Technical and Regulatory Issues Associated with Per- and Polyfluoroalkyl Substances (PFAS)

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Nomenclature

- Per- and Polyfluoroalkyl Substances (also written as PFAS)
  - Perfluoroalkyl substance – carbon-chain molecules with all carbon atoms bonded to fluorine atoms
  - **Most well-known compounds**
    - **Perfluorooctanoic acid (PFOA)**
    - **Perfluorooctane sulfonic acid (PFOS)**
  - Polyfluoroalkyl substance – carbon-chain molecules with at least one carbon bonded to something other than a fluorine atom
- Incorrectly referred to as "PFCs"
  - Greenhouse gases regulated by Kyoto Protocol *(perfluorocarbons)*
  - PFCs are one family of PFAS

~5,000 manufactured compounds

Unique Chemistry = Forever Chemicals

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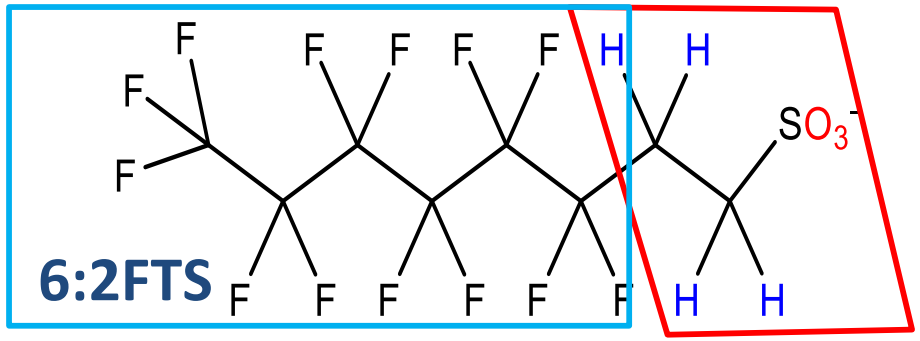
Very water soluble	Hydrophobic (tail)
Heat Resistant	Lipophobic (tail)
Surfactant	Resistant to Degradation

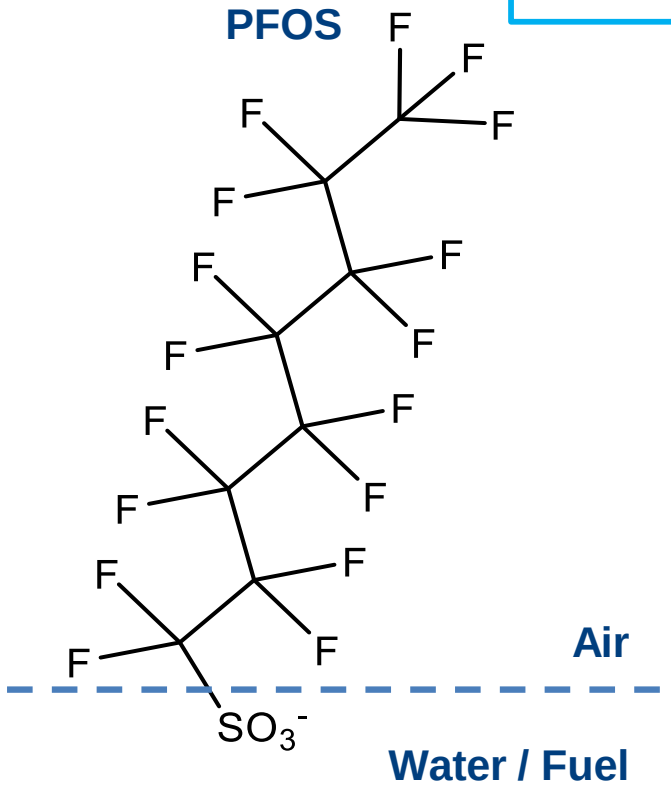


<u>Polyfluorinated</u>

- Partially fluorinated
- CH_2 – linkages = 'weakness' in molecule, open to chemical and biological degradation
- "Precursors"

<u>Perfluorinated</u>

- Fully fluorinated
- "Terminal PFAS"



