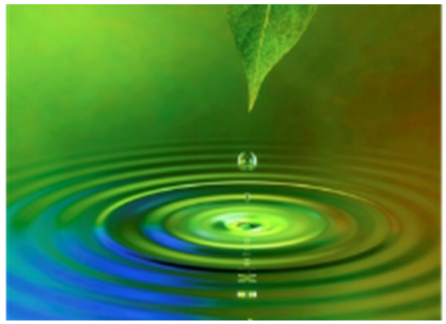



Emerging Contaminants in the Landfill Industry: What to Expect. How to Manage.

Presented to:
Engineering Society of Detroit's 28th Annual Solid Waste Technical Conference

By: Nikki Delude Roy and Ken Quinn

April 11, 2018

Objectives

- Avoid Surprises
  - Don't have a regulator or 3rd party identify a previously unknown contaminant of concern
  - For example: New Hampshire has required every landfill to analyze for PFAS in their monitoring programs
  - Vermont: One attempt to break the PFAS cycle
- Manage Sites Proactively
  - Develop responses prior to a site
  - becoming an emergency
  - But what constituents might become an issue?

Q

Developing a Balanced Approach

- What are emerging contaminants & which ones have regulatory concerns?
- What's the probability they're in my landfills?
- What regulatory limits are being considered or implemented?
- What's their fate and transport. In the landfill? In the environment, especially in groundwater?
- How do I manage the risk of contaminants of emerging concern?
- Other considerations

Q

Emerging Contaminants – Who Identifies them?

- DOD Emerging Contaminants Program
  - Watch & Action Lists
  - Actions: Perchlorate, RDX, 1,4-dioxane, Strontium, PFAS, Lead
- EPA Unregulated Contaminant Monitoring Program (UCMR)
  - Under the 1996 Clean Water Act: every 5 years
  - UCMR3 – 2012, Assessed 28 constituents in 4,850 water supplies
    - 1,4-dioxane detected in 7%
    - PFOS & PFOA detected in 0.9% and 0.3%

      https://www.epa.gov/sites/production/files/2017-02/documents/ucmr3-data-summary-january-2017.pdf
  - UCMR4 – 2018 to 2020, list of 30 contaminants

    https://www.epa.gov/dwucmr/fourth-unregulated-contaminant-monitoring-rule
- USGS Emerging Contaminant Program
  - 253 Constituents included in a research program
    - Surface water, Sediment, Tissue, Groundwater

      https://toxics.usgs.gov/regional/emc/methods_devel.html
- Others: Universities and individuals (e.g., 1,4-dioxane by Tom Mohr)

Q

What Contaminants are of Emerging Concern?

- Nationwide Now
  - 1,4-Dioxane
  - Per- and Poly-Fluoroalkyl Substances (PFAS)

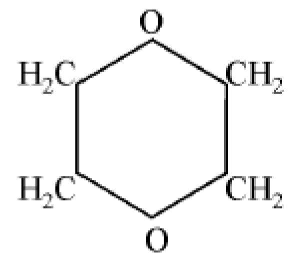
- Nationwide Future??
  - Nothing else foreseen in the short term
  - Longer term: strontium, pharmaceuticals, endocrine disrupters

- Changing/Evolving Role of U.S. EPA
  - State-by-state response

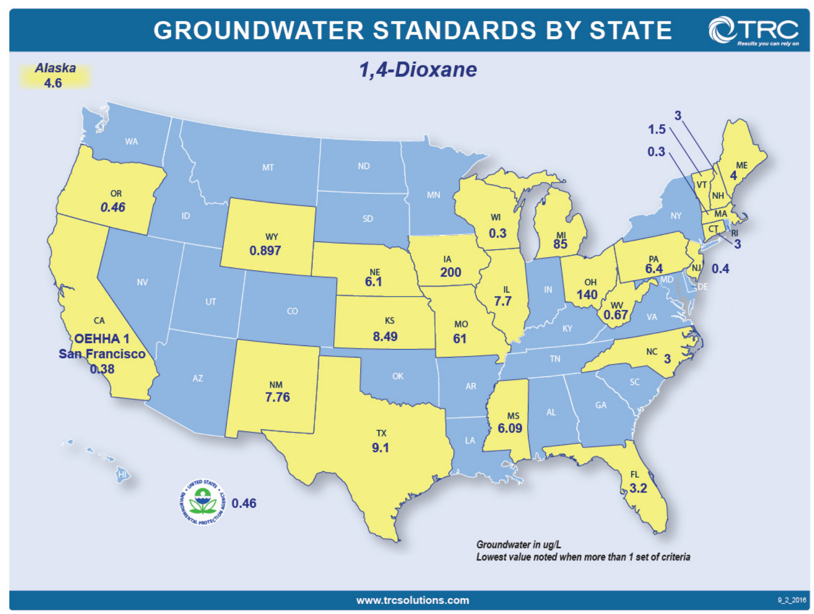
R

1,4-Dioxane?

- Cylclic ether
- Solvent stabilizer for 1,1,1-TCA (PCE & TCE in some settings)
- Also used in or by-product present in numerous commercial
  - Detergents, shampoos, cosmetics
  - Brake cleaning sprays and fluids
  - Aerosol propellants
  - Adhesives, paints, coatings, inks,
- Completely miscible with water
  - Rapid migration in groundwater
- Resistant to biodegradation
- U.S. EPA – Group B2 human carcinogen
- Low (sub 1 ppb) regulatory limit in drinking water/groundwater



1,4-dioxane



What are PFAS?

