Development of Standard Procedures for Sampling PFAS in Surface Water and Groundwater

Andrea Tokranov

Team: Joe Duris, Jerry Casile, Irene Fisher, Heather Heckathorn, Lee Eicholtz, Allison Casile, Tim Oden, Stan Skrobialowski

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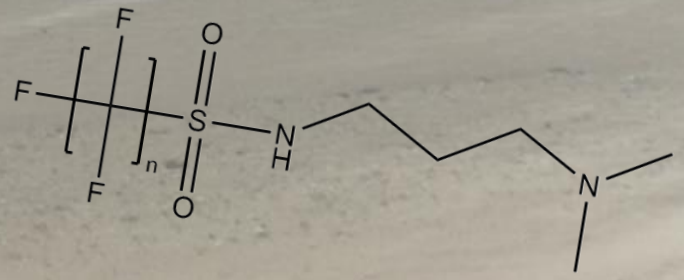
Chesapeake Bay Program's Toxic Contaminants Workgroup



U.S. Department of the Interior

U.S. Geological Survey

Contact Info:

atokranov@usgs.gov

Status of sampling protocols

Many guidelines exist for PFAS sampling. For example:

- DoD: Bottle Selection and other Sampling Considerations When Sampling for PFAS
- Michigan Department of Environment, Great Lakes, and Energy
- Interstate Technology Regulatory Council (ITRC)
- Massachusetts Department of Environmental Protection

And many, many more…however, these are guidelines based on presumed best practices, and have not been tested.

Additionally, SOPs/guidelines are focused on eliminating sources of PFAS, but have not evaluated sample representativeness (e.g. loss of PFAS during sampling)

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	DOD	Michigan Department of Environment, Great Lakes, and Energy
Prohibited Materials	Teflon	Fluoropolymers
	LDPE	PFAS treated paper, notebooks, clipboards, paper towels, etc.
	Polypropylene	New or unwashed clothing
	Paper products	Clothes washed with fabric softener
	Sticky notes	Decon 90 or other soaps with fluorinated surfactants
	Glue	Water resistant, waterproof or stain resistant clothing or shoes
	Markers	
	Blue ice packs	
	Decon 90 or other soaps with fluorinated surfactants	
	Water resistant, waterproof or stain resistant clothing or shoes	
Recommendations	Do not use personal care products such as creams, cosmetics, etc.	Do not use personal care products such as creams, cosmetics, etc. in sampling area
	Use only PFAS-free sunblock or insect repellent	Only use personal care products that have been verified as PFAS-free
	No food or drink except bottled water and hydration drinks	Screen Aluminum foil
	No fabric softener	Screen blue ice
	Clothes should be washed 6 times	No food or drink except bottled water and hydration drinks (outside sampling area)
		Screen LDPE bottles
		Screen Post-It® Notes
		Screen latex gloves
Allowed Materials	HDPE	HDPE, silicone, polypropylene, stainless steel
	Silicon	Loose paper, Rite in the Rain® notebooks
	Acetate liners	Nitrile gloves
	Nitrile gloves	Cotton clothing
	Pens	Wax-coated, polyurethane, polyvinyl chloride, rubber, neoprene, or uncoated Tyvek® rain gear
	Bags of ice	Aluminum, polypropylene clipboards
	Alconox® or Liquinox®	Bags of ice
	Cotton clothing	Alconox® or Liquinox®
	Wax-coated or polyurethane rain gear	Sharpie® markers (fine or ultra-fine)
		Pens, pencils
		LDPE tubing
		Natural rubber, nylon, polyethylene, glass jars for fish/wildlife samples

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Recent work on field sampling materials

Rodowa et al, 2020: https://doi.org/10.1021/acs.estlett.0c00036

- Analyzed 66 materials important for sampling
  - *"Of the 22 materials with potential to come in direct contact with samples during sampling, none had quantifiable concentrations of routinely measured PFAS."*

Table 2. Group Category, Material, Summed Concentration of PFOA and PFOS[a] for Materials with Detectable Levels of PFOA/PFOS and Area (cm^2) of Materials Needed to Reach the LC-MS/MS Limit of Quantification (10 ng/L) and EPA HAL (70 ng/L) in a 1 L Water Sample, Assuming All PFAS Mass Released into Water

