Introduction to PFAS: Source, Fate and Transport in Surface Waters and Relevant Advisories

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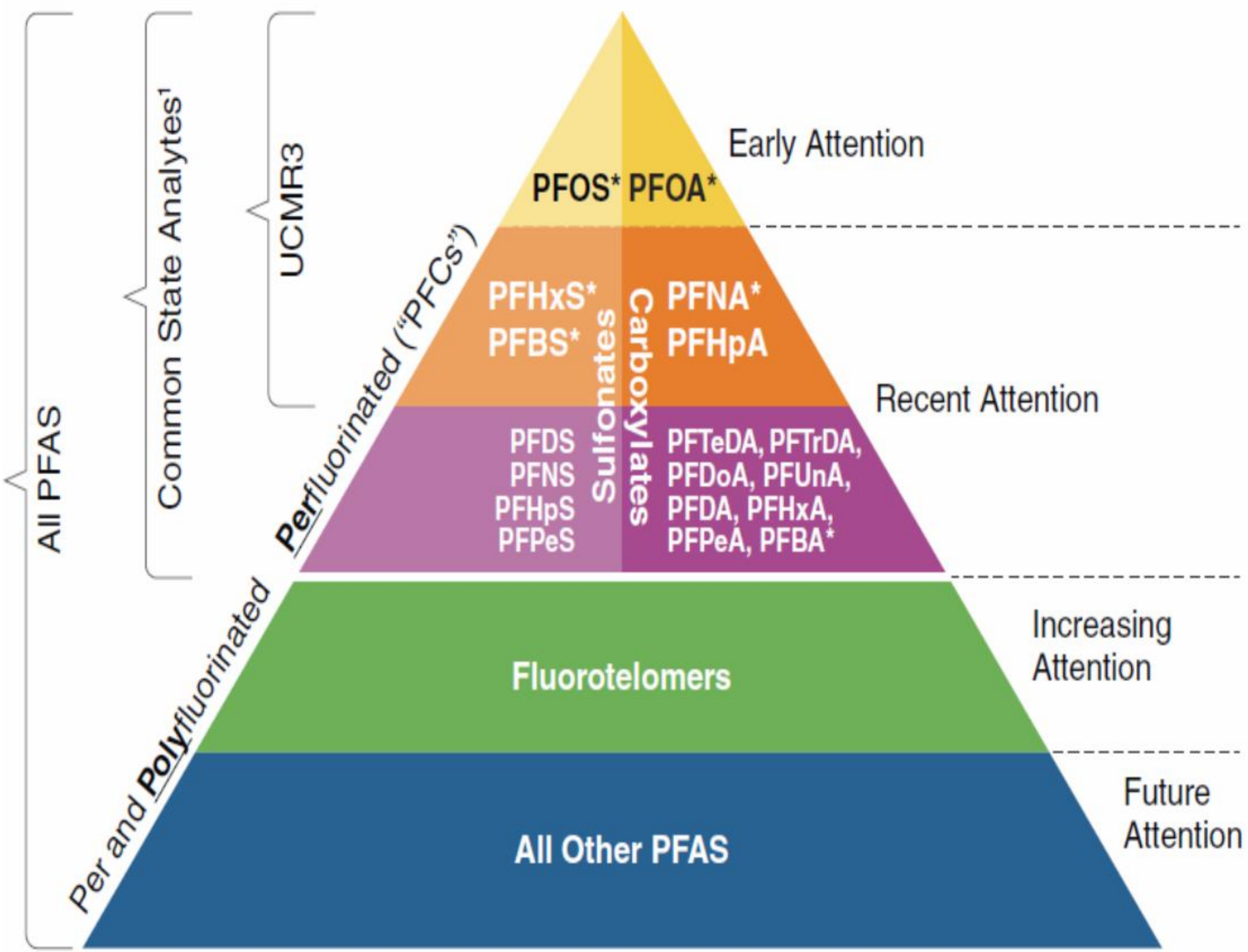


(From ITRC Fact Sheet, 2017, History and Use of PFAS)

Outline

- Compound classes and structure
- Health advisories
- Use and Sources
  - Highlight on major sources
  - General distribution
- Fate and Transport Characteristics
- Example groundwater/surface water studies
- Bioaccumulation

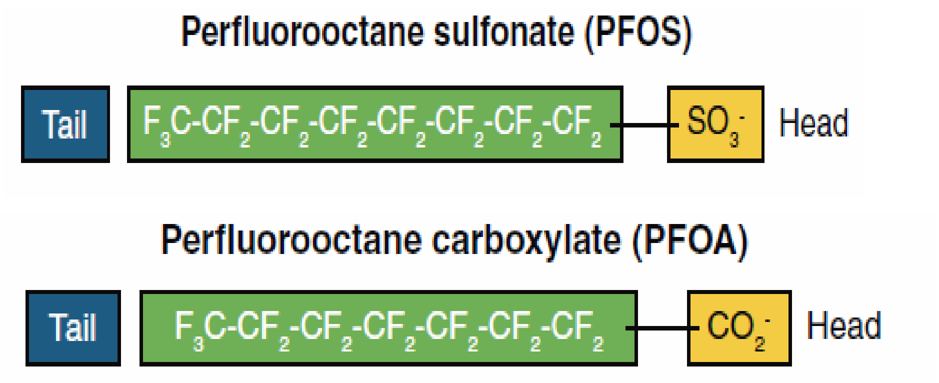
Perfluorinated

- Perfluoroalkyl acids (PFAAs) include two major groups, with PFOS and PFOA the most commonly tested in each
  - Anionic and acid forms but anionic most common
  - Believed to be essentially non-degradable
  - "Terminal degradation products" of polyfluoroalkyl substances
  - Up to 14 carbon chain lengths
- Perfluoroalkane sulfonamides (FASAs)
  - Can degrade to form PFAAs such as PFOS
  - Examples: N-Methyl perfluorooctane sulfonamide (MeFOSA) and N-Ethyl perfluorooctane sulfonamide (EtFOSA)

Polyfluorinated

- Fluorotelomer and perfluoroalkane sulfonamido substances
- Not fully fluorinated; a non-fluorine atom (typically H or O) attached to at least one carbon; creates 'weakness'
- Some are key raw materials, and some are degradation products
- Precursors that can degrade to PFAAs

More than 3,000 Synthetic Chemicals



6:2 Fluorotelomer sulfonate (6:2 FtS)

$$\overbrace{F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2}^{6}\text{-}\overbrace{CH_2CH_2}^{2}\text{-}SO_3H$$

(Structure figures from ITRC Fact Sheet, 2018, Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS))

Health Advisories

Jurisdiction		PFOA (ppt)	PFOS (ppt)	Notes
Advisory or Regulatory Standard				
U. S. EPA, 2016	**Advisory**	**70**		for combined
New Hampshire, 2016, AGWQ	**Standard**	**70**		for combined
Vermont, 2016	**Standard**	**20**	**20**	
Australia, January 2017 interim drinking water guidance	**Advisory**	**5,000**	**500** (includng PFHxS)	
Australia, April 2017 final drinking water guidance	**Advisory**	**70**	**560** (including PFHxS)	
Canada, proposed June 2016; screening values November 2017	**Advisory**	**200**	**600**	
Michigan, non-cancer values, 2014		**420**	**11**	
Minnesota drinking water (as of 2016) (as of 2017)	**Standard** **Advisory**	**300** **35**	**300** **27**	PFBA & PFBS = 7000 Adopted 5/2017
New Jersey health-based guidance Proposed	**Advisory**	**40** **14**		
West Virginia (as of 2016)	**Standard**	**400** or **500**		
Maine CDC, 2014, health-based MEG		**100**		

