TECHNICAL REPORT

Assessing the Potential for Bias in PFAS Concentrations during Groundwater and Surface Water Sampling

SERDP Project ER19-1205

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14. ABSTRACT

This report provides science-based recommendations to minimize sampling bias while limiting unnecessary costs and efforts associated with overly conservative sampling recommendations or procedures. The examination of potential bias was motivated by widespread assumptions that PFAS can be introduced during or after sampling due to cross-contamination from field equipment and materials used during sample collection, as well as PFAS transformation in the laboratory during sample storage, even when standard field procedures are followed. This report summarizes the scientific state of knowledge regarding the potential for bias in PFAS sampling, presents findings of new research conducted under this Strategic Environmental Research and Development Program (SERDP) project ER19-1205, and provides scientifically based guidelines for practical field sampling equipment and procedures to minimize the potential for bias.

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List of Acronyms and Abbreviations

°C	degrees Celsius
AFFF	aqueous film forming foam
CA SWRCB	California State Water Resources Control Board
CA	California
DOC	dissolved organic carbon
DoD	U.S. Department of Defense
EDQW	Environmental Data Quality Workgroup
EF	enrichment factor
EGLE	Michigan Department of Environment, Great Lakes, and Energy
EPA	Environmental Protection Agency
EtFOSAA	N-ethyl-perfluorooctane sulfonamido acetic acid
FAQs	frequently asked questions
FDEP	Florida Department of Environmental Protection
FHxSA	perfluorohexane sulfonamide
FTCA	fluorotelomer carboxylic acid
FTSA	fluorotelomer sulfonic acids
g/L	grams per liter
HDPE	high density polyethylene
ITRC	Interstate Technology and Regulatory Council
LC-MS/MS	liquid chromatography tandem mass spectrometry
LC-QToF	liquid chromatography and quadrupole time of flight
LDPE	low density polyethylene
LOQ	limit of quantitation
MaDEP	Massachusetts Department of Environmental Protection
Maine DEP	Maine Department of Environmental Protection
MeFOSAA	N-methylperfluorooctane sulfonamidoacetic acid
mg/L	milligrams per liter
MIP	membrane interface probe
mL	milliliters
MPCA	Minnesota Pollution Control Agency
MRM	multiple reaction monitoring

NaCl	sodium chloride
NAVFAC	Naval Facilities Engineering Command
N-EtFOSA	N-ethyl perfluorooctane sulfonamide
N-EtFOSAA	N-ethyl perfluorooctane sulfonamido acetic acid
N-EtFOSE	N-ethyl perfluorooctane sulfonamido ethanol
ng/cm2	nanograms per square centimeter
ng/L	nanograms per liter
NHDES	New Hampshire Department of Environmental Services
N-MeFOSA	N-Methylperfluorooctanesulfonamide
N-MeFOSAA	N-methylperfluorooctane sulfonamidoacetic acid
N-MeFOSE	N-methyl perfluorooctanesulfonamidoethanol
NYSDEC	New York State Department of Environmental Conservation
PFAA	perfluoroalkyl acids
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonate
PFCA	perfluorinated carboxylic acid
PFDA	perfluorodecanoic acid
PFDoDA	perfluorododecanoic acid
PFEtCHxS	perfluoro-4-ethylcyclohexane sulfonate
PFHpS	perfluoroheptane sulfonate
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate
PFNA	perfluorononanoic acid
PFNS	perfluorononane sulfonate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFPeA	perfluoropentanoic acid
PFSA	perfluorinated sulfonic acid
PFUnDA	perfluoroundecanoic acid
PIGE	particle-induced gamma-ray emission
PPE	personal protective equipment
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride

PVDF	polyvinylidene fluoride
RPM	Remedial Project Managers
SERDP	Strategic Environmental Research and Development Program
SOP	Standard Operating Procedure
SPE	solid phase extraction
SPr-FHxSA	N-sulfo propyl perfluorohexane sulfonamide
SWF	surface water foam
SWRCB	State Water Resources Control Board
U.S.	United States
UPLC/MS/MS	ultra-performance liquid chromatography/tandem mass spectrometry
USEPA	U.S. Environmental Protection Agency

1. INTRODUCTION

1.1. Project Motivation and Background

Per- and polyfluoroalkyl substances (PFAS) are a large group of anthropogenic compounds present in fire-fighting foams and many consumer products that have drawn increasing regulatory attention over the past 25 years. Adverse human health and ecological effects of some PFAS, including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)[1], have been documented. These PFAS are highly stable and bioaccumulate over time. Other PFAS (known as perfluoroalkyl acid (PFAA) precursors) will transform over time to PFOS, PFOA, and similarly stable PFAAs. PFAS can now be detected at sub-nanogram per liter (ng/L) concentrations; widespread detections of PFAS have been reported. Standards and guidance issued by states for individual PFAS have followed an ever-declining trend and are now being issued in the single digit ng/L range.[2]

The combination of these factors has led to regulatory concern over false positive sampling results and other forms of bias that may affect PFAS sampling results. A variety of government agencies and other organizations have developed sampling guidance for PFAS in drinking water, groundwater, soil, and other environmental media. Guidance documents commonly recommend an abundance of caution and may prohibit or suggest avoidance of specific equipment or materials used to collect samples if PFAS may be present.

1.2. Report Objectives

This report provides science-based recommendations to minimize sampling bias while limiting unnecessary costs and efforts associated with overly conservative sampling recommendations or procedures. The examination of potential bias was motivated by widespread assumptions that PFAS can be introduced during or after sampling due to cross-contamination from field equipment and materials used during sample collection, as well as PFAS transformation in the laboratory during sample storage, even when standard field procedures are followed. This report summarizes the scientific state of knowledge regarding the potential for bias in PFAS sampling, presents findings of new research conducted under this Strategic Environmental Research and Development Program (SERDP) project ER19-1205, and provides scientifically based guidelines for practical field sampling equipment and procedures to minimize the potential for bias.

1.3. Potential Bias Examination Approach

This report summarizes interim findings from a recent 1.5-year course of literature review, laboratory experiments, and field experiments. The project team evaluated several potential sources for bias during PFAS sampling, including the following:

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[1] The term perfluorooctanoic acid is used for consistency with United States Environmental Protection Agency (USEPA) and includes the associated perfluorooctanoate anion, which is the typical form of PFOA in the environment.

[2] Michigan Department of Environment, Great Lakes, and Energy (EGLE), 2020. Michigan adopts strict PFAS in drinking water standards. Press Bulletin. 22 July.

- **Field equipment and materials**: A systematic evaluation of field materials and procedures used for collecting groundwater and surface water samples to provide a scientific basis for sampling protocols was conducted (Section 2);
- **Laboratory sample storage**: Prior research indicates that laboratory sample hold times and storage conditions (i.e., temperature) can lead to potential bias in measured concentrations of specific PFAS, as summarized in this guidance document (Section 3); and
- **Emerging research on stratification**: Other factors can impact PFAS concentrations in water samples, such as stratification due to accumulation at the air/water interface, association with natural organic matter, and salinity. Preliminary research findings to inform future groundwater and surface water sampling guidance are summarized inSection 4.

Based on the findings to date, the project team is conducting outreach to communicate best practices to state and federal project managers, consultants, and contract laboratories. In addition to this document, key findings and recommendations will be communicated through other publications, webinars, and short courses.

2. BIAS FROM FIELD EQUIPMENT AND MATERIALS

Field sampling equipment, materials, and sampling procedures have long been suspected as sources of potential bias that can affect PFAS concentrations measured in surface water and groundwater samples. A variety of different PFAS sampling guidelines have been published by the United States (U.S.) Department of Defense (DoD), USEPA, state regulatory agencies, commercial laboratories, and consulting firms. A limited number of these restrictions and recommended best practices are substantiated by scientific studies. Most PFAS sampling recommendations are based on the precautionary principle and may unnecessarily restrict field materials, equipment, or procedures that actually present a low risk of biasing sample results.

The following activities were completed to assess potential sources of bias from PFAS sampling equipment, materials, and procedures:

- A list of existing PFAS sampling guidance documents was compiled and reviewed to understand which recommendations were common and which were presented in a limited number of sources, reflecting a lack of consensus within the industry;
- Published papers were reviewed that provided scientific support or refutation of PFAS sampling restrictions and recommendations;
- Unpublished data sets from field equipment blank samples were reviewed; and
- Industry practitioners and regulators were surveyed through the Interstate Technology and Regulatory Council (ITRC) PFAS team to solicit input on each step of the process and request other relevant resources (**Appendix A**).

Key findings from the review of PFAS sampling guidance, peer-reviewed literature, equipment blank data, and ITRC survey results are described in this section as follows:

- There is a variety of existing guidance on PFAS sampling procedures, equipment, and materials and the guidance varies from one organization to another (Section 2.1). The reasons for differences in the guidelines are not clearly explained. As guidance documents are updated, consensus appears to be developing to inform best practices for PFAS sampling. However, the consensus is not necessarily based on scientific studies.
- Peer-reviewed literature published to date provides data supporting the possibility of biasing PFAS concentrations due to various materials commonly used during sampling. Some materials resulted in detectable PFAS concentrations after 24 hours of soaking in water (Section 2.2.2); others did not (Section 2.2.1). These data were considered by the project team in light of realistic field conditions to assess whether the use of these materials during field sampling poses a realistic risk of potentially biasing PFAS concentrations (Section 2.2.3).
- A review of equipment blanks collected from a variety of field sampling equipment provided insight into potential PFAS contributions from field equipment, i.e., whether a particular type or brand of equipment contributed to PFAS blank detections. Non-detects provide evidence that use of the equipment did not result in a positive bias in measured

PFAS concentrations in soil and water (Section 2.3). Several PFAS detections were also identified.[3] Equipment blanks with positive detections were used to identify equipment that was further tested in the laboratory to determine their potential PFAS concentration (Section 2.2.4).

