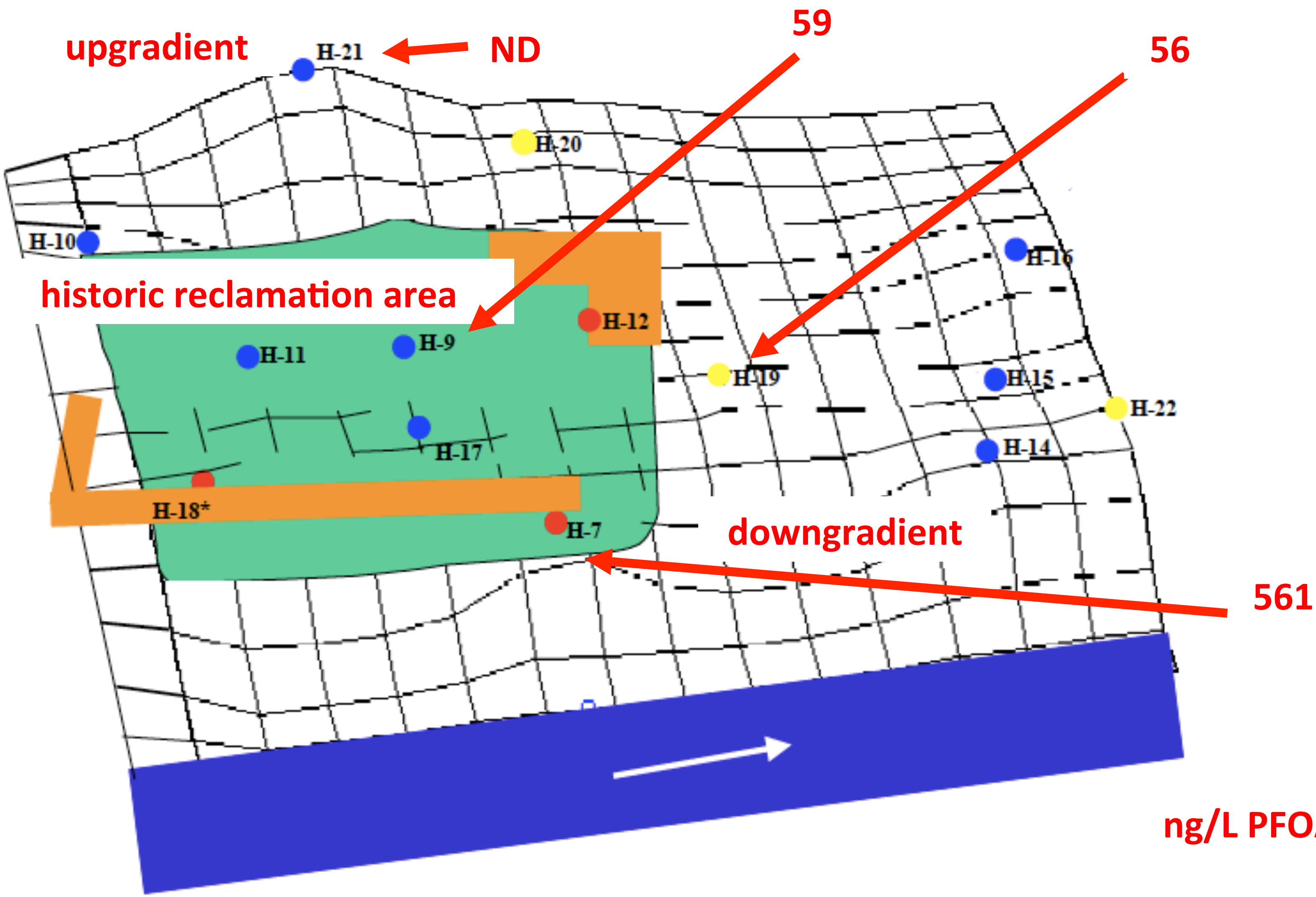
Monitoring well testing at biosolids monofill

- Monofill used in 1980s. Since ~1996, all biosolids from WWTP (11.5 MGD) have been land applied, some on farm field shown.
- Likely a worst-case scenario



Monitoring well testing at reclamation site

- Historic land application use to ~2001.
- Likely a worst-case scenario



ng/L PFOA + PFOS

Residuals management is being negatively impacted right now.

Regulatory response in March 2017 drives recycle paper mill residuals to landfill and composting business to laying off workers.

Residuals management is being negatively impacted right now.

November 2017 drinking water well test result that regulatory agency thinks may be related to long-term land application site. More research needed.

Sample ID:	**MTBE_4999**	
Client Data		
Name:	New Hampshire DES	
Project:	General Investigation-Ag Sites	
Date Collected:	03-Nov-2017 9:20	
Location:	96 W Portsmouth St.	
Analyte	**Conc. (ng/L)**	**RL**
PFBA	32.6	2.03
PFPeA	89.5	2.03
PFBS	83.3	2.03
PFHxA	105	2.03
PFHpA	91.0	2.03
PFHxS	15.5	2.03
6:2 FTS	ND	2.03
PFOA	88.5	2.03
PFHpS	ND	2.03
PFOS	ND	2.03
PFNA	ND	2.03

EPA PHA = 70 ug/L (ppt) for PFOA + PFOS

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PFAS Risk and Wastewater Residuals (Mobility/Leaching)

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). Other modeling suggest ~140 ug/kg may be appropriate. These are the numbers states want to set!
- Observation in groundwater can follow release to surface soils by years if not decades, especially for longer chain PFAS (C8 and higher)

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States trying to set numbers…

NY:

- DEC did some cursory leaching studies & modeling; promised a number for paper mill residuals. Have not released it.
- Latest: "We don't think today's biosolids/residuals with typical levels of PFAS are significant contributors to impacts."