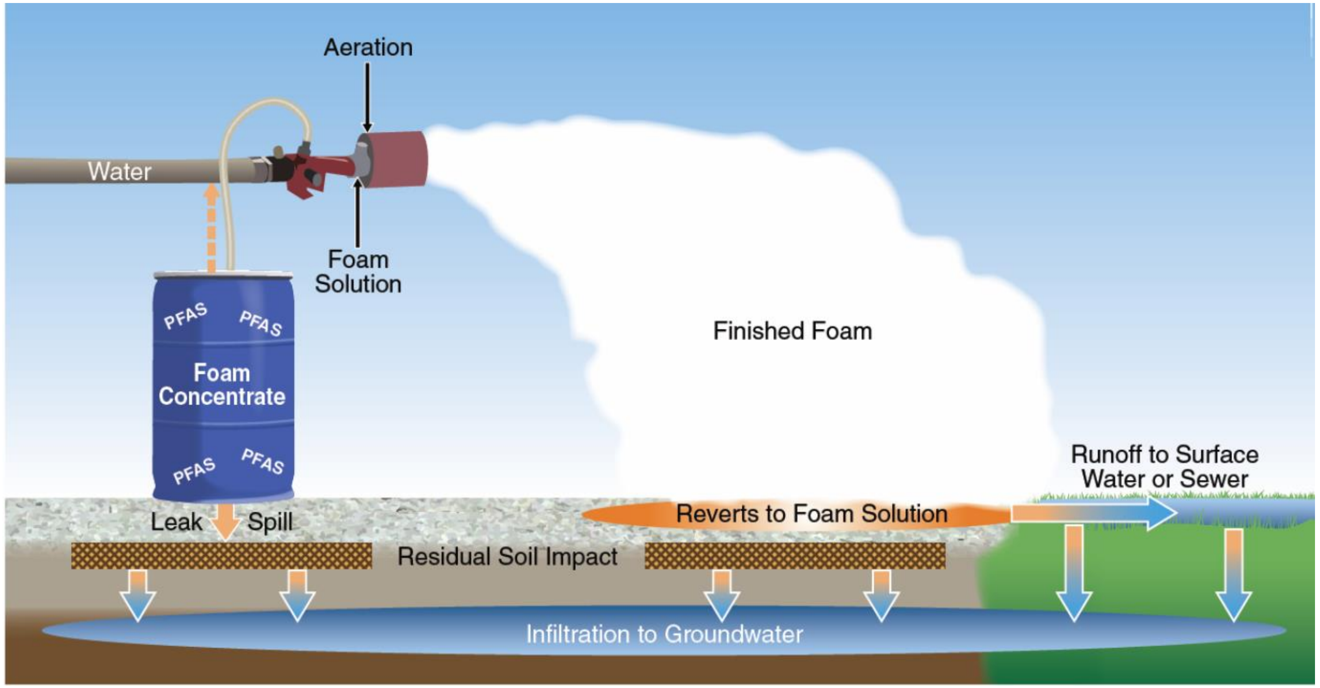
PFAS Uses and Sources

- Wide variety of industry and commercial/household products, including for fire resistance, dust suppression, and oil, stain, grease, and water repellence (began in 1940s; AFFF in 1960s)
- Waste disposal sources
  - Industrial wastes
  - Landfills
  - Wastewater treatment plant effluent
  - Biosolids land application
  - Air (vapor and particulates)
- AFFF (aqueous film forming foam) users
  - Military and civilian airports, train yards
  - Fire training areas
  - Chemical refineries

Many military bases and airports located in coastal areas, including Chesapeake Bay area.

- 3M AFFF
  - PFOS was a major component of 3M AFFF
  - PFHxS (C6) > PFOS in 3M AFFF
  - PFOA minor component in AFFF
  - Ultra-short sulfonates as well as cationic and zwitterionic structures
  - Many PFOS-like structures due to 'messy' chemistry
- Telomer-based AFFF
  - PFOS not present in telomer-based AFFF
  - Fluorotelomer sulfonates (FTSAs) minor component
  - Anionic, cationic and zwitterionic structures

SERDP and ESTCP Webinar Series (#23)



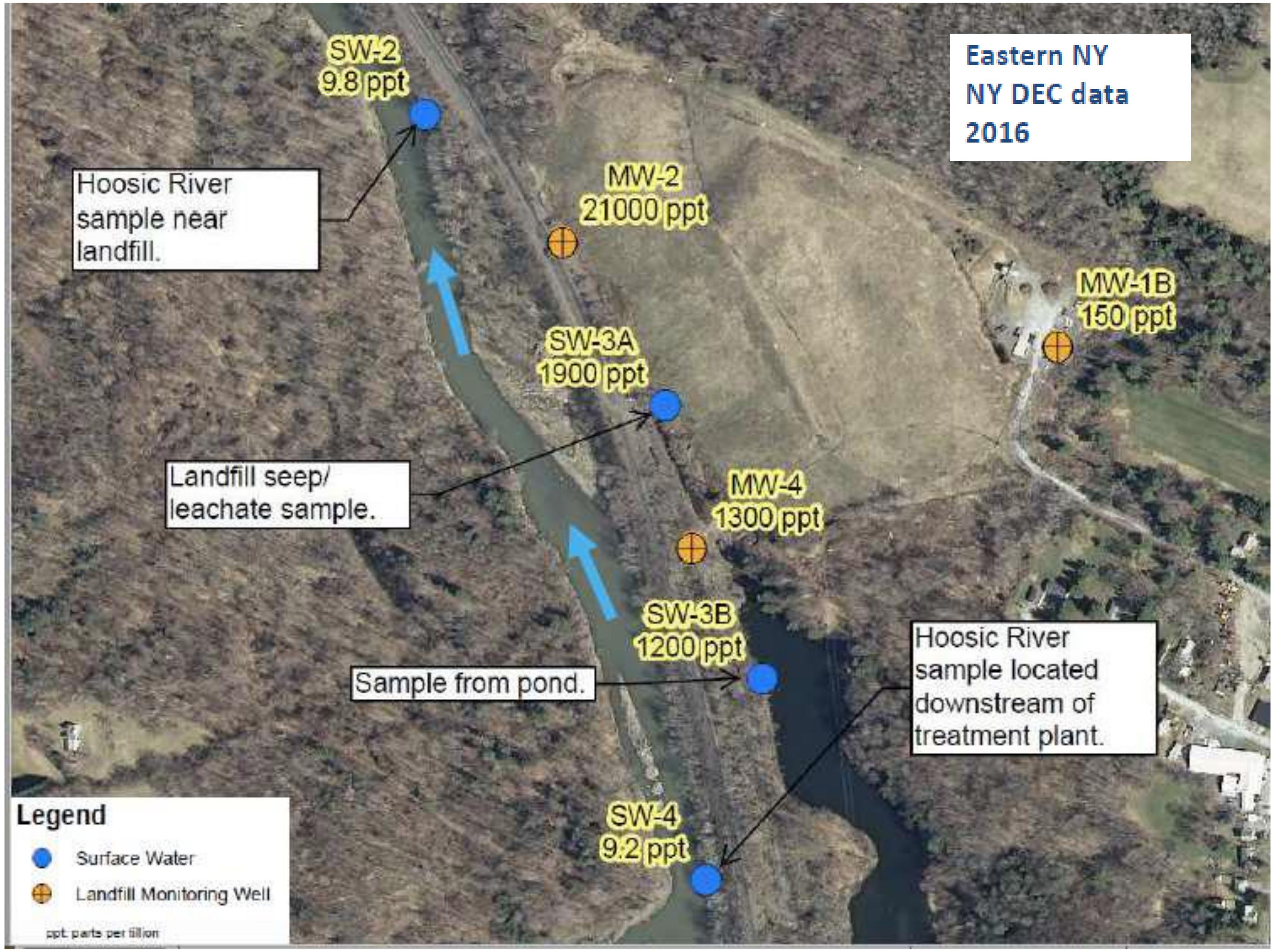
(From ITRC Fact Sheet, 2017, History and Use of PFAS)

(From Denis LeBlanc, Cape Cod site)

Landfills

Landfills commonly located near or adjacent to surface-water bodies.

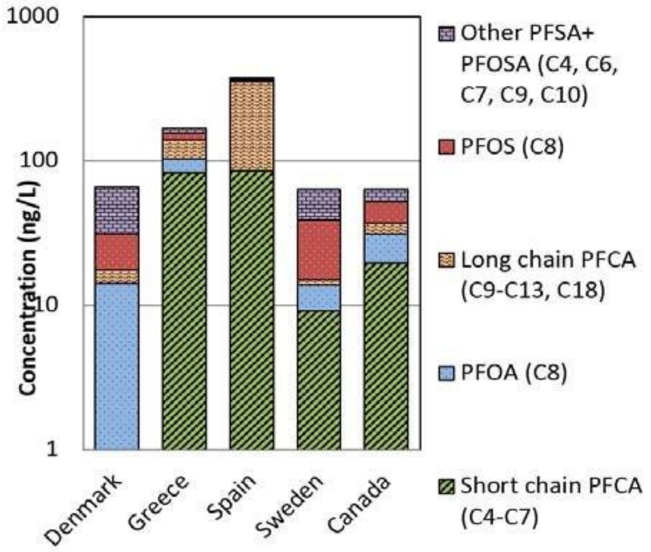
- Repositories for PFAS-contaminated consumer goods, PFAS-contaminated industrial waste and sewage sludge, and municipal sewage sludge in some cases.
- Landfills containing PFAS sources release PFAS at slow but steady rates for decades.
- Unlined landfills have a higher potential of contributing PFAS to groundwater or surface water.
- Leachate volume released typically is low compared to the flow volume in most wastewater treatment plants, but industrial landfills a significant source.



