Oklahoma Department of Environmental Quality
Protocols for PFAS Sampling
Standard Operating Procedures

Surface Water Sampling SOP

May 2022

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1.0 General

The objective of this protocol is to give general guidelines for the collection of surface water samples for PFAS analysis. Due to the high water solubility and persistence of most PFAS compounds, any surface water hydrologically connected to the target site is susceptible to contamination and should be sampled. PFAS can readily migrate to surface water from drains, stormwater runoff, or leaching to and from groundwater systems. This guidance is based on the DEQ's research, USEPA method 537.1, and USEPA Draft Method 1633. The PFAS General Sampling Guidance should be referred to for what to include in a QAPP for PFAS sampling, information on cross-contamination, additional information on field clothing, and many other details.

2.0 Field Clothing and PPE

Field clothing and other personal protective equipment (PPE) may consist of PFAS-containing materials, especially those advertised as water-resistant, water repellent, or stain-resistant. Refer to Tables 1-4 and 8 in the Quick Reference Field Guide for general guidance regarding field clothing and PPE.

Sunscreen and biological protection also require screening, and recommendations are provided in Tables 5 and 7 in the Quick Reference Field Guide.

For guidance on specific brands and product names, refer to Table 6 in the Quick Reference Field Guide.

While PFAS-containing apparel and PPE should be avoided, the safety of samplers should never be compromised. Any deviation from the DEQ's guidance should be recorded in the field notes.

3.0 Equipment

All equipment used during sample collection should be assessed for the presence of PFAS to eliminate or reduce the probability of cross-contamination. Refer to Table 10 in the Quick Reference Guide at the end of this document for details on sampling containers that are and are not allowed. Internal components of sampling equipment that contain PFAS are acceptable if there is no direct contact with the surface water or the sample, but any equipment that comes into contact with the surface water should be PFAS-free. For surface water sampling, liner-less HDPE or polypropylene containers with HDPE or polypropylene lids are recommended for collection. Sampling container size may vary depending on which analytical laboratory method is used; refer to the Sampling Techniques and Collection Methods section for guidance.

Automated samplers used for surface water sampling, such as telescope/swing samplers, submersible devices (e.g., Kemmerer® and Van Dorn® bottles), or peristaltic pumps, are not recommended for PFAS sampling. Automated samplers typically consist of multiple components that may contain PFAS. If this equipment is necessary for depth-interval sampling, ensure that all the components (i.e. tubing, seals, cables) consist of HDPE, stainless steel, PVC, or silicone. Refer to Table 11 in the Quick Reference Guide at the end of this document for a list of common materials which are allowed or prohibited. Food packaging can contain PFAS, so food packaging and products should be kept in a designated eating area as noted in Table 9 of the Quick Reference Guide at the end of this document.

4.0 Sampling Techniques and Collection Methods

The following section provides guidance for surface water sample collection for PFAS analysis. DEQ approves multiple surface water sampling techniques. The selected sampling technique may vary depending on what is most suitable for the sampling entity, selected laboratory, site characterization, and release type. USEPA Method 537.1 and USEPA Draft Method 1633 are the acceptable laboratory analysis methods for surface water, and the differences in sampling methods are highlighted below. While Draft Method 1633 guidance is not promulgated as regulation, it is highly recommended by the USEPA for individual permits. Sample preparations should be outlined in a site-specific sampling plan, such as a Sampling Analysis Plan (SAP).

Current research indicates PFAS concentrate in the air-water interface and in any foam/scum present on the surface of the water body (Costanza et al., 2019). Therefore, sampling the foam and/or surface microlayer of a water body will provide a different (generally higher) PFAS concentration than sampling deeper in a water body. The project-specific requirements will clarify whether the air-water interface or water body will be sampled.

USEPA Draft Method 1633 Sampling Equipment: 500-mL (HDPE or propylene) sampling bottles with (HDPE or propylene) linerless screw caps will be provided by the laboratory.

USEPA Method 537.1 Sampling Equipment: 250-mL (HDPE or propylene) sampling bottles and (HPDE or propylene) linerless screw caps will be provided by the laboratory.