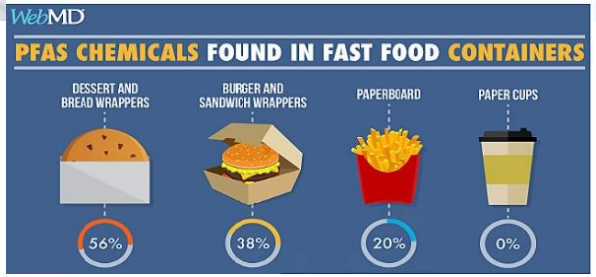
Basic chemical structure include a chain (**tail**) with a charged functional **head** (commonly carboxylic or sulfonic acid that is hydro- and lipophillic)

C-F bond is shortest and strongest bond in nature

- Hydrophobic and lipophobic
- Resist chemical & biological degradation

PFAS Uses

- **Aqueous film forming foams (AFFF)** – propriety mixtures of fluorinated and hydrocarbon surfactants, water, corrosion inhibitors, solvents
  - ~1-10% PFAS by weight
  - <5% of PFAS production
- Aerospace
- Chemical manufacturing
- Electronics
- Healthcare
- Leather products
- Medical supplies
  - Implants, patches, grafts
- **Metal plating and etching**
- Mining
  - Odor and dust control
- Paint, varnish, sealant, wax, polish



- Paper coatings
- **Personal care products**
  - **Cosmetics, bug spray, sunscreen, dental floss, shampoo, body wash**
- Pesticides (Sulfuramid)
- Pharmaceuticals
- Photolithography
- Plastics
  - Polymer manufacturing, Resins
- Performance chemicals
  - Building and construction
  - Hydraulic fluids, fuels
  - Industrial surfactants
  - Oil and gas – enhanced recovery
- **Textiles**
  - **Weather resistant apparel and equipment**
  - **Stain resistant fabrics**

PFAS Usage Timeline

- 1930's – PTFE (Teflon) discovered
- 1940's – PFAS in consumer products begins
- 1950's – Stain resistant products
- 1960's – AFFF, packaging
- 1970's – Detected in the blood serum of workers and consumers
- 1990's – Chromium plating dust suppressant
- 2000's – C8 Study suggests human toxicity (Dupont)
  - **2006 – 2015 – Voluntary Stewardship Program phases out manufacture of PFOA and PFOS in the United States (8 largest producers)**
  - 2019 – PFOA and PFOS no longer manufactured in US, but present in imported raw, finished, and waste materials

Potential Sources

“The only places we’re not finding PFAS are places we’re not looking”

Heidi Grether, Director, Michigan Department of Environmental Quality

- Industrial Sites
  - Primary manufacturing facilities (product and feedstocks)
  - Secondary manufacturing facilities that use products as part of industrial processes or worker safety (dust suppression)
- Fire Training/Fire Response Sites
- Landfills
  - Leachate
  - Odor and dust control
- Wastewater treatment plants
  - Effluent
  - Biosolids (land application)

