Ecotoxicity of Per- and Polyfluoroalkyl Substances

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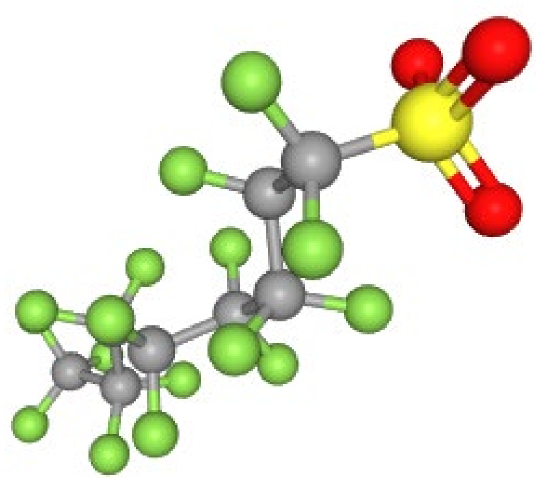
Overview

- Background and sources
- Chemistry of PFAS
- How do we analyze PFAS in water and sediment?
- What happens to PFAS in the environment?
- Where are PFAS found?
- What are the ecotoxicological effects?

Background: What are PFAS?

"Highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms" – Buck et al., 2011



Perfluorooctanesulfonic acid (PFOS)

Image from NIH PubChem

PFAS Applications

Construction coatings and paints

Solar power

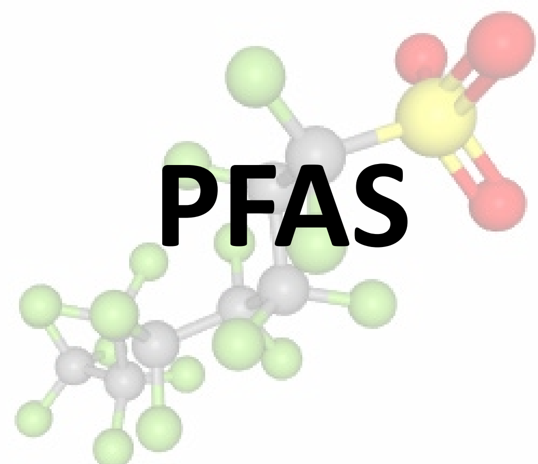
Batteries

Food packaging

Electrical and communications

Consumer electronics

Pesticides



Fire protection

Aviation

Personal care products

Automotive industry

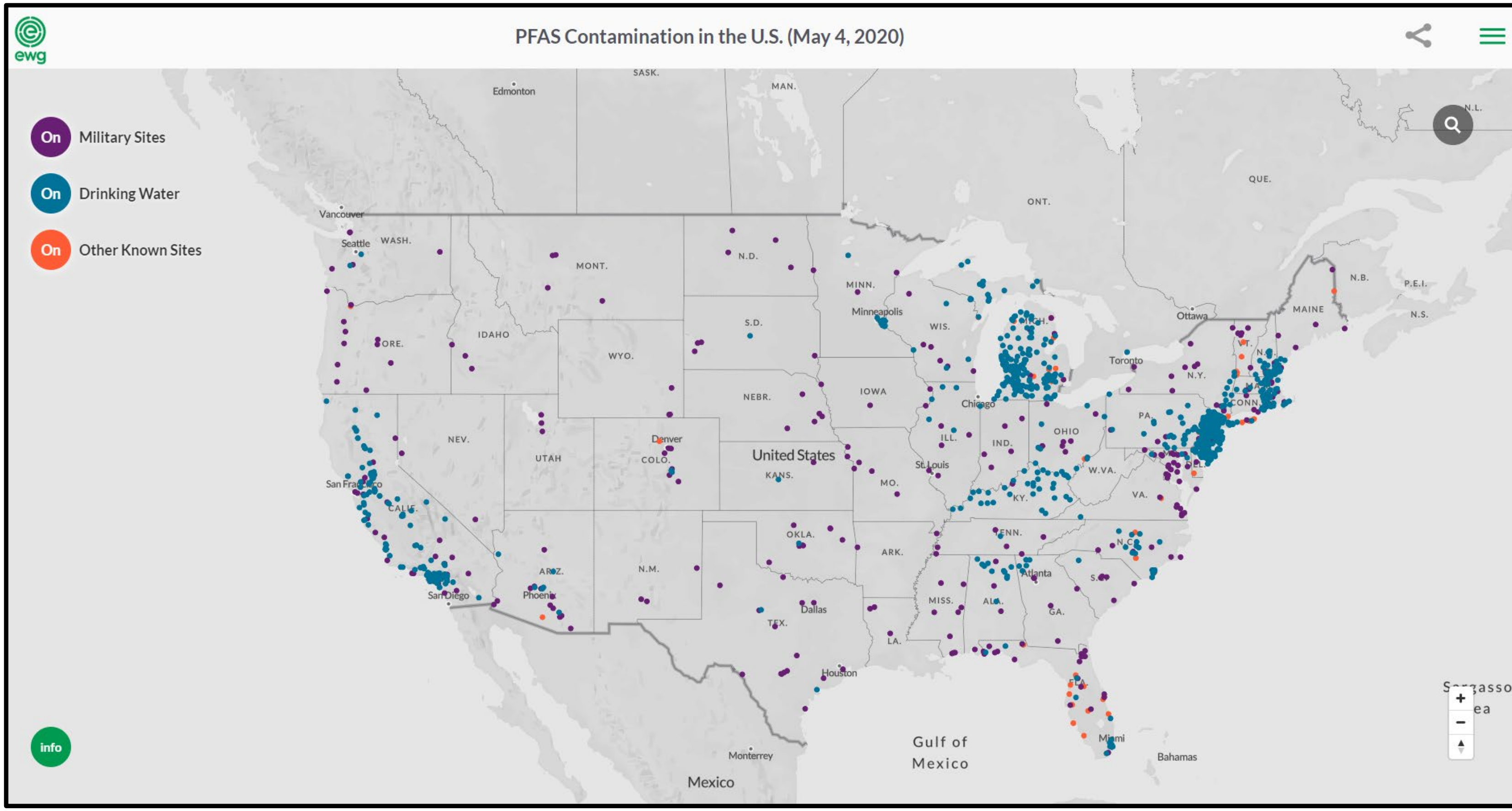
Water, stain, fire resistant textiles

Boating and marine

Chrome plating

Primary applications are for water, stain, chemical, temperature, fire and friction resistance

PFAS Contamination is Widespread



From the Environmental Working Group
https://www.ewg.org/interactive-maps/pfas_contamination/