2.1. Current PFAS Sampling Guidelines and Restrictions

To gain an understanding of PFAS sampling guidance being followed by field teams, the team compared PFAS recommendations listed in readily available guidance documents and highlighted areas of commonality and areas where there was a broader range of recommendations. The PFAS guidance documents that were reviewed are summarized in **Table 2-1**.

Table 2-1. Guidance documents on PFAS sampling materials, equipment, and procedures

Type	Organization	Year	Title
Industry	ITRC	2020	PFAS technical and regulatory guidance document and fact sheets, PFAS-1. Washington, D.C. https://pfas-1.itrcweb.org/
	National Groundwater Association (NWGA)	2018	Groundwater and PFAS: State of knowledge and practice
Federal	USEPA Region 4	2015	Field equipment cleaning and decontamination at the FEC, SESDPROC-206-R3, Science and Ecosystems Support Division, Athens, Georgia
	USEPA	2020	PFAS technical brief
	DoD Environmental Data Quality Workgroup (EDQW)	2017	Bottle selection and other sampling considerations when sampling for PFAS
	Naval Facilities Engineering Command (NAVFAC)	2017	Interim PFAS site guidance for NAVFAC remedial program managers
States	California State Water Resources Control Board (CA SWRCB)	2020	PFAS sampling guidelines for non-drinking water
		2019	Drinking water sample collection for PFAS sampling guidance
	Florida Department of Environmental Protection (FDEP)	2019	Draft Standard Operating Procedure (SOP) – PFAS sampling
	Maine Department of Environmental Protection (Maine DEP)	2019	Addendum A – Development of a sampling and analysis plan, additional requirements for the sampling of PFAS, and Attachment A - PFOA and PFOS sampling and analysis plan form template, SOP No. RWM-DR-014-ADDENDUM
	Massachusetts Department of Environmental Protection (MaDEP)	2020	Fact sheet. Interim guidance on sampling and analysis for PFAS at disposal sites regulated under the Massachusetts Contingency Plan. October 21
		2018	Groundwater PFAS sampling
		2018	General PFAS sampling guidance

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[3] Some types of equipment blanks are typically collected after sample collection and decontamination before moving to the next sample location, to assess the adequacy of the decontamination process. Therefore, an equipment blank detection does not imply that the equipment contains PFAS.

Type	Organization	Year	Title
	EGLE	2018, 2019	Guidance specific to PFAS sampling of residential wells, groundwater, surface water, surface water foam, wastewater, and more
	Minnesota Pollution Control Agency (MPCA)	2018	Currently using Michigan's 2018 guidance and may develop guidance for sampling foam on surface waters
	New Hampshire Department of Environmental Services (NHDES)	2019	Laboratory testing guidelines for PFAS at waste sites
		2018	Master quality assurance project plan of the Hazardous Waste Remediation Bureau Waste Management Division
		2017	Frequently asked questions (FAQs) for sampling and analysis of PFAS at waste management and disposal sites
	New York State Department of Environmental Conservation (NYSDEC)	2020	Sampling, analysis, and assessment of PFAS under NYSDECs Part 375 Remedial Programs. October
	Ohio EPA	2020	DDAGW SOP for PFAS sampling at public water systems, Ohio EPA LOE contractors, Revision 1.1, Final. March
	Utah Department of Environmental Quality	2020	Sampling and analysis plan, Statewide PFAS monitoring Phase I: Drinking water systems. October.
	Washington Department of Ecology	2016	Quality assurance project plan, Statewide survey of PFAS in Washington state rivers and lakes
		2020	PFAS draft chemical action plan. Publication 20-04-035. October

Each of the guidance documents promote awareness of the potential presence of PFAS in a variety of commonly-used materials, sampling equipment, personal care products, and consumer products that are used during field sampling events. Some of the guidance documents also raise awareness of potential field sources of low bias in PFAS results, including field filtration and sorption to low density polyethylene (LDPE) tubing or to the sides of containers that are used for sample collection (e.g., field composites). The guidance documents provide differing recommendations on how to best reduce sample bias, typically by categorizing materials and equipment into allowable and prohibited items (i.e., do's and don'ts) or specifying whether they can be used in direct contact with a sample, adjacent to the sample, or in the staging area only. Guidance documents also provide brand-specific information on products that have been tested at least once in the past and found to be PFAS-free. Examples of recommendations in current PFAS sampling guidance documents are provided in **Table 2-2**. A summary of current PFAS guidance recommendations for acceptable, do not use, or use under certain circumstances is provided in **Appendix B**.

In general, earlier sampling guidance (produced prior to 2018) was more precautionary and restrictive of materials that could be used during PFAS field sampling. This approach can be beneficial because it bolsters confidence in sampling results, reduces the need for discussions regarding the acceptability of data for decision-making, and avoids the potential need to re-sample or to collect additional samples. However, some of the earlier and more restrictive precautions still remain in use. Overly precautious guidance can increase the cost and duration of field sampling events and increase the amount of waste generated.

Table 2-2. Examples of differing recommendations for PFAS sampling materials in various guidance documents

Example Topic	Guidance from CA RWQCB	Guidance from EGLE	Guidance from NAVFAC
Markers for labeling and field notes	Acceptable to use ballpoint pens or pre-printed labels from the laboratory. Avoid regular or thick-size markers (Sharpie® or otherwise as they may contain PFAS). Acceptable to use Fine or Ultra-Fine Sharpie® markers to label empty sample bottles in the staging area provided that the lid is on the sample bottle and that gloves are changed following sample bottle labeling.[4]	Acceptable to use ballpoint pens, pencils, and Fine or Ultra-Fine Sharpie® markers. Other markers need screening, i.e., equipment blank samples should be taken to verify that the product is PFAS-free prior to use during sampling.[5]	Waterproof pens may contain PFAS.[6] EDQW guidance is referenced. Markers are prohibited; pens are recommended.[7]
Plastic bags	LDPE should not be used for any items that will come into direct contact with sample media (e.g., plastic bags, tubing, containers and bottles). Samples and ice should be double-bagged using LDPE bags (e.g., Ziploc®).[8] *Note that this 2019 guidance was replaced in 2020 with the following:* Sampling equipment that have parts made of LDPE should be avoided if the part comes in direct contact with the sample. However, if it is absolutely necessary, equipment that have parts made of LDPE may be used if an equipment blank has confirmed it to be PFAS-free. LDPE bags should be kept separate from other sampling supplies in the staging area and should not come into direct contact with the sample media. Gloves are changed after handling LDPE bags.[9]	LDPE should not be used for any items that will come into direct contact with sample media (e.g., plastic bags, tubing, containers and bottles). However, LDPE may be used if an equipment blank has confirmed it to be PFAS-free. LDPE does not contain PFAS in the raw material but may contain PFAS cross-contamination from the manufacturing process. LDPE bags (e.g., Ziploc®) that do not come into direct contact with the sample media and do not introduce cross-contamination with samples may be used.[10] Surface water foam has been successfully sampled using various high density polyethylene (HDPE) bottles and polyethylene plastic bags (e.g., Ziploc®). Polyethylene plastic bags are preferred for sample collection because the wide openings facilitate the placement of surface water foam.[11]	Plastic bags may contain PFAS.[12] EDQW guidance is referenced. LDPE or polypropylene containing materials (e.g., bags or containers used to transport samples) are prohibited. HDPE and silicon materials are recommended. Acetate liners are recommended for direct push technologies. Bags of ice are recommended.[13]

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[4] CA SWRCB, 2020. PFAS sampling guidelines for non-drinking water.

[5] EGLE, 2018. General PFAS Sampling Guidance. 16 October.

[6] NAVFAC, 2017. Interim Per- and Polyfluoroalkyl Substances (PFAS) Site Guidance for NAVFAC Remedial Project Managers (RPMs). September.

[7] EDQW, 2017. Bottle selection and other sampling considerations when sampling for PFAS. DoD.

[8] CA SWRCB, 2019. Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidelines. 20 March. *Note this is older guidance that was updated in 2020.*

[9] CA SWRCB, 2020. PFAS sampling guidelines for non-drinking water.

[10] EGLE, 2018. General PFAS Sampling Guidance. 16 October.

[11] EGLE, 2019. Surface water foam PFAS sampling guidance.

[12] NAVFAC, 2017. Interim Per- and Polyfluoroalkyl Substances (PFAS) Site Guidance for NAVFAC Remedial Project Managers (RPMs). September.

[13] EDQW, 2017. Bottle selection and other sampling considerations when sampling for PFAS. DoD.

Example Topic	Guidance from CA RWQCB	Guidance from EGLE	Guidance from NAVFAC
Glass	PFAS may adsorb to glass containers and therefore should not be used for water, leachate, or other aqueous samples. Glass containers may be used for dry or solid samples, provided that absorbed PFAS can be extracted by laboratory as part of the sample preparation procedure.[14]	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 a long period of time (e.g., being 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.[15]	Drinking water samples must be collected in accordance with USEPA Method 537, which requires sample collection in polypropylene bottles with a polypropylene screw cap. All other samples must be collected in an HDPE container with an unlined plastic screw cap.[16]

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[14] CA SWRCB, 2020. PFAS sampling guidelines for non-drinking water.

[15] EGLE, 2018. General PFAS Sampling Guidance. 16 October.

[16] NAVFAC, 2017. Interim Per- and Polyfluoroalkyl Substances (PFAS) Site Guidance for NAVFAC Remedial Project Managers (RPMs). September.

Many state guidance documents were updated in 2019 or 2020, building on significant engagement of state regulators in the development of ITRC team's technical and regulatory guidance for PFAS.[17] Inter-agency initiatives such as ITRC and cross-DoD working groups appear to be effective in reaching consensus on PFAS sampling best practices and developing and communicating industry best practices. Despite this convergence, questions still remain regarding the scientific basis for PFAS sampling precautions.