4.1 Direct Sampling

- Collect the samples in sequence from the locations expected or determined to be least contaminated to most contaminated.
- Submerge the sampling container with a screw cap secured. Open the sampling container underwater if avoiding surface film collection. Replace the screw cap before bringing the sampling container to the surface.
- If using a preservative, gently agitate the sample to dissolve.

4.2 Sampling with Submersible Equipment

- Collect the samples in sequence from the locations that are expected or determined to be least contaminated to most contaminated.
- Before sampling, decontaminate the sampling equipment per recommended guidance in the Decontamination section.
- Follow proper procedures when using submersible equipment, such as Kemmerer® bottles and Van Dorn® samplers.
- When filling the sampling container, do not place any tubes or other materials inside the bottle. Do not place the screw cap on any surface.
- If using a preservative, after closing the container, gently agitate the sample to dissolve.
- When collecting samples, either direct sampling when wearing waders or using submersible equipment from a boat, always sample upstream from self or boat.

If further information regarding each sampling technique is desired before sampling, please reference the respective USEPA method documents mentioned.

5.0 Decontamination

Refer to Table 13 in the Quick Reference Field Guide at the end of this document for guidance on decontamination methods and materials which are allowed or prohibited while sampling. The following general decontamination principles for PFAS sampling should be followed:

- Sampling equipment must be decontaminated after sampling at each location or at the end of the workday.
- Wash hands with PFAS-free water and put on new nitrile gloves before decontamination.
- Decontaminate equipment with a triple rinse of verified PFAS-free water and remove particulates with a polyethylene or PVC brush.
- PFAS-free detergents such as Alconox®, Liquinox®, or Citranox® may be used.
- Dry equipment with a cotton cloth, untreated paper towels, or place decontaminated equipment on a PFAS-free surface to air-dry.

6.0 Quality Assurance / Quality Control

The DEQ recommends following the Quality Assurance/Quality Control (QA/QC) Guidelines outlined in section 5.0 of the General PFAS Sampling document to ensure project-specific Quality Assurance Project Plan (QAPP), Standard Operating Procedures (SOP), and Sampling Analysis Plan (SAP) consistency between sampling events. Additionally, the following guidelines should be followed for surface water-specific sampling events.

- Collect a rinsate/equipment blank at the rate of 1 per day per sampling team to ensure the sampling has not introduced PFAS cross-contamination to the sampling results. This process should be conducted on each piece of equipment. (Required)
- Laboratory sources of water used for equipment decontamination and blank sample collection should be certified as PFAS-free or addressed for background concentrations of PFAS. (Required)
- Collect field quality control samples such as duplicates at the rate of 1 per 10 samples, trip blanks at the rate of 1 per cooler per sampling team, and field blanks at the rate of 1 per day per sampling team to assist in evaluating soil sampling and handling activities at the investigation site. (Required)
- If possible, a control sample/background sample should be collected from an upstream portion of stream not affected by the possible contaminants of concern and submitted with the other sample(s). (Required)

7.0 Documentation

Keep a sampling log during the sampling event. In the sample log, record the following:

- Sample point location
- Sampling equipment
- Duplicate sample(s)
- Visual description of samples
- Use of any unapproved PPE
- Other sampling specific (applicable) observations

Ensure documentation materials are PFAS-free; refer to Table 12 in the Quick Reference Field Guide. Pre-printed labels for sample containers are preferred.

8.0 Shipment

The following is recommended for sample shipment. Information is also provided in the Quick Reference Field Guide Table 14.

- Use regular ice, double-bagged, in place of chemical (blue) ice and maintain the temperature between +4ºC and - 2ºC in a cooler.
- Check the cooler periodically to ensure samples are well iced and at the proper temperature.
- The cooler should be taped closed with a custody seal.
- Double bag Chain of Custody and other applicable forms and tape to the inside of the cooler lid.
- Ship within 48 hours or per the holding time determined by the laboratory or the selected laboratory analysis method.