(from Beecher and Rainey, 2018, MWEA Biosolids Conference)

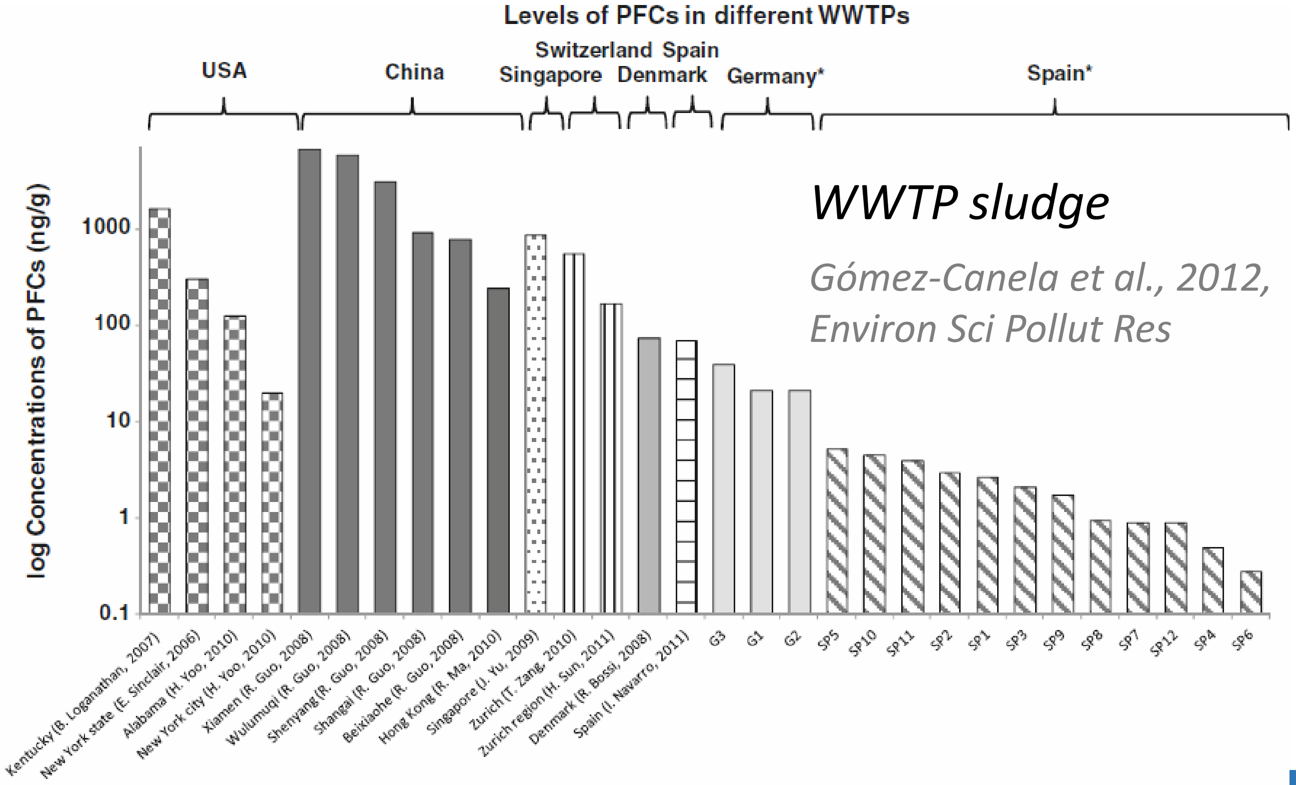
Wastewater Treatment Plants

- PFAAs may increase in effluent compared to influent from the oxidation of precursors during the treatment process.
- Conventional WWTPs have limited efficiency in removing PFAS from water.
- Maximum in surface waters near typical WWTPs: PFOS, 24 ng/L; PFOA: 25 ng/L
  - 4x higher in WWTP located near industry (Becker et al., 2008; Boulanger et al. 2005; Wilkinson et al. 2017; MDH 2008)
- PFAS can be concentrated in solid waste
  - biosolids soil amendment common in agriculture and reclamation
  - provide a pathway for PFAS run-off to surface water and infiltration to groundwater