Group No.	Material	PFOA + PFOS (ng/cm^2)	Material area to achieve 70 ng/L in (cm^2)	Material area to achieve 10 ng/L (cm^2)
1: Pre-staging	First aid adhesive wrapper	0.45	160 (4.7 wrappers[b])	22 (0.7 wrappers)
2: Staging	PTFE tape 2	0.44	160 (130 cm)	23 (19 cm)
2: Staging	Aluminum foil	2.7	26	3.7
2: Staging	Paper towel 1	0.49	140	20
2: Staging	Lab notebook cover	0.39	180	26
4: Shipping	Resusable ice pack	0.023[d]	3000 (6.7 ice packs)	430 (1.0 ice packs)

Source: Rowowa et al, 2020: https://doi.org/10.1021/acs.estlett.0c00036

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Recent work on field sampling materials

Denly et al, 2019: https://doi.org/10.1002/rem.21614

- Leached sampling materials for 24 hours and analyzed PFAS in leachate
  - Represents an upper bound, as items are not usually in contact with sample for 24 hours.

	Sample	Silastic tubing		Nitrile gloves		Field book pages		Field book cover		PTFE bladder		Time-released bentonite pellets
PFAS	Batch	2		2		3		3		3		5
PFBA		7.20	6.96	2.12	2.48	NR	NR	71.99	94.40	61.79	62.53	2.0 U
PFBS		2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.16	3.17	2.0 U	2.0 U	2.0 U
PFPeA		NR	NR	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	80.34	64.94	2.0 U
PFHxA		2.0 U	2.0 U	2.0 U	2.0 U	2.17	2.21	2.0 U	2.0 U	11.87	8.97	2.0 U
PFHxS		2.0 U	2.0 U	4.24	4.28	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U
PFHpA		2.0 U	2.0 U	2.0 U	2.0 U	2.06	2.17	4.98	9.98	11.81	8.95	2.0 U
PFOA		2.0 U	2.0 U	2.0 U	2.0 U	2.27	2.35	2.0 U	2.0 U	2.93	2.04	2.24
PFNA		2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.10	2.0 U	2.0 U	2.74	2.13	2.0 U
PFUnA		2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	3.12	2.44	2.0 U
PFTrDA		2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	3.07	3.44	2.0 U
PFTeDA		2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	2.24	2.0 U	2.0 U

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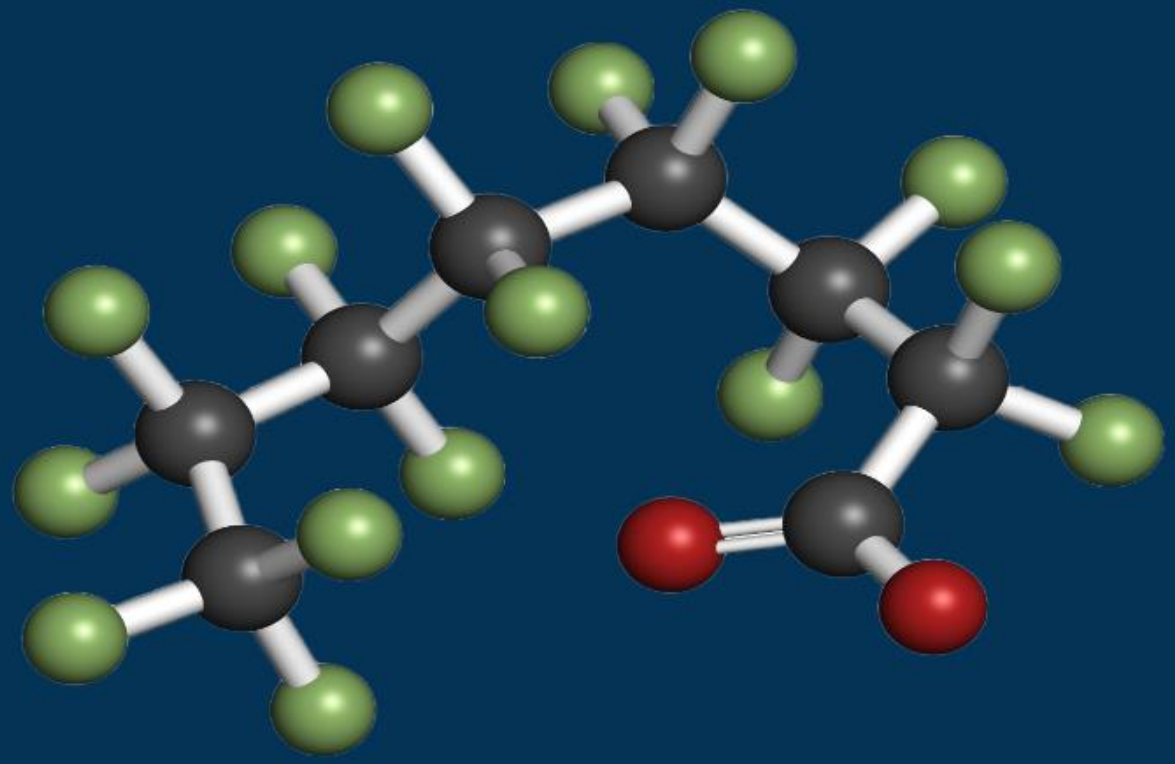
Source: Denly et al, 2019: https://doi.org/10.1002/rem.21614