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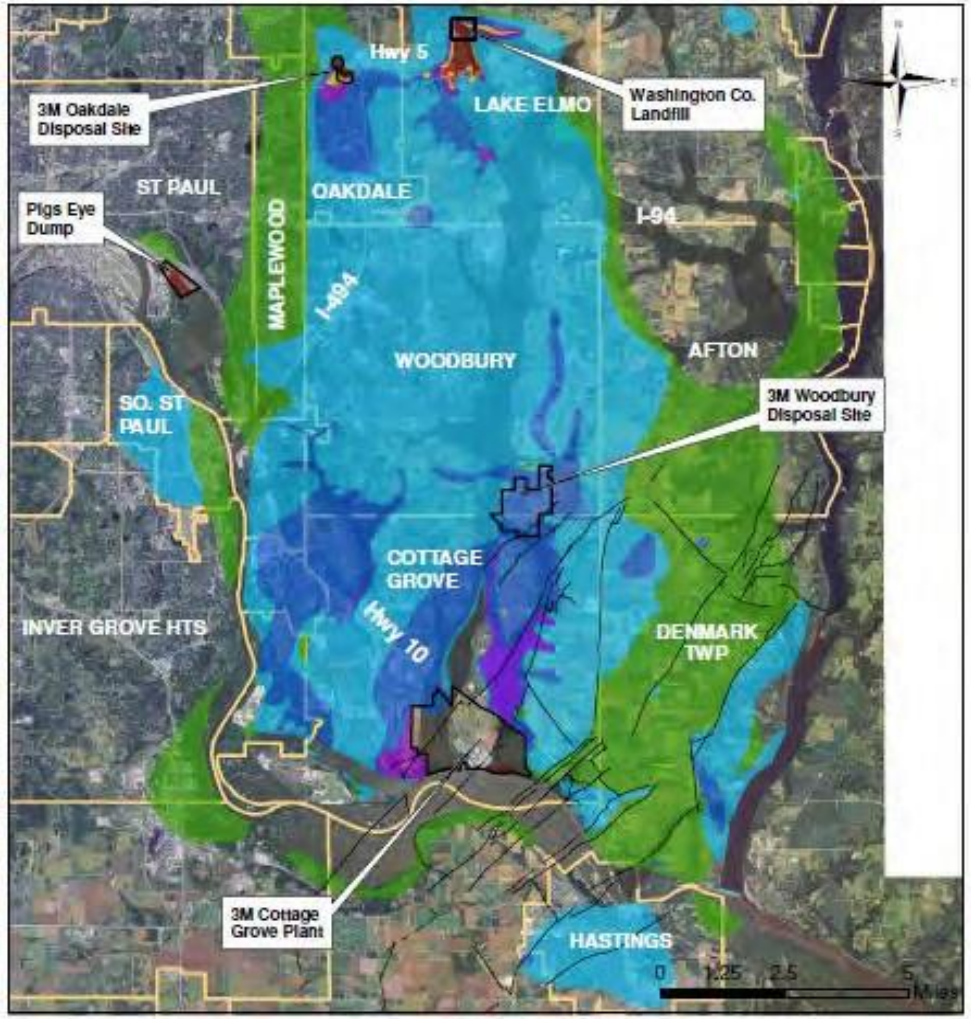
Fate, Transport, and Exposure

Environmental Fate and Transport

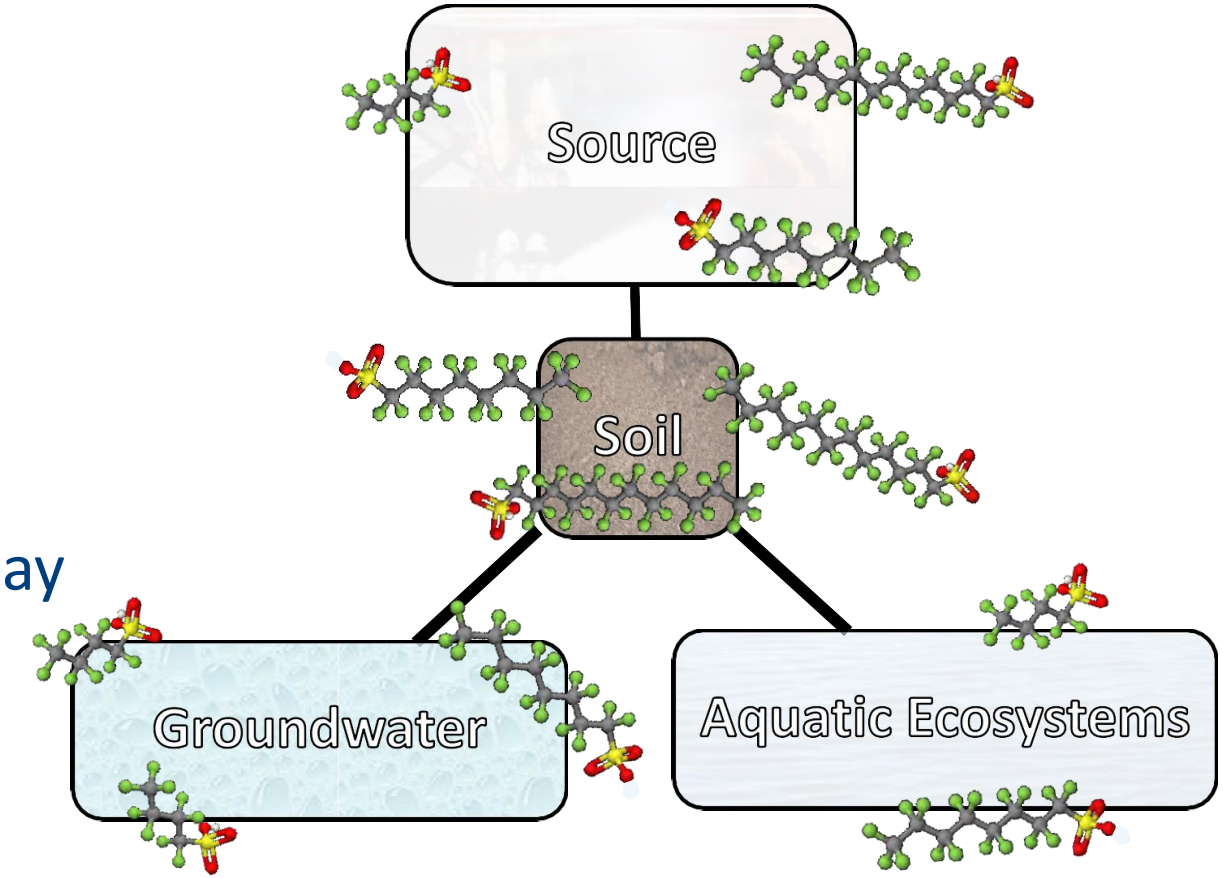
- Moderate-high water solubility and mobile
  - Groundwater plumes from contaminated areas many miles long
- Why?
  - Low volatility
  - No degradation
  - Can partition to soils and sediment (organics) - serves as ongoing source to leach to groundwater