WWTP effluent

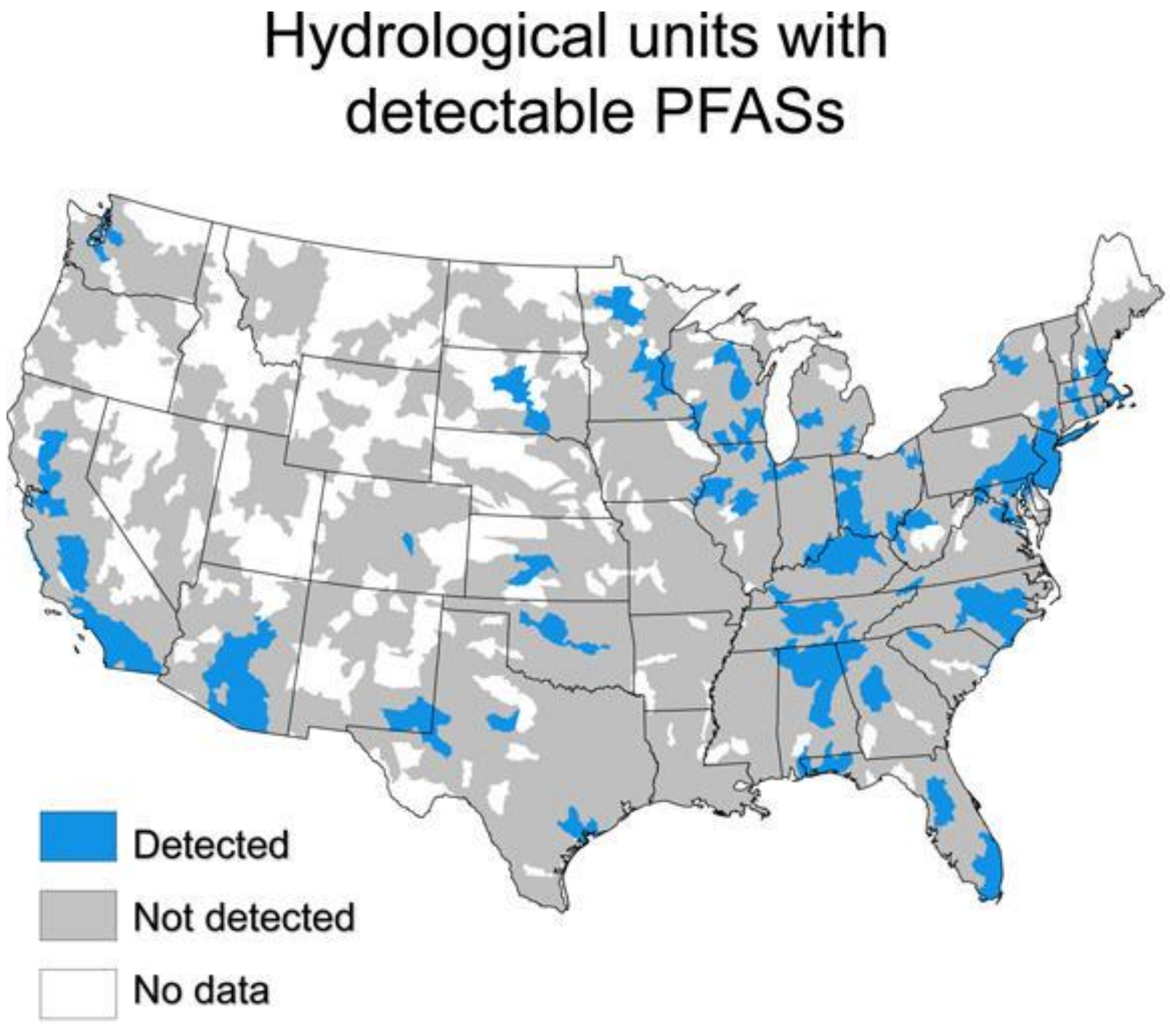
Hamid, 2016, Ecocycles 2

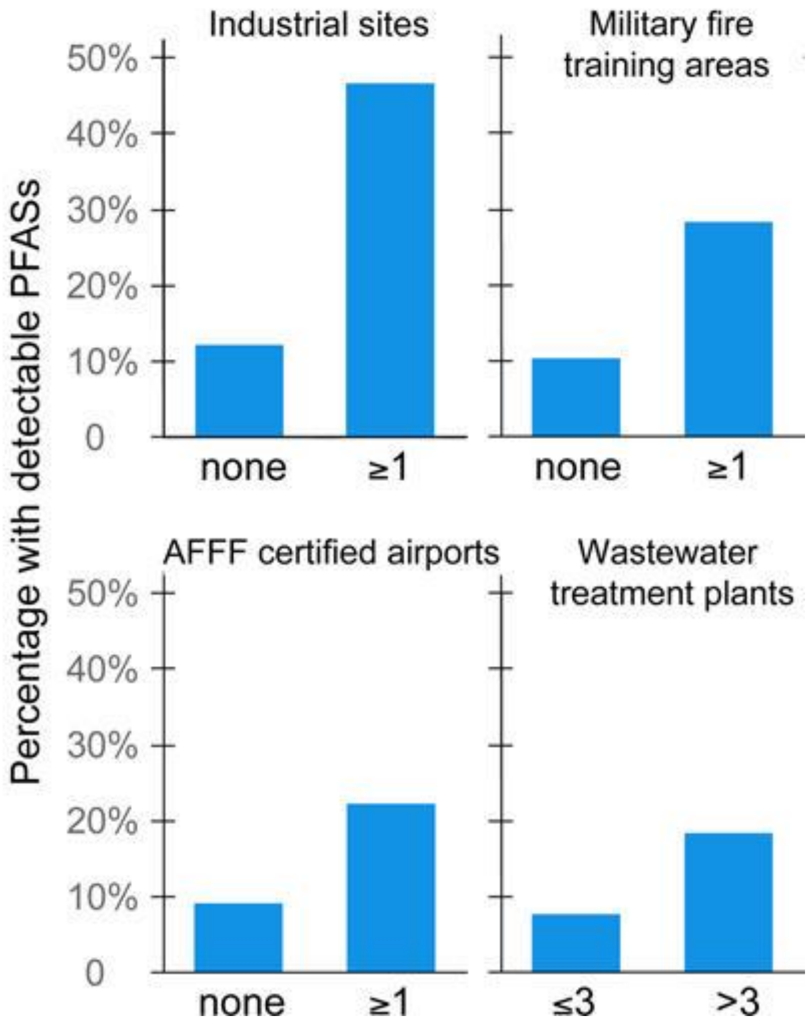


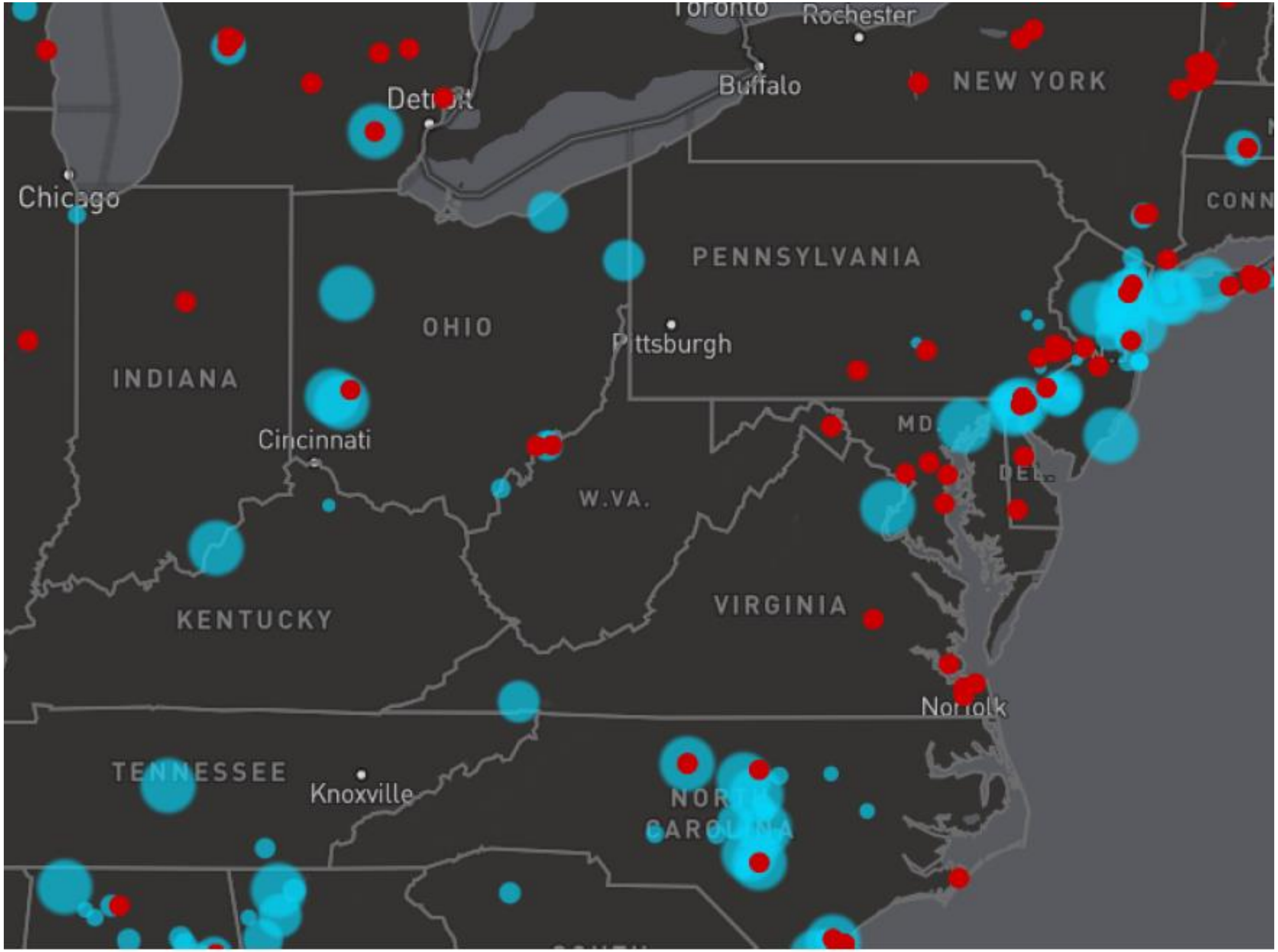
WWTP sludge

Gómez-Canela et al., 2012, Environ Sci Pollut Res

Hu et al., 2016, ES&T: Spatial regression analysis of 2013−2015 national drinking water PFAS concentrations from the EPA third Unregulated Contaminant Monitoring Rule (UCMR3) program.







(Environmental Working Group and SSEHRI at Northeastern University)

- Focus on northeast region here
- Publicly known PFAS pollution from 94 sites in 22 states:
  - industrial plants, dumps
  - military air bases
  - civilian airports
  - fire training sites
- EPA testing program of large public water systems under the Unregulated Contaminant Monitoring Rule, 2013-16
  - Detections in 194 systems serving 16 million people
  - Not a complete sampling of public systems; no private wells

Industrial or Military Contamination Site

EPA Tap Water Detection

DoD Sampling

About 60 % of DoD wells samples exceeded EPA LHA.
PFAS detected across groundwater, soil, sediment, surface water.

Component	Total Installations with known or suspected release of PFOS/PFOA (as of August 31, 2017)	Number of Installations Sampled where results exceeded EPA LHA (as of August 31, 2017)	Total number of groundwater wells sampled	Number of groundwater wells that tested above the EPA LHA
Army	64	9	258	104
Navy/USMC	127	40	1,368	784
Air Force	203	39	1,022	719
DLA	7	2	20	14
Total	401	90	2,668	1,621

(Maureen Sullivan, March 2018)

Compound	Surface Soil	Subsurface Soil	Sediment	Surface Water	Groundwater
PFOA	79.1%	48.1%	66.7%	88.0%	89.9%
PFOS	98.9%	78.8%	93.9%	96.0%	84.1%
PFHxS	76.9%	59.6%	72.7%	88.0%	94.9%

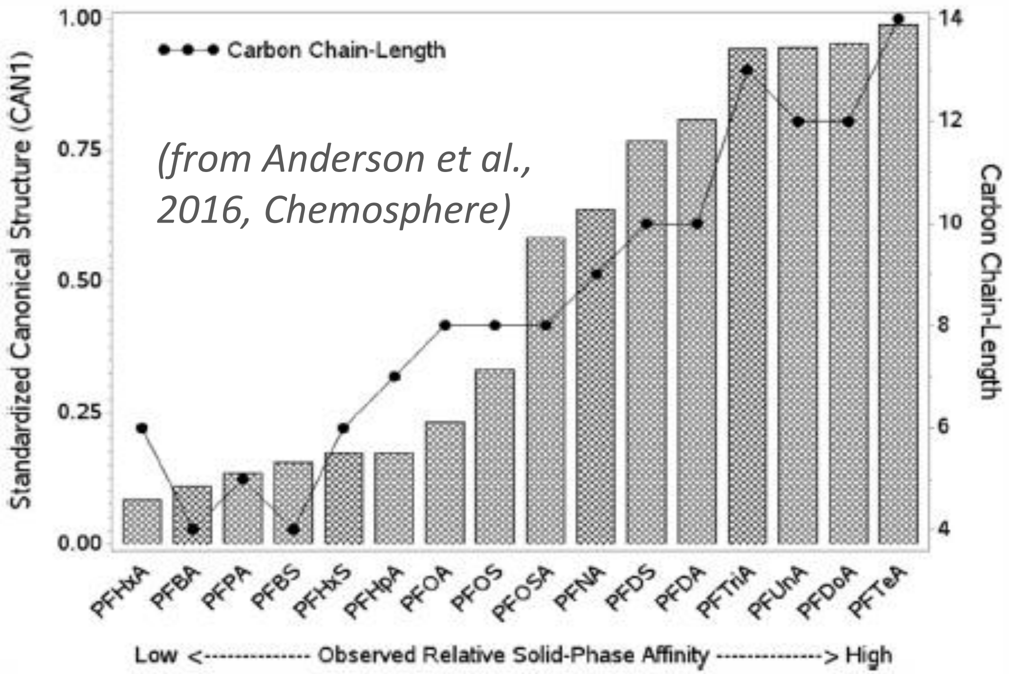
Detection frequency in several hundred samples at U.S. Air Force sites.