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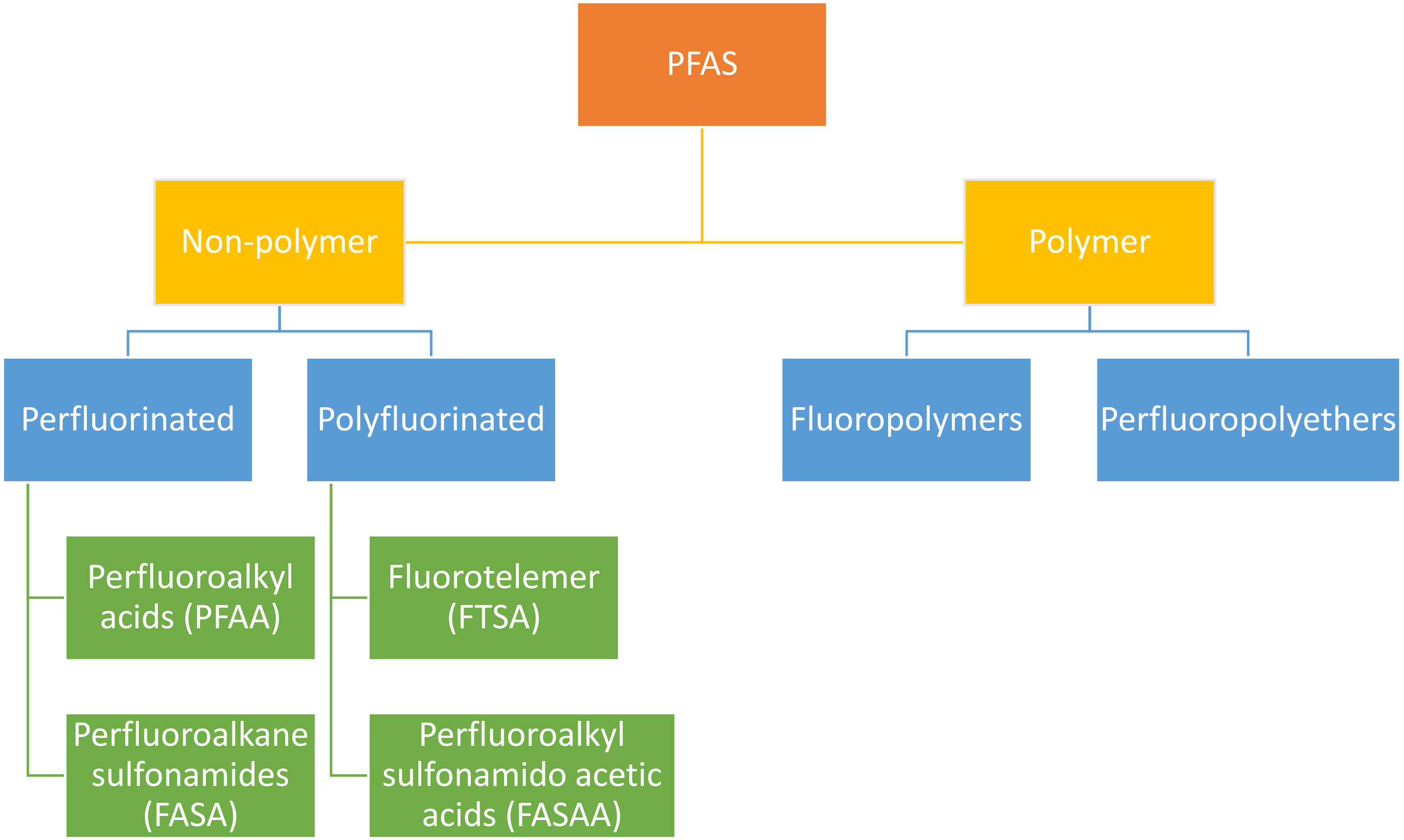
PFAS Classification

If you thought PCBs were complicated….

there are over <u>4,500 PFAS</u> congeners….



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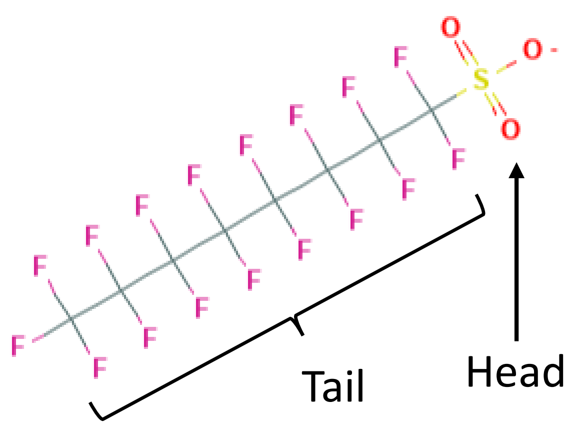
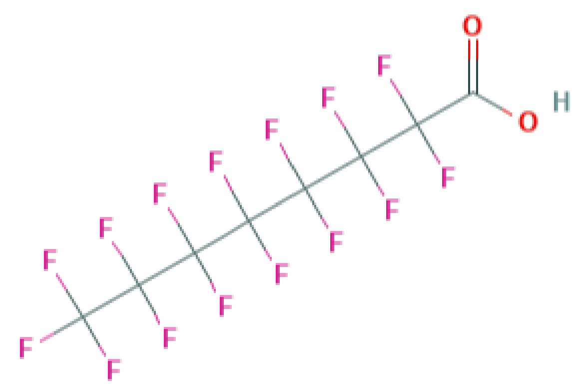
Perfluorinated Alkyl Acids (PFAA) Structure

- Fully fluorinated chain
- Functional group with a carboxylate (COO^-) or sulfonate group (SO_3^-)



Perfluorooctane sulfonate (PFOS)



Perfluorooctanoic acid (PFOA)