Minnesota 3M PFAS plumes in groundwater 10+ miles long, cover over 100 miles² (MDH, 2012)

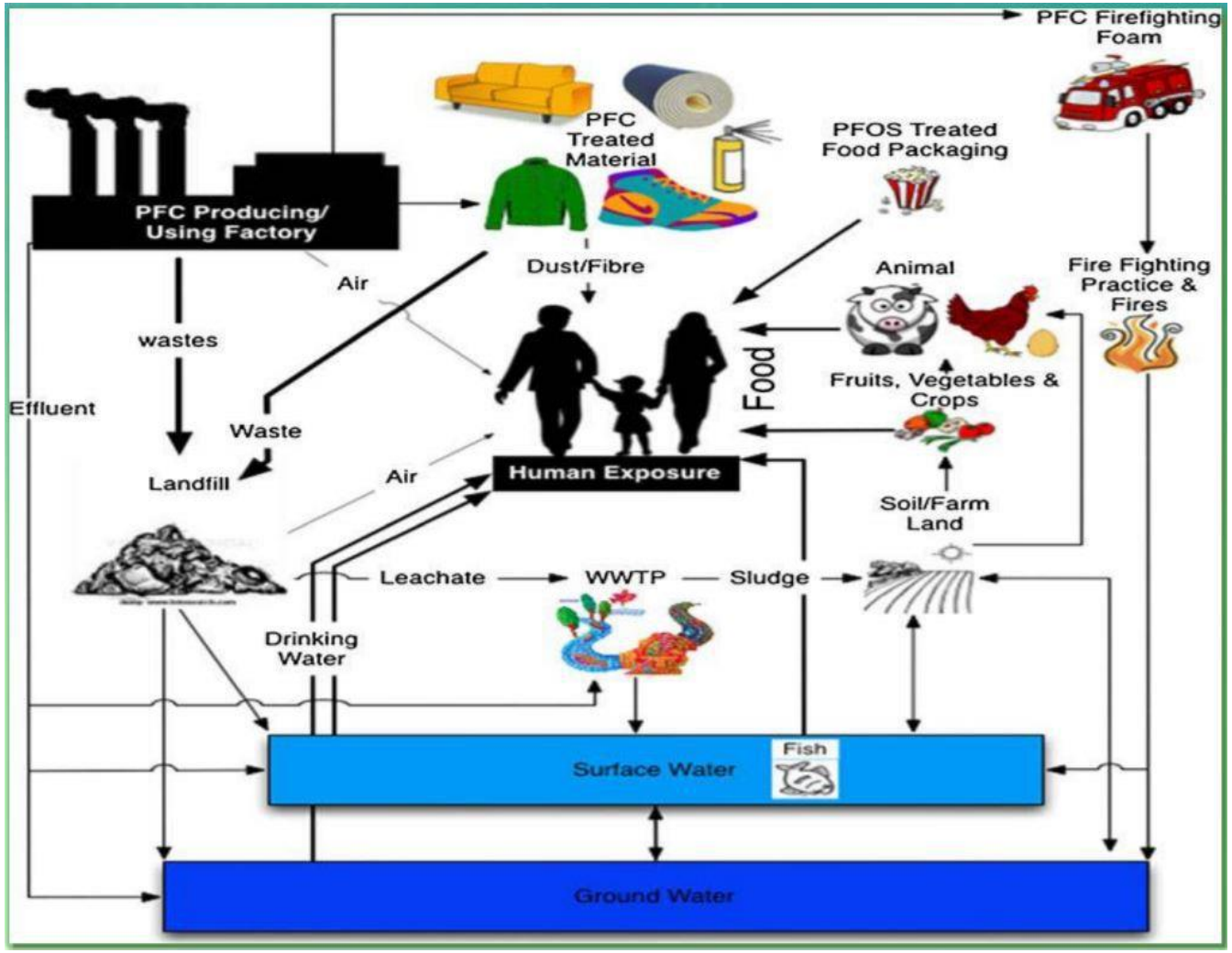
Environmental Fate and Transport

- Hydrophobic/lipophobic tail competes with hydrophilic head, partitioning to interfaces (soil/water, water/air, etc.)
- Advection drives mobility in groundwater
- Dispersion limited (narrow plumes)
- Diffusion in groundwater is slow but diffusion of contaminant mass into lower permeability soil, bedrock, and concrete may enhance long-term persistence in groundwater
- These traits typically mean PFAS concentrations do not decrease along flow paths



Human Health Impacts and Exposure Pathways

- Essentitally all US populations have detectable levels of PFAS in blood
- Links to cancer and non-cancer diseases
- Major pathways[1,2]
  - **Drinking water**
  - Incidental soil/dust ingestion
  - **Diet (bioaccumulation)**
    - Fish and seafood
    - Homegrown produce
- Insignificant or minor pathways
  - Dermal absorption
  - Inhalation



[1] Oliaei et al., 2013. Environ. Sci. Pollut. Res. Manag. 20:1977-1992
[2] Domingo, 2012. Environment International 40:187-195

Regulatory Framework

Federal Regulatory Framework

- 2016 - EPA established **lifetime health advisory level of 70 ng/L for PFOA, PFOS, and PFOA+PFOS**
- December 2019 - EPA released *Interim Recommendations to Address Groundwater Contaminated with Perfluorooctanoic Acid and Perfluorooctanesulfonate*
- 2020 National Defense Authorization Act (NDAA)

Does Not	Does
Designate PFAS as haz waste under CERCLA	Prohibits military use of PFAS-containing AFFF after 10/1/24 and immediately prohibits use in training
List PFAS on CWA toxic pollutant list	Adds PFOA, PFOS, and other PFAS to the Toxics Release Inventory (report releases and disposal if use >100 lbs)
Set national drinking water standard und SDWA	Requires SDWA monitoring by most public water system for PFAS which EPA has a valid method for measuring
	USGS required to establish performance standard for detecting PFAS and conduct nationwide PFAS sampling program of various waterbodies and soil

- U.S. states are taking the lead…

Florida's Regulatory Framework: Provisional CTLs and SLs

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Provisional PFOA and PFOS Cleanup Target Levels/Screening Levels							
Media	Groundwater - PGCTL**	Soil – PSCTL			Irrigation - IWSL		
		Residential	Commercial/ Industrial	Leachability	Residential	Commercial/ Industrial	Produce
Perfluorooctanoic acid (PFOA)	70 ng/L (0.07 µg/L)	1.3 mg/kg	25 mg/kg	0.002 mg/kg	6.7 µg/L	750 µg/L	NA
Perfluorooctane sulfonate (PFOS)	70 ng/L (0.07 µg/L)	1.3 mg/kg	25 mg/kg	0.007 mg/kg	72 µg/L	370 µg/L	0.6 µg/L