- PFAS = Per- and Poly-Fluoroalkyl Substances
- A large family of chemicals – not naturally occurring
- Used for decades (1940s to early 2000s)

AFFF; firefighting foam

aviation fluids

- Wide range of industrial applications:
  - Fire-fighting foams (AFFF - Aqueous Film Forming Foam)
  - Fluoropolymer production/application (Teflon®, Gore-Tex®, Stainmaster®, Scotchgard®)
  - Metal plating, electronic and semiconductor applications, aviation hydraulic fluid, oil/mining production, wire coating, etc.
- Found globally, even in remote places – transported by air

R

Sources of PFAS Contamination

- Point sources:
  - Class B firefighting foam use/storage
  - Fluoropolymer manufacturing facilities
  - Waste water treatment plants
  - Landfills
- Non-point sources:
  - Biosolids application
  - Atmospheric deposition
- Emerging sources:
  - Car washes
  - Granite/stone cutting/sealing facilities
  - Auto salvage yards
  - Carpet cleaning facilities, automotive detailing
  - Residential and commercial septic systems
  - Building construction materials

R

The Chemistry of PFAS

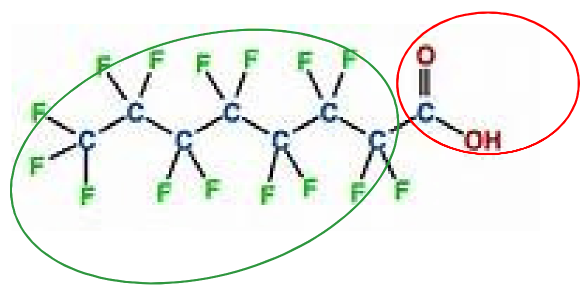
PFAS = **per** and **poly**fluoroalkyl substances

perfluoroalkyl substances – fully fluorinated alkyl tail

PFOA (a perfluoroalkane carboxylate) – C8

Tail

- Hydrophobic *(makes it a great surfactant)*
- Very stable and strong - carbon bonds shielded by fluorine *(persistent in environment, bioaccumulative in wildlife and humans)*



Head

- **Hydrophilic**
- **All but 1 carbon are surrounded by fluorine *(resistant to degradation)***

Chain length matters: more carbons = more difficult/toxic

There are hundreds of other PFAS compounds

Many poly-fluorinated compounds will degrade to the stable per-fluorinated compounds, like PFOA

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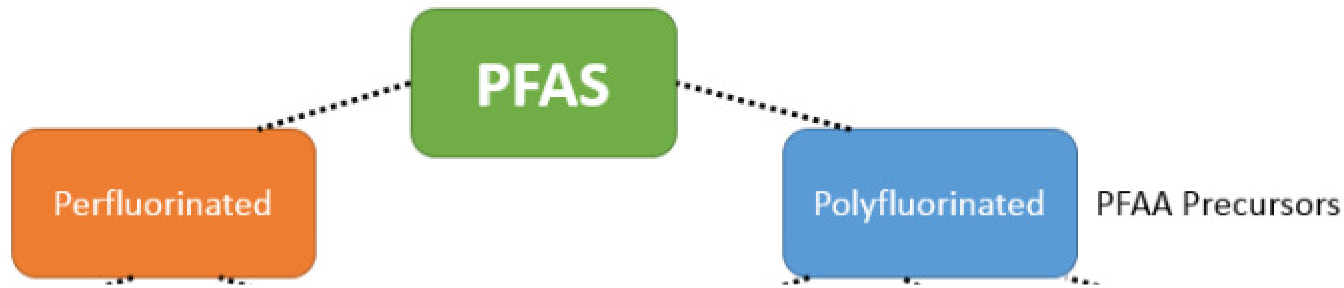
The Chemistry of PFAS



Adapted from Buck et al., 2011

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Developing a Balanced Approach

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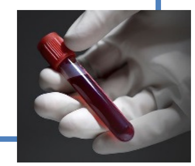
A Brief History of PFAS

1938-1949
- Teflon (PTFE) developed by DuPont
- PTFE used in products

1956
- Stain-resistant products (PFOS)

1968
- Navy developed AFFF (aqueous film forming foam)

1978
- Detected in blood of manufacturing workers



2002
- PFOS manufacturing phased out

2006-2015
- 2006 PFOA Phased out
- EPA PFOA Stewardship Program
- 2009 Stockholm Convention
- 2009 EPA released provisional health advisories (PHAs) for PFOA/PFOS (400/200 ppt)

2012-2014
- UCMR-3 Sampling identifies PFAS in 97 public drinking water supplies

2016
- EPA Revises Health Advisory for PFOA/PFOS (70 ppt)
- Manufacturing facility in Hoosick Falls, NY first PFAS-related Superfund site for PFOA
- 100k Alabama residents advised not to drink their local water

2011-2015
- Several States establish SW & GW standards for PFAS for remediation

2017-2018
- POTWs considering sampling influents
- States taking active roles (e.g., NH requires GW permits to analyze for PFAS)

Conclusion: they're in most (all?) landfills

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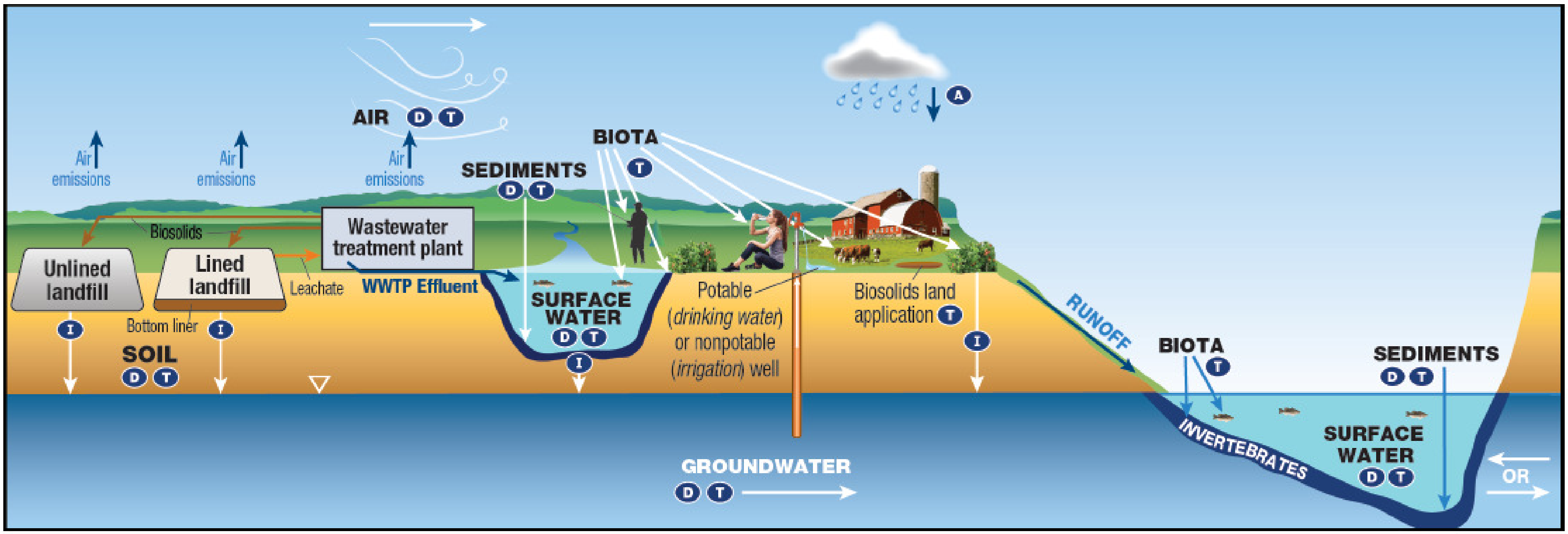
The PFAS Cycle