Image from NIH PubChem

Nomenclature of PFAA

AB C D

- AB = PF is perfluoro
- C = number of carbon

  B, buta, 4 carbon

  Pe, penta, 5 carbon

  Hx, hexa, 6 carbon

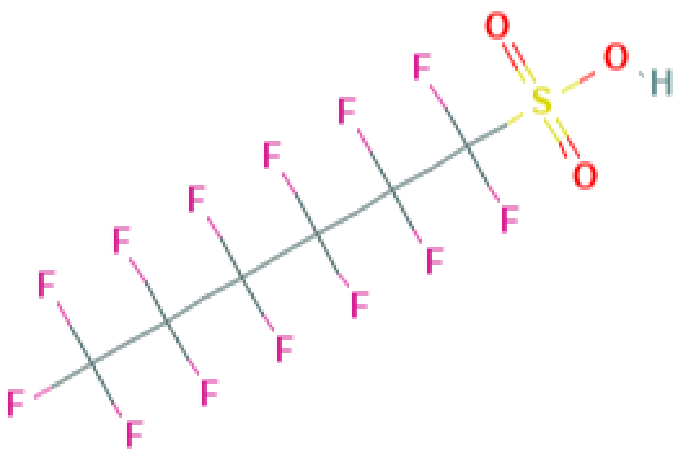
  Hp, hepta, 7 carbon

  O, octa, 8 carbon

  N, nona, 9 carbon

  D, deca, 10 carbon

- D = functional group
  - Sulfonate = S
  - Carboxylate = A



PF Hx S

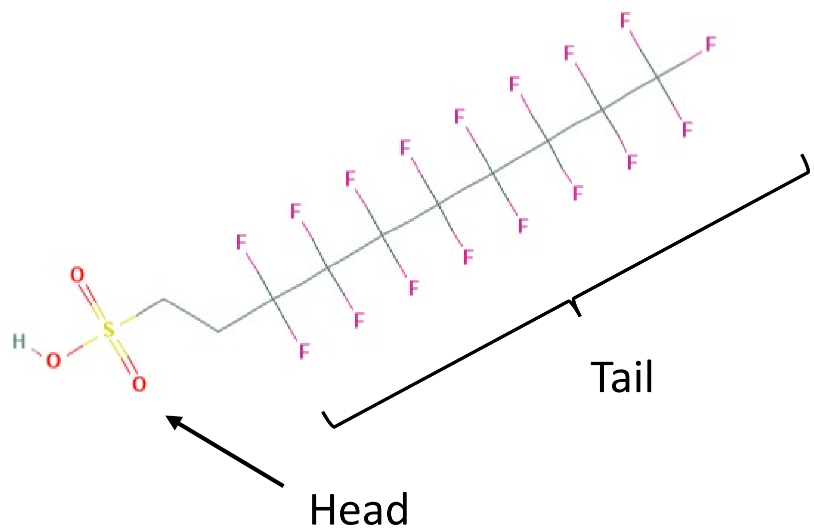
Image from NIH PubChem

X	Y	Acronym	Name	Formula	CAS No.
B = buta (4 carbon)	A = Carboxylate or carboxylic acid	PFBA	Perfluorobutanoate	$C_3F_7CO_2^-$	45048-62-2
			Perfluorobutanoic acid	C_3F_7COOH	375-22-4
	S = Sulfonate or sulfonic acid	PFBS	Perfluorobutane sulfonate	$C_4F_9SO_3^-$	45187-15-3
			Perfluorobutane sulfonic acid	$C_4F_9SO_3H$	375-73-5
Pe = penta (5 carbon)	A = Carboxylate or carboxylic acid	PFPeA	Perfluoropentanoate	$C_4F_9CO_2^-$	45167-47-3
			Perfluoropentanoic acid	C_4F_9COOH	2706-90-3
	S = Sulfonate or sulfonic acid	PFPeS	Perfluoropentane sulfonate	$C_5F_{11}SO_3^-$	NA
			Perfluoropentane sulfonic acid	$C_5F_{11}SO_3H$	2706-91-4
Hx = hexa (6 carbon)	A = Carboxylate or carboxylic acid	PFHxA	Perfluorohexanoate	$C_5F_{11}CO_2^-$	92612-52-7
			Perfluorohexanoic acid	$C_5F_{11}COOH$	307-24-4
	S = Sulfonate or sulfonic acid	PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_3^-$	108427-53-8
			Perfluorohexane sulfonic acid	$C_6F_{13}SO_3H$	355-46-4
Hp = hepta (7 carbon)	A = Carboxylate or carboxylic acid	PFHpA	Perfluoroheptanoate	$C_6F_{13}CO_2^-$	120885-29-2
			Perfluoroheptanoic acid	$C_6F_{13}COOH$	375-85-9
	S = Sulfonate or sulfonic acid	PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_3^-$	NA
			Perfluoroheptane sulfonic acid	$C_7F_{15}SO_3H$	375-92-8
O = octa (8 carbon)	A = Carboxylate or carboxylic acid	PFOA	Perfluorooctanoate	$C_7F_{15}CO_2^-$	45285-51-6
			Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1
	S = Sulfonate or sulfonic acid	PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3^-$	45298-90-6
			Perfluorooctane sulfonic acid	$C_8F_{17}SO_3H$	1763-23-1
N = nona (9 carbon)	A = Carboxylate or carboxylic acid	PFNA	Perfluorononanoate	$C_8F_{17}CO_2^-$	72007-68-2
			Perfluorononanoic acid	$C_8F_{17}COOH$	375-95-1
	S = Sulfonate or sulfonic acid	PFNS	Perfluorononane sulfonate	$C_9F_{19}SO_3^-$	NA
			Perfluorononane sulfonic acid	$C_9F_{19}SO_3H$	474511-07-4
D = deca (10 carbon)	A = Carboxylate or carboxylic acid	PFDA	Perfluorodecanoate	$C_9F_{19}CO_2^-$	73829-36-4
			Perfluorodecanoic acid	$C_9F_{19}COOH$	335-76-2
	S = Sulfonate or sulfonic acid	PFDS	Perfluorodecane sulfonate	$C_{10}F_{21}SO_3^-$	126105-34-8
			Perfluorodecane sulfonic acid	$C_{10}F_{2}1SO_3H$	335-77-3

From ITRC fact sheet at https://pfas-1.itrcweb.org/

Polyfluorinated (FASA) Structure

- Partially fluorinated chain, replaced with hydrogen
- Functional group with a carboxylate (COO^-) or sulfonate group (SO_3^-)



8:2 Flurotelomer sulfonic acid (8:2 FTSA)

Image from NIH PubChem

Relevant Chemical Properties

Solubility (S)	Some are soluble ranging from insoluble up to tens of thousands PFOS ~ 910 mg/L PFOA ~ 3,000 – 10,000 mg/L PFHS ~ 6.2 – 7.6 mg/L
Log K_{oc}	1.2 to 6.2
Vapor pressure	Relatively low and do not expect significant volatility
Stability	Extremely stable to temperature, chemicals, and oxidation Little to no degradation under natural conditions

The carbon-fluorine bond is very strong

C-F = 485 kJ/mol
C-Cl = 339 kJ/mol

Carbon chain length and functional group affect environmental behavior

↑ chain length = ↑ uptake in organisms

How to Sample?

- Conventional sample and handling
  - Water – 250 ml polypropylene (PP) or high-density polyethylene (HDPE) - no glass bottles with lined lids
  - Solid samples – 5 grams in PP or HDPE
  - Get containers from analytical lab – confirmed to be PFAS free
- Challenges with contamination
  - Avoid Teflon™ and aluminum foil
  - Double bag samples
  - Minimize exposure to light
  - Avoid chemical packs (blue ice) to keep samples cool
- Trip blanks are critical
- Keep inventory of supplies (with lot numbers) used for sampling
- Personal protection equipment (PPE)
  - Be sure to wear PPE! Nitrile gloves
  - Avoid wearing water, stain proof clothing

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Chemical Analysis

<u>Water – solid phase extraction then LC-MS</u>

- EPA Method 537.1 (tests for 18 PFAS) – uses surrogates for internal standard
- EPA Method 533 (tests for 25 PFAS) – uses isotopically labeled compounds for internal standard

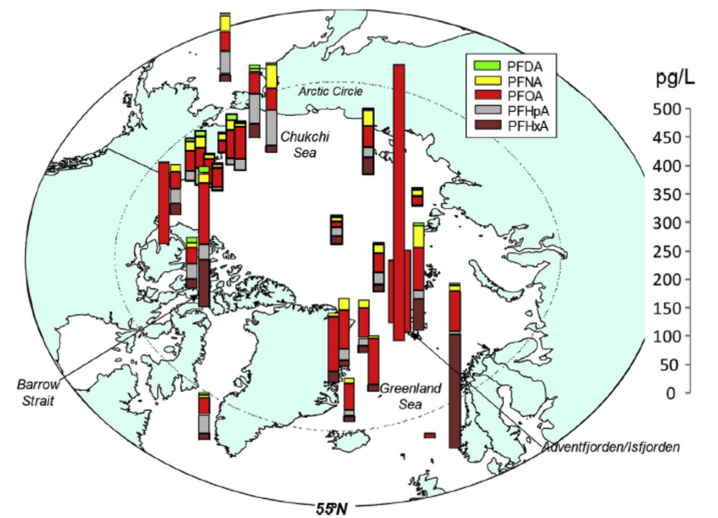
Solid samples – labs use modification of the methods above

<u>Alternative method - TOP assay (Total Oxidizable Precursors)</u>

- Oxidize sample to convert all precursors to PFAA
- Provides a conservative estimate of total PFAS concentration

Where are PFAS found?