2.2. Scientific Basis for PFAS Sampling Restrictions

The scientific basis for PFAS sampling material restrictions was evaluated by conducting a literature review of peer reviewed scientific studies. Readily available scientific studies were summarized to determine which materials or equipment had previously been evaluated for PFAS contribution to samples. Several peer-reviewed studies[18, 19, 20] evaluated equipment rinsate blanks or conducted soak tests for various materials to evaluate the presence of PFAS and/or total fluorine (Section 2.2.1 and Section 2.2.2).

In addition to the literature review, Oregon State University conducted methanol extraction tests for a variety of different field sampling materials for PFAS to determine the potential for sample bias.[21] Rodowa et al. analyzed 66 materials for 52 PFAS using liquid chromatography tandem mass spectrometry (LC-MS/MS) following sample extraction according to a previous publication.[22] Particle-induced gamma-ray emission (PIGE) spectroscopy was performed by the University of Notre Dame to quantify total fluorine. Items were categorized into materials and products used for pre-staging, staging, sampling, and transport. Results indicated that none of the 22 materials that gave quantifiable concentrations of individual PFAS had the potential to come into direct contact with sample media. Detailed results from the project laboratory study and other published studies are summarized in the following subsections.

Studies yielded relevant information about materials, field equipment, various consumer products, and personal protective equipment (PPE). Results were extrapolated to assess the extent of potential biasin PFAS samples when standard field procedures are followed (Section 2.2.3).

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[17] ITRC, 2020. PFAS technical and regulatory guidance document and fact sheets, PFAS-1. https://pfas-1.itrcweb.org/

[18] Denly, Elizabeth, Jim Occhialini, Phil Bassignani, Michael Eberle, and Nidal Rabah. 2019. Per- and polyfluoroalkyl substances in environmental sampling products: Fact or fiction? *Remediation*, 29:65-76. DOI: 10.1002/rem.21614.

[19] Bartlett, Samuel A., and Katherine L. Davis, 2018. Evaluating PFAS cross contamination issues. *Remediation*, 28:52-57. DOI: 10.1002/rem.21549.

[20] van der Veen, Ike, Anne-Charlotte Hanning, Ann Stare, Pim E.G. Leonards, Jacob de Boer, and Jana M. Weiss, 2020. The effect of weathering on per- and polyfluoroalkyl substances (PFASs) from durable water repellent (DWR) clothing. *Chemosphere*, 249: 126100. DOI: 10.1016/j.chemosphere.2020.126100.

[21] Rodowa, Alix E., Emerson Christie, Jane Sedlak, Graham F. Peaslee, Dorin Bogdan, Bill DiGuiseppi, and Jennifer A. Field, 2020. Field Sampling Materials Unlikely Source of Contamination for Perfluoroalkyl and Polyfluoroalkyl Substances in Field Samples. *Environmental Science & Technology Letters*, 7:156-163. DOI: 10.1021/acs.estlett.0c00036.

[22] Robel et al., 2017. Closing the mass balance on fluorine on papers and textiles. *Environ. Sci. Technol.* 51: 9022–9032.

2.2.1. Materials, Equipment, and Products That Did Not Contribute PFAS

The following studies used a variety of techniques to test consumer products and found that many commonly used field materials, equipment, and products did not contribute PFAS to analytical samples.

- Denly et al.[23] tested various materials by soaking them in a sample of PFAS-free water for 24 hours and then measuring the resulting PFAS concentrations in the water. Samples were then extracted using solid-phase extraction (SPE) and analyzed for 24 individual PFAS using LC-MS/MS analysis. Results indicate the following products and equipment will not contribute detectable PFAS to analytical samples: aluminum foil;[24] adhesive notes; bubble wrap; most bentonite plugs, bentonite chips, time-release pellets, and granular bentonite;[25] protein bar wrapper;[26] passive diffusion bags; and, polyvinylidene fluoride (PVDF) water level tape.[27]
- Bartlett and Davis collected equipment blanks from testing various fabrics sprayed with insect repellants and analyzed the samples for 17 different PFAS using an ultra-performance liquid chromatography/tandem mass spectrometry (UPLC/MS/MS) method with isotope dilution method. Three insect repellants were tested and none contributed detectable PFAS to equipment blanks: Insect Shield Insect® pretreated clothing, OFF! Deep Woods® Spray for clothing or skin, and Sawyer® do-it-yourself permethrin treatment for clothing.
- Rodowa et al. tested a variety of items that had no detections of individual PFAS or total fluorine including the following: dryer sheets, aluminum foil (other than non-stick), paper towel adhesive, adhesive notepads, binder plastic cover, nitrile gloves, putty caulk, clear resin, white glue, polyethylene bladder, core bag, elastic sealing film, and plastic bags.

A summary of compiled study results is provided in **Table 2-3**.

Conditions during PFAS sampling are typically more conservative than the methods used for sample preparation (i.e., extraction with methanol [Table 2-3, Note 1] or a 24-hour soak of material directly in water [Table 2-3, Note 2]). [28] Therefore, these studies effectively establish that many materials prohibited by current sampling guidance are unlikely to cause bias.

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[23] Denly, Elizabeth, Jim Occhialini, Phil Bassignani, Michael Eberle, and Nidal Rabah, 2019. Per- and polyfluoroalkyl substances in environmental sampling products: Fact or fiction? *Remediation*, 29:65-76. DOI: 10.1002/rem.21614.

[24] Other studies have reported PFAS detections on non-stick aluminum foil – see Rodowa et al., 2020. Published studies are limited in their ability to account for differences in brand name, manufacturing batch, or manufacturing methods.

[25] A PFOA detection was reported for time-released bentonite pellets analyzed by Denly et al. (2019). The authors noted that the detection was just above the limit of quantification (LOQ) and that further confirmation may be prudent.

[26] Other types of food wrappers had low PFAS detections.

[27] Other types of water level tape tested by Denly et al. (2019) had low PFAS detections.

[28] An exception is down-hole dedicated equipment that is in contact with the water and purging is not conducted prior to sample collection (e.g., passive samplers).

Table 2-3. Materials, equipment, and products that were tested and found to be PFAS-free

Material, Equipment or Product	Equipment Preparation and Analytical Method	Reference(s)
Adhesive notepad	LC-MS/MS and PIGE spectroscopy; 24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	1, 2
Aluminum foil (not treated for nonstick)	LC-MS/MS and PIGE spectroscopy; 24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	1, 2
Bentonite 3/8-inch chips	Leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Bentonite granular	Leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Bentonite medium chips	Leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Bentonite plugs	Leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Bentonite time-release pellets	Leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Binder plastic cover	LC-MS/MS and PIGE spectroscopy	1
Bubble wrap	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Clear resin	LC-MS/MS and PIGE spectroscopy	1
Core bag	LC-MS/MS and PIGE spectroscopy	1
Dryer sheets	LC-MS/MS and PIGE spectroscopy	1
Elastic sealing film	LC-MS/MS and PIGE spectroscopy	1
Insect repellant (Insect Shield Insect® pretreated clothing)	Equipment blank from fabric sprayed with product analyzed for 17 PFAS with USEPA 537 modified method	3
Insect repellant (OFF! Deep Woods® Spray for clothing/skin)	Equipment blank from fabric sprayed with product analyzed for 17 PFAS with USEPA 537 modified method	3
Insect repellant (Sawyer® do-it-yourself permethrin treatment for clothing)	Equipment blank from fabric sprayed with product analyzed for 17 PFAS with USEPA 537 modified method	3
Lab tissue packaging	LC-MS/MS and PIGE spectroscopy	1
Paper towel adhesive	LC-MS/MS and PIGE spectroscopy	1
Passive diffusion bag	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Plastic bags	LC-MS/MS and PIGE spectroscopy	1
Polyethylene bladder	LC-MS/MS and PIGE spectroscopy; 24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	1, 2
Protein bar wrapper	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Putty caulk	LC-MS/MS and PIGE spectroscopy	1
Polyvinyl chloride (PVC) pipe	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Resealable plastic storage bags	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Silicone tubing	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
White glue	LC-MS/MS and PIGE spectroscopy	1

Notes: (1) Rodowa et al., 2020; (2) Denly et al., 2019; (3) Bartlett and Davis, 2018.

2.2.2. Materials, Equipment, and Products That Could Contribute PFAS

Certain materials are known to contain fluorinated compounds and have been considered likely sources of PFAS bias in field samples. These include polytetrafluoroethylene (PTFE) materials such as Teflon™ and Hostaflon®, fluoroelastomers such as Viton™, and fluoropolymer-based stain- or water-resistant materials. Because these materials are known to contain fluorinated compounds, they have not been an area of particular focus for some laboratory researchers. However, the extent to which these fluoropolymers contribute soluble PFAS to water samples under realistic field conditions over time and as a function of equipment age has not been fully studied.

Several peer-reviewed scientific studies have identified common sampling materials comprised of fluorinated materials that did contribute detectable concentrations of PFAS to equipment blanks after 24 hours of soaking in water. For example, Denly et al. detected PFAS in soak tests with PTFE tubing, a PTFE bladder, some water level tape meters, one type of bentonite (time-release pellets), bailer line/twine, nitrile gloves, sample labels, and a waterproof field book cover. Denly et al. also identified perfluorobutanoic acid (PFBA) concentrations in 1 out of 3 types of HDPE tubing and PFBA, perfluoropentanoic acid (PFPeA), and other PFAS in 2 types of new LDPE tubing. Rodowa et al. identified one or more individual PFAS were detected in first aid packaging, first aid adhesive wrapper, PTFE tape, nonstick aluminum foil, laboratory tissue, paper towel, laboratory notebook, marker ink, and duct tape samples.

