NAVFAC
Naval Facilities Engineering Systems Command
EXWC Engineering and Expeditionary Warfare Center

Best Practices for PFAS Sampling and Analysis

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Presentation Overview

- Introduction
- Avoiding Cross-Contamination
- Field Sampling Considerations
- Analytical Best Practices
- Conclusions

Introduction

- PFAS are used in a wide array of products, creating potential for cross-contamination when sampling
- Preventing cross-contamination is critical to ensure sample integrity and produce defensible data for decision making
  - Especially important considering low ppt screening and action levels
  - e.g., proposed USEPA MCLs of 4.0 ppt for PFOS and PFOA

Existing PFAS Sampling Guidelines

Federal	State
▪ Naval Facilities Engineering Command (NAVFAC) ▪ DoD Environmental Data Quality Workgroup (EDQW) ▪ USEPA ▪ USEPA Region 4	▪ Michigan Department of Environment, Great Lakes, and Energy (EGLE) ▪ California State Water Resources Control Board (CA SWRCB) ▪ Florida Department of Environmental Protection (FDEP) ▪ Maine Department of Environmental Protection (Maine DEP) ▪ Massachusetts Department of Environmental Protection (MaDEP) ▪ Washington Department of Ecology ▪ Minnesota Pollution Control Agency (MPCA) ▪ New Hampshire Department of Environmental Services (NHDES) ▪ New York State Department of Environmental Conservation (NYSDEC)

***Non-exhaustive list*

- Consider your agency and/or state sampling guidance when developing sampling work plan

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Sampling Equipment Considerations

- To produce defensible data, it is important to ensure samples are not compromised by contaminants originating from sampling equipment
- Review Safety Data Sheets (SDS) for sampling materials – things to look for:
  - PFAS
  - terms containing ‘fluoro’ or ‘halo’
- Your work plan should document materials to be excluded due to PFAS content
- Consider including ultra-clean sample handling protocols in work plan, such as ‘clean hands/dirty hands’

Example materials that could introduce PFAS

- ❑ polytetrafluoroethylene (PTFE)
- ❑ waterproof coatings containing PFAS
- ❑ fluorinated ethylene-propylene (FEP)
- ❑ ethylene tetrafluoroethylene (ETFE)
- ❑ low-density polyethylene (LDPE)
- ❑ polyvinylidene fluoride (PVDF)
- ❑ pipe thread compounds and tape

Commonly Prohibited Materials and Equipment

Materials and Equipment to Avoid
Teflon®-containing materials, when possible, should be avoided (e.g., tubing, bailers, tape, and plumbing paste). In cases where Teflon®-containing materials are unavoidable, ensure adequate purging is performed prior to sampling (e.g., in-well pumps) and/or rinse blanks are collected prior to sampling
LDPE-containing materials (e.g., bags or containers used to transport samples)
Paper products such as waterproof field books, plastic clipboards, binders, spiral hard cover notebooks, sticky notes or glue materials
Markers
Chemical (blue) ice packs
Decontamination soaps containing fluoro-surfactants such as Decon 90®
Water that is not verified to be "PFAS-free" to be used for trip and decontamination blanks and decontamination processes
Water-resistant, waterproof, stain-treated clothing or shoes including Gore-Tex™ and Tyvek® materials

Brand names are included for illustration only and do not imply endorsement of the product.

Recommended Materials and Equipment

Recommended Materials and Equipment
HDPE and silicon – Materials include: tubing, bailers, tape, plumbing paste
Acetate liners for direct push technologies
Nitrile gloves – Change often
Loose paper with Masonite or aluminum clipboards
Pens
Bags of ice
Alconox® or Liquinox® , potable water followed by deionized rinse (for decontamination)
Laboratory supplied and verified “PFAS-free” water to be used for trip and decontamination blanks and decontamination processes
Cotton construction is recommended for field clothing and should be well-laundered from time of purchase due to possible PFAS-related treatments. Fabric softener must be avoided. Rain gear should be made from polyurethane and wax-coated materials

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PFAS Detected in Sampling Materials

Category	Material	Target PFAS (µg/m^2)		Total PIGE (F/m^2)
Prestaging	First Aid packaging and adhesive wrapper	PFBA 0.88 PFHxA 0.68 PFHpA 0.22, 0.40	PFBS 1.1 PFOS 0.19,0.32 PFOA 0.09, 3.9	660,000 ± 83,000
Staging	PTFE tape	PFOA 4.4 and 27		56,000,000 ± 11,000,000
	Aluminum Foil (non-stick only)	PFOA 4.4	PFBS 4.5	
	Label backing	6:2 FTS - 2.7	8:2 FTS - 5.7	63,000 ± 13,000
	Paper towel	PFOS 1.1, 3.8		
	Lab notebook	PFHxA 1.4	PFOS 2.2,1.7	
Sample Collection	PVC liner			10,000 ± 3,300
	Nitrile glove packaging			160,000 ± 33,000
Shipping	Marker	PFOA 83		16,000 ± 5,700
	Cold pack			250,000 ± 33,000
	Duct Tape	PFBS 0.77		

Rodowa et al. 2020 Study Summary

- 66 Materials analyzed for 52 PFAS and PIGE
- 22 materials had no quantifiable PFAS concentrations
- 10 materials had quantifiable concentrations (<0.45–83 µg/m^2) of target PFAS
- 15 had total fluorine (8000 to >11,000,000 µg F/m^2).