- Highest concentrations found near sources of contamination, but are detected globally in all matrices
- Main sources:
  - Fire training sites
  - Industrial sites
  - Landfills
  - Wastewater treatment plants / biosolids



Concentrations of PFAS in Artic water (Muir et al., 2019)

PFAS	Water		Soil/Sediment	
	Typical	High	Typical	High
PFOS	5 ng/L	5,900 ng/L	1 ng/g	11 ng/g
PFOA	5 ng/L	33,900 ng/L	1 ng/g	203 ng/g

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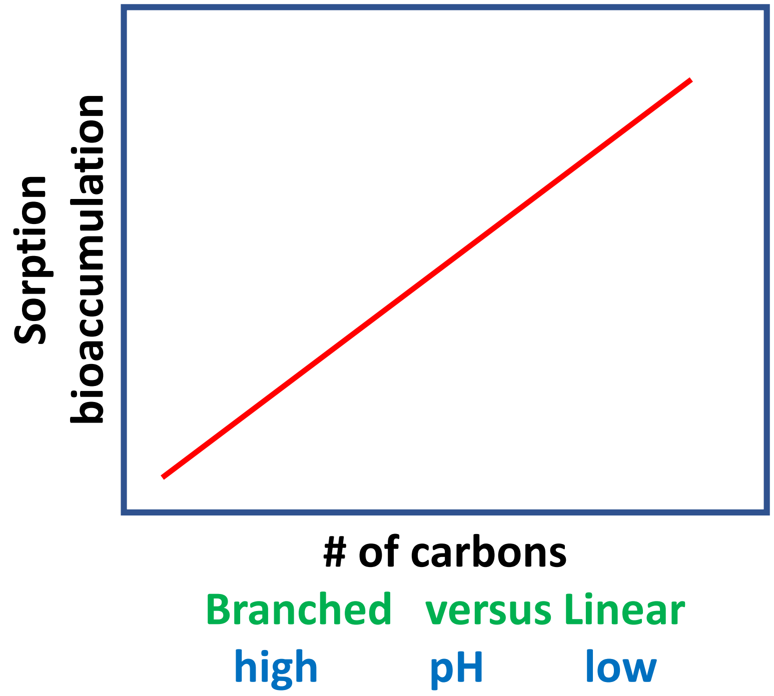
Fate and Transport

- Fate
  - PFAS extremely persistent in the environment because of strong C-F bond
  - Precursors transform to PFAA
    (ex, 8:2 FTS to PFOA)
- Transport
  - Deposition and leaching from soils/sediments
  - Groundwater – dispersion, dilution, due to solubility
  - Surfactant properties -> accumulation on surface of water



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Bioaccumulation

- PFAS have been detected in most plants, fish, wildlife and birds – in most tissues
- PFAS are readily absorbed and distribute in blood to liver, kidney and eliminated in feces and urine – half-life for PFOS is 5.4 years
- Partitioning is different from other contaminants (PCB) and partition to protein as opposed to fat
- Lipid normalization and use of octanol-water partition coefficients is not effective (suggested use of protein normalization)

Congener	Matrix and sample size				
Perfluorocarboxylic acids (PFCAs)	Egg n = 40	Plasma n = 20	Liver n = 10	Brain n = 10	Diet n = 6
PFBA					
PFPeA	5 (13%)				
PFHxA	5 (13%)		6 (60%)		4 (67%)
PFHpA	6 (15%)	2 (10%)			
PFOA			2 (20%)		5 (83%)
PFNA			1 (10%)		2 (33%)
PFDA	33 (82%)				
PFUnA	36 (90%)		3 (30%)	5 (50%)	
PFDoA	26 (65%)	15 (75%)			
Perfluorosulfonates (PFSAs)					
PFBS					
PFHxS				8 (80%)	5 (83%)
PFOS					
PFOSA		19 (95%)	9 (90%)	9 (90%)	

100% detected ≥50% detected <50% detected 0% detected

PFAS in Tree Swallows at Oscoda, Michigan (Custer et al., 2019); Picture by Tom Custer

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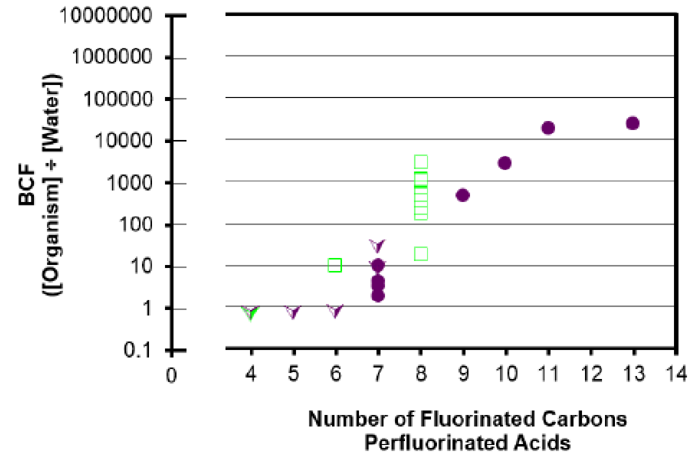
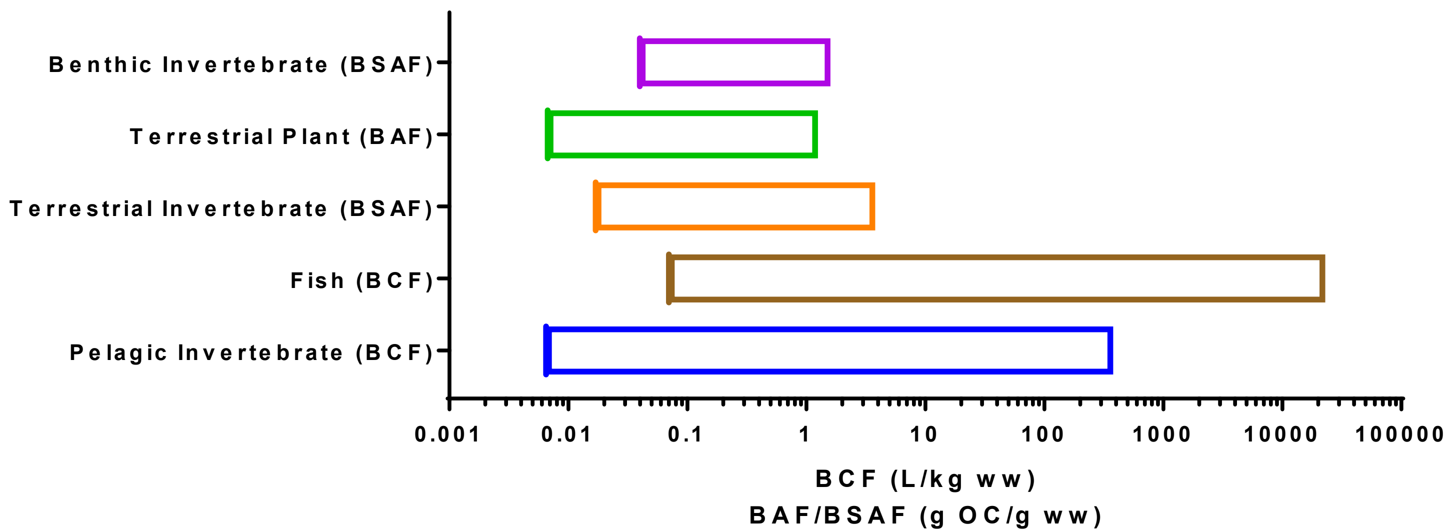
Bioaccumulation