In other studies, PFAS were not directly measured in samples, but total fluorine was, indicating the presence of undetected PFAS (Rodowa et al., 2020) in label backing, waterproof notepaper, plastic shovel packaging, nitrile glove packaging, PVC liner, PVC screen, core catcher, core catcher liner, vinyl end caps, membrane interface probe (MIP) membrane, electrical tape, and cold packs. The materials, equipment, and products that were tested in these studies are summarized in **Table 2-4**.

Table 2-4. Materials, equipment, and products that yielded PFAS and/or total fluorine detections

Material, Equipment or Product	Equipment Preparation and Analytical Method	Reference(s)
Bailer line	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Cold pack (outside)	PIGE spectroscopy	1
Core catcher	PIGE spectroscopy	1
Core catcher liner	PIGE spectroscopy	1
Duct tape	LC-MS/MS and PIGE spectroscopy	1
Electrical tape	PIGE spectroscopy	1
Field book cover	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Field book pages	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
First aid adhesive wrapper	LC-MS/MS and PIGE spectroscopy	1
First aid packaging (box)	LC-MS/MS and PIGE spectroscopy	1
HDPE tubing	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Lab notebook	LC-MS/MS and PIGE spectroscopy	1
Lab tissue	LC-MS/MS and PIGE spectroscopy	1

Material, Equipment or Product	Equipment Preparation and Analytical Method	Reference(s)
Label backing	LC-MS/MS and PIGE spectroscopy	1
Labels	PIGE spectroscopy; 24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	1, 2
LDPE tubing	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
MIP membrane	PIGE spectroscopy	1
Nitrile glove packaging	PIGE spectroscopy	1
Nitrile gloves	LC-MS/MS and PIGE spectroscopy; 24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	1, 2
Nonstick aluminum foil	LC-MS/MS and PIGE spectroscopy	1
Paper towels	LC-MS/MS and PIGE spectroscopy	1
Permanent marker ink	LC-MS/MS and PIGE spectroscopy	1
Pizza box	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Plastic shovel packaging	PIGE spectroscopy	1
PTFE bladder	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
PTFE tape	LC-MS/MS and PIGE spectroscopy	1
PTFE tubing	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
PTFE-lined tubing	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
PVC liner	PIGE spectroscopy	1
PVC screen	PIGE spectroscopy	1
Silastic tubing	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Time-release bentonite pellets	Leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Vinyl end caps	PIGE spectroscopy	1
Water level tape	24-hour leaching on shaker table, SPE and analysis of 24 PFAS by LC-MS/MS	2
Waterproof notepaper	PIGE spectroscopy	1
Waterproof outdoor clothing	Sequential organic solvent extraction and LC-MS/MS analysis	4

Notes: (1) Rodowa et al., 2020; (2) Denly et al., 2019; (3) Bartlett and Davis, 2018; (4) Van der Veen et al., 2020.

It may be difficult to generalize these results to similar products, as manufacturing methods may vary and may change over time. Particular products that are tested and found to contain PFAS may no longer need to be avoided if the manufacturer changes their practice to avoid PFAS.

2.2.3. Evaluation of Potential Pathways for PFAS to Enter a Sample

The literature search confirmed that PFAS are present in some materials used during sample collection and that these materials can leach PFAS to water after 24 hours of soaking. The literature does not evaluate whether use of these materials in the field, consistent with industry standard sampling procedures, will introduce PFAS bias to field samples. Therefore, the research team also evaluated pathways by which PFAS could potentially be introduced to the environmental samples.

Several pathways for field materials and equipment to bias PFAS sampling results were identified:

- ***Direct sample contact with sampling equipment*** – Sampling equipment that comes into direct contact with the sample media, such as laboratory sample containers, tubing, pump components (i.e., O-rings), bailers, sleeves and liners, samplers, and filters is the most likely pathway to impact PFAS concentrations in the sample. Some materials and equipment are in prolonged contact with the sampled water (e.g., passive diffusion bags), while others may have only brief contact (e.g., momentary contact with a pump O-ring). Some materials are in direct contact with specific types of samples only. For example, aluminum foil could be used when collecting fish tissue samples but is not typically used during groundwater or surface water sampling). The quantity of material potentially in contact with a sample is also important to consider.
- ***Incidental contamination while sample bottle is open*** – Cross-contamination could theoretically occur during the brief time that field staff have a sample container open and are filling it prior to capping the bottle. Cross-contamination could theoretically come from personal care products the sampler has used, dust or soil particles that enter the sample, or volatile PFAS entering the sample container. To avoid the transfer of PFAS or introduction of unintended particles, PFAS guidance typically specifies that the field personnel change to a clean pair of gloves immediately prior to sample collection. To be present at concentrations above the reporting limit (e.g., >2 ng/L) in a 250-milliliter (mL) sample, approximately 0.5 ng of PFAS would need to be introduced. As presented in **Appendix C**, this equates to at least 0.2 mg of makeup, 1 to 2 drops of pure sunscreen product, a peak rainfall rate for 20 minutes or more into the sample bottle, or peak rainfall near an active PFAS manufacturing facility into the sample container for over 3 minutes. Cross-contamination due to volatile PFAS is unlikely to occur at most sites because PFAA concentrations measured in outdoor air are far too low (picograms per cubic meter)[29] to result in detectable PFAA concentrations in a sample bottle. PFAA concentrations are higher in indoor air but are still approximately 2 to 3 orders of magnitude lower than needed to result in detectable PFAA concentrations (**Appendix C**).
- ***Contamination during shipping*** – Guidance documents for PFAS sampling typically provide recommendations or restrictions for field staff regarding sample packaging (e.g., no blue ice) for transport to the laboratory. However, there are no plausible pathways for non-volatile PFAS from these materials to enter into a sample bottle. Sample bottles are capped, making it extremely unlikely that PFAS could diffuse into a sample bottle even if the outside of a blue ice pack was contaminated from the breakage of highly concentrated PFAS samples during a prior cooler shipment. Field blanks and trip blanks provide data that support assumptions regarding the integrity of shipping containers.

Many of the materials identified in the literature review as having potential to contribute PFAS to water samples are not in direct contact with environmental samples and other pathways seem unlikely sources of detectable quantities of PFAS in samples. The potential for direct contact for some sampling equipment and materials known to contain PFAS is summarized in Table 2-5.

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[29] ITRC, 2020. Table 17-1A. PFAS Technical and Regulatory Guidance Document and Fact Sheets PFAS-1. Washington, D.C.: Interstate Technology & Regulatory Council, PFAS Team. https://pfas-1.itrcweb.org/.

Other materials have low PFAS concentrations such that incidental direct contact with a sample would not provide enough PFAS mass to bias sample results in low ng/L. Therefore, some materials that have been tested or are known to contain PFAS may be acceptable to use.

Table 2-5. Potential exposure pathways for materials, equipment, and products that contain PFAS to affect PFAS samples when following standard field procedures

Material, Equipment, or Product	Potential for Direct Contact with Sample	No Potential Pathway to Affect PFAS Sample when Following Standard Field Protocols
Bailer line	X	
Cold pack (outside)		X
Core catcher*	X	
Core catcher liner*	X	
Duct tape		X
Electrical tape		X
Field book cover		X
Field book pages		X
First aid adhesive wrapper		X
First aid packaging (box)		X
HDPE tubing	X	
Laboratory notebook		X
Laboratory tissue		X
Label backing		X
Labels		X
LDPE tubing	X	
MIP membrane*		X
Nitrile glove packaging		X
Nitrile gloves	X	
Nonstick aluminum foil*	X	
Paper towels		X
Permanent marker ink		X
Plastic shovel packaging		X
PTFE bladder	X	
PTFE tape		X
PTFE tubing	X	
PTFE-lined tubing	X	
PVC liner	X	
PVC screen	X	
Silastic tubing	X	
Time-release bentonite pellets	X	
Vinyl end caps	X	
Water level tape	X	
Waterproof notepaper		X
Waterproof outdoor clothing		X

*Not applicable for groundwater and surface water sampling

Current PFAS sampling guidance does not adequately recognize whether a plausible pathway exists for materials to affect PFAS concentrations in environmental samples. More careful consideration and communication of these aspects of guidance can begin to shift industry perceptions from a "contamination" mindset to a more scientifically based perspective of PFAS transport pathways and relative concentrations. When thinking about PFAS sampling from a contamination mindset, any material which contains trace amounts of PFAS is suspect and should not be allowed in proximity to the sample. From a scientifically informed perspective, some of the restrictions and recommendations provided in current PFAS guidance are unnecessary. PFAS sampling guidance can also be improved by describing standard protective measures that apply to all environmental sampling activities and highlighting areas where additional measures are needed to ensure the representativeness of surface water and groundwater samples. Industry standard sampling procedures are specifically designed to avoid extraneous material from entering a sample bottle.

2.2.4. Review of Unpublished Equipment Blank Sample Datasets

The project team completed a review of unpublished field equipment datasets (i.e., empirical data) to determine if field equipment and procedures systematically resulted in positive PFAS detections in groundwater samples. Equipment rinsate blanks and/or equipment soak blanks were collected during PFAS site inspections at over 30 large U.S. Navy installations and 13 PFAS remedial investigations conducted in the state of Michigan. Data were evaluated to assess whether any commonly used, yet untested, groundwater sampling equipment should be considered for PFAS analysis under this SERDP project.

Equipment blank datasets were filtered using a number of criteria as summarized in Figure 2-1. PFAS were detected in one or more equipment blanks at eight (8) out of the 30 U.S. Navy installations. In Michigan, 13 out of 121 equipment blanks collected over a three-year timeframe had detections of PFOS and/or PFOA.