Rodowa et al. 2020. Field Sampling Materials Unlikely Source of Contamination for Perfluoroalkyl and Polyfluoroalkyl Substances in Field Samples. *Environ. Sci. Technol. Lett.* 7, 156−163.

Potential Pathways for PFAS to Enter a Sample

Direct sample contact with sampling equipment	Incidental contamination while sample bottle is open	Contamination during shipping
• Direct contact is the most likely pathway for introducing PFAS into a sample • For example, sample containers, tubing, pump components, bailers, sleeves and liners, samplers, and filters	• Cross-contamination could theoretically occur while sample bottle is open via dust/soil particles, volatile PFAS, etc. • Approximately 0.5 ng of PFAS would need to be introduced to a 250 mL sample to exceed reporting limit concentrations (>2 ng/L) • Equivalent to 1-2 drops of sunscreen entering bottle	• Guidance documents typically provide restrictions regarding sample packaging (e.g., no blue ice) for transport to the laboratory • There are no plausible pathways for non-volatile PFAS from these materials to enter a sample bottle

- Low potential for cross-contamination from sampling materials that are not likely to contact the sample or through incidental contact
- **Place greater focus on equipment and materials that come in direct contact with the sample**

Field et al. 2021. Assessing the Potential for Bias in PFAS Concentrations during Groundwater and Surface Water Sampling. SERDP Project ER19-1205.

Potential Pathways for PFAS to Enter a Sample

Material, Equipment, or Product	Potential for Direct Contact with Sample	No Potential Pathway to Affect Sample When Following Standard Field Protocols
Cold pack (outside)		X
Duct/electrical tape		X
Field book cover/pages		X
HDPE tubing	X	
Nitrile gloves	X	
Paper towels		X
Permanent marker ink		X
PTFE tubing	X	
PVC liner/screen	X	
Waterproof outdoor clothing		X

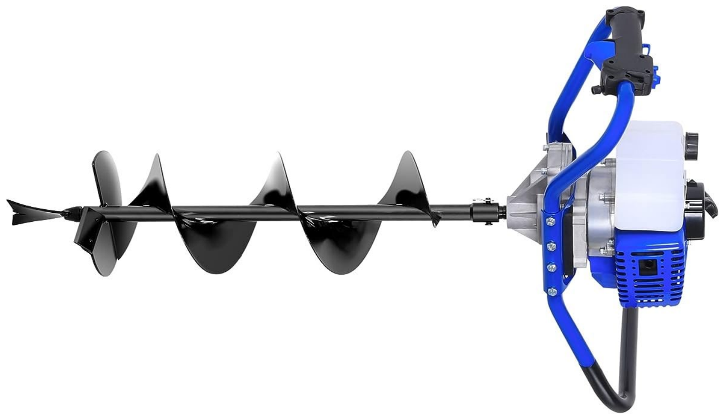
KEY POINT

Consider a scientifically-informed approach for selecting sampling materials based on probability of direct contact with sample and relative PFAS concentrations

Field et al. 2021. Assessing the Potential for Bias in PFAS Concentrations during Groundwater and Surface Water Sampling. SERDP Project ER19-1205.