- Accumulation varies based on the congener
- Long chain PFAS accumulate more in invertebrates and fish
- Short chain PFAS accumulate more in plants





Data from From Conder et al. 2008, Conder et al., 2019

Ecotoxicity of PFAS

- Toxicity Studies
  - Most with aquatic organisms (fish > inverts)
  - PFOS and PFOA greatest amount of data
  - Some data for plants, birds, amphibians, and reptiles
  - Data for mammals is from human health studies (rodents)
  - Few chronic studies

Effects

- Growth
- Hepatic effects
- Immunological effects
- Developmental effects
- Endocrine (thyroid implicated)
- Reproductive effects
- Tumors

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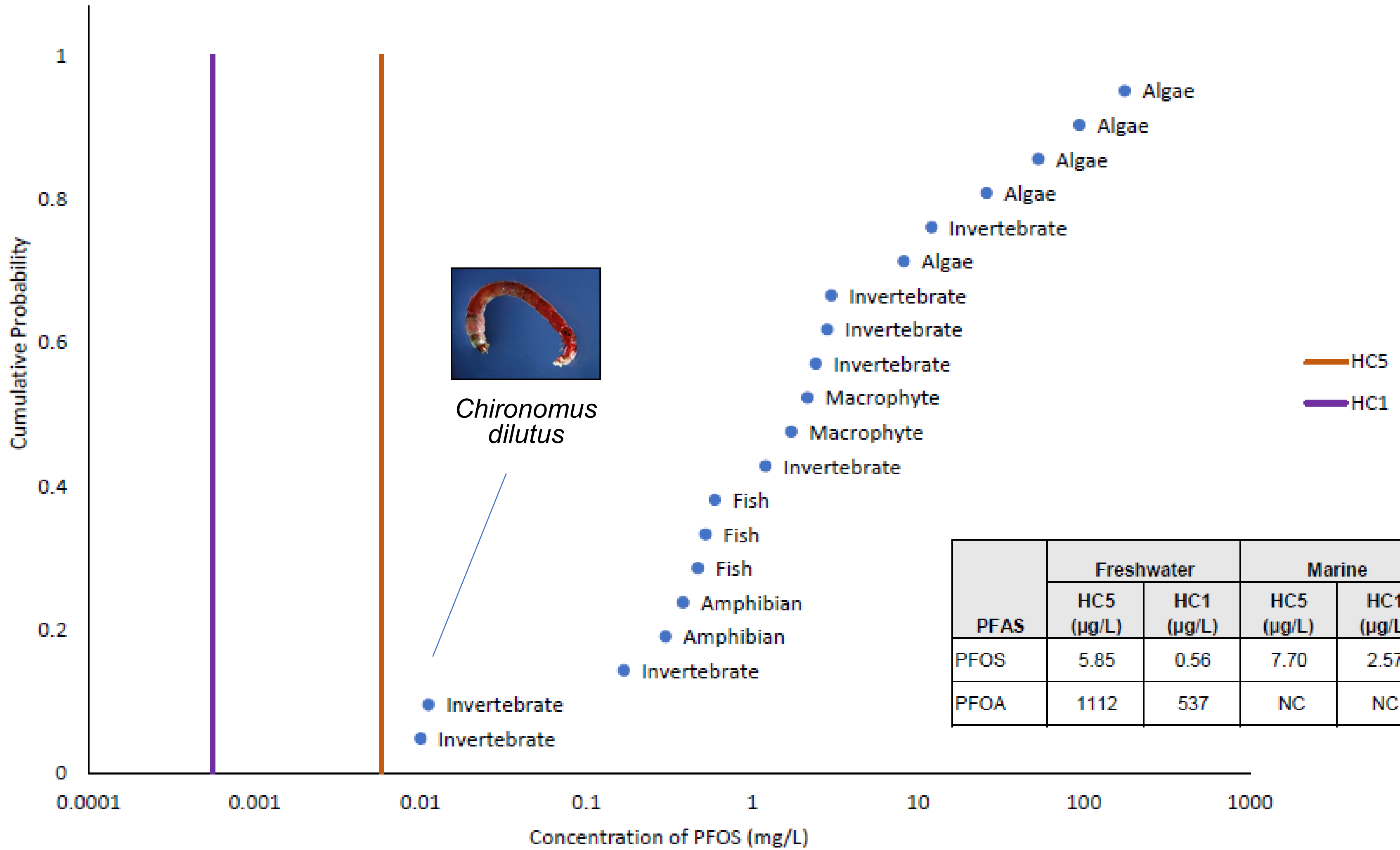
Ecotoxicity of PFOS



PFAS	Freshwater HC5 (µg/L)	Freshwater HC1 (µg/L)	Marine HC5 (µg/L)	Marine HC1 (µg/L)
PFOS	5.85	0.56	7.70	2.57
PFOA	1112	537	NC	NC