KEY A Atmospheric Deposition D Diffusion/Dispersion/Advection I Infiltration T Transformation of precursors (abiotic/biotic)

Figure 3. Conceptual site model for landfills and WWTPs.
(Source: Adapted from figure by L. Trozzolo, TRC, used with permission)

https://pfas-1.itrcweb.org/fact-sheets/

Q

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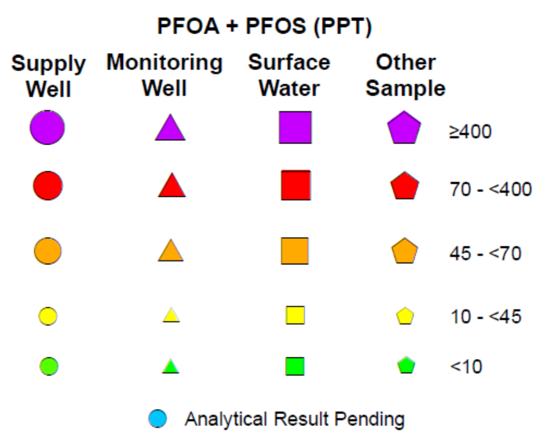
LLS (C&D) Landfill, Salem, NH

- Monitoring wells up to 820 ppt combined PFOS and PFOA
- Nearby private water supply wells: up to 14 ppt combined PFOS and PFOA



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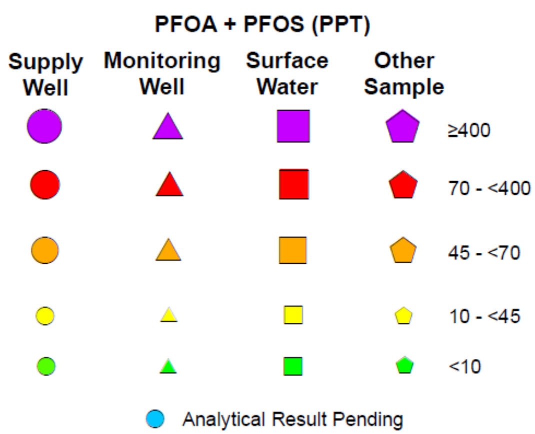
Coakley Landfill, Rye, NH

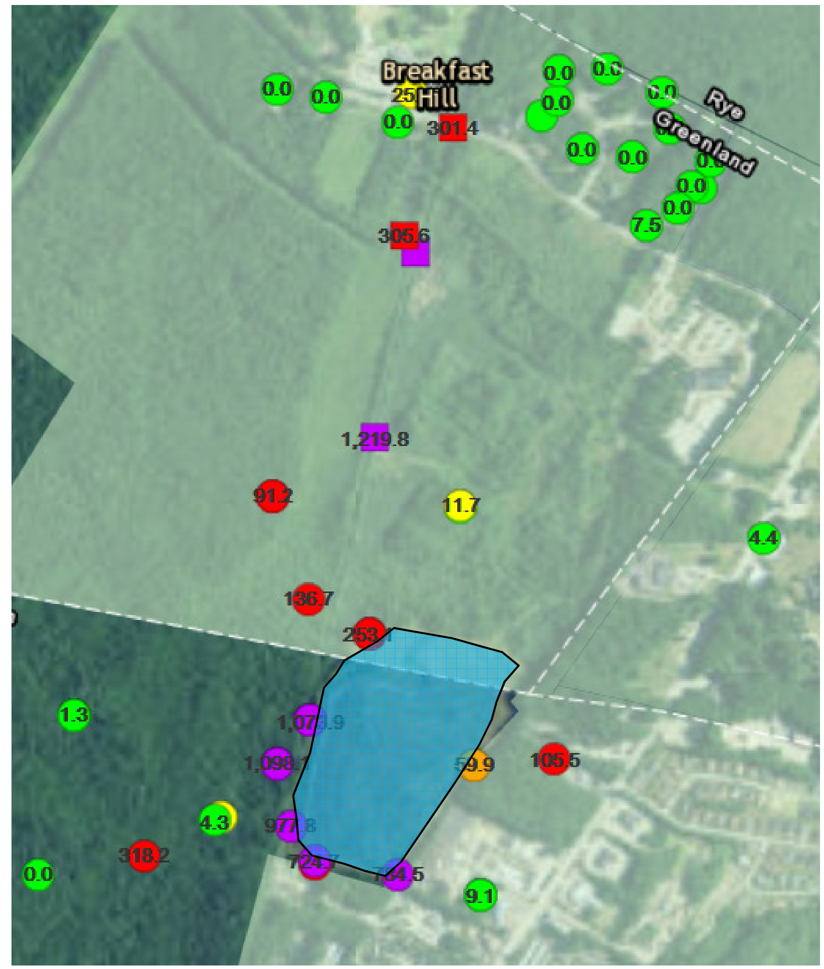
Groundwater

- PFOA up to 756 ppt
- PFOS up to 452 ppt

Surface Water

- PFOA and PFOS up to 1,200 ppt





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PFAS: The Rapidly Changing Regulatory Landscape