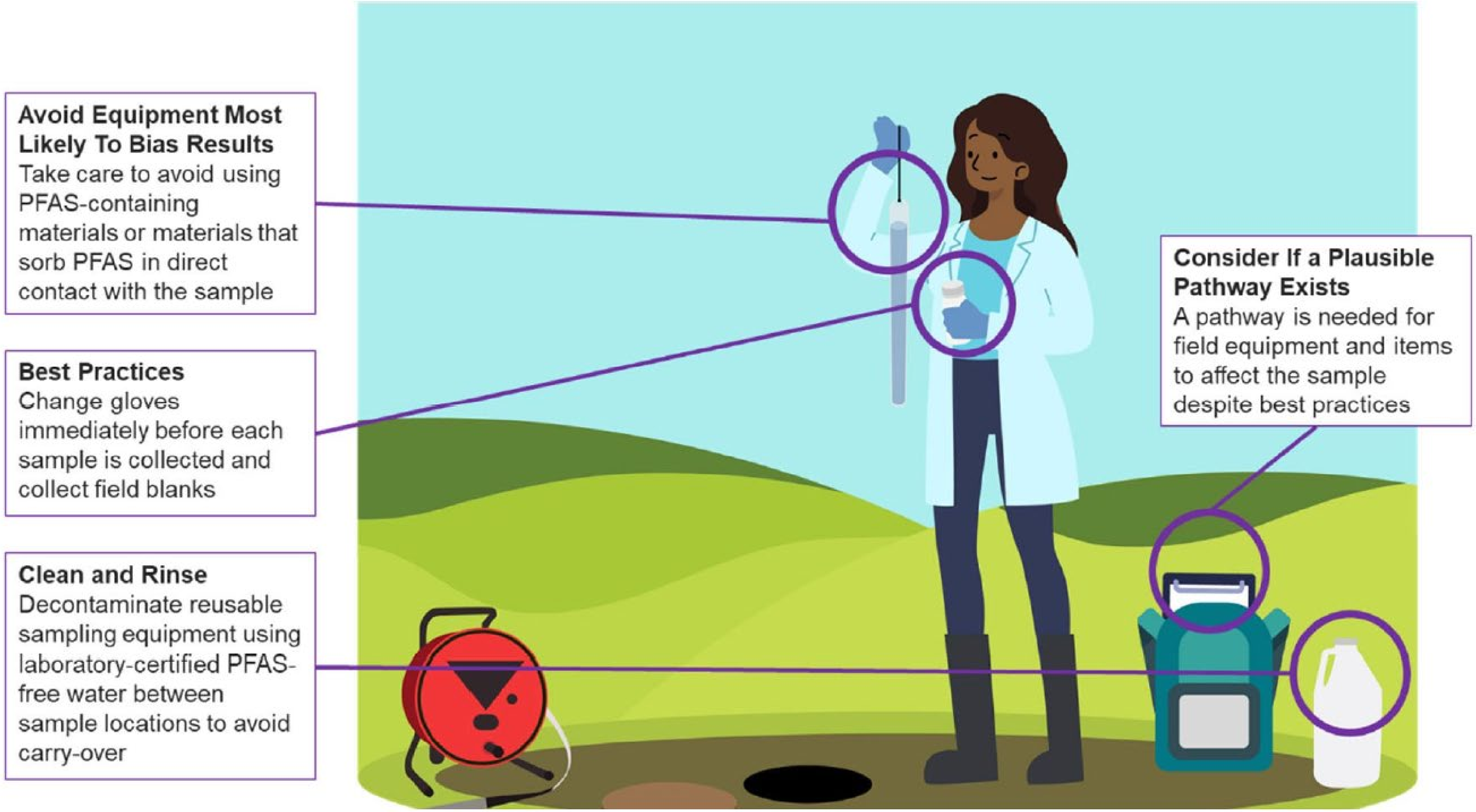
Equipment Decontamination

- Ensure equipment is decontaminated before mobilization to each investigation area and between sample locations at each investigation area
- Review SDS sheets for detergents or soaps for presence of fluorosurfactants
- Equipment should be rinsed with laboratory-verified PFAS-free water immediately before use, especially for equipment coming in direct contact with sample
  - Potable water can be used for larger equipment (augers, rigs, etc.)
  - During work plan development/prior to field mobilization, potable water sources should laboratory-verified PFAS-free to extent practicable
  - Include collection of source and equipment blank samples in work plan



Thoroughly decontaminate sampling equipment with hinges and difficult-to-access cavities

Key Points for Avoiding Cross Contamination



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- **Field Sampling Considerations**
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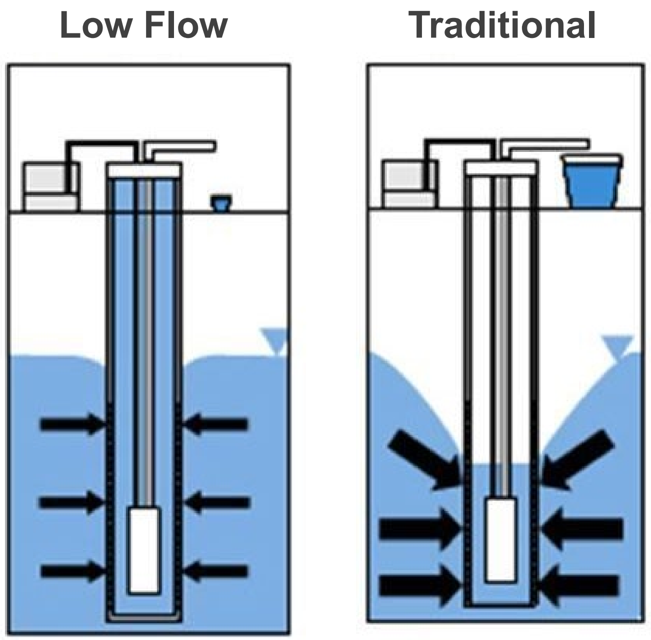
Sampling Considerations: Groundwater