Notes:
PGCTL – provisional groundwater cleanup target level
PSCTL – provisional soil cleanup target level
ISWL – irrigation water screening level
NA – not applicable, model not applicable based on K_{ow}
ND – No data available for this calculation
** - sum of PFOA and PFOS should be compared to the PGCTL
µg/L – micrograms per liter
ng/L – nanograms per liter
mg/kg – milligrams per kilogram

PFOA and PFOS Surface Water Screening Levels				
Criteria	Human Health		Ecological	
	Freshwater	Marine	Freshwater	Marine
Perfluorooctanoic acid (PFOA)	0.15 µg/L (150 ng/L)	0.15 µg/L (150 ng/L)	1,300 µg/L	ND
Perfluorooctane sulfonate (PFOS)	0.004 µg/L (4 ng/L)	0.004 µg/L (4 ng/L)	37 µg/L	13 µg/L

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PFAS Site Investigations and Lessons Learned

PFAS Site Investigations

- Large Federal facility (over 650 samples and 150 locations)
- 14 other AFFF-use facilities in Florida
- **Prepared PFAS-specific SOPS**

Why PFAS-Specific SOP?

- Avoid cross-contamination, false positive results
  - PFAS potentially present in variety of commonly-used materials
  - Low method detection limits (low to sub ng/L)
- Current sampling guidance reflect abundance of precaution, rather than scientific findings
  - Guidance varies state by state, still in infancy
  - Rapid changes to state of knowledge, state and federal guidance and regulations

PFAS Considerations – Field Personnel

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Try to Avoid

- X Water or stain-resistant boots and clothing
- X Clothing recently laundered with a fabric softener
- X Coated HDPE suits
- X Latex gloves
- X Sunscreen and insect repellants containing fluorinated compounds
- X Cosmetics, moisturizers, hand cream, and other related products which may contain PFAS
- X Food wrapper and packaging

Safe to Use

- ✓ Boots made of polyurethane, polyvinyl chloride (PVC), rubber, or untreated leather
- ✓ Other field boots covered by PFAS-free (e.g., polypropylene) over-boots
- ✓ Rain gear made of polyurethane, PVC, wax-coated, vinyl or rubber
- ✓ Clothing made of synthetic (e.g. polyester) or natural (e.g. cotton) fibers
- ✓ Uncoated HDPE suits
- ✓ Sunscreen and insect repellant tested and found to be PFAS free

❖ If an item cannot be easily avoided, use QA/QC samples to confirm no cross-contamination (e.g., field blanks)

PFAS Considerations – Field Personnel

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Attachment A. Daily Sampling Checklist