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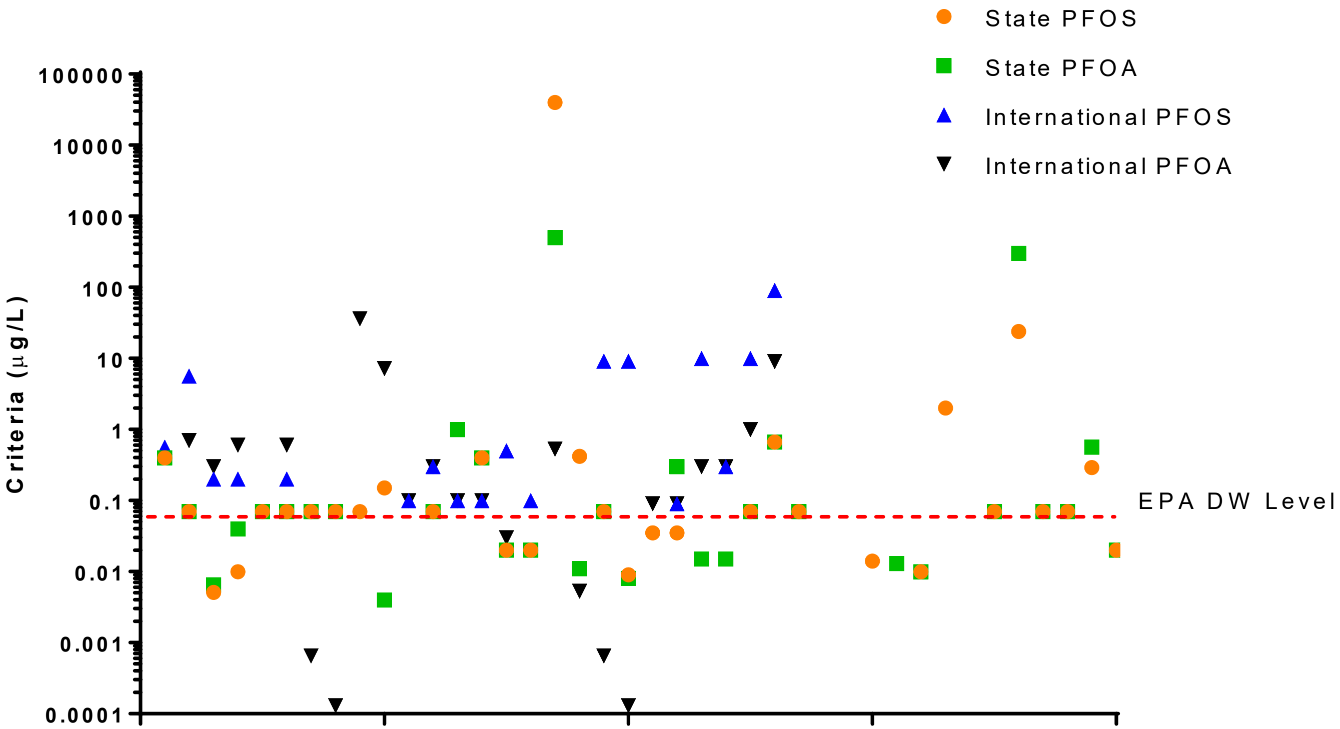
Figure from Conder et al., 2019

Screening Levels:

- EPA Drinking water level for PFOS/PFOA is 70 ng/L
- Numerous human health criteria interim or released (23 states, EPA, 11 countries) for DW/GW/SW.



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Data from ITRC Factsheet

Ecological Screening Values

Location		Criteria	(µg/L)
United States			
	Minnesota	PFOS aquatic	19
		PFOA aquatic	1700
	Michigan	PFOS aquatic	140
		PFOA aquatic	880
		PFOS avian	0.035
		PFOS mammals	0.084
Canada		water, avian dietary, mammal dietary (PFOS and PFOA)	
EU		freshwater and saltwater (PFOS)	
Italy		freshwater and saltwater (5 PFAS)	
Australia		freshwater and saltwater (PFOS and PFOA)	
New Zealand		freshwater and saltwater (PFOS and PFOA)	

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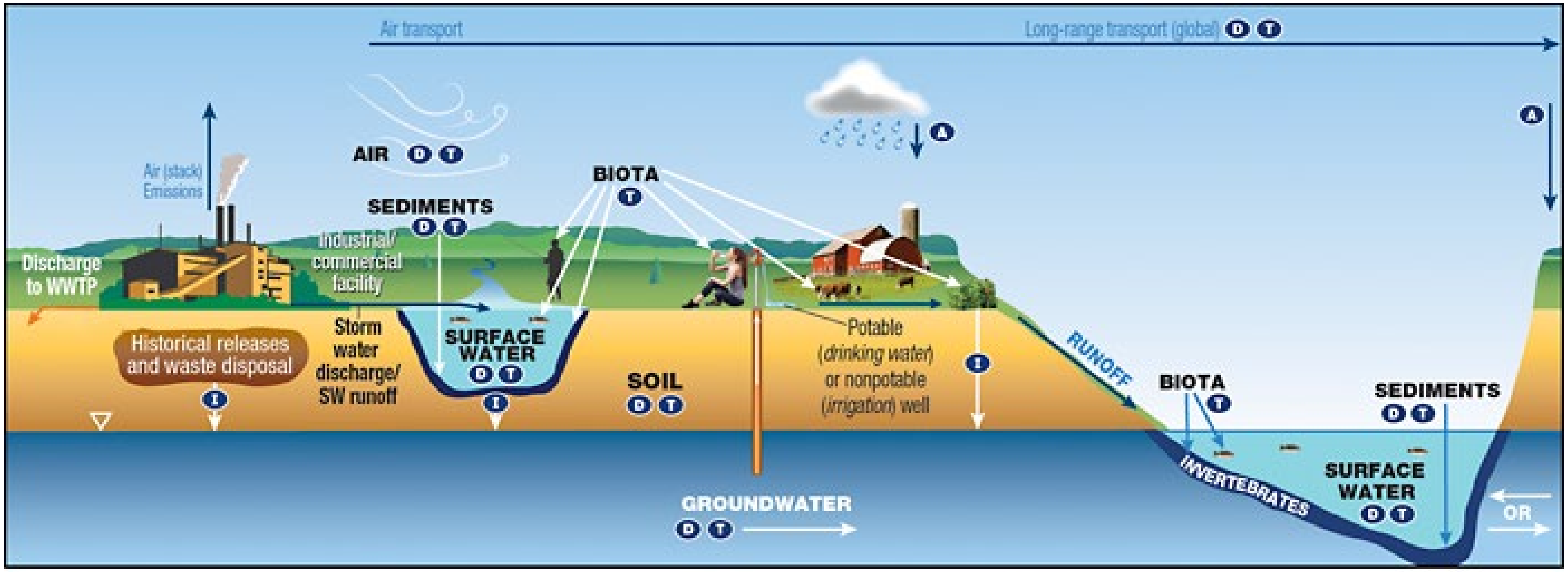
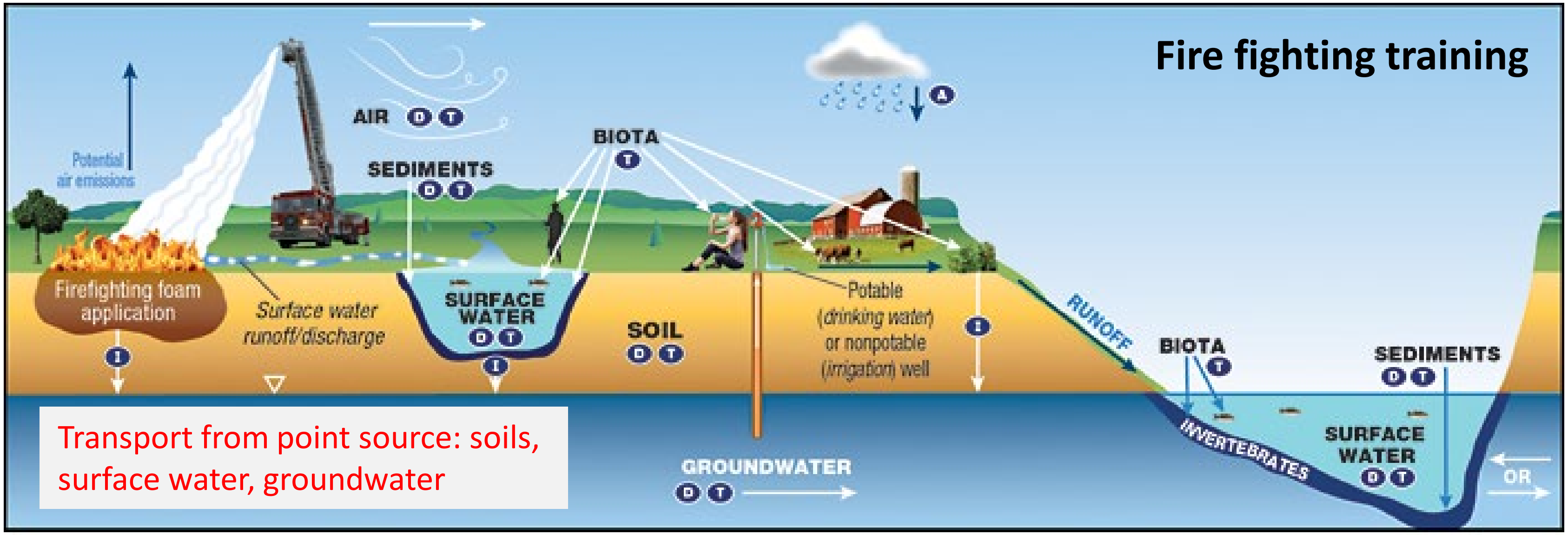
Characterizing Risk or Injury