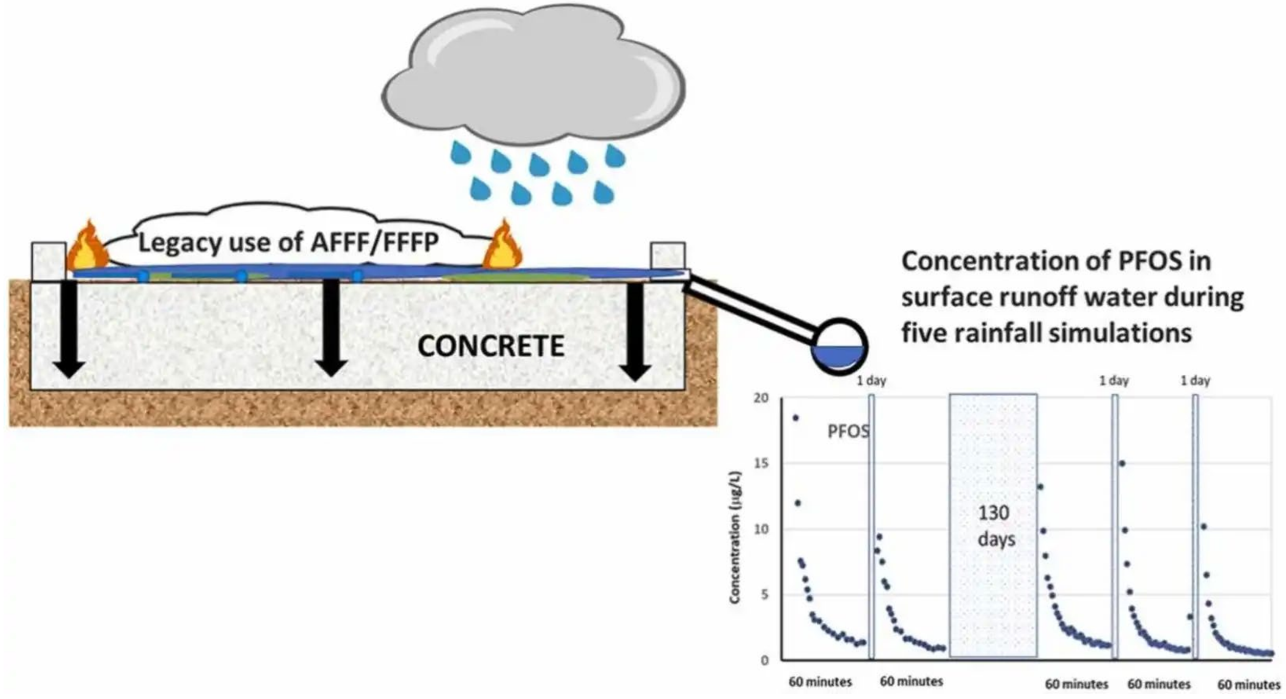
- Low-flow or passive sampling techniques are preferred to **minimize turbidity of samples and purge-water volume**
  - Preferred for use in risk assessments and for site management decisions
- Sample depth selection should consider potential:
  - stratification of PFAS within the aquifer
  - phase partitioning
  - accumulation of PFAS at the air-water interface
- Samples should not be filtered due to adsorption of PFAS to the filter
  - Centrifugation can be used as an alternative if absolutely necessary for certain analytical methods



Minimizes drawdown, turbidity, and purge volume

Sampling Considerations: Groundwater

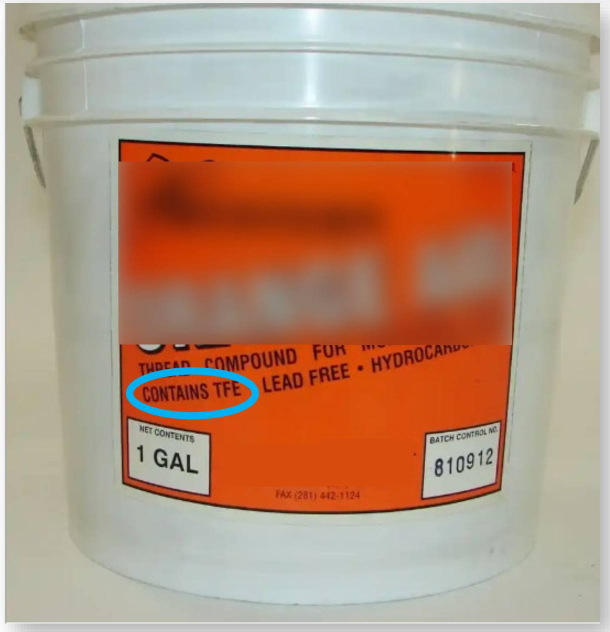
- For sampling location selection, consider potential impact of runoff and storm water conveyance systems
- Environmental sequence stratigraphy may be useful to place wells at sites with evidence of geologic preferential pathways
- Additional data may support the CSM and improve understanding of migration/ transformation potential:
  - Dissolved oxygen
  - oxidation-reduction potential
  - pH
  - total oxygen demand
  - Common anions and cations



Thai et al., 2022. Release of perfluoroalkyl substances from AFFF-impacted concrete in a firefighting training ground (FTG) under repeated rainfall simulations. *Journal of Hazardous Materials Letters*, *3*, 100050.