ME:

- Proposed new screening numbers for materials put on land that are not for agronomic use (Chapter 418 regulations, Appendix A).
- Switched to Regional Screening Levels (RSLs) for most chemicals, but modeled PFBS, PFOA, & PFOS with Maine's SESOIL model:
  PFOA: 0.000438 ppb
  PFOS: 0.000908 ppb
- NEBRA & other comments → new proposed RSL numbers:
  PFOA: 2.5 ppb
  PFOS: 5.2 ppb

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PFAS Risk and Wastewater Residuals (Mobility/Leaching)

- Sorption in the soil does occur and is best described as a sorption equilibrium reaction
- PFAS sorption equilibria are influenced by:
  - **PFAS carbon chain length**
  - **Organic carbon content**
  - pH
  - [Ca^{+2}]
  - Clay content
  - Specific surface area
- More research needed.

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PFAS Risk and Wastewater and Residuals - Perspective

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
- A little perspective on PFAS risk from wastewater and residuals:
  - PFAS are in wastewater & residuals because they have been widely used for decades and are persistent in the environment
  - Presence in wastewater & residuals is not evidence of risk or even significant exposure in excess of current everyday exposure
  - Uncertainty on extent of public health risk; health studies vary.
  - PFOA & PFOS are phased out in No. America. Human blood serum levels down 50% over ~15 years.
  - Is this is a legacy issue, at least for PFOA & PFOS?

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NEBRA Response to PFAS Issue

- NEBRA pursuing answers via facilitation of relevant research and guidance:
  - Fact Sheets
  - Sampling and Analysis Guidance
  - Proposal for PFAS Research - UNH
  - PFAS Advisory Group
  - Webinars on PFAS issues
- Working with state agencies and legislatures to deal with PFAS risk in a measured and thoughtful manner (need to avoid regulatory over-reaction)
- Nationwide PFAS conference call – last Tuesday of each month, 1:30 Eastern

PFAS Risk and Wastewater Residuals

NEBRA proactively facilitating research to address the **potential** risk to public health from land application of wastewater residuals containing PFAS.

Research question:

"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?"

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NEBRA Resources (see members-only page: click button on right side of https://www.nebiosolids.org)

CORE NEBRA DOCUMENTS

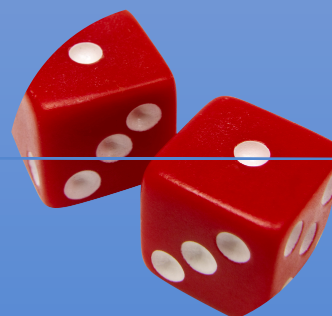
- **PFAS in Biosolids & Residuals - Fact Sheet** (v. 3.3, Jan. 9, 2018)
- **PFAS & Recycling: Putting Them In Perspective, a 2-page fact sheet re concerns about PFAS in residuals**
- **FAQ: PFAS & Wastewater/Residuals/Biosolids, Jan. 18, 2017. Working draft. Should you test?**
- **Guidance: Sampling & Analysis of PFAS in Biosolids and Associated Media - v. 2, Jan. 5, 2018**
- **Concentrations of PFAS in NE Biosolids, Residuals, Wastewater, & Associated Media - a spreadsheet dataset coming soon...**

PFAS Research Proposal Summary, Dec. 2017. UNH will begin site evaluations in 2018, funded by NH DES with NEBRA help.

Where do normal, modern biosolids applications lie on the continuum of PFAS impacts to groundwater?

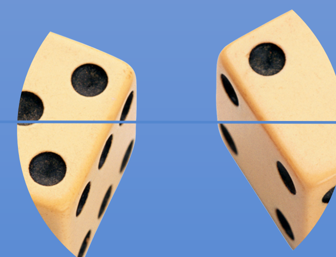
Historic residuals impacted by PFAS manufacturer

(e.g. 3M, Decatur, AL; NE farm with high PFOS likely from 1980s papermill residuals use)



Historic / modern residuals heavily applied repeatedly

(Sepulvado et al. 2011



Modern residuals applied semi-annually with setbacks, etc.

EQ biosolids used for several years - home settings

(e.g. 3 sites in NH)

Higher concern

Where drinking water standards are set determine our level of concern.

Minimal to no concern

Reactions Can Impact Recycling

- NH Legislation – a dozen bills in 2017 & 2018
  - Pushing lower drinking, groundwater, and surface water standards
- NJ proposed: 14 ppt for PFOA in drinking water
- PA proposed: 6 ppt for PFOA in drinking water

This is where water quality professionals need to engage. It is premature for anyone to set lower drinking water numbers (MCLs, etc.); EPA PHA is being applied and provides high level of protection

It is premature to set <u>any</u> soil or wastewater or residuals concentration number. The science is not there yet!

Weigh in wherever & whenever these are proposed!

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QUESTIONS?