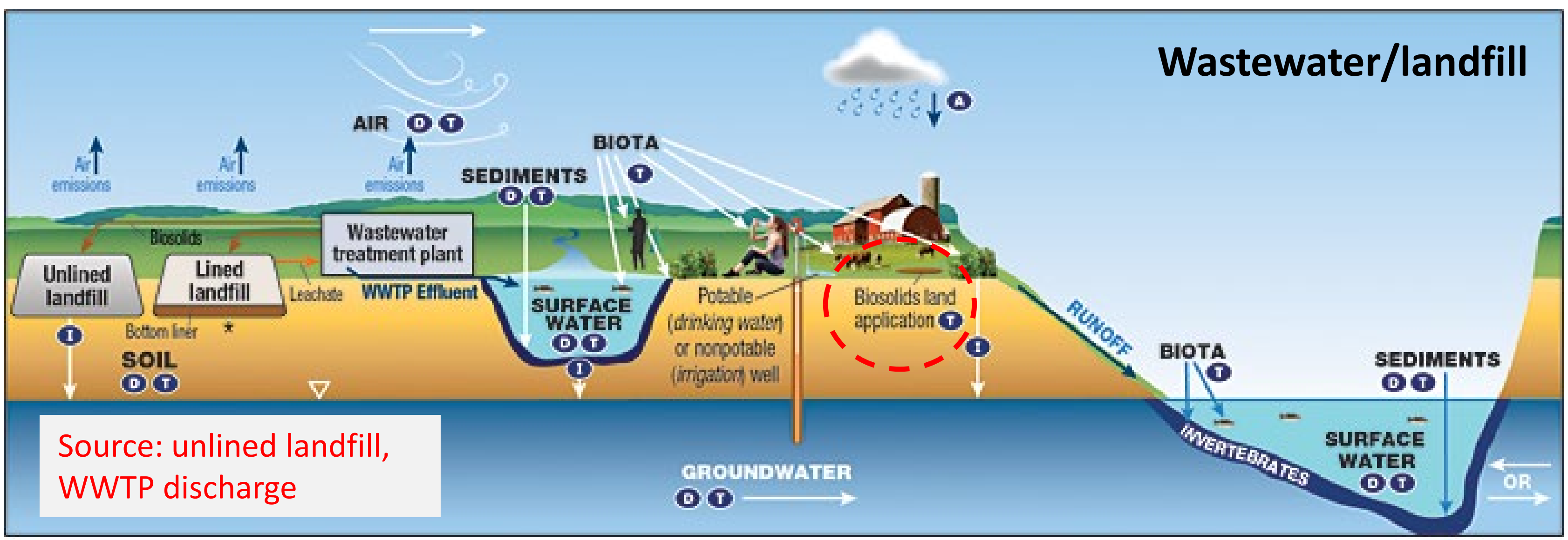
<u>Considerations</u>

- Primary release pathways: disposal, air, WWTP
- Transport via water to aquatic resources overland flow, ground water, surface water
- Receptors likely to be aquatic organisms and wildlife/birds connected to food web

Figure by Laura Trozzolo, TRC Companies Inc



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



*Leachate release from lined landfills could occur in the event of a liner leak

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

Figure by Laura Trozzolo, TRC Companies Inc

Ongoing Activities/Research

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- USGS is conducting research and developing a research strategy (summer 2020)
    - Sampling and analytical methods
    - Sources and models
    - Monitoring
    - Fate and Transport
    - Bioaccumulation and ecotoxicity

- SETAC
    - Special issue of ET&C
    - Focused Topic Meeting last August, subgroups developing manuscripts

SERDP
DOD ▪ EPA ▪ DOE

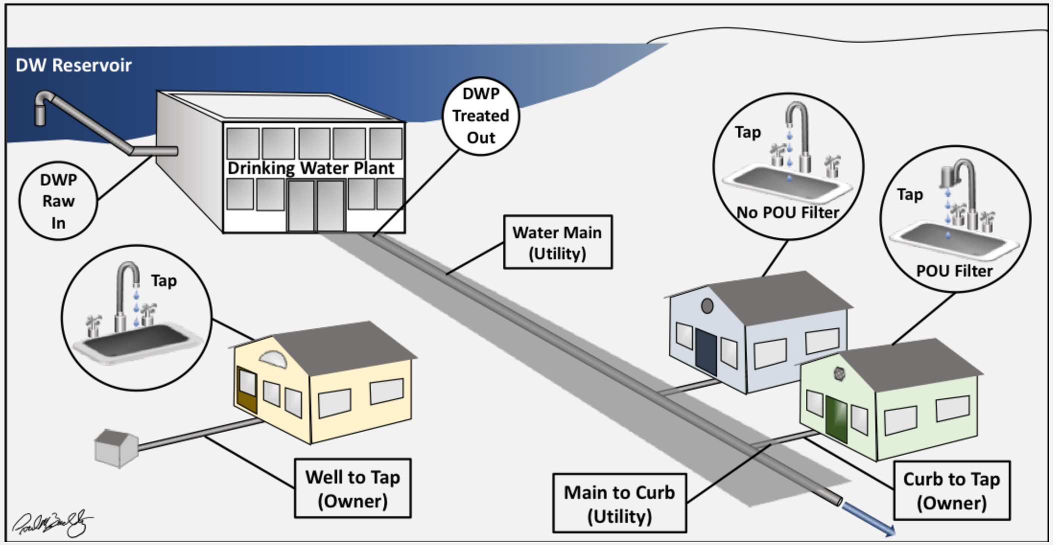
- US DoD through SERDP/ESTCP
    - Developing ecological risk-based screening values
    - Bioaccumulation
    - T&E Species
    - Remediation technologies

- US EPA evaluating availability of data for AWQC
    - PFOS and PFOA for single chemical have sufficient data
    - Other chemicals not likely enough data

Assessing Exposures from Drinking Water at the Point of Use: USGS Collaborative Tapwater Research

DW Resource → Treated DW → DW Exposure?