State	Year	Type	Promulgated?	PFOA	PFOS	PFNA	Other PFAS	Gen-X
				(µg/L)				
Alaska (AK)	2016	GW	Y	0.40	0.40			
Connecticut (CT)	2016	GW		0.07	0.07	0.07	Y	
Colorado (CO)	2017	DW		0.07	0.07		Y	
Delaware (DE)	2016	GW		0.07	0.07		N	
	2016	GW		0.07	0.07		Y	
Iowa (IA)	2016	Protected GW	Y	0.07	0.07		N	
		Non-protected GW	Y	0.7	1		N	
Maine (ME)	2016	DW		0.07	0.07		N	
	2016	GW		0.13	0.56		N	
	2016	RW		0.05	1.2		N	
Michigan (MI)	2015	SW	Y	0.42	0.011		N	
	2018	GW	Y	0.07	0.07		N	
Minnesota (MN)	2017	GW		0.035	0.027		Y	
	2017	GW		0.035	0.027		Y	
	2017	GW		0.035	0.027		Y	
Nevada (NV)	2015	DW		0.667	0.667		Y	
New Hampshire (NH)	2016	GW	Y	0.07	0.07		N	
New Jersey (NJ)	2015	GW	Y			0.010	N	
	2017	GW	P			0.010	N	
	2017	DW	P			0.013	N	
	2017	DW	Y	0.014			N	
North Carolina (NC)	2006	GW	Y	2			N	
	2017	DW					N	0.14
Oregon (OR)	2011	SW	Y	24	300	1	Y	
Texas (TX)	2017	GW	Y	0.29	0.56	0.29	Y	
Vermont (VT)	2016	GW/DW	Y	0.02	0.02		N	

International:
Australia
Canada
Denmark
Germany
Italy
Netherlands
Sweden
UK

Residential soil and soil leaching standards exist also.

R

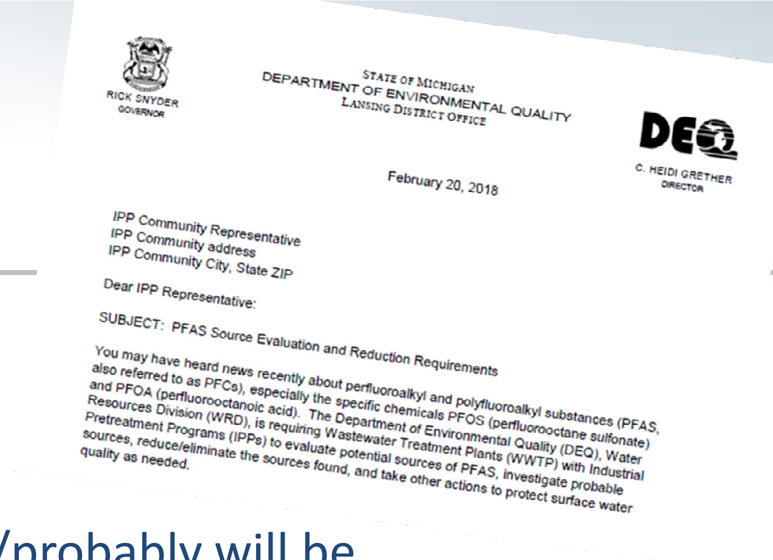
PFAS – The New Frontier

- Parts per million (ppm, equivalent to mg/L)
  - 0.000001, 10^{-6} or $\frac{1}{1\,000\,000}$
  - 1.25 2-Liter bottles in 1 Olympic-size swimming pool

- Parts per billion (ppb, equivalent to µg/L)
  - 0.000000001, 10^{-9}, or $\frac{1}{1\,000\,000\,000}$
  - ½ tsp in Olympic-size swimming pool

- Parts per trillion (ppt, equivalent to ng/L)
  - 0.000000000001, 10^{-12} or $\frac{1}{1\,000\,000\,000\,000}$
  - 1 drop of water (0.05 milliliters) in 2 Olympic-size swimming pools

PFAS: The Rapidly Changing Regulatory Landscape



RICK SNYDER
GOVERNOR

STATE OF MICHIGAN
DEPARTMENT OF ENVIRONMENTAL QUALITY
LANSING DISTRICT OFFICE

DEQ

C. HEIDI GRETHER
DIRECTOR

February 20, 2018

IPP Community Representative
IPP Community address
IPP Community City, State ZIP

Dear IPP Representative:

SUBJECT: PFAS Source Evaluation and Reduction Requirements

You may have heard news recently about perfluoroalkyl and polyfluoroalkyl substances (PFAS, also referred to as PFCs), especially the specific chemicals PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid). The Department of Environmental Quality (DEQ), Water Resources Division (WRD), is requiring Wastewater Treatment Plants (WWTP) with Industrial Pretreatment Programs (IPPs) to evaluate potential sources of PFAS, investigate probable sources, reduce/eliminate the sources found, and take other actions to protect surface water quality as needed.

- Waste Water Treatment Plants:
  - MI DEQ has issued letters to POTWs rolling out the expectation that all landfill leachate being disposed to POTWs may be/probably will be analyzed BY THE POTW for PFAS

- New Hampshire has required all landfill groundwater monitoring programs to analyze for PFAS

- NYSDEC environmental sites sampling for PFAS, PFOA and PFOS are now on the hazardous substance list, and fire fighting foams that contain PFOA or PFOS are prohibited
  - Colonie Landfill (Colonie, NY) is applying for expansion permit. A group opposed to the expansion collected samples: PFOA was detected by in stormwater (68 ppt), in seeps near the Mohawk River (519 ppt), and in samples from the River (1-3 ppt)

R

PFAS: The Rapidly Changing Regulatory Landscape

- Another attempt to break the PFAS cycle: Vermont PFOA and PFOS Guideline Levels for Accepting Landfill Leachate at permitted WWTF

PFAS analyte:	Column 2:	Column 3:	Column 4:
	Landfill Leachate concentration requiring no restrictions	Landfill Leachate concentration which may require restrictions	Landfill Leachate concentration requiring pretreatment
PFOA	0.120 mg/L	0.120 mg/L to 1.2 mg/L	>1.2 mg/L
PFOS	0.001 mg/L	0.001 mg/L to 0.010 mg/L	>0.010 mg/L

WWTP

Leachate ?