Sampling Considerations: Groundwater

- Critical to ensure well construction materials are PFAS-free – things to consider:
  - Avoid shrink- and crack-resistant **concrete formulations** using fluorinated surfactants
  - Avoid **greases and thread** compounds containing fluorinated chemicals
  - **Purging and sampling equipment** components may include PFAS (e.g. pump components: O-rings, gaskets, bladders, etc.) – consult with equipment vendor to see if PFAS-free alternatives are available
  - **Coated bentonite** formulations should be avoided as much as possible due to potential for leaching of PFAS



NAVFAC/Jacobs/Battelle Bentonite Study

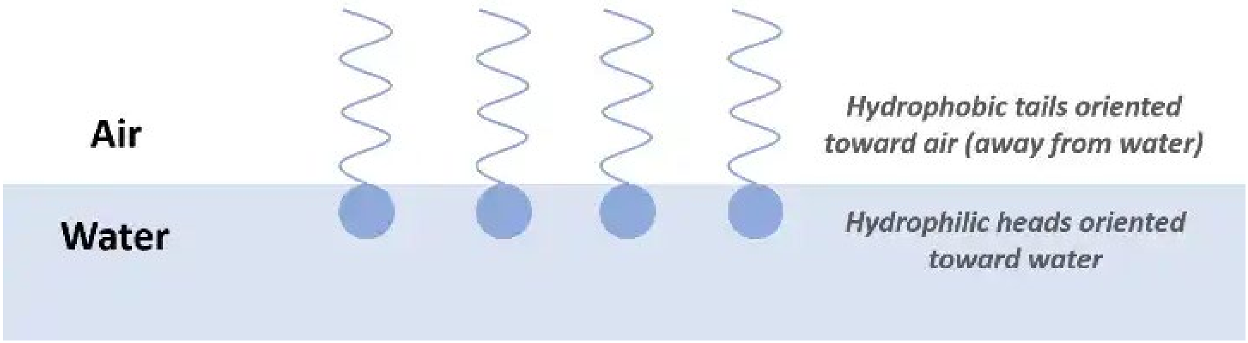
- Various types of bentonite pellets were leached for 24 hours
  - **Coated pellet leachate contained PFBA, PFPeA, and PFHxA at higher concentrations than the control and uncoated pellets**
  - Triple coated pellet concentrations were roughly triple the concentration of the single coated pellets, **supporting the premise that the pellet coating was the source of PFAS**
- NAVFAC EXWC recently completed additional leaching studies using bentonite pellets from multiple vendors (three types of gw at 1, 24, and 72 hr timepoints)
  - Preliminary TOF results indicate presence of fluorinated organic compounds in coated bentonite pellets

KEY POINT

Use of coated bentonite pellets during well installation presents a potential for low-level false positives. It is recommended that coated bentonite pellets be avoided during the installation of monitoring wells at sites identified for PFAS evaluation

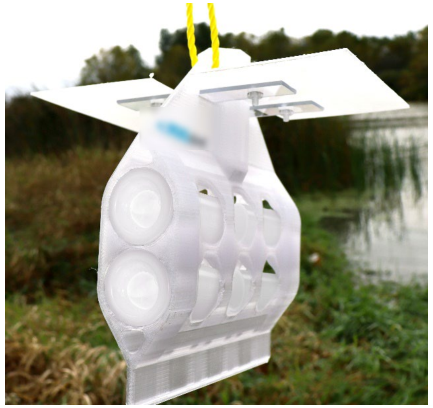
Sampling Considerations: Surface Water & Sediment

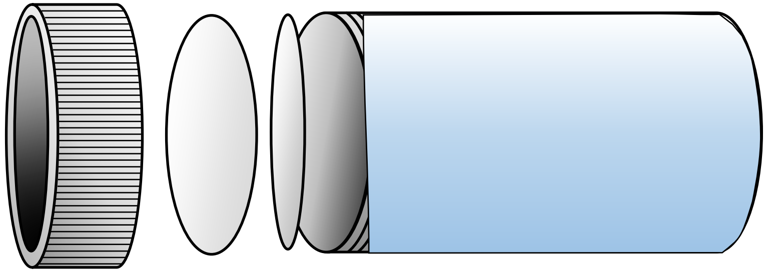
- Collect surface water samples prior to sediment samples to avoid introduction of particulates into sample
- For flowing water bodies (streams, rivers), sample downstream to upstream and during base flow conditions (not during or within 48 hours after storm event)
- Sample location in the water column should consider the potential stratification of PFAS in solution and tendency to accumulate at the air/water interface
  - Surface water depth interval sampling dependent on data quality objectives
  - Typically collected within the water column for risk assessment
  - Concentrations at the air-water interface could be higher and may be useful for some types of treatment planning