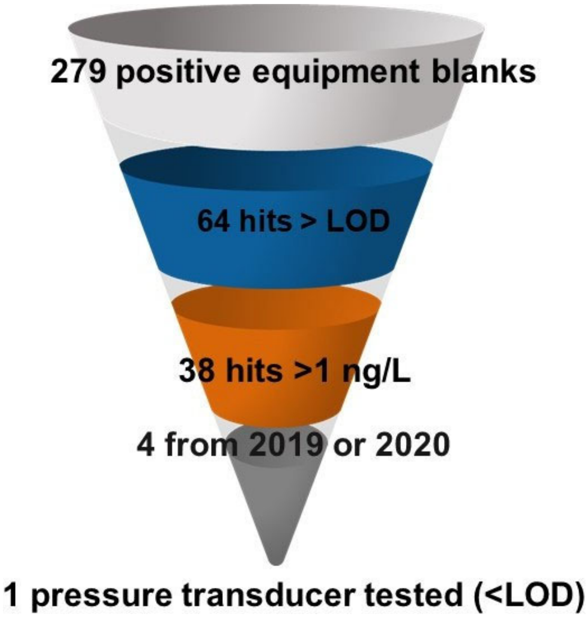

Figure 2-1. U.S. Navy installation equipment blank dataset characteristics

The majority of equipment blank samples collected from U.S. Navy installations were collected after the equipment had been used for sampling and had been decontaminated before moving to the next sample location. In this manner, equipment blanks offer data to assess the adequacy of the decontamination process and a detection does not imply that the equipment contained PFAS materials. Rather, carryover from one sample location to the next may explain positive PFAS detections (**Appendix D**). Most of the reported detections were qualified as approximate values (J flag) or uncertain due to detections below method detection limits, recoveries outside of the accepted range, or detection in the associated field blank, trip blank, or laboratory blank (B flag).

The data review resulted in the identification of three pumps with Teflon or PTFE components as candidates for additional testing, including Grundfos Redi-Flo2 (electric impeller pump), Geotech (bladder pump), and the Monsoon Proactive Stainless-Steel (electric impeller pump). However, these pumps, or their components, were not tested by this research group because prior testing had been completed. The Grundfos Redi-Flo2 impeller pump and Geotech bladder pump (with PTFE and polyethylene bladders) were tested during earlier phases of a sampling program and did not result in any detectable PFAS concentrations.[30] The Monsoon pump was previously tested by the equipment manufacturer. A conservative soak test (15 months of soaking in deionized water) was completed to represent a valid worst-case assessment of the pump with a resulting PFAS concentration of 9.4 ng/L or less (**Appendix D**).

Equipment blanks from Michigan sites were typically collected in the field by pouring PFAS-free water over large sampling equipment, pumping PFAS-free water through a pump/tubing setup similar to a sample, or soaking smaller sampling materials and tools in PFAS-free water in a Ziploc® or other self-sealing polypropylene bag for 24 to 48 hours. A Level Troll and Rugged Troll from In-Situ, Inc. were two types of equipment identified for further testing. The project team received a loan of a new identical Level Troll pressure transducer from In-Situ, Inc to conducta soak test. The pressure transducer (surface area 0.01120 square meters) was soaked in 40 mL ofmethanol for 24 hours and analyzed for PFAS by LC-MS/MS. No PFAS were detected.

The preponderance of non-detect results in the datasets reviewed indicates that typical equipment used to collect environmental samples did not contaminate field samples with PFAS. Blanks that yielded non-detect results were taken from sampling equipment including hand augers, steam cleaners, truck water tanks and water totes, sampler screens, submersible pumps, trash bags, hand tools, water level meters, and more (**Appendix D**).

These data support the conclusion that there is a low likelihood of systemic cross-contamination from PFAS-containing field equipment and materials. The Michigan equipment blank dataindicate a greater potential for cross-contamination may come from source water used fordecontamination or during drilling.

Figure 2-2 summarizes key aspects of science-based guidelines for avoiding bias in PFAS sampling results from common field equipment and materials.

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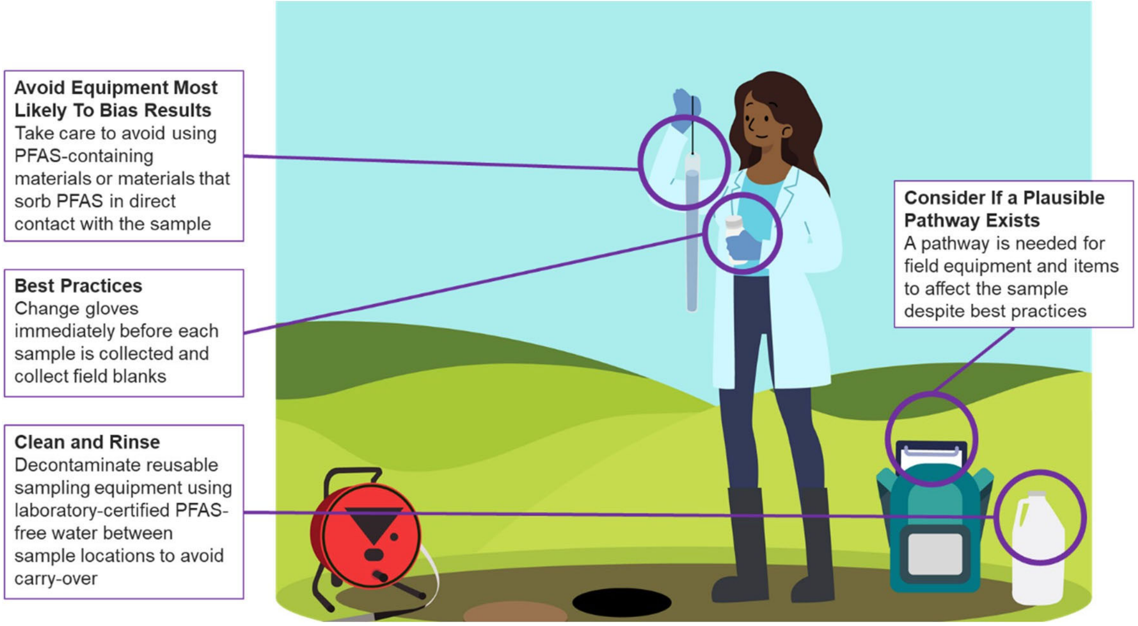
[30] DiGuiseppi, W.H., Winter, D., Gwinn, T., Field, J., and Barzen-Hanson, K., 2014. Groundwater Sampling Interference from Per- and Polyfluoroalkyl Substances in Sampling Equipment, Battelle's Ninth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 19-22.



Avoid Equipment Most Likely To Bias Results
Take care to avoid using PFAS-containing materials or materials that sorb PFAS in direct contact with the sample

Best Practices
Change gloves immediately before each sample is collected and collect field blanks

Clean and Rinse
Decontaminate reusable sampling equipment using laboratory-certified PFAS-free water between sample locations to avoid carry-over

Consider If a Plausible Pathway Exists
A pathway is needed for field equipment and items to affect the sample despite best practices

Figure 2-2. Science-based guidelines for field equipment and materials used during PFAS sample collection

3. BIAS FROM SAMPLE STORAGE

Many PFAS, particularly the perfluorinated PFAS including PFOS, PFOA, and their carbon-chain length homologs, are typically long-lived and difficult to degrade. However, at present, there is widespread concern that reported PFAS concentrations may be biased as a result of groundwater or surface water sample storage conditions. A low bias can result from PFAS interactions with the sample container material, and a high or low bias can result from the transformation of some PFAS precursors to others during storage.

The extent to which these processes occur within a sample may vary depending on the type of storage container, hold time, storage temperature, mixture of PFAS originally present in the sample, and other water quality parameters. Current guidance for groundwater and surface water PFAS samples recommends sample collection into wide-mouth 250-mL HDPE bottles fitted with an HDPE screw cap and storage at 4 degrees Celsius (ºC) or less for a hold time of up to 14 days prior to extraction. No preservative is needed for non-drinking water samples.[31]

Questions arise as to the scientific basis for these restrictions, particularly the 14-day hold time. A longer hold time for PFAS samples could reduce the need for resampling if shipping delays occur and could enable some samples to be placed on hold following receipt by a commercial laboratory, allowing application of cost-saving sample strategies where the analysis of samples could be contingent on results of a subset of the samples. Another benefit of longer hold times would be for researchers who wish to store samples or subsamples for future evaluation. Some of these questions have been thoroughly reviewed by previous scientific studies; key findings are describedin this section.

3.1. Research Findings Regarding PFAS Sample Storage and Hold Times

Several researchers have evaluated the effect of sample storage times and containers on PFAS analytical results. In early research (2011), Berger et al.[32] evaluated the recovery of perfluorinated carboxylates (PFCAs), perfluorinated sulfonic acids (PFSAs), and fluorotelomer alcohols over a period of three months of storage in a polypropylene container. Of those PFAS, the percent recovery rates steadily decreased and were unacceptably low (<70%) after 90 days for two longer chained PFAS: perfluoroundecanoic acid (PFUnDA) and perfluorododecanoic acid (PFDoDA). Additional PFAS mass was recovered upon rinsing the containers with methanol, indicating significant PFAS losses to the container that could be mitigated by a methanol rinse or other measures. HDPE containers were then suggested as preferable and have since become common practice. In 2018, the USEPA Method 537.1 demonstrated the stability of PFSAs, PFCAs, ether carboxylates, sulfonates, N-methylperfluorooctane sulfonamidoacetic acid (MeFOSAA), and

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[31] Drinking water samples require the addition of 5 grams per liter (g/L) Trizma® as a dechlorinating agent, i.e., to remove free chlorine from chlorinated drinking water. The presence of free chlorine was found to affect the recovery of PFAS during Method 537 development. Trizma® also serves as a pH buffer. Trizma® itself does not appear to have an effect on PFAS in non-chlorinated water samples.