Landfill

R

PFAS: The Rapidly Changing Knowledge Landscape

GOLDER

TRC Results you can rely on

In the last few months:

- ✓ NGWA: Published groundwater and PFAS: State of Knowledge and Practice
- ✓ ITRC: Published first six of seven PFAS Fact Sheets
- ✓ U.S. EPA: Launched a cross-agency effort to address PFAS
- ✓ Bipartisan legislation to fund the federal government for fiscal year 2018 also directs the Defense Department to complete a $7 million, first-ever national health study on PFAS exposure in drinking water
- ✓ Michigan: POTW focus
- ✓ California: added PFOS and PFOA to its list of Prop 65 chemicals
- ✓ Colorado: Scheduled a hearing for an Aquifer Specific PFOA/PFOS groundwater standard (70 ppt) for April 18, 2018
- ✓ Wisconsin: WDNR Published Feb. 1, 2018 RR Report stating it has authority to regulate PFAS compounds, relying on soil standards and EPA's Health Advisory (70 ppt)
- ✓ Soil standards – leaching

Q

Developing a Balanced Approach

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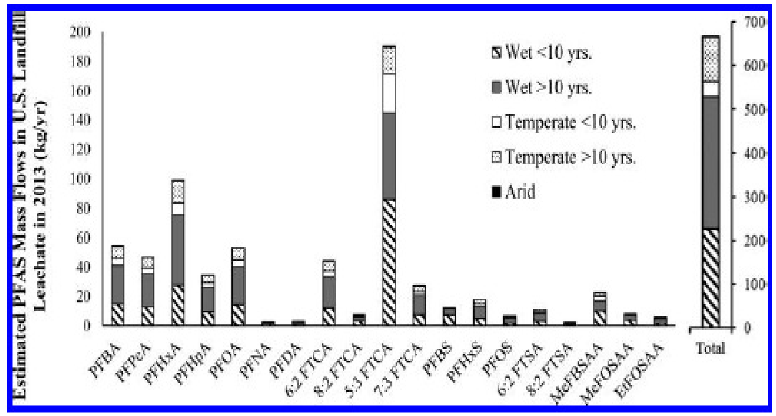
Q

PFAS in Landfill Leachate

- US Landfill Study (Lang et al., 2017) – 95 samples from 18 landfills
  - 70 PFAS measured, 19 PFAS detected in >50% of samples
  - PFOS: 3 to 200 ppt
  - PFOA: 100 to 1,000 ppt
  - Total PFAS: 2,000 to 29,000 ppt
  - 5:3 FTCA (precursor) dominant in most leachates: 400 to 15,000 ppt

National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate ES&T 2017

J. R. Lang, B. McKay Allred, J.A. Field, J.W. Levis, & Morton A. Barlaz



- Canadian Landfill Study (Li, 2012) – samples for 28 landfills
  - PFAS detections in all 28 samples
  - PFOA detected in all samples, mean concentration of 439 ppt

- German Landfill Study (Busch, 2009) – 22 German landfills
  - 38 PFAS detected
  - Total PFAS: 30.5 ppt to 13,000 ppt

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Leachate PFAS Composition Observations

- Highly variable - between sites and seasonally within same landfill
- But there are general observations:
  - PFAS present in leachate of >50% of landfills tested.
  - PFOA & PFOS ranges of key PFAS
    - PFOA – 100 – 1,000 ng/L
    - PFOS – 3 -200 ng/L
  - Short-chain PFAS typically found at greater concentrations than PFOA and PFOS, possibly due to degradation of precursors, like 5:3FTCA or preferential release from waste
  - Similar overall concentrations of PFAS in old and new waste.

Managing Leachate PFAS Strategies

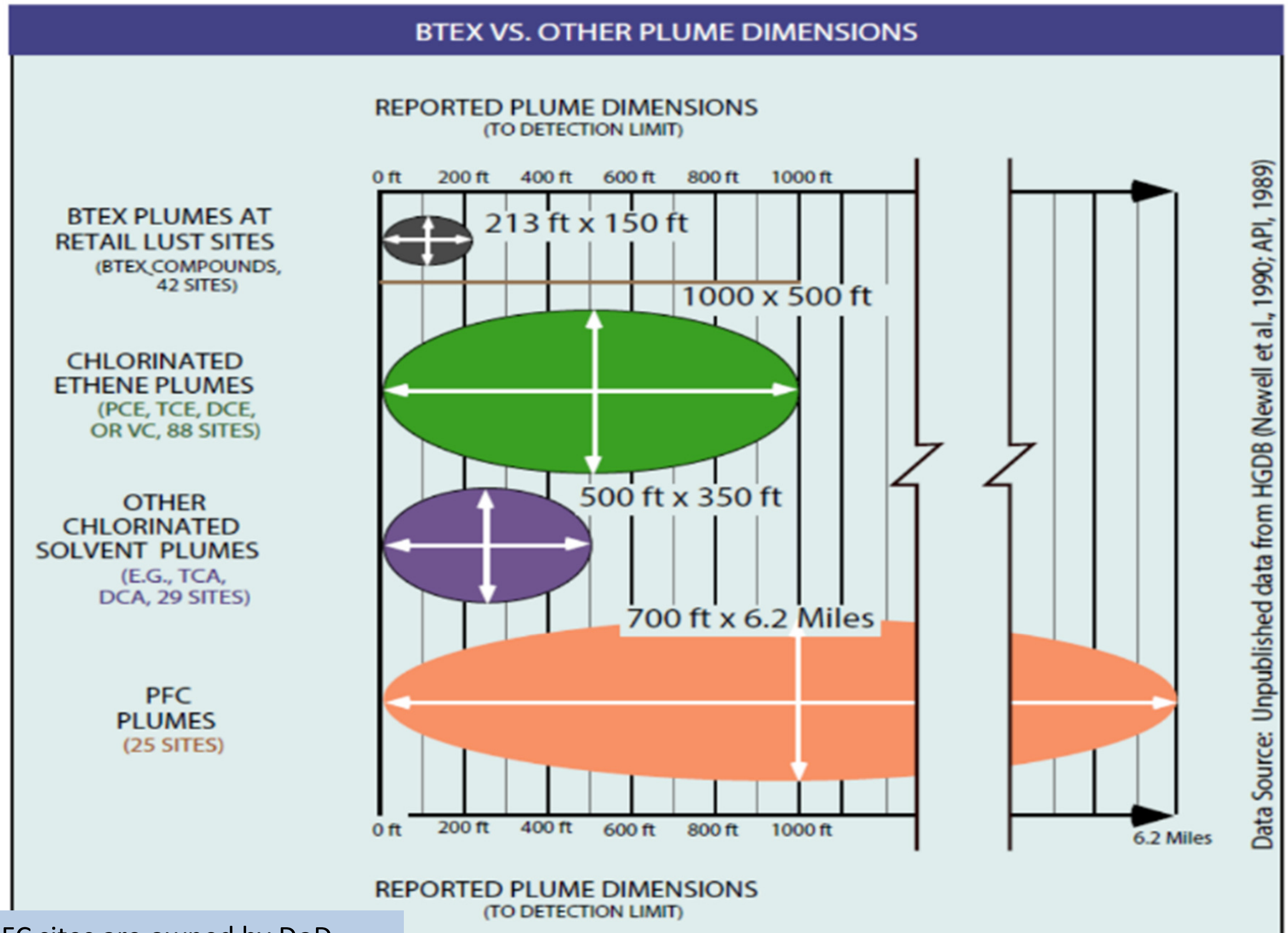
- Will your POTW target your landfill leachate for analysis of PFAS?
  - No? If your site qualifies as "typical" (i.e., no waste from industries identified in the DEQ list, no AFFF used at a landfill fire, etc.).
  - If yes: Leachate loading to the POTW could be assessed using the Lang data and impact assessed with a dilution factor:
    (e.g., 120,000 gal/yr of leachate to 5MGD POTW is a 15,000 times dilution)
  - DEQ standards for POTW effluents[1]:

	HNV (nondrinking)	HNV (drinking)	FCV	FAV	AMV
PFOS (ng/L)	12	11	140,000	1,600,000	780,000
PFOA (ng/L)	12,000	420	880,000	15,000,000	7,700,000

  - For HNV standards, leachate could be up to 180 ug/L PFOS

Q 1.From: presentation entitled "IPP PFAS Initiative Regional Information Meetings, PFAS AND POTWS," by Carla Davidson, MI DEQ March 2018

PFAS Mobility



Theses PFC sites are owned by DoD and are mostly Airforce bases

Developing a Balanced Approach

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- What regulatory limits are being considered or implemented?

- What's their fate and transport. In the landfill? In the environment, especially in groundwater?

- How do I manage the risk of contaminants of emerging concern?
  - Sampling & Analysis
  - Separate landfill impacts from other impacts
  - Remediation Alternatives

R

PFAS – Sampling and Analysis

When to sample?

- Sampling required by State, POTW, etc.
- In high risk settings:
  - Historical waste types, nearby water supplies, public scrutiny?
- Analytical techniques
  - Laboratory selection
  - What PFAS target compound list?
    - Report PFOA & PFOS only (varies from state to state)?
    - Others for forensics?
  - Data Validation

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PFAS – Sampling and Analysis

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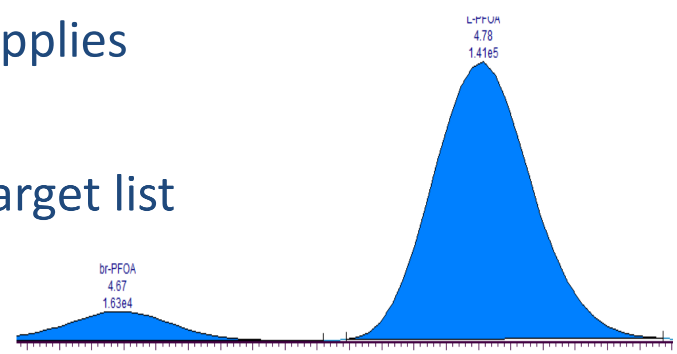
TRC
Results you can rely on

EPA United States Environmental Protection Agency

Technical Advisory- Laboratory Analysis of Drinking Water Samples for Perfluorooctanoic Acid (PFOA) Using EPA Method 537 Rev. 1.1

Analytical Method	Media
EPA Method 537	Drinking water (1-40 ppt)
ASTM D7979-16	Water, sludge
ASTM D7968-14	Soil

- Method 537
  - *“as specifically written”*
  - Is not amenable to expanded list of compounds or other sample matrices without modification
  - Addresses both linear & branched isomers
- Designed/certified for chlorinated public water supplies
  - UCMR 3 method
  - Amenable to a specific 14 compound PFAS target list
- Method 537 Modified
  - *“Laboratory proprietary method”*



815-B-16-021, September 2016

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PFAS – Sampling and Analysis

- Understand site history, and surrounding property use
- Determine target analyte list
- Establish sampling SOP: communicate prohibited materials/practices to field staff
  - Teflon containing materials (Teflon tubing, waterproof notebooks, blue ice packs)
  - Clothing or PPE treated with PFAS (Gore-Tex, Tyvek, fabric softener)
  - Morning cleaning/shower routine
  - No containers with LDPE or glass (sorption), no Teflon-lined caps
  - No food or drink packaging
- Because of anthropogenic background, QA samples are essential
- Background samples are important
  - There are many potential PFAS “background” sources, even in rural areas