U = less than the limit of quantitation; NR = Not reported (≤5% recovery of extracted internal standard)

DOD SERDP RFP



Development of Improved Sampling and Analytical Methodologies for the Determination of Per- and Polyfluoroalkyl Substances (PFAS) in the Environment

SERDP, Environmental Restoration Program Area

Released November 3, 2022

FY 2024

Specific objectives include: Development and validation of sampling methods relative to thermal treatment, stormwater sampling, surface water, and sediment sampling

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USGS approach

- Test surface water and groundwater sampling equipment/methods in use at the USGS
- Use USGS methods outlined in the National Field Manual, to the extent possible
    - E.g. use “clean hands, dirty hands” approach
    - Work inside a sample collection chamber if feasible
- No restrictions on what people eat or drink or wear
- Goal: collect a representative sample

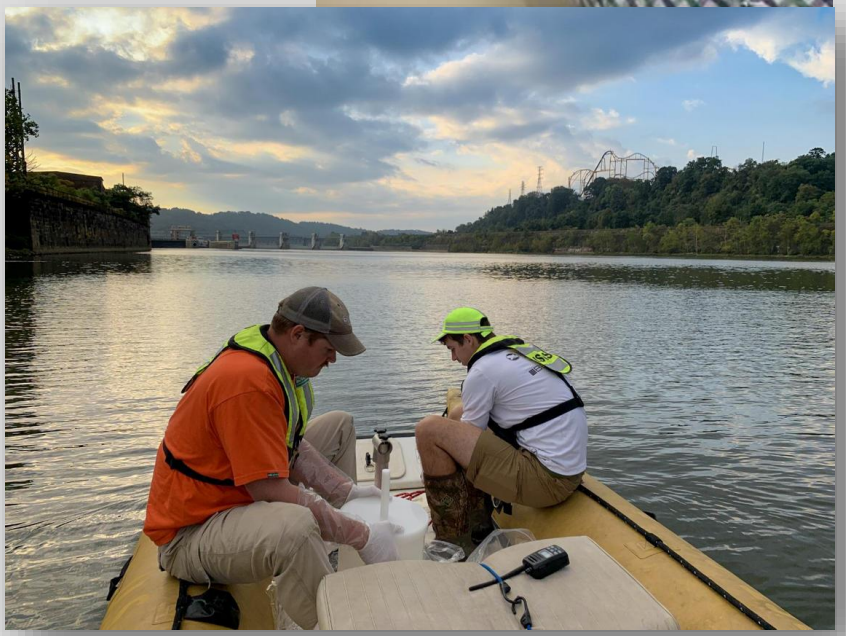
USGS testing

For groundwater and surface water:

- Equipment was blanked
- A PFAS-containing solution was made at a low (20 ng/L) and high (1,000 ng/L) concentration
- Surface water and groundwater equipment was used to collect the PFAS-containing solution
  - For GW: Fultz pump, Grundfos Redi-flo2, Bennett pump, and Acetyl bodied pump. Tested with 50 ft of HDPE and FEP tubing.
  - For SW: see next slide
- Equipment was cleaned and a final methanol rinse collected to determine cleaning effectiveness
- Testing allows evaluation of recovery (or evaluation of any loss to container/tubing) and cleaning effectiveness at two different PFAS concentrations for every sample configuration tested