[32] Berger, Urs, Mary A. Kaiser, Anna Kärrman, Jonathan L. Barber, Stefan P. J. van Leeuwen, 2011. Recent developments in trace analysis of poly- and perfluoroalkyl substances. *Analytical and Bioanalytical Chemistry* 400: 1625-1635. DOI: 10.1007/s00216-011-4823-8.

and N-ethyl-perfluorooctane sulfonamido acetic acid (EtFOSAA) in drinking water samples over a 14-day period. Data were not provided to demonstrate the validity of hold times specified by other analytical methods (ISO 25101 or ASTM International D7979-17).

In 2019, Woudneh et al.[33] performed experiments to assess the effect of temperature, sample matrix, and storage time on PFAS analytical results. Sample matrices consisted of spiked bottled water, surface water, and two types of wastewater treatment plant effluent. HDPE or amber glass containers were used for sample storage. Samples were stored at -20, 4, and +20 ºC. Twenty-nine PFAS were tested, including 11 PFCAs, 8 PFSAs, 3 fluorotelomer sulfonic acids (FTSAs), 3 perfluorooctane sulfonamides, 2 perfluorooctane sulfonamide ethanols, and 2 perfluorooctane sulfonamide acetic acids. Key findings of the study were as follows:

- All 29 of the PFAS that were tested were stable over a period of 180 days at -20°C regardless of the sample matrix.
- PFCA and PFSA concentrations remained stable over a period of 180 days at 4°Cregardless of sample matrix.
- Other PFAS showed decreasing or increasing trends when stored at 4°C or 20°C. Changes in concentrations of other PFAS were observed within 7 days, in both surface water and wastewater matrices. Increasing the storage temperature led to greater concentration differences, as expected. PFAS that decreased over time included N-Methylperfluorooctanesulfonamide (N-MeFOSA), N-ethyl perfluorooctane sulfonamide (N-EtFOSA), N-methyl perfluorooctanesulfonamidoethanol (N-MeFOSE) and N-ethyl perfluorooctane sulfonamido ethanol (N-EtFOSE), likely due to volatility of these compounds. 8:2 FTSA concentrations decreased over time as this compound biodegraded. Formation of PFOA, perfluorononoic acid (PFNA), N- methylperfluorooctane sulfonamidoacetic acid (N-MeFOSAA), and N-ethyl perfluorooctane sulfonamido acetic acid (N-EtFOSAA) were observed over time, likely from the degradation of N-MeFOSE and N-EtFOSE precursors also present in the sample.
- At 20°C, PFOS and other PFSA concentrations remained stable over a period of 180 days regardless of the sample matrix.
- Amber glass bottles and HDPE containers showed comparable recovery of analytes. The most significant losses occurred for PFUnDA and PFDoDA in the polypropylene container; however, these losses were demonstrated to be reversible by rinsing the container with methanol.

As part of the process for the development of PFAS analytical method 8327, USEPA ran time-based studies on PFAS degradation and loss during sample storage over a 45-day timeframe.[34] USEPA also assessed the effects of different container types including plastic and glass on

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[33] Woudneh, Million B., Bharat Chandramouli, Coreen Hamilton, and Richard Grace, 2019. Effect of sample storage on the quantitative determination of 29 PFAS: Observation of analyte interconversions during storage. *Environmental Science & Technology* 53 (21): 12576-12585. DOI: 10.1021/acs.est.9b03859.

[34] USEPA, 2019. Method 8327 PFAS using external standard calibration and multiple reaction monitoring (MRM) liquid chromatography/tandem mass spectrometry (LC-MS/MS). Revision 0. June.

analyte recovery. USEPA recommended the use of HDPE containers, 'whole bottle' preparation (i.e., rinsing the sample bottle with methanol), and a hold time of up to 28 days prior to sample extraction. The written USEPA method 8327 summary also references freezing to prevent loss and degradation of some target PFAS. USEPA plans to develop guidelines for field sampling and currently references the ITRC team fact sheets for use as sampling guidelines.

For USEPA Method 533, a maximum hold time of 28 days is recommended for samples prior to sample extraction. Extracts should be analyzed within 30 days after sample extraction.[35] These recommendations are based on a preliminary holding time study.

3.2. Summary and Implications for PFAS Sample Storage

The research study by Woudneh et al. indicates that **all 29 PFAS tested remained stable for up to 180 days when the samples were frozen**. Broader awareness of this finding could encourage commercial laboratories to conduct further evaluation and adjust SOPs to allow for longer sample hold times when samples are frozen. For example, laboratories could assess transformation over time from a variety of different PFAS precursors, using dilute aqueous film forming foam (AFFF) or samples from AFFF source areas. Laboratories could also assess matrix effects such as the impact of iron oxidation or precipitation over time. Allowing for longer sample storage times would avoid possible rework if shipping delays cause hold time exceedances or would provide site investigators with more flexibility for placing PFAS samples on hold and deciding whether or not to analyze them based on the results from other samples.

Research studies indicate that **at 4ºC, transformations of some PFAS in surface water and wastewater (e.g., N-MeFOSE, N-EtFOSE, 8:2 FTSA) began occurring within the first 14 days**, i.e., within the current hold times. PFAS transformations were observed in surface water as well as wastewater samples. Effects were significant within 7 days of storage; therefore, Woudneh et al. recommended laboratory storage of PFAS samples at -20°C for all PFAS samples.

Figure 3-1 summarizes key findings from the Woudneh et al. study related to PFAS stability in samples stored at different temperatures.

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[35] USEPA, 2019. Method 533: Determination of PFAS in drinking water by isotope dilution anion exchange solid phase extraction and liquid chromatography/tandem mass spectrometry. Office of Water. November.

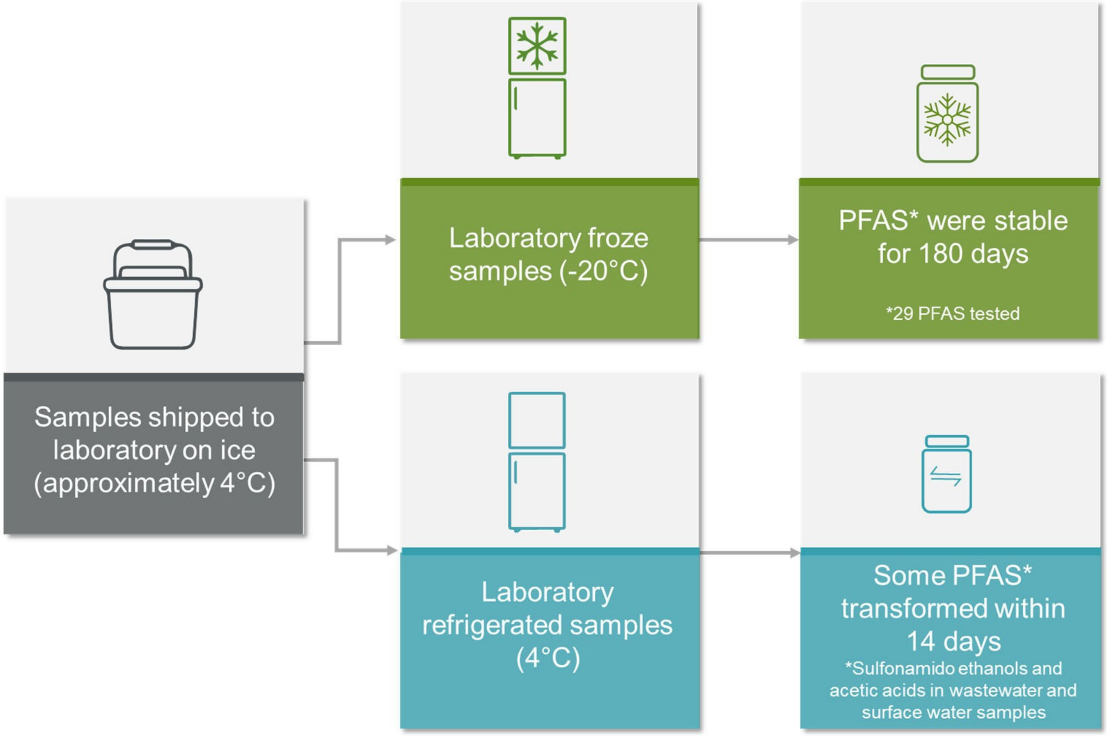

Figure 3-1. PFAS stability at different storage temperatures and hold times

4. BIAS DUE TO STRATIFICATION: EMERGING RESEARCH

Some PFAS, including PFAAs, are amphiphilic and are designed to accumulate at interfaces due to their chemical structure – they are comprised of a hydrophobic fluorinated carbon chain that is attached to a water-soluble, polar head group. Many PFAS have surfactant properties and many industrial PFAS applications depend on this surfactant property – PFAS are used in AFFF in order to facilitate the spread of an aqueous film on the surface of a liquid fuel in addition to the formation of foam that blankets the liquid fuel, preventing the fire from mixing with air and cooling the fuel and adjacent surfaces.[36]

The propensity of PFAS to accumulate at interfaces, including the air/water interface, has implications for PFAS sample collection and measured PFAS concentrations. For example, a recent laboratory study measured surface tension of various PFOS and PFOA solutions with concentrations ranging from 0.1 to >1,000 milligrams per liter (mg/L) and found that accumulation of PFOS and PFOA at the air-water interface was substantial.[37] This enrichment at the surface has the potential to lead to overall stratification in a water column. The accumulation of PFAS at the air-water interface has potential to bias results, as does stratification of bulk water, particularly under certain geochemical conditions (e.g., salinity, organic matter, and colloidal material). Evaluation of these potential issues and their impact on surface water and groundwater sampling are summarized below.