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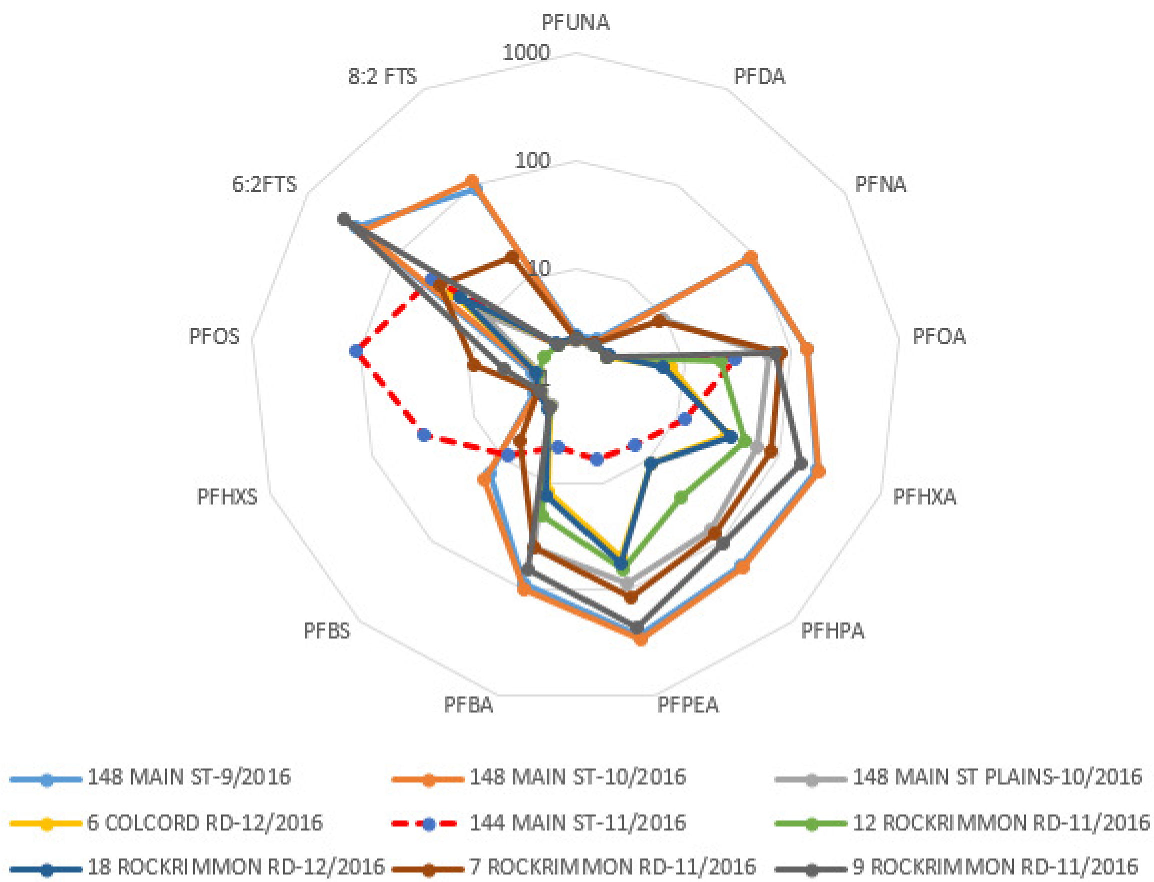
Separating Impacts
Example: Interpreting the Results – Drinking Water Samples Near a Rural Fire Department



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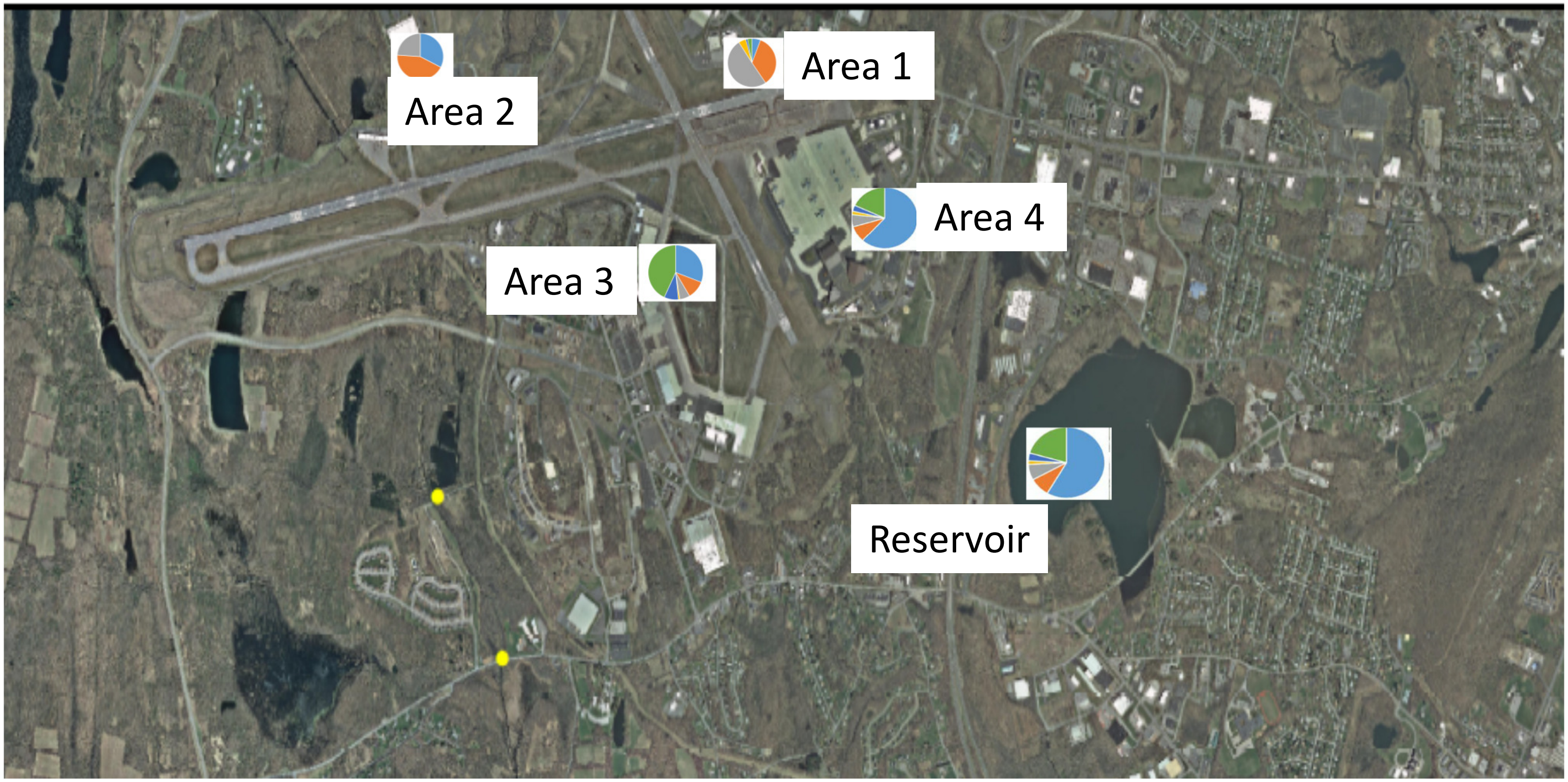
Separating Impacts
Example: Fingerprinting Multiple Sources of Fire Fighting Foam