(from Anderson et al., 2016, Chemosphere)

PFAS Fate Characteristics

- High solubility, low sorption, and low degradation potential can lead to long groundwater plumes.
  - increases chance of surface-water discharge
- Sorption generally increases with chain length and soil organic content
  - PFAS can be cationic, anionic or zwitterionic and greatly affects their fate and transport
  - Anionic > zwitterionic > cationic
  - pH and saltwater affects
  - Electrostatic effects can vary sorption
- Tend to accumulate at interfaces
  - hydrophobic C-F tail oriented towards the air and the hydrophilic head dissolved in the water
  - effect on transport poorly understood

Chemical Properties	PCB (Arochlor 1260)	PFOA	PFOS	TCE
Molecular Weight	357.7	414.07	538	131.5
Solubility	0.0027 mg/L @24°C	**3400–9500 mg/L @25°C**	519 mg/L @20°C	1100 mg/L @ 20°C
Vapor Pressure (25°C)	4.05×10^{-5} mmHg	**0.5-10 mmHg**	**2.48×10^{-6} mmHg**	77.5 mmHg
Henry's Constant	4.6×10^{-3} atm-m³/mol	0.0908 atm-m³/mol	**3.05×10^{-6} atm-m³/mol**	0.0103 atm-m³/mol
Organic Carbon Part. Coeff. (Log K_{oc})	4.8-6.8	2.06	**2.57**	2.42

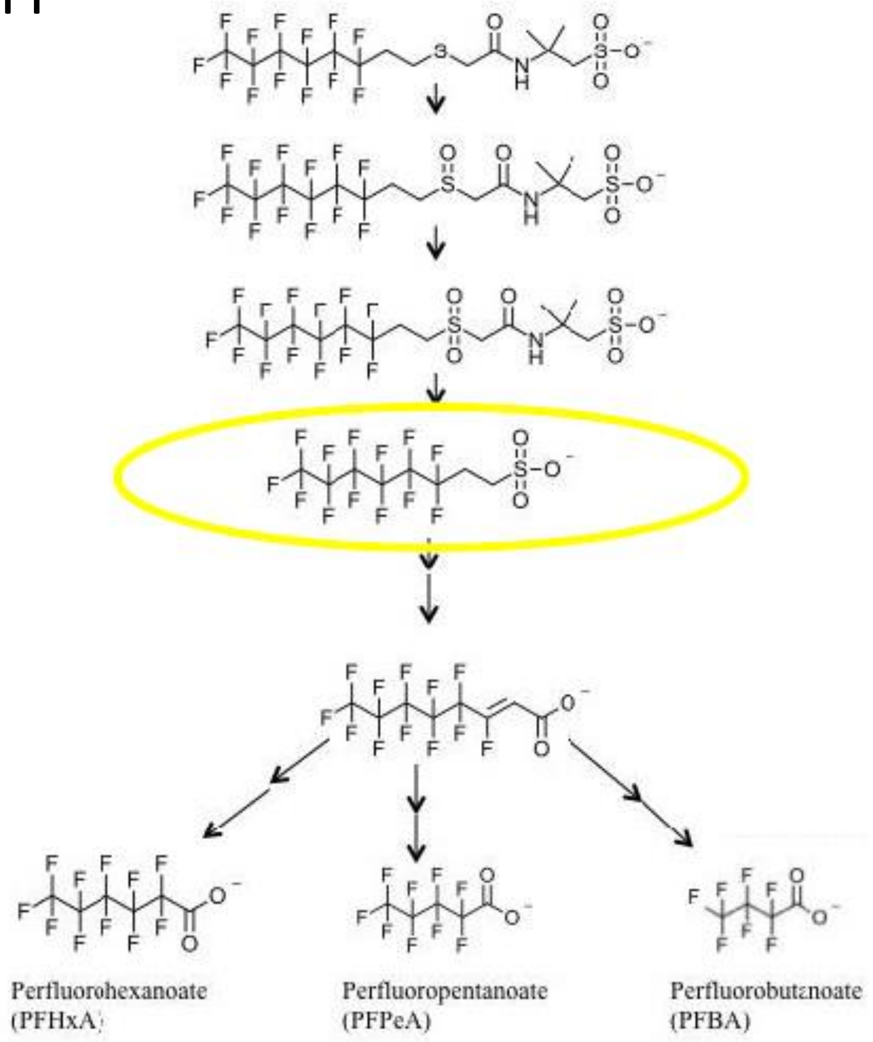


(from Anderson et al., 2016, Chemosphere)

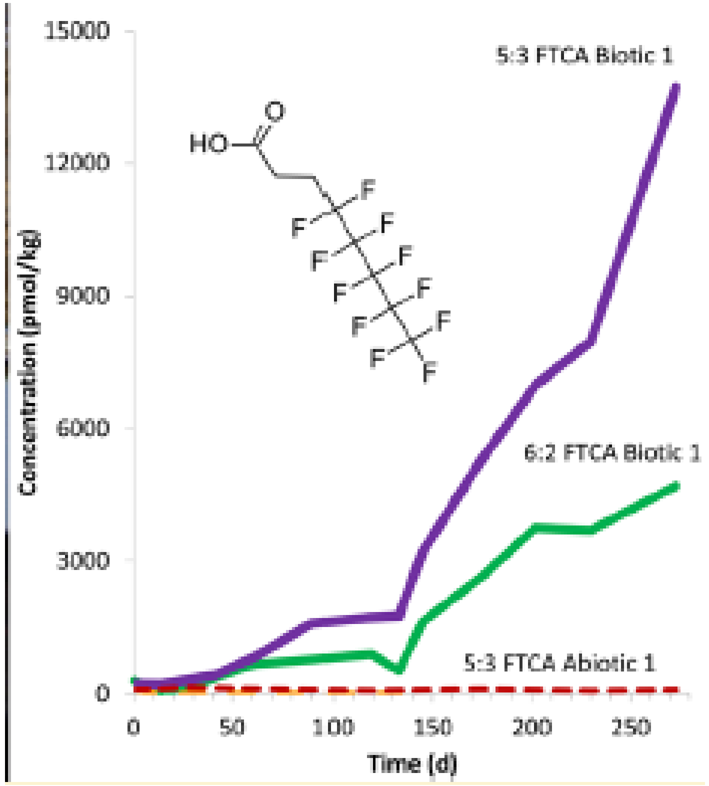
PFAS Biodegradation

- C-F bond is shortest and strongest in nature.
- Precursor abiotic or biotic transformation to PFAAs can greatly affect fate and lead to increases in PFOA and PFOS downgradient of original sources.
- Precursors transformation to PFAAs can occur in all matrices.
- Few data for anions.
- No data for zwitterions and cations.

(SERDP and ESTCP Webinar, 2016)



Telomer sulfonates are biodegradation products and aerobically degrade to PFAAs.