Sampling Considerations: Passive Samplers

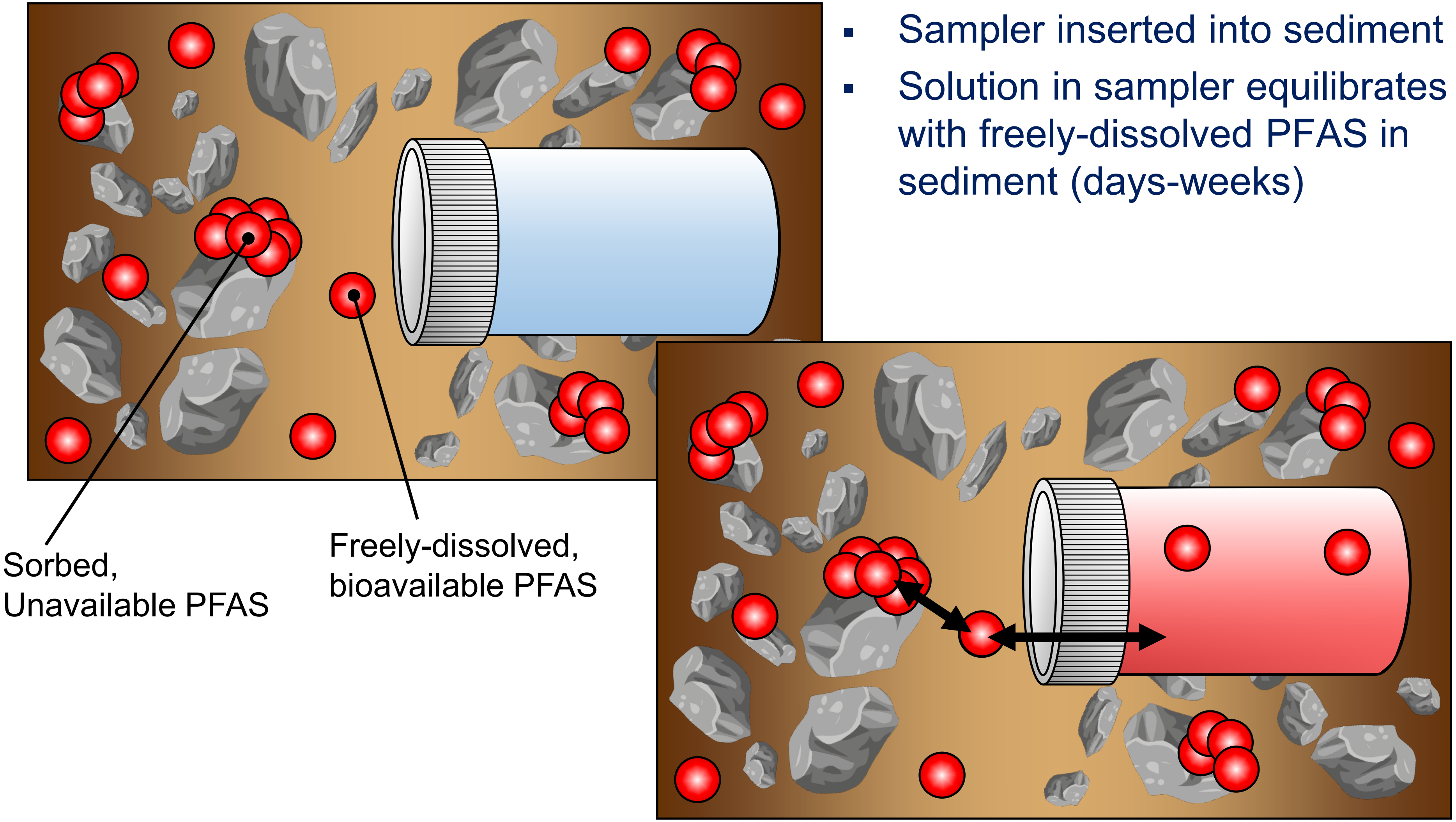
- Small, durable samplers for measuring bioavailable PFAS in sediment, groundwater or surface water
- Deploy for 2 to 4 weeks, sample collection via equilibration. PFAS diffuses across membrane in sample bottle cap
- DoD demonstration ongoing now via ESTCP Project ER23-B3-7741





- Small container capped with semi-permeable membrane
- Can also have protective outer cap (with open permeations)
- Filled with PFASE-free ultrapure water