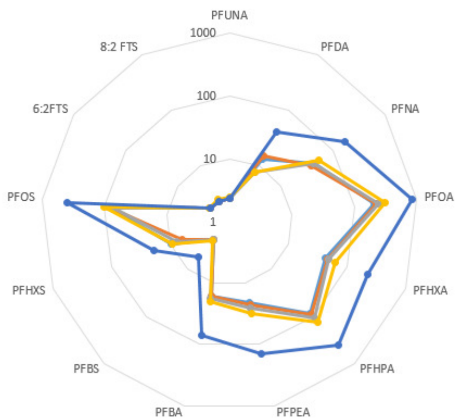


Blue – PFOS *Green- PFHxS*

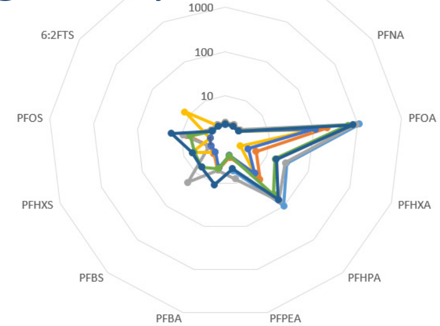
Q*Orange PFOA* *Grey PFHxA*

Separating Impacts
Example: Interpreting the Results – Comparison of Results from Different Sources

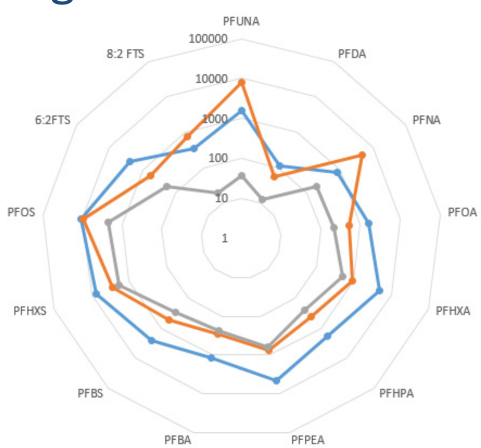
Surface water near a landfill



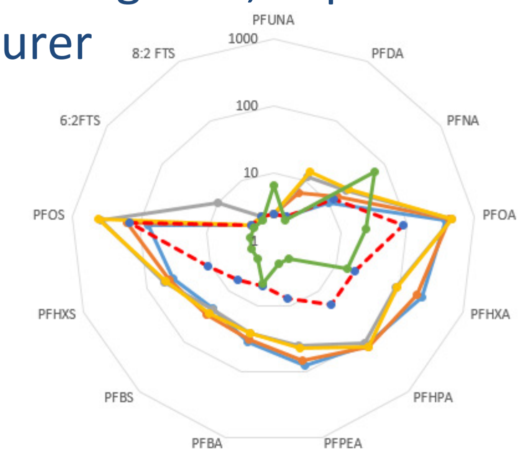
Drinking water near a fluoropolymer manufacturing facility



Fire Training Area



Wastewater Lagoons, Paper Manufacturer



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PFAS Remediation Alternatives - Water

Fate and Transport/ Remediation Challenges

- Low Volatility (rules out stripping)
- Moderate solubility
- Strength of C-F Bond
- Treatment efficiency must be very high because of low (ppt) remediation objectives

Ex Situ Technologies

- Carbon Sorption*
  - *inefficient
- Emerging technologies:
  - Reverse Osmosis
  - Membrane filtration
- AOP

In Situ Technologies

- Emerging technology:
  - Carbon injection
  - PRB
  - Chemical Oxidation

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Biosolids

- PFAS are present in WWTP influent, effluent, and sludge. WWTP treated effluent (WRF, 2016)
  - PFOS: 3.0 to 86 ppt
  - PFOA: 15 to 1,050 ppt
- Waste water treatment processes can increase mass of some PFAS through conversion of precursors
- PFAS are present in soils amended with biosolids (Sepulvado et al., 2011)
  - PFOS was present in biosolids amended soils at concentrations between 2 to 11 ug/kg in plots amended for 3 years, and at up to 483 ug/kg in plots amended for more than 3 years
  - Estimated that normal application rates would result in pore water concentrations over 200 ppt

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Amended Compost with Paper Sludge

- Total PFAS – 26,000 ppm to 45,000 ppm
- PFOA – 2,400 ppm to 4,900 ppm
- PFOS – 9,500 ppm to 17,000 ppm
- Analysis didn't include precursors

Compare to Connecticut soil mobility standards: 1,400 ppm to 14,000 ppm

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Landfill Gas

- PFAS detected in:
  - Landfill Gas
  - Landfill gas condensate
  - Ambient air around landfill (and waste water treatment plants)
- Volatile Precursors
  - Some PFAS (e.g. fluorotelomer alcohols like 8:2-FTOH) have moderate volatility
  - These compounds can break down to form PFCs in the environment
  - Significant PFAS (mostly FTOH) emissions (>1000 g/year) have been calculated from WWTPs and landfills (Ahrens et al, 2011)

Compound	Vapor Pressure (at 25-C)
2,3,7,8-TCDD	2E-07
Dieldrin	7E-04
PFOA	1.3
Naphthalene	10.6
8:2-FTOH	212
PCE	2550
TCE	9900
Benzene	12800

Conclusions

- Contaminants of emerging concern have the potential to create unwanted surprises
- Each contaminant has challenges in identification, characterization, analyses, and remediation
- Rely on proactive approach and experts to consider:
  - Hydrogeology
  - Chemistry
  - Remedial Alternatives
- The science (and policy) around contaminants of emerging concern is constantly evolving
- Know what's going on, take control, and manage the outcome

Thank you

Questions?

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