Date: _____

Site Name: _____

Weather (*temperature/precipitation*): _____

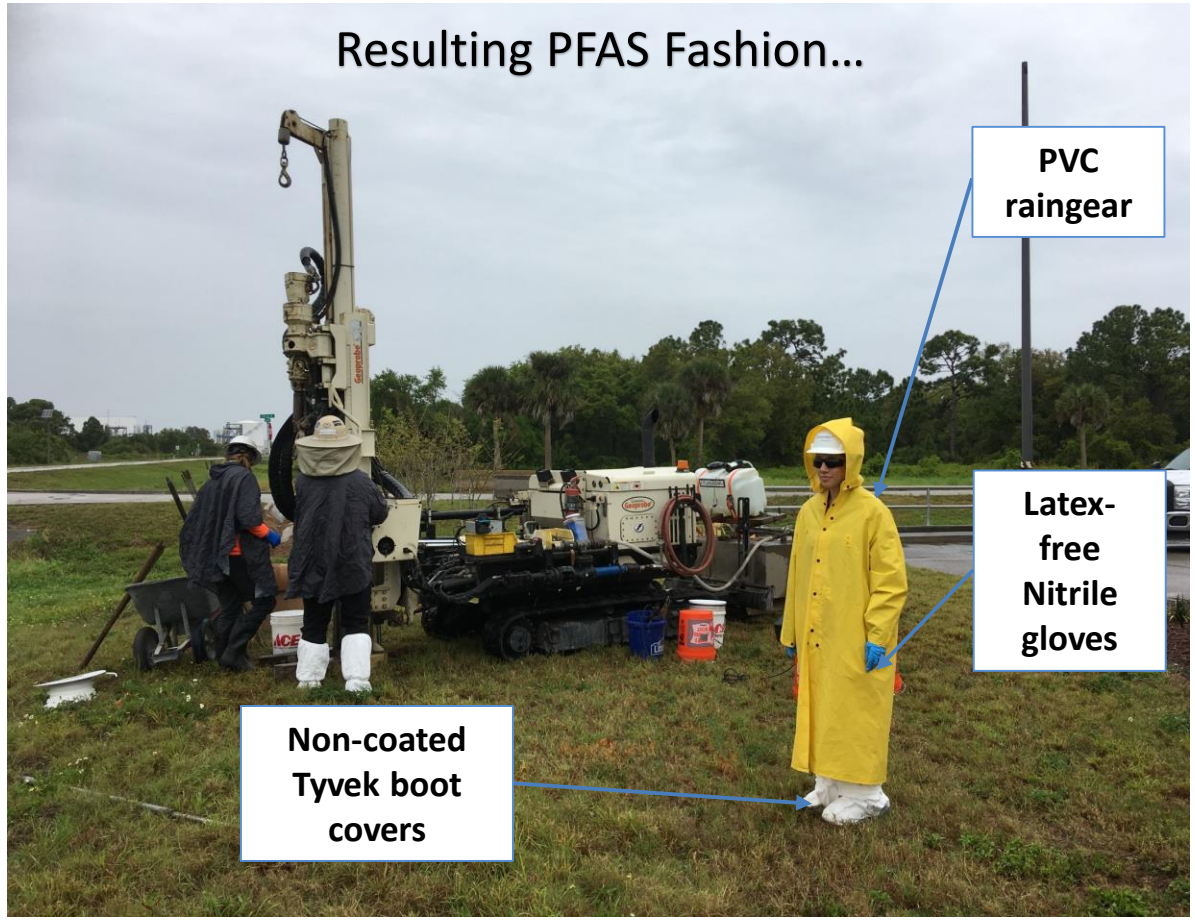
Please check all boxes that apply and describe any exceptions in the notes section below along with QA/QC methods used to assess potential sample cross-contamination as a result.

Field Clothing and PPE:

- ☐ No water- or stain-resistant boots or clothing (e.g., GORE-TEX®)
- ☐ Boots made of polyurethane, PVC, rubber, or untreated leather
- ☐ Clothing has not been recently laundered with a fabric softener
- ☐ No coated HDPE suits (e.g., coated Tyvek® suits)
- ☐ Field crew has not used cosmetics, moisturizers, or other related products today
- ☐ Field crew has not used sunscreen or insect repellants today, other than products approved as PFAS-free

Field Equipment:

- ☐ Sample containers are made of HDPE or polypropylene, not LDPE
- ☐ Sample caps are made of HDPE or polypropylene and are not lined with Teflon™
- ☐ No materials containing Teflon™, Viton™, or fluoropolymers
- ☐ No materials containing LDPE in direct contact with the sample (e.g., LDPE tubing)
- ☐ Equipment in direct contact with the sample is made from stainless steel, HDPE, acetate, silicon, or polypropylene
- ☐ No plastic clipboards, binders, or spiral hard cover notebooks
- ☐ No waterproof field books
- ☐ No waterproof or felt pens or markers (e.g., certain Sharpie® products)
- ☐ No chemical (blue) ice, unless it is contained in a sealed bag



Other Considerations - Decon Water Sources: Pros and Cons

- Laboratory-certified PFAS-free water
  - Known source
  - Small volume and expensive
- On-site water source
  - Large volumes and least expensive
  - Potential PFAS detections and client sensitivities
- Drilling subcontractor and/or Geosyntec office water source
  - Large volumes and less expensive
  - Potential PFAS detections

Other Considerations – Investigation Derived Waste

- Cradle-to-grave liabilities
  - Landfill leachate
  - “Treated” aqueous discharge
  - Biosolids
- Landfills and water treatment facilities practices for accepting waste derived from PFAS/AFFF sources are evolving

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