DEQ PFAS Sampling Quick Reference Field Guide

Table 1: Clothing[1]		
Allowed	**Not Allowed**	**Needs Additional Research**
• Well laundered clothing (recommended six times prior to sampling) • 100% cotton (preferred) • Synthetic fabrics • Polyvinyl Chloride (PVC) • Polyurethane • Uncoated Tyvek® clothing • Wax-coated fabrics. • Rubber/Neoprene	• New/unwashed clothing • Clothing applied/washed with fabric softeners, fabric protectors including ultraviolet (UV) protection, water, dirt or stain-resistant chemicals, or insect-resistant chemicals • Clothing containing Tyvek® • Flame resistant (FR) clothing • Clothing made of Gore-Tex or other known PFAS containing materials.	• Tyvek® suits, clothing that contains Tyvek®, or coated Tyvek®

[1]Clothing should be kept dust and fiber free.

Table 2: Boots		
Allowed	**Not Allowed**	**Needs Additional Research**
• Polyurethane boots • PVC boots • PFAS-free boot covers	• Gore-Tex® boots • Boots made from water-resistant synthetics	

Table 3: Gloves		
Allowed	**Not Allowed**	**Needs Additional Research**
• Powderless nitrile gloves*	• Gore-Tex gloves • Any glove made with PFAS-containing materials.	• Latex gloves • Water and dirt-resistant leather gloves • Any special gloves required by a Health and Safety Plan (HASP).

[1]Samplers must wash their hands with PFAS-free water before putting on any gloves.

Table 4: PPE[1]		
Allowed	**Not Allowed**	**Needs Additional Research**
• Hard hats made of HDPE • Hard hat covers/liners (i.e. Head Gaiters) made of cotton or other natural fabric • Safety glasses made of HDPE • Life jackets made of polyethylene foam and nylon shell fabric • Waders made of Neoprene or other PFAS-free material	• Waders made of Gore-Tex or other known PFAS containing materials	• Hard hats or safety glasses not made of HDPE

[1]PPE should be kept dust and fiber free.

Table 5: Sun Protection		
Allowed	**Not Allowed**	**Needs Additional Research**
• Approved Sunscreens (See Table 6)	• No unauthorized sunscreen	

Table 6: Allowed/Approved Sunscreens[1]
• Banana Boat® for Men Triple Defense Continuous Spray Sunscreen SPF 30
• Banana Boat® Sport Performance Coolzone Broad Spectrum SPF 30
• Banana Boat® Sport Performance Sunscreen Lotion Broad Spectrum SPF 30
• Banana Boat® Sport Performance Sunscreen Stick SPF 50
• Coppertone® Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50
• Coppertone® Sport High-Performance AccuSpray Sunscreen SPF 30
• Coppertone® Sunscreen Stick Kids SPF 55
• L'Oréal® Silky Sheer Face Lotion 50
• Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 50
• Meijer® Sunscreen Continuous Spray Broad Spectrum SPF 30
• Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50
• Meijer® Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70
• Neutrogena® Beach Defense Water+Sun Barrier Lotion SPF 70
• Neutrogena® Beach Defense Water+Sun Barrier Spray Broad Spectrum SPF 30
• Neutrogena® Pure & Free Baby Sunscreen Broad Spectrum SPF 60+
• Neutrogena® UltraSheer Dry-Touch Sunscreen Broad Spectrum SPF 30

[1]Baby sunscreens that are "free" or "natural" are not guaranteed PFAS-free and need additional research.

Table 7: Insect Protection[1]		
Allowed	**Not Allowed**	**Needs Additional Research**
• OFF® Deep Woods • Sawyer® Permethrin	• No unauthorized insect protection	

[1]Approved sunscreens and insect repellents should not be applied near the sample collection area. Hands should be well washed after application or handling of these products, and afterwards; an uncontaminated clean/new pair of powderless nitrile gloves should be worn.

Table 8: Prohibited Water Repellant Field Clothing and PPE Brand and Product Names	
• Ultra Release Teflon®	• Release Teflon®
• Repel Teflon® Fabric Protector	• High-Performance Release Teflon®
• High-Performance Repel Teflon® Fabric Protector	• Advanced Dual Action Teflon® Fabric Protector
• NK Guard® S Series	• GreenShield®
• Tri-Effects Teflon® Fabric Protector	• Lurotex Protector RL ECO®
• Oleophobol CP®	• Repellan KFC®
• Rucostar® EEE6	• Unidyne™
• Bionic Finish®	• RUCO-GUARD®
• RUCOSTAR®	• RUCO-COAT®
• RUCO-PROTECT®	• RUCOTEC®
• RUCO®	• Resist Spills™
• Resists Spills and Releases Stains™	• Scotchgard™ Fabric Protector
• GoreTex®	