Sampling Considerations: Passive Samplers



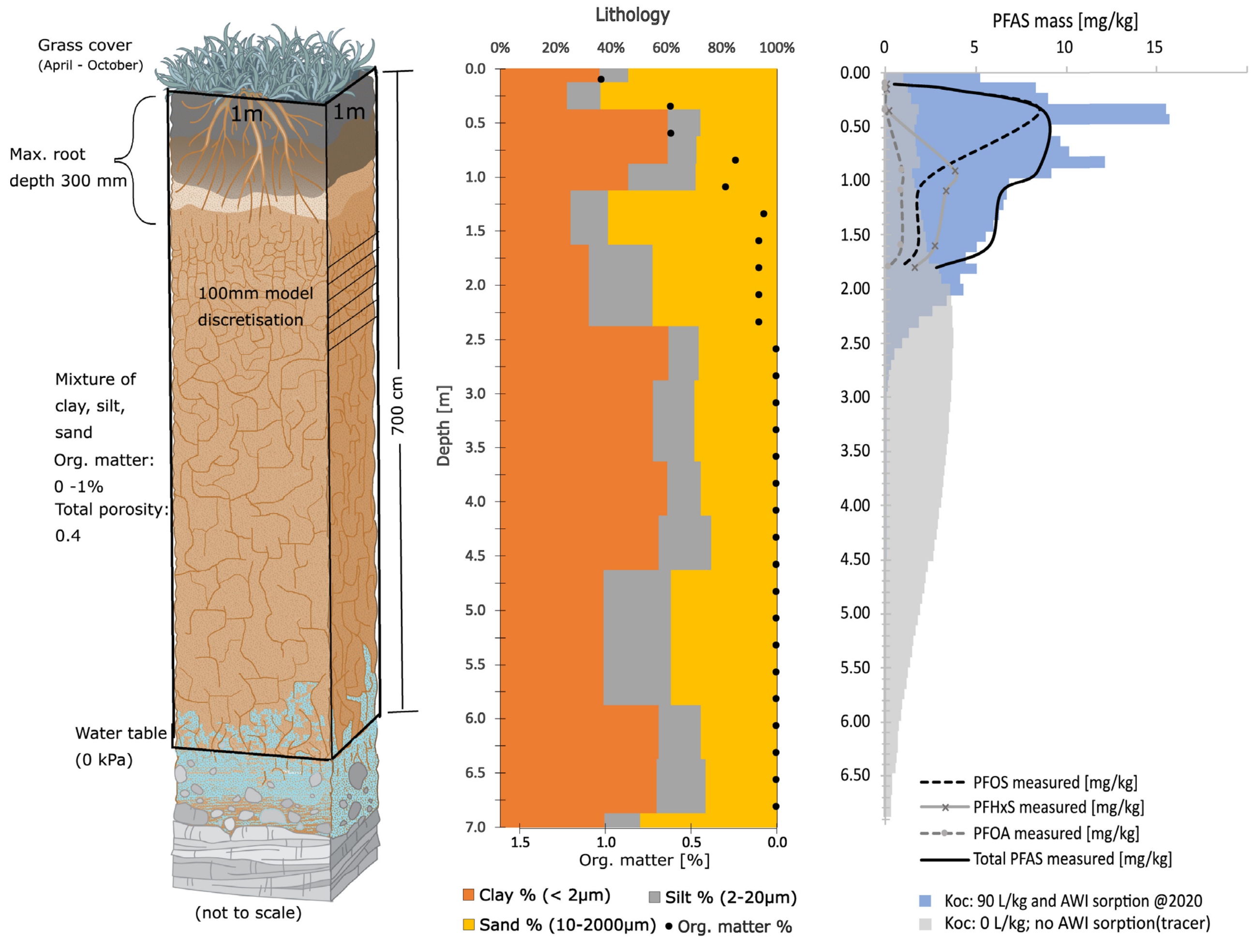
- Sampler inserted into sediment
- Solution in sampler equilibrates with freely-dissolved PFAS in sediment (days-weeks)

Benefits

- Eliminates the problem of purge water disposal
- May reduce/eliminate turbidity compared to pumped samples
- May reduce sampling costs

Sampling Considerations: Soils

- Sample different soil horizons to assess higher concentration strata and migration as well as vertical extent
  - Delineation should consider the extent of PFAS that pose unacceptable risk from direct exposure and the extent of PFAS which may leach to groundwater at levels of concern
- Consider collecting concurrent total organic carbon, pH, total oxygen demand, anion/cation exchange capacity (subset of samples), and redox measurements to address potential for desorption/transformation



Wallis et al. 2022. Model-based identification of vadose zone controls on PFAS mobility under semi-arid climate conditions. *Water Research* 225, 119096.

Sampling Considerations: Biota

- Biota sampling should be considered if there is a confirmed PFAS release to abiotic media AND there is complete pathway for biota exposure
- Species of fish collected, as well as the portion of fish sampled (whole versus fillet), depends on the project goals (e.g. human health risk)
- Before work plan development, consider previous aquatic biota sampling performed by local agencies and conduct a site survey to determine if fish/shellfish can be collected
- Consider including the use of standard reference material (e.g., NIST standards) to add to the QA/QC of sampling

Sampling Considerations: Air

USEPA Other Test Methods (OTM) for measuring PFAS source emissions

Method	Analytes	No. Analytes
OTM-45: *Measurement of selected PFAS from stationary sources*	Semivolatile/nonvolatile, polar, particulate-bound PFAS	50
OTM-50: *Sampling and analysis of volatile fluorinated compounds (VFCs) from stationary sources using passivated stainless-steel canisters*	Nonpolar, volatile VFCs indicative of incomplete combustion/destruction of PFAS from thermal treatment control technologies	30