4.1. PFAS Stratification and Enrichment

Laboratory testing is being conducted at Oregon State University and CDM Smith to assess PFAS stratification in bulk groundwater and surface water under freshwater and brackish conditions. Model groundwater wells were constructed using 2.5-inch-diameter PVC with sampling ports located at multiple vertical intervals (4, 30, and 54 inches from the top). Three of the seven columns were filled with freshwater (groundwater collected from a site where AFFF had been used), three with brackish water (groundwater from the same site amended with 11.9 g/L sodium chloride (NaCl) which resulted in a salinity measurement of 21.8 microsiemens per centimeter), and one with deionized water. The columns were sampled following setup and then the columns were allowed to sit undisturbed for three months and five months prior to sampling the ports again. The top sampling port was not positioned at the interface; thus, the surface microlayer was not assessed. Samples were analyzed for PFAS using tandem liquid chromatography quadrupole time of flight mass spectrometry (LC-QToF). Preliminary results indicated that PFAS stratification did not have a measurable effect on bulk water concentrations in either the fresh or brackish water.

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[36] Chemguard, 2005. General Foam Information. Data Sheet #D10D03010. Revision Sept. Available online at https://www.chemguard.com/about-us/documents-library/foam-info/general.htm#:~:text=Foam%20works%20in%20the%20following,fuel%20surface%20smothering%20the%20fire.&text=The%20foam%20cools%20the%20fuel,that%20can%20mix%20with%20air.

[37] Costanza, J., M. Arshadi, L.M. Abriola, and K.D. Pennell, 2019. Accumulation of PFOA and PFOS at the Air-Water Interface. *Environ. Sci. Technol. Lett.* 6 (8): 487-491. https://doi.org/10.1021/acs.estlett.9b00355.

In surface waters, accumulation of natural organic matter occurs in the surface microlayer.[38] Surface water foam (SWF) formation may be generated from the microlayer in lakes and streams where air is mixed into the water by waves or by turbulent flow and where the surface tension is reduced by the presence of natural organic matter (a natural surfactant resulting from the presence of decaying plant matter).[39] Such SWFs serve as a potential reservoir of PFAS because of the large number of air/water interfaces in SWF, and thus may impact PFAS concentrations if SWF is captured while sampling surface water.

Ju et al. measured PFOS and PFOA concentrations in coastal waters in China and reported significantly higher concentrations in the sea surface microlayer of 50 ±10 µm relative to surface water and subsurface water.[40] Enrichment factors (EFs), defined as the ratio of the concentration of a compound in the surface microlayer to that in bulk water, were as high as 24 to 109 for PFOS.

In a recently published study from Oregon State University,[41] foam samples and bulk water samples were collected from nine locations in a freshwater lake in the state of Michigan that was known to be impacted by multiple sources of AFFF, landfill leachate, and potentially septic systems. Foam and bulk water samples were analyzed for up to 50 target PFAS and >1,400 non-target PFAS, as well as dissolved organic carbon (DOC). The DOC in two pairs of foam and bulk samples were characterized by nuclear magnetic resonance. The data for PFAS in foam and the bulk water were used to calculate EFs, evaluate the nature of DOC, and calculate preliminary estimates of exposure and risk due to incidental ingestion.

Sixteen different PFAS were present above the LOQ in the foam, but onlyfive PFAS were present in bulk water samples: PFOS, PFOA, perfluorohexane sulfonate (PFHxS),perfluorohexanoic acid (PFHxA), and 6:2 FTSA. For PFAS that were detected in both bulk waterand foam samples, EFs ranged from 10 to 2,830. EF trends were evaluated as a function of PFAScarbon chain length, head group, and structure. EFs were typically greater for linear isomers relative to branched isomers, that is, linear isomers of longer chain PFAS with sulfonate head groups had a higher tendency to accumulate in SWFs compared with shorter chain or branched PFAS and PFAS with carboxylate head groups.[42]

Several PFAS were detected in SWF but not in surface water, including PFNA at concentrations ranging from 130 to 1,500 ng/L, perfluorodecanoic acid (PFDA) at concentrations of 260 to 960 ng/L, PFUnDA at concentrations of 110 to 660 ng/L, perfluoroheptane sulfonate (PFHpS) at concentrations of 160 to 2,800 ng/L, and perfluorononane sulfonate (PFNS) at 130 ng/L. Longer

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[38] Wurl, O., W. Ekau, W.M. Landing, C.J. Zappa, and J. Bowman, 2017. Sea surface microlayer in a changing ocean – A perspective. *Elementa: Science of the Anthropocene*, vol. 5.

[39] Wegner, C., and M. Hamburger, 2002. Occurrence of stable foam in the upper Rhine River caused by plant-derived surfactants. *Environmental science & technology*, *36*(15), pp.3250-3256.

[40] Ju, X., Y. Jin, K. Sasaki, and N. Saito, 2008. Perfluorinated surfactants in surface, subsurface water and microlayer from Dalian coastal waters in China. *Environmental Science and Technology*, *42* (10): 3538-3542.

[41] Schwichtenberg, T., D. Bogdan, C.C. Carignan, P. Reardon, J. Rewerts, T. Wanzek, and J.A. Field, 2020. PFAS and dissolved organic carbon enrichment in surface water foams on a northern U.S. freshwater lake. *Environ. Sci. Technol*. 54 (22): 14455-14464. https://doi.org/10.1021/acs.est.0c05697.

[42] Schwichtenberg, T., D. Bogdan, C.C. Carignan, P. Reardon, J. Rewerts, T. Wanzek, and J.A. Field, 2020. PFAS and dissolved organic carbon enrichment in surface water foams on a northern U.S. freshwater lake. *Environ. Sci. Technol*. 54 (22): 14455-14464. https://doi.org/10.1021/acs.est.0c05697.

chain compounds such as PFNA, PFDA, PFUnDA are not typically detected in surface water; this study documented their presence in SWFs. Other PFAS were detected in SWF but not in bulk water samples included 220 to 730 ng/L perfluoro-4-ethylcyclohexane sulfonate (PFEtCHxS), 690 to 1,100 ng/L perfluorohexane sulfonamide (FHxSA), 100 to 130 ng/L EtFOSAA, 140 ng/L N-sulfo propyl perfluorohexane sulfonamide (SPr-FHxSA). Fluorotelomer-based PFAS compounds including 5:3 fluorotelomer carboxylic acid (5:3 FTCA) and 8:2 FTSA were detected in foam samples at concentrations of 190 ng/L and 100 to 130 ng/L, respectively.

DOC concentrations in SWF and bulk surface water were on average 250 mg/L and 15 mg/L, respectively. Because DOC concentrations were three orders of magnitude higher than PFAS concentrations in SWF samples, and PFAS concentrations were far below critical micelle concentrations,[43] DOC is likely the primary cause of SWF formation, not PFAS.

Bench-scale studies were recently completed to assess PFAS stratification in surface water that could lead to bias during surface water sample collection; publication of results is pending. Synthetic surface water with multiple organic components and ten different PFAS was created for use in bench-scale experiments. Each PFAS had a target concentration of 3 nanomolar (nmol/L) in the bulk liquid (e.g., 1,500 ng/L PFOS). Experiments were conducted under both low (NaCl = 0.2 g/L) and high (NaCl = 5 g/L) ionic strength conditions, as well as in deionized water at low salinity. The synthetic surface water was mechanically agitated to form a foam that had a stability of several hours, similar to natural SWFs. After 48 hours of agitation, PFAS concentrations in the surface microlayer and bulk water were measured and used to calculate EFs in fresh and brackish waters, with and without foam present.

In general, EFs were greater for brackish water compared to freshwater, which was expected due to the increased ionic strength that enhances PFAS accumulation at air-water interfaces of some longer chain PFAS. EFs for PFAS ranged from 1.0 (PFHxA, perfluorobutane sulfonate [PFBS]) to 32 (PFOS) in freshwater and from 1.0 (PFHxA, PFBS) to 51 (PFOS) in synthetic brackish water. After 72 hours, foam was no longer present and PFAS were no longer enriched at the surface of the synthetic surface waters. This finding suggests that foam formation may play a key role in enriching PFAS at the water surface, at least for the specific water tested. In contrast, measurement of PFAS partitioning using partially condensed foams showed that PFAS was equally distributed between the condensed foam and foam phases when normalized to the liquid volume. Thus, the extent of PFAS enhancement in SWFs versus organic-rich surface microlayers versus bulk water may be very dependent upon the nature of the organics and SWFs composition present in natural environments.

4.2. Implications for Groundwater and Surface Water Sampling

Preliminary results of the laboratory study suggest that stratification in groundwater wells does not occur to a measurable extent over the study period. PFAS concentrations in the well were not stratified with depth after three months with no disturbance, neither in freshwater nor in brackish

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[43] The critical micelle concentration is an important characteristic of surfactants – at concentrations above this concentration, the surfactant will form micelles, that is, aggregates of molecules in a colloidal solution.

groundwater. **Therefore, current guidance for PFAS sampling from groundwater monitoring wells does not need to be amended at this time**.

PFAS have been shown to accumulate in SWF that forms on surface waters due to the presence of DOC. The inclusion of SWF in surface water samples can therefore potentially bias sample results high relative to PFAS concentrations in bulk surface water. **This finding suggests that bulk surface water samples be collected in a manner that does not include SWF or the surface microlayer**. In areas where SWF is present on surface water, bulk water samples can be collected by fully submerging the sample bottle beneath the liquid surface before opening it and then closing the sample bottle before bringing it to the surface. If surface water sampling is being done remotely (e.g., using a sampling pole) and this technique is not possible, SWF should be removed from the surface of the water prior to sample submittal to the laboratory for analysis. In shallow water, a common method of collecting surface water samples is to use a peristaltic pump and HDPE tubing. This method would avoid over-representing the surface microlayer during sampling and also avoid suspending sediment.

Beyond assessing bias, SWF sampling may provide new information regarding PFAS signatures and likely sources, because several longer chained indicator PFAS may be present in SWF or surface microlayers, but not in bulk surface water. In addition, SWF and microlayer sampling can provide site-specific information for risk assessment related to exposure to or incidental ingestion of surface water foam and can inform the need for posted signs or institutional controls. The need for SWF and microlayer sampling and PFAS analysis should be considered in the context of project objectives. If SWF is present and site-specific sampling is not conducted, EFs published by these research studies may be useful for estimating PFAS concentrations in SWF based on PFAS concentrations in bulk surface water.