2016 Reconnaissance of Chemical & Biological Contaminant Exposures from Residential and Workplace Tapwaters at Selected Sites in the US



PFAS: 9% of detected; 84% of samples (med: 2 ng L-1)

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EPA United States Environmental Protection Agency

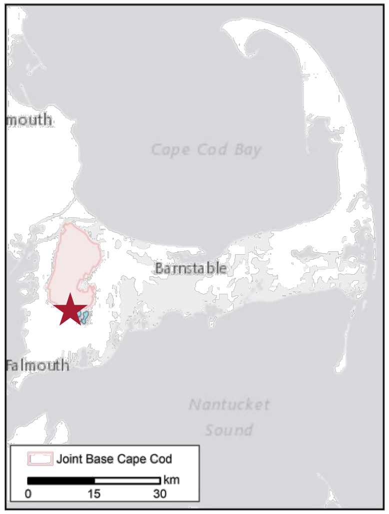
NIH National Institute of Environmental Health Sciences Your Environment. Your Health.

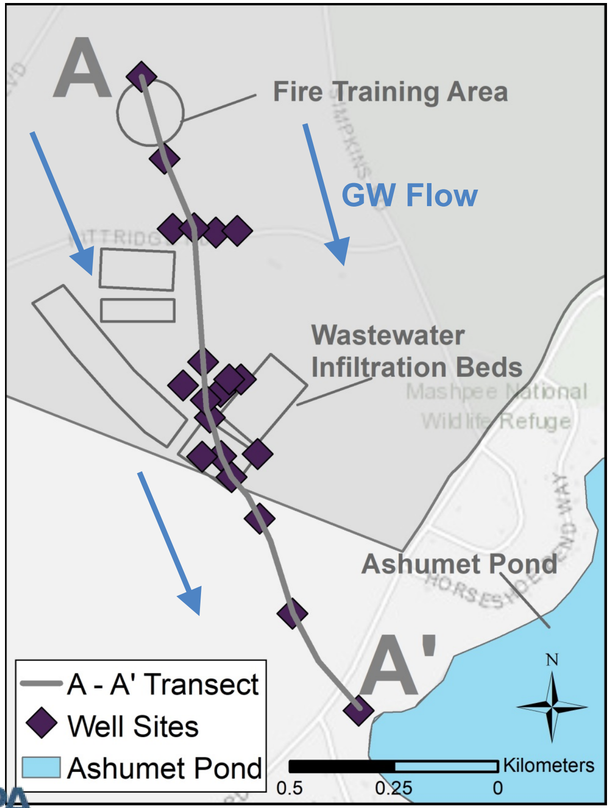
COLORADO SCHOOL OF MINES EARTH • ENERGY • ENVIRONMENT

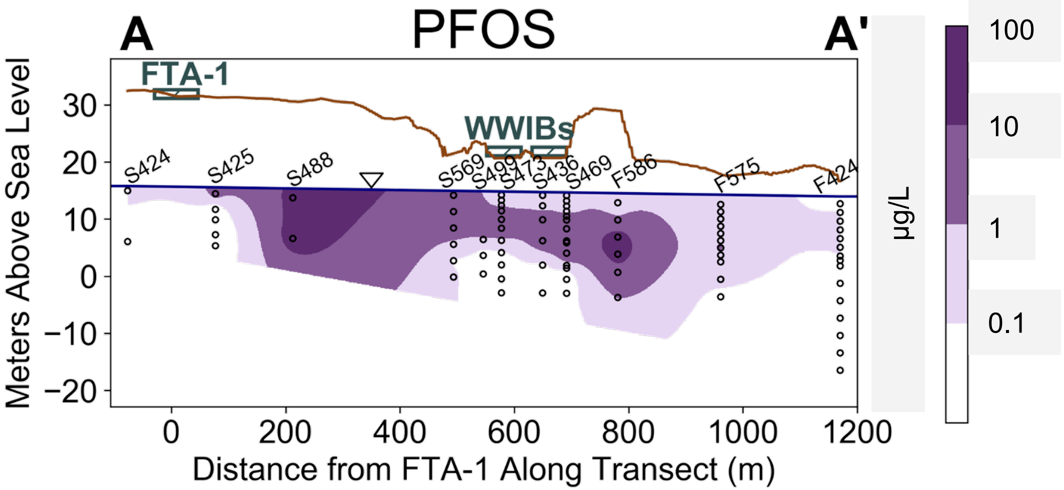
Bradley, USGS

Fate and Transport: Cape Cod

- USGS Cape Cod Research Site – used as a field laboratory
- Site is impacted by AFFF (pre-1997) and wastewater (pre-1995)



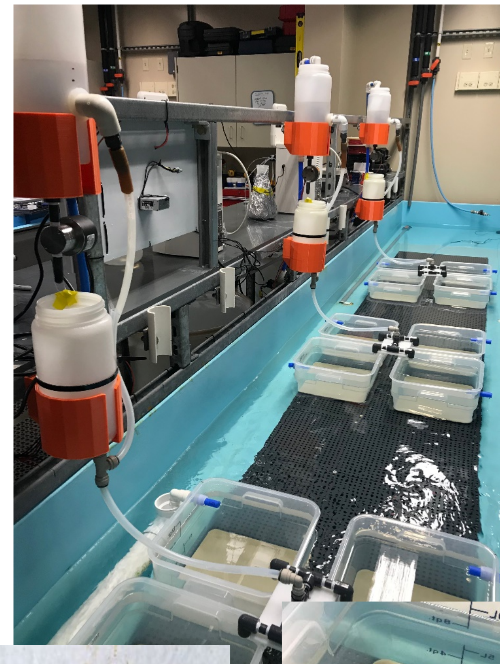




Tokranov, Weber, Barber, Jasmann, USGS

Laboratory mussel and mayfly toxicity and bioaccumulation study

- Bioaccumulation – PFAS mixture Eastern Pond mussel (ongoing); four chemicals selected because commonly observed on DoD facilities
- Water, mussel tissue analyzed through collaboration with Baylor University and through contract lab.
- Data will be used to parameterize bioaccumulation model and to inform conditions for field-based studies
- Toxicity - PFOS and PFOA using mayfly and mussel (planned this summer)



N. triangulifer

L. nasuta

BAYLOR UNIVERSITY 1845

EPA United States Environmental Protection Agency

Steevens, Dorman, Walters, USGS

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Acknowledgements

- Chris McCarthy, Jacobs Engineering
- USGS PFAS team
- Society of Environmental Toxicology and Chemistry
- Interstate Technology Regulatory Council

Questions?

- **Jeff Steevens**
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- **Cell: 573-702-9121**

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Image of spotted sandpiper by Steevens

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