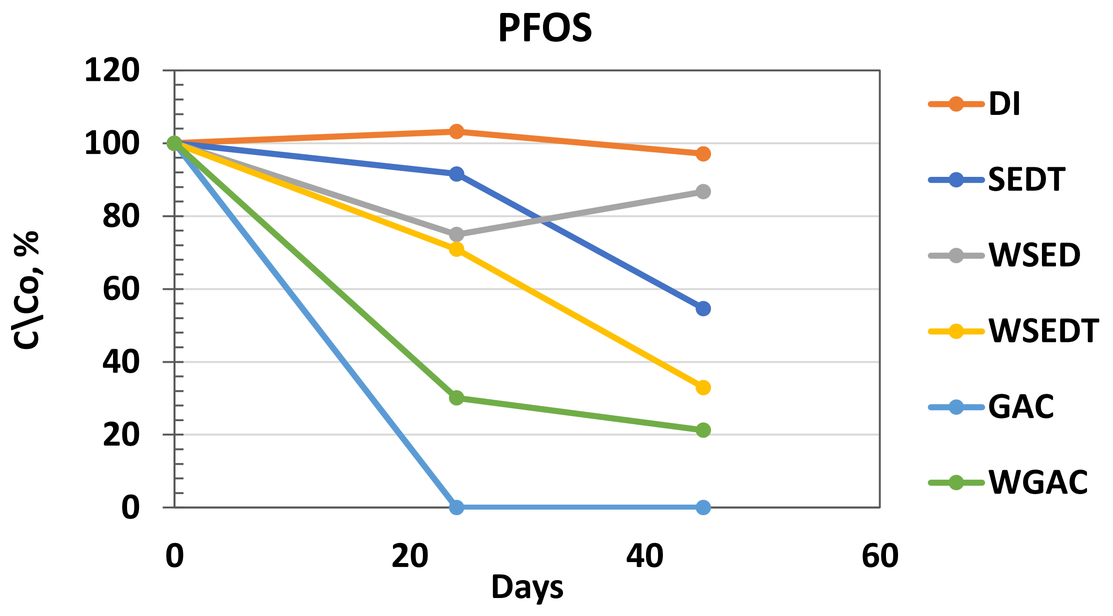


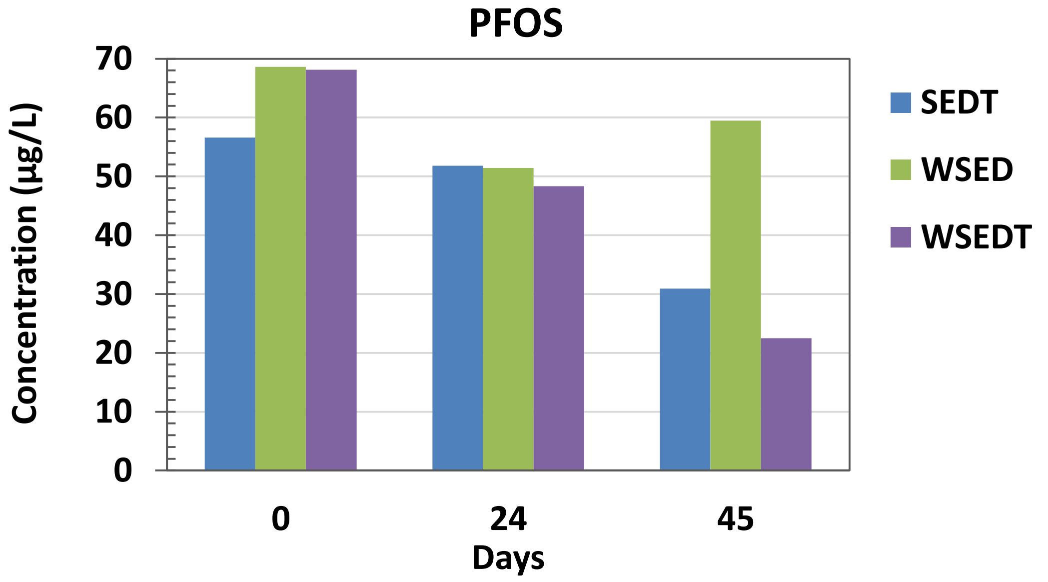
Methanogenic biotransformation products in municipal landfill waste bioreactors.

(from Allred et al., 2015, ES&T 2016)

Microcosms with PFOS-Amended Water and Sediment

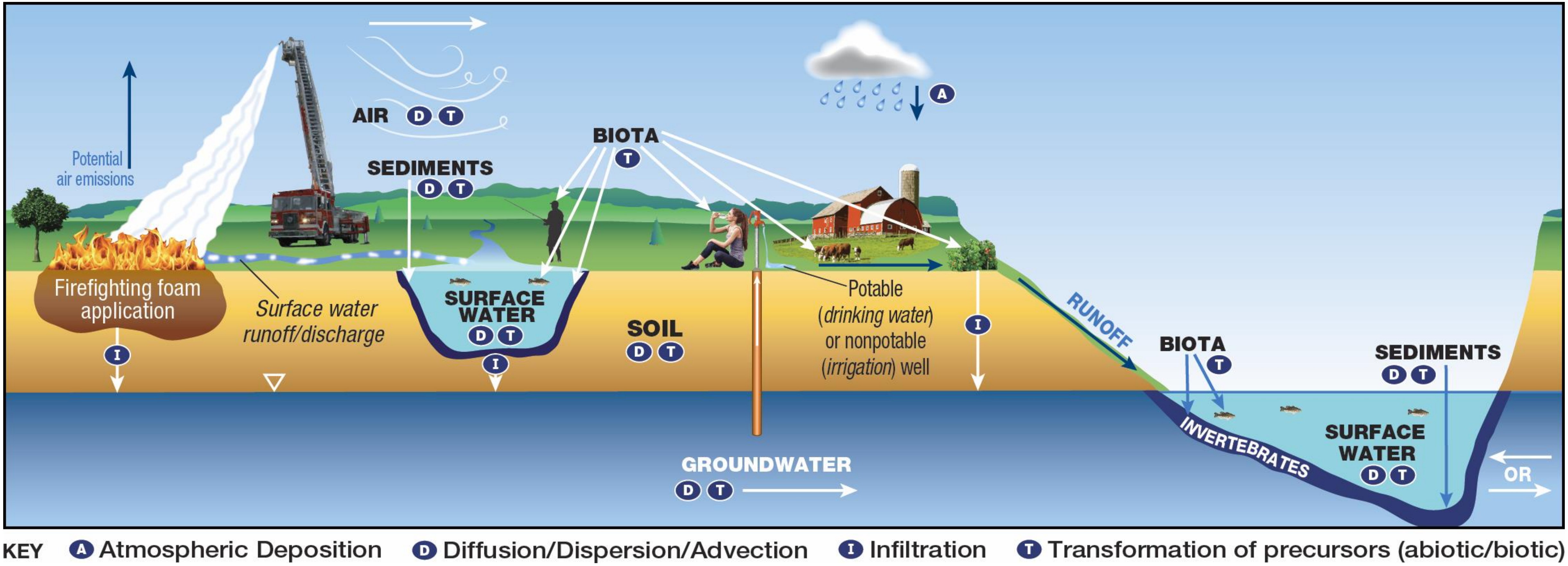
- Preliminary tests by Michelle Lorah in cooperation with USCOE and USGS Toxic Substances Hydrology Program (Infrastructure Team)
- PFOS removal in two treatments with added cVOCs, which included site sediment with and without the dechlorinating culture WBC-2
- 25 to 45% removal (after account for loss in DI control)
- PFOS removal in sediment microcosms highest in WSEDT where cVOC degradation was greatest



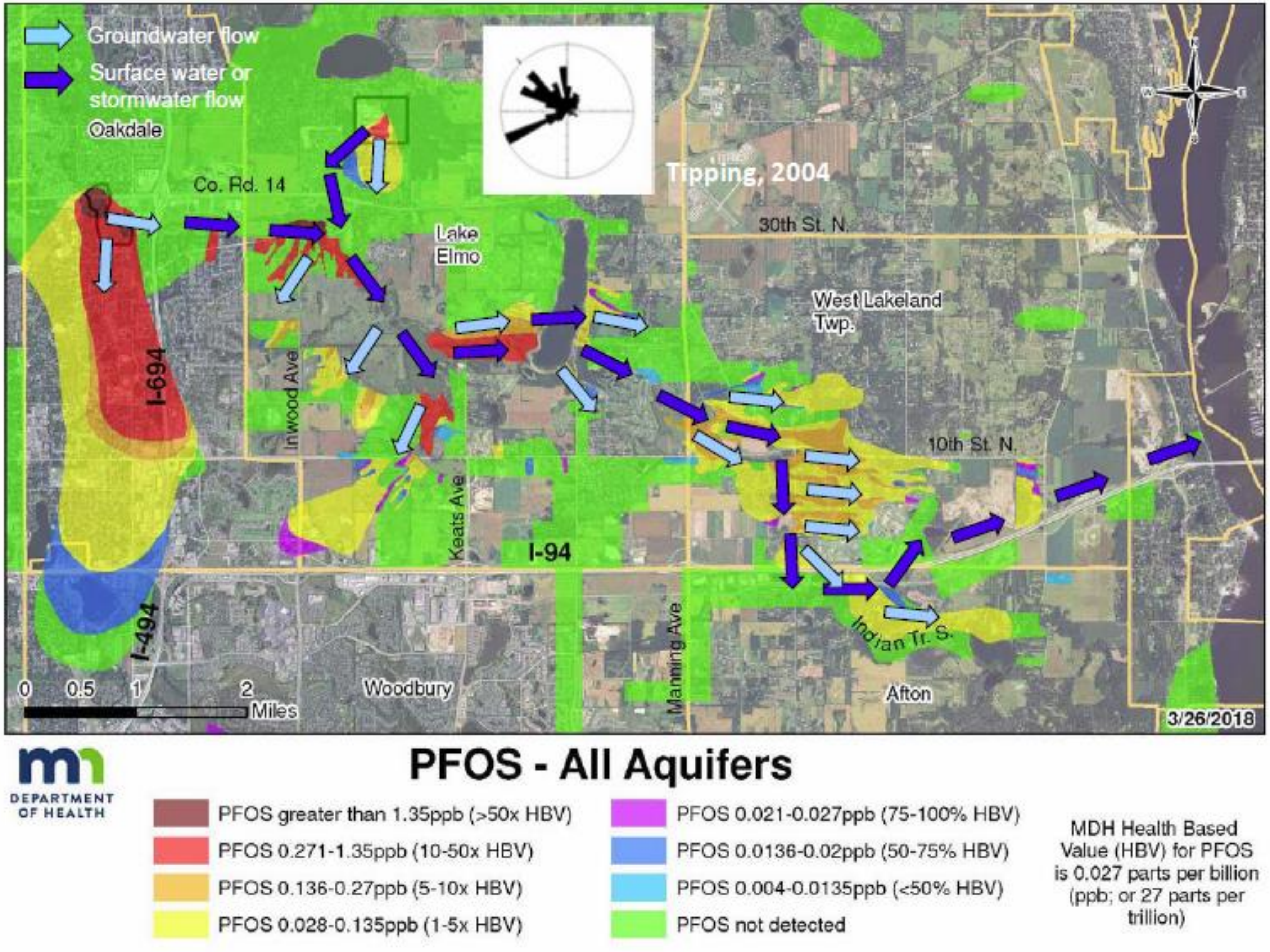


All results provisional.