Table 9: Food Containers		
Allowed	**Not Allowed**	**Needs Additional Research**
• Food packaging and products in a designated eating area set up for food and beverage consumption	• Food packaging and products in the staging or sampling areas	• Bringing foods rewrapped in PFAS-free materials

Table 10: Sampling Containers		
Allowed	**Not Allowed**	**Needs Additional Research**
• HDPE also known as polyethylene high-density (PEHD) • Polypropylene • Stainless Steel • Unlined bottle caps • LDPE resealable bags (Ziplock) that will not come in contact with the sample media	• Polytetrafluoroethylene (PTFE) lined bottles or caps (i.e.Teflon® and Hostaflon®) • LDPE containers that will contact the sample media • Aluminum foil is not to be used due to the possibility of it being coated with PFAS. Utilize an alternative sample preparation and storage material.	• Glass bottles and containers[1]

[1]Glass bottles or containers may be used if they are known to be PFAS-free; however, PFAS have been found to adsorb to glass, especially when the sample is in contact with the glass for an extended period of time (e.g., stored in a glass container). If the sample comes into direct contact with the glass for a short period of time (e.g., using a glass container to collect the sample, then transferring the sample to a non-glass sample bottle), the adsorption is minimal. Generally, glass bottles or containers should not be used for PFAS samples.

Table 11: Sampling Equipment		
Allowed	**Not Allowed**	**Needs Additional Research**
• HDPE (also PEHD) • Polypropylene • Stainless Steel • Acetate • Silicone	• Polytetrafluoroethylene (PTFE) • Polyvinylidene fluoride (PVDF) • Polychlorotrifluoroethylene (PCTFE) • Ethylene-tetrafluoroethylene (ETFE) • Low-density polyethylene (LDPE) which will contact the sample media	• Glass equipment

Table 12: Field Materials		
Allowed	**Not Allowed**	**Needs Additional Research**
• Aluminum, polypropylene, or Masonite field clipboards • Rite in the Rain® notebooks • Loose paper (non-waterproof, non-recycled) • Ballpoint pens and pencils	• Clipboards coated with PFAS-containing materials • Notebooks made with PFAS treated paper • PFAS treated loose paper • Post-It® Notes or other adhesive paper products • Sharpie® markers • Coated materials, including paper towels • Aluminum foil is not to be used due to the possibility of it being coated with PFAS. Utilize an alternative sample preparation and storage material.	• Plastic clipboards, binders, or spiral hardcover notebooks • Waterproof field books • All markers not listed as allowable

Table 13: Decontamination Procedures		
Allowed	**Not Allowed**	**Needs Additional Research**
• Alconox®, Liquinox®, or Citranox® • Triple rinse with PFAS-free water • Cotton cloth or untreated paper towels • Polyethylene or PVC brush to remove particulates	• Decon 90® • PFAS treated paper towels • Reusing non-dedicated equipment without decontaminating	• Municipal water[1] • Recycled or treated paper towels

[1]Decontamination procedures should include a triple rinsing with PFAS-free water for equipment such as dippers, balers, spades, etc. Laboratory supplied PFAS-free deionized water is preferred for cleaning and decontamination. However, commercially available deionized water may be used for cleaning and decontamination if the water is verified to be PFAS-free. Municipal drinking water may be used for cleaning or decontamination if the water is known to be PFAS-free.

Table 14: Sample Shipment		
Allowed/Required	**Not Allowed**	**Needs Additional Research**
• Coolers filled with regular ice • Maintaining sample temperature between +4ºC and -2ºC • Double-bagging of samples and ice using bag materials made of HDPE (preferred) or LDPE (if sample does not come in contact) • Chain of Custody and other forms should be single bagged in LDPE (e.g. Ziploc®) storage bags and taped to the inside of the cooler lid.	• Aluminum foil is not to be used due to the possibility of it being coated with PFAS. Utilize an alternative sample preparation and storage material. • Chemical (blue) ice packs	• Chemical (blue) ice packs that are verified PFAS free