KEY POINT

OTMs not promulgated – instead, promote consistency with what EPA believes is the current best practices for sampling and analysis

Sampling Considerations: Background PFAS

- Atmospheric and rainwater transport contribute background levels of PFAS in groundwater and soil, with concentrations of PFAS in rainwater ranging from 50–850 ng/L (Pike et al., 2021)
- In a compiled dataset of >30,000 samples collected from >2,500 sites worldwide, PFAS were present in almost all soil samples, even in remote regions far from PFAS sources (Brusseau et al., 2020)
- A meta-analysis of 21,000 data points compiled from 96 publications indicated presence of PFAS in groundwater, surface water, soil, and precipitation in all regions tested, including areas far removed from PFAS sources (Johnson et al., 2022)
- PFAS were detected extensively in Vermont soils with PFOS detected in 100% of background soil samples ranging from 0.1 to 9.7 µg/kg (Zhu et al., 2019)

KEY POINT

Given low ppt screening/action levels, consideration of PFAS background levels may be important to generate data that supports defensible project decisions and final remedy selection

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Analytical Methods

Method	Matrices	Analytes	Multilaboratory-validated
USEPA Method 537.1 ☆	Drinking Water	18 PFAS analytes (including 4 PFAS not included in USEPA Method 533)	X
USEPA Method 533	Drinking Water	25 PFAS analytes (including 11 not included in USEPA Method 537.1)	X
USEPA Draft Method 1633 ☆	Wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue	Up to 40 PFAS analytes depending on the matrix of the sample (includes all analytes from USEPA Method 537.1, 533, and 8327 and 11 additional PFAS analytes)	
USEPA SW-846 Method 8327	groundwater, surface water, and wastewater	24 PFAS analytes (DoD EDQW considers Method 8327 to be a screening method and is not used for collection of definitive data)	X
DOD AFFF01	AFFF	PFOA and PFOS	X
USEPA OTM-45	Air	50 semi-volatile and nonvolatile polar PFAS	
USEPA OTM-50	Air	30 volatile, nonpolar VFCs	

☆ Currently used by DoD for CERCLA investigations

Analytical General Considerations

- Sample container recommendations are dependent on the analytical method and should be supplied by the laboratory and be laboratory-verified PFAS-free
  - USEPA Draft Method 1633: high-density polyethylene (HDPE) containers
  - USEPA Method 533 and Method 537.1: polypropylene or polyethylene, etc.
- Follow sample preservation, shipping, storage, and holding time requirements prescribed by the analytical method used
- Work closely with laboratory to ensure samples generate data that meet project objectives

KEY POINT

Ensure to follow all QA/QC requirements (bottle selection, hold times, etc.) during sampling and sample shipment based on your selected analytical method

Analytical QC Sample Examples

Sample Type	Purpose
FIELD QC SAMPLES	
Field Duplicate	Used to evaluate the precision of sample collection, preservation, storage, and laboratory methods
Equipment Blank	Final rinse sampling equipment with laboratory-verified PFAS-free water; prior to the sampling event – evaluates potential contribution of PFAS from equipment
Source Water Blank	Evaluate PFAS content of potable water that is used during sampling processes (e.g. decontamination)
Field Reagent Blank	Laboratory-provided PFAS-free reagent water that is poured into empty sample bottle or sample bottle containing only preservative (USEPA Methods 537, 537.1 and 533)
Proficiency Test (PT) Sample	Deionized water sample spiked with known concentrations and sent blind to the lab with drinking water samples to assess accuracy of laboratory analysis
LABORATORY QC SAMPLES	
Method Blank	Used to confirm absence of PFAS contamination in laboratory equipment, supplies, and reagents
Sample Duplicate	Ensures the laboratory's subsampling procedures are capable of achieving a known level of precision as defined in work plan
Laboratory control sample (LCS), ongoing precision and recovery (OPR), or laboratory fortified blank (LFB)	Used to evaluate bias associated with sample preparation and analytical processes
Matrix spike (MS) and MS duplicate (MSD)	Accounts for the influence of matrix interferences (not required if isotope dilution analysis is used, which accounts for the influence of matrix interferences in each sample)

Conclusions

- Consider a scientifically-informed approach for selecting sampling materials based on probability of direct contact with sample and relative PFAS concentrations
- Follow media-specific sampling recommendations to collect representative samples
- Given low ppt screening/action levels, consideration of PFAS background levels may be important to generate data that supports defensible project decisions
- Ensure to follow field sampling and sample shipping/storage protocols for the analytical method to be used for samples

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Questions

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Brusseau et al., 2020. PFAS concentrations in soils: Background levels versus contaminated sites. *Science of The Total Environment*, 740, 140017. https://doi.org/10.1016/j.scitotenv.2020.140017

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Zhu et al. (2019), PFAS background in Vermont shallow soils, report commissioned by Vermont Department of Environmental Conservation (DEC).