Summary of sampling methods tested

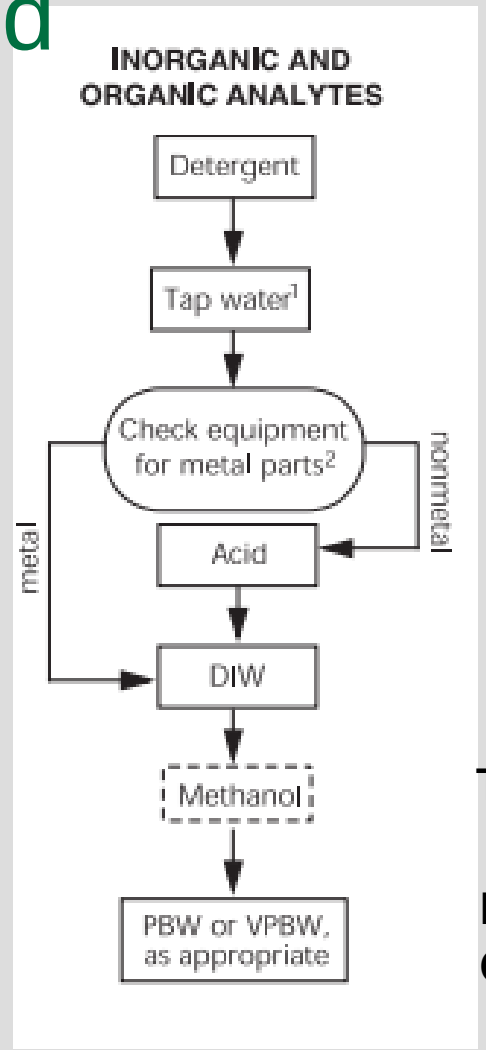
- Trace (ppt) sampling protocols
- No special rules for attire, food, product use, etc.
  - Clean-Hands/Dirty-Hands (i.e. 2 people sampling)
    - https://water.usgs.gov/owq/FieldManual/
  - Specially selected & cleaned equipment (next slide)
  - Person opening sample bottle should be wearing elbow length poly gloves, covered with nitrile gloves
  - Normal cautions
    - Only open bottle when you're ready to fill
    - Close bottles promptly
    - If you drop a bottle and it's open, get a new one
    - Avoid any contact with inside of bottle
    - Avoid spraying or creating aerosols where samples are being collected or processed.
    - Water in the bottle should only ever be in contact with sampling equipment



Equipment Cleaning Process Implemented

All equipment used for PFAS sampling will be cleaned with the following process:

1. Tap water rinse
2. Liquinox detergent soak (30 min)
3. Scrub equipment with soft bristle brush
4. Warm tap water rinse
5. DI (lab produced) water rinse
6. Methanol rinse (from a PFAS-free spray bottle)
7. 2nd methanol rinse (from a PFAS-free spray bottle)
8. Rinse with copious amounts of blank water (Optima)
9. Allow to air dry
10. Stored double bagged in chamber bags



Twice!

Rinse with Optima

https://water.usgs.gov/owq/FieldManual/

Spiking, cleaning, blanking of SW sampling equipment

Equipment	Material	Contact Time	Low Spike Samples	Cleaning	Blank Samples	High Spike Samples	Cleaning	Blank Samples
Bottle, nozzle, cap 	poly and Teflon	~ 20 seconds, triplicate	~20 ng/L ΣPFAS	collect multiple MeOH rinses	triplicate	~1,000 ng/L ΣPFAS	collect multiple MeOH rinses	triplicate
Bags from bag samplers 	poly and Teflon	~ 20 seconds, triplicate	~20 ng/L ΣPFAS	no rinse collected, disposable	no blanks, disposable	~1,000 ng/L ΣPFAS	no rinse collected, disposable	no blanks, disposable
Churn splitter 	poly and Teflon	60 minutes, triplicate	~20 ng/L ΣPFAS	collect multiple MeOH rinses	triplicate	~1,000 ng/L ΣPFAS	collect multiple MeOH rinses	triplicate

Work in progress

- Data release of spike/blank data is being prepared
- Journal article to follow (for both SW and GW) related to USGS equipment
- National Field Manual will be updated using the data and journal articles as references

Thank you! Questions?

Contact information:
Andrea Tokranov: atokranov@usgs.gov 508.490.5017

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