Conceptual site model for fire training areas.



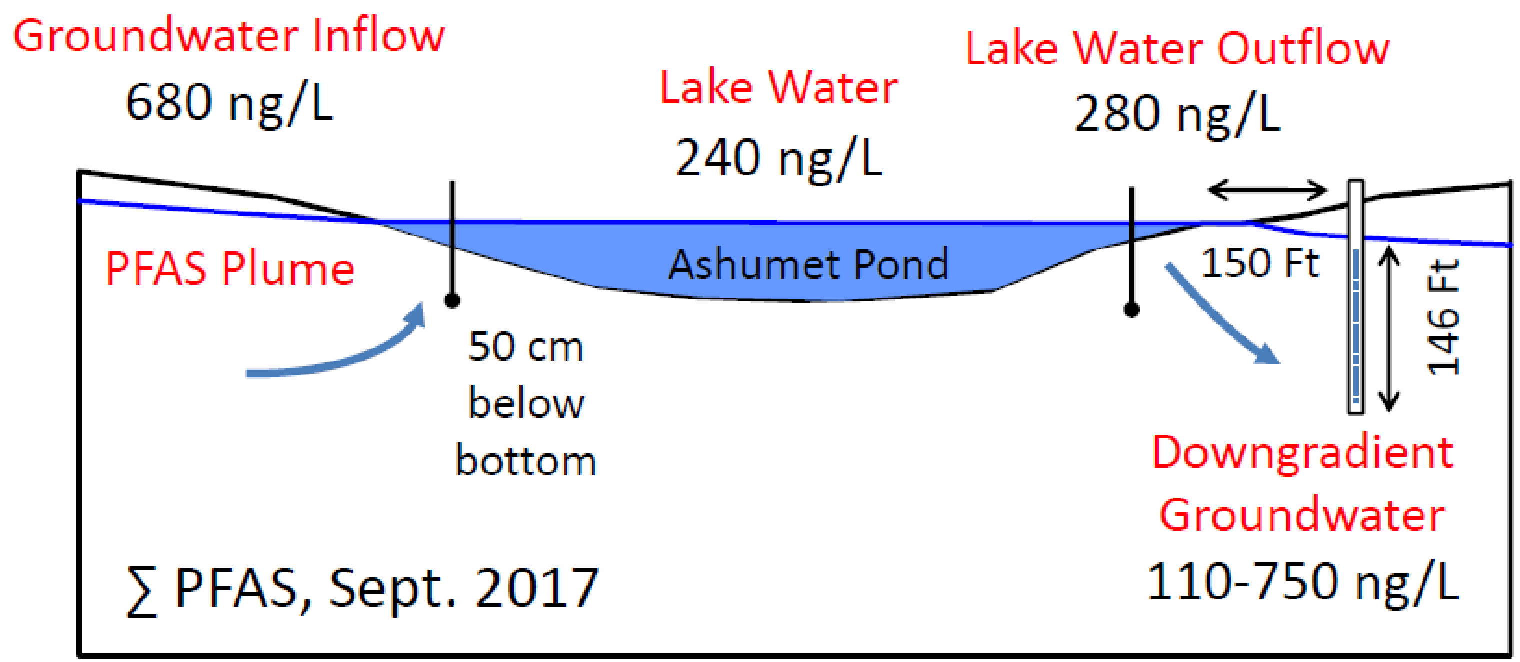
(From ITRC Fact Sheet, 2018, Fate and Transport for PFAS)

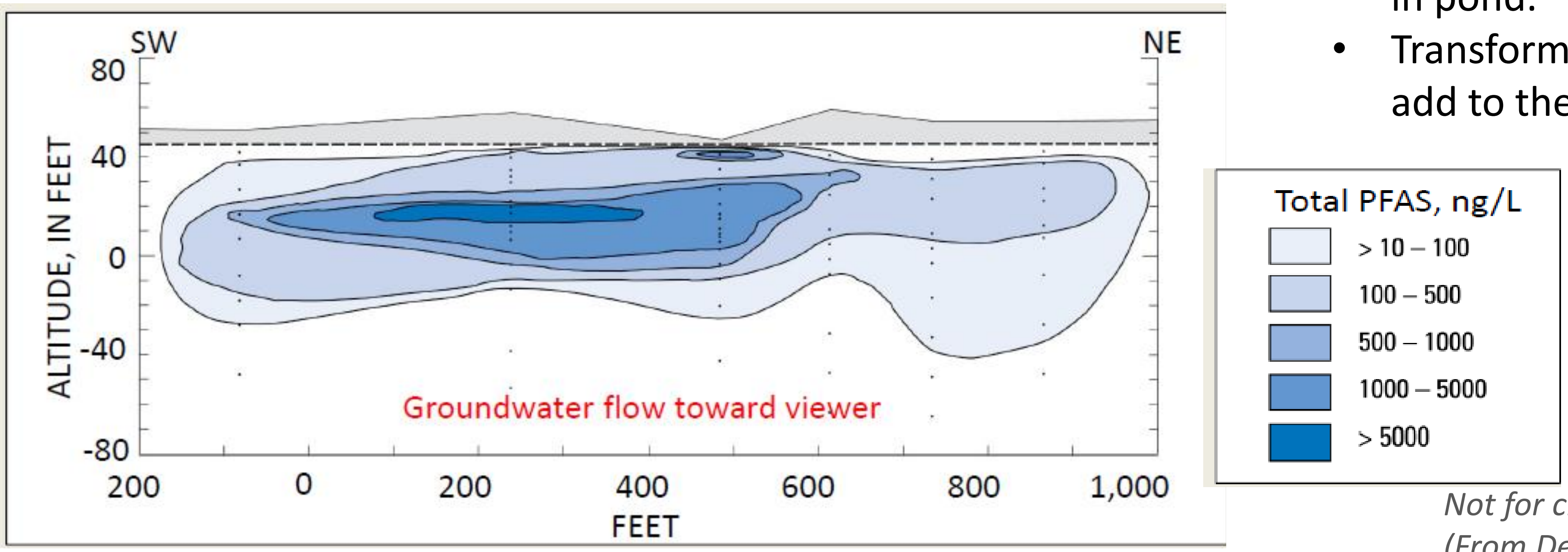


Minnesota Site

- Groundwater-surface water interactions are a critical element in transport and fate of PFAS.
- Groundwater discharge can contaminate surface-water bodies distant from the source.
- Surface-water transport can move PFAS many miles from source areas.
- Infiltration along surface-water pathway can create discrete groundwater plumes isolated from their source.

(From Yingling, 2018, Battelle Conference, A8_0850-754)





Cape Cod Site

- Discharge to surface water and recharge to groundwater again.
- Relatively extensive sampling network.
- Mass flux from groundwater across section explains 25% or measured PFAS concentration in pond.
- Transformations of precursors add to the measured PFAS.

Not for citation or release.
(From Denis LeBlanc, Cape Cod site)

PFAS Bioaccumulation

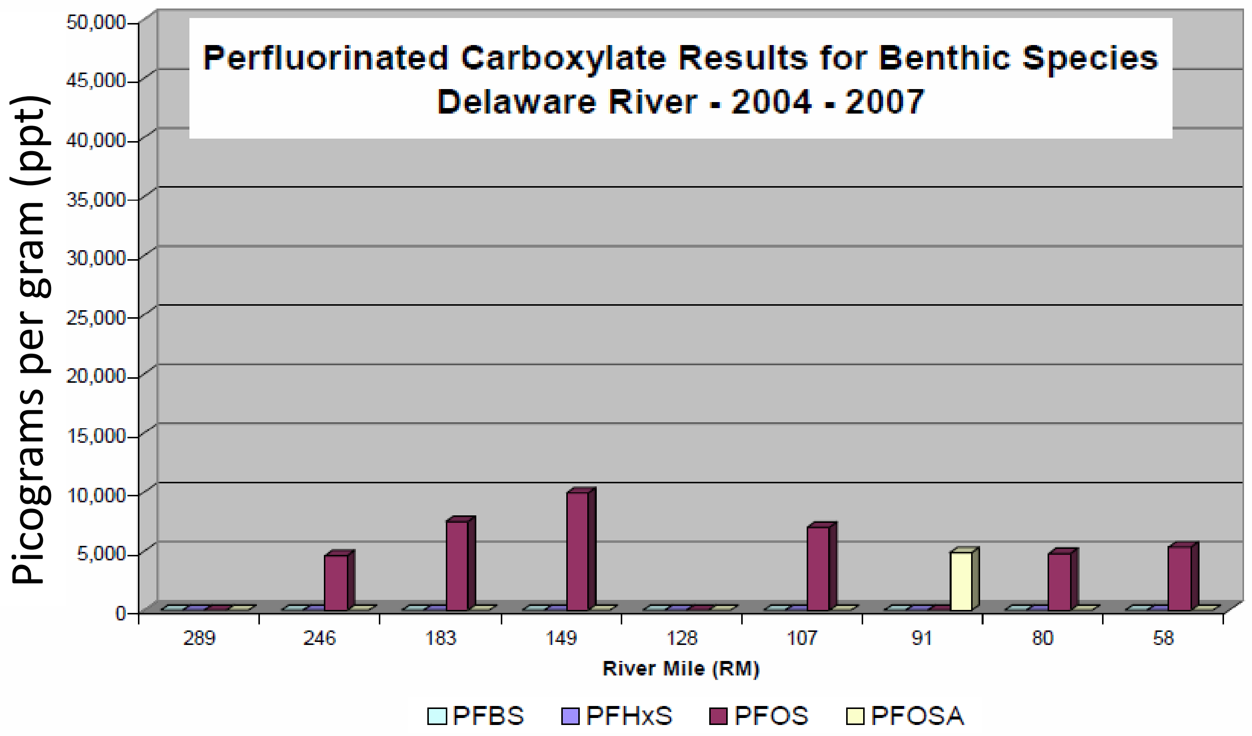
- Occur widely in plants, invertebrates, fish, and humans through bioaccumulation.
- Concentrations in biota may not reflect concentrations in other media because of precursor transformation within biota.
- PFAS accumulation in fish generally greatest for longer-chain PFAS (>8 C).
    - PFOS tends to partition to protein in fish, not fat like other organics
    - PFOS concentration from water is the predominant accumulation process

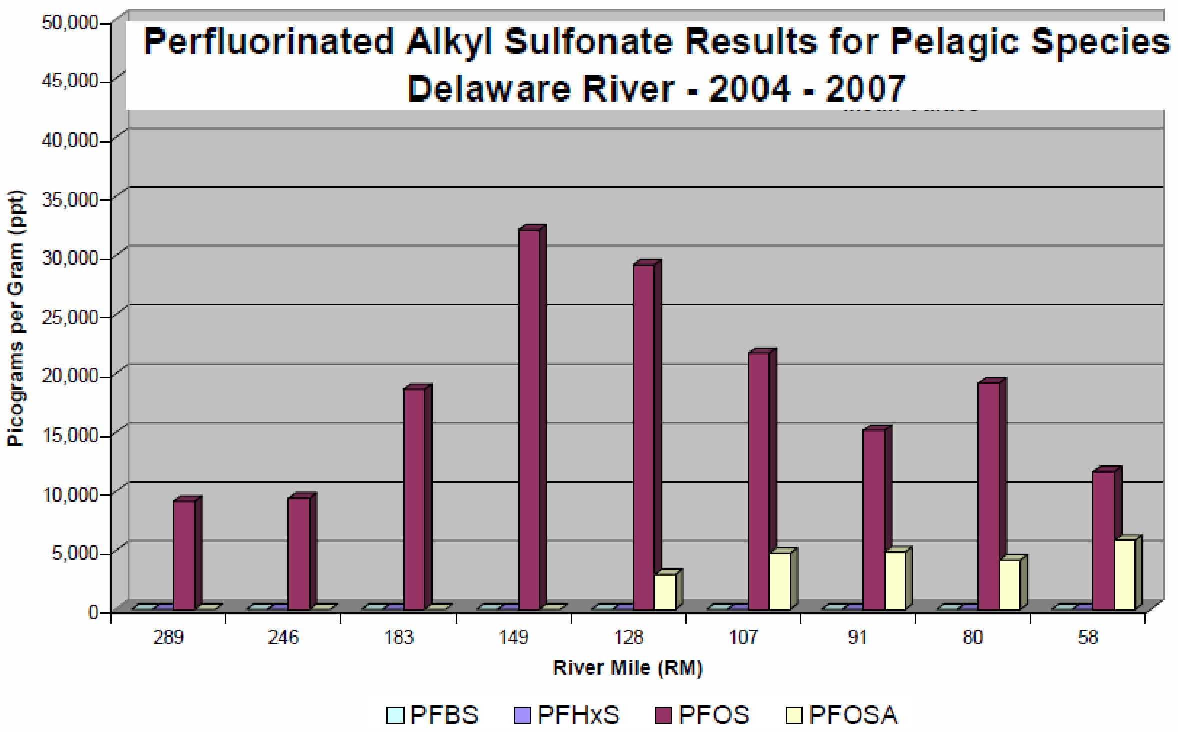
Table 4.5
Observed PFAS concentrations in fish (ITRC Fact Sheet, 2018, Fate and Transport for PFAS)

Location	Information	Concentrations (µg/kg)
Industrial (Oliaei et al. 2013; Delinsky et al. 2010)	Near PFAS production plants, individual fish tissues such as liver, blood, and muscle have been reported to have elevated PFOS.	Maximum PFOS: • Liver: 6,350 • Blood: 29,600 • Muscle: 2,000
AFFF spill (Moody et al. 2002; Gewurtz et al. 2014; Lanza et al. 2017)	PFOS in fish liver, muscle, and whole fish samples were detected following an AFFF spill.	Maximum PFOS: • Liver: 72,900 • Muscle: 6,160 • Whole fish: 9,350
Wastewater treatment plant (Becker, Gerstmann, and Frank 2010; Li et al. 2008; Schuetze et al. 2010)	PFOS concentrations have been detected in fish collected near the outfall of wastewater treatment plants.	Maximum PFOS: Liver: 400 Serum: 84 Muscle tissue: 225

Delaware River Basin

- In 2004, PFAS was added to ongoing fish monitoring in tidal and non-tidal portions.
- Fish samples from 2 species collected from 8 stations in each portion.
    - Tidal: white perch, channel catfish
    - Non-Tidal: smallmouth bass, white sucker
- PFAS higher in pelagic compared to benthic species
- PFOS/PFOSA higher in pelagic species near urban areas





Fish Consumption Advisories

August 2018
"The Michigan Department of Health and Human Services (MDHHS) has issued an emergency 'Do Not Eat' fish advisory for all fish between the Huron River at Milford (Oakland County) to the Huron River at Base Line and Portage Lakes (Livingston and Washtenaw county lines) due to PFOS. "

NJ Department of Environmental Protection, **June 2018**, SR15-010. PFAS detected in 100 % of sampled fish (n= 32)

Table 8: DRAFT Preliminary Fish Consumption Advisory Triggers

	General Population			High Risk Population*		
	PFOA (ng/g; ppb)	PFNA (ng/g; ppb)	PFOS (ng/g; ppb)	PFOA (ng/g; ppb)	PFNA (ng/g; ppb)	PFOS (ng/g; ppb)
Unlimited	0.62	0.23	0.56	0.62	0.23	0.56
Weekly	4.3	1.6	3.9	4.3	1.6	3.9
Monthly	18.6	6.9	17	18.6	6.9	17
Once/3 months	57	21	51	N/A	N/A	N/A
Yearly	226	84	204	N/A	N/A	N/A
Do Not Eat	>226	>84	>204	>18.6	>6.9	>17

Ongoing/Planned Work

- USGS Toxic Substances Hydrology Program- Drinking Water and Municipal Wastewaters (Infrastructure) Team
  - Lorah, Akob, and Oremland- Mitigating Risks from Drinking Water and Wastewater Resources Containing Chlorinated and Fluorinated (PFAS) Contaminants through Biological Processes
  - LeBlanc et al.- Transport and transformation of mixed contaminants, including PFASs, along the groundwater pathway from sources to drinking water and environmental receptors (Cape Cod area)
  - Not focused in Chesapeake Bay area with current funds, although Carol Morel, Pathways intern, working to add PFAS to some sites sampled as part of Back River Watershed, Baltimore City, PCB project