A secondary ongoing project objective is to systematically study the procedures for sampling the surface microlayer for PFAS. EGLE has published guidance for SWF PFAS sampling.[44] PFAS-containing SWF has been detected in Michigan surface water bodies, studied to assess notable and seasonal observations, and sampled to assess PFAS concentrations and EFs. Continued collaboration with EGLE, USEPA, and other organizations is planned to better understand parametersthat influence form formation, how environmental conditions affect SWF formation and PFAS occurrence in SWF as well as the role of SWF in PFAS fate and transport.[45] SWF can be sampled using clean polypropylene bags and gloved hands to gather foam from surface waters and collect approximately 20 times the volume of required liquid as SWF. Bags of foam are allowed to rest until the SWF collapses and the collapsed SWF is then consolidated into one sample container. The resulting liquid may be viscous or gelatinous and may require dilution prior to PFAS analysis.A recent publication summarizes the sample extraction and analytical methods used for foam.[46]

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[44] EGLE, 2019. Surface water foam PFAS sampling guidance.

[45] AECOM, 2019. Appendix C - Preliminary Foam Assessment. Available online at https://3msettlement.state.mn.us/sites/default/files/Appendix%20C%20-%20Preliminary%20Foam%20Assessment_FullReport.pdf

[46] Schwichtenberg, T., D. Bogdan, C.C. Carignan, P. Reardon, J. Rewerts, T. Wanzek, and J.A. Field, 2020. PFAS and dissolved organic carbon enrichment in surface water foams on a northern U.S. freshwater lake. *Environ. Sci. Technol*. 54 (22): 14455-14464. https://doi.org/10.1021/acs.est.0c05697.

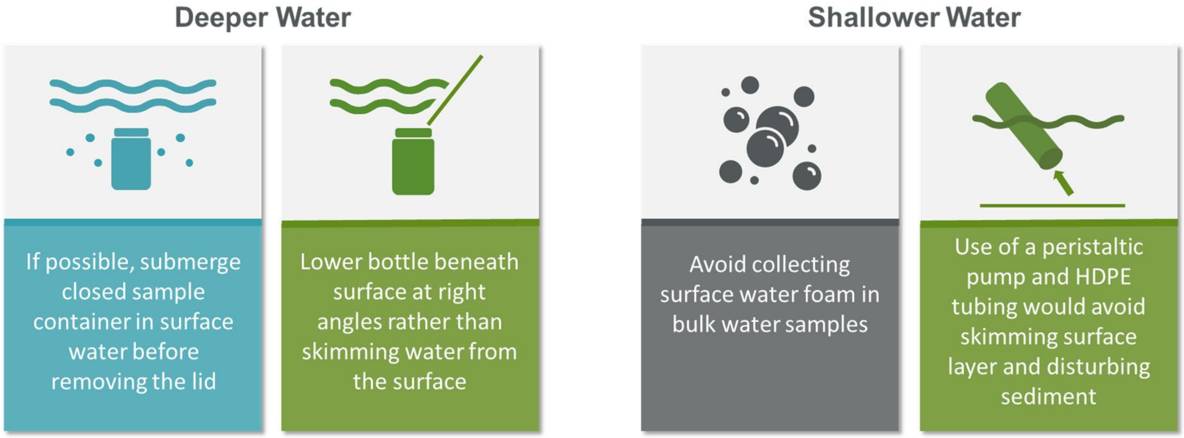

Figure 4-1. Tips for collecting representative samples of bulk surface water

5. SUMMARY AND RECOMMENDATIONS

This report addressed the potential for bias to be introduced in PFAS sample results due to the use of specific sampling materials or equipment, laboratory sample storage, or stratification of PFAS in the water column. Current guidance documents on PFAS sampling from federal and state agencies and professional organizations list multiple sampling restrictions and recommendations that are intended to reduce sample bias. A comparison of various guidance documents indicated several inconsistencies from one organization to another as well as a trend towards greater consensus as guidance documents are revised; however, guidance still lacks a demonstrated scientific basis.

This report evaluated the scientific basis for PFAS sampling restrictions by reviewing relevant scientific publications, evaluating several large datasets of field equipment blank results, summarizing key findings of ongoing studies under SERDP project ER19-1205, and surveying industry professionals to identify and review other available resources. Results indicate that many PFAS sampling restrictions in current guidance are not science-based but rather are based on the precautionary principle. For example, some guidance documents unnecessarily restrict the use of materials and equipment in the field that are never in direct contact with water inside sample bottles and have no credible pathway for biasing sample results (e.g., waterproof field notebooks, permanent markers, post-it notes, blue ice).

Sampling protocols already provide an additional layer of sample protection by specifying glove changes prior to the collection of each sample and the collection of field QA/QC samples. Guidance that is highly specific and restrictive increases the time and effort required for field work planning and implementation, resulting in higher cost and more waste generated. Because PFAS sampling has become more routine, sampling guidance can be improved by differentiating between the limited field practices and equipment that are scientifically known to result in PFAS detections in laboratory tests (e.g., PTFE bailers or tubing), best practices to provide a measure of safety against potential cross-contamination (e.g., glove changes, collection of field blanks, decontamination practices to prevent carryover from one sample location to the next), as well as the broader list of field practices and equipment that are not likely to result in measurable or significant differences in PFAS concentrations based on scientific studies to date.

Key aspects of current guidelines that are supported by science conducted to date include the following:

- Avoid using materials and field equipment in direct contact with the sample if they have yielded detectable PFAS in scientific soak studies or equipment blanks, as these items have the potential to bias sample results high.
- Avoid using materials in direct contact with the sample if they are known to sorb PFAS, as these items have the potential to bias sample results low.
- Follow best practices to keep samples clean and free from debris. Change gloves immediately before each sample is collected, avoid touching the inside of the sample bottle

or cap, and minimize the amount of time that the sample bottle is uncapped. Collect field blanks to assess the adequacy of sample handling procedures.

- Clean reusable sampling equipment and rinse the equipment using PFAS-free water. This will reduce the potential for carryover from one sample location to the next. Collect field equipment blanks to assess the adequacy of decontamination procedures.

Published research has demonstrated that current sample hold times for PFAS samples are unlikely to introduce bias, and could be extended without introducing bias, provided that samples are frozen upon receipt at the laboratory. Extended hold times would provide site investigators and researchers with more flexibility and provide options to reduce analytical costs by placing some of the samples on hold and analyzing them only if needed based on results of a subset of samples. Key findings from published research support the following:

- PFAS samples are shipped to the laboratory on ice, consistent with typical environmental sample shipment procedures. Although blue ice packs have been discouraged out of an abundance of precaution, there is no scientific evidence or plausible pathway for blue ice to bias sample results;

- Samples that are received by the laboratory and stored in a freezer at a temperature of -20 degrees Celsius have been analyzed for a suite of standard PFAS compounds up to 180 days later with no adverse effects on data quality. This suggests that laboratories may be able to revisit hold times specified in their SOPs.

Experiments conducted under SERDP project ER19-1205 demonstrate that groundwater stratification in well casings may not be a source of significant bias in measured PFAS concentrations, but that stratification of surface water can potentially introduce bias during surface water sampling, particularly if there is SWF on the water surface. Research is ongoing to quantify the enrichment of various PFAS in the surface microlayer. Key findings regarding the effect of the surface microlayer on surface water sampling procedures suggest the following:

- Surface water sampling methods may need to be adjusted to avoid over-representing the surface microlayer when collecting samples that are meant to represent bulk water quality;
    - Avoid collecting surface water foam in the sample;
    - When collecting a grab surface water sample (stream access and depth permitting), submerge the closed sample container in the surface water before removing the lid to collect the sample;
    - When using a sampling pole to collect a grab surface water sample (depth permitting), lower the bottle beneath the surface at right angles rather than skimming water from the surface;
    - In shallower water, the common surface water sampling method of using a peristaltic pump and HDPE tubing provides a method to avoid over-representing the surface water interface in the collected sample without suspending sediment.

- In contrast, the surface microlayer does not appear to bias PFAS groundwater sample results. This finding is supported by theoretical calculations as well as field sample results.

The findings presented in this document suggest that agencies who have published PFAS sampling guidance should regularly review and update their guidance based on the latest published scientific literature. Field practitioners who sample groundwater and surface water for PFAS shouldsimilarly review and update SOPs to be consistent with applicable regulatory requirements and toreflect science-based evidence, as summarized in this document. Removing restrictive specific requirements from guidance and SOPs and instead requiring field staff to take general precautions to prevent and demonstrate sample integrity (e.g., glove changes, field blanks) will reduce the effort and cost associated with PFAS sampling without compromising sample results or introducing sample bias.

APPENDIX A:

Interstate Technology and Regulatory Council (ITRC) Survey Results

ITRC Survey Questions

1. PFAS sampling protocols in the following guidance documents have been reviewed as part of this study. Please list any other published sampling guidance(s) that may be relevant:

Industry guidance documents:

- ITRC, 2020. PFAS Technical and Regulatory Guidance Document and Fact Sheets PFAS-1. Washington, D.C.: Interstate Technology & Regulatory Council, PFAS Team. https://pfas-1.itrcweb.org/.
- NWGA, 2017. Groundwater and PFAS: State of Knowledge and Practice.
- Federal guidance documents:
- USEPA, 2015. Region 4, Science and Ecosystems Support Division, Athens, GA, Field Equipment Cleaning and Decontamination at the FEC, SESDPROC-206-R3.
- DoD EDQW, 2017. Bottle Selection and other Sampling Considerations When Sampling for PFAS.
- NAVFAC, 2017. PFAS Site Guidance for NAVFAC RPMs. September 2017 Update.

State guidance documents:

- California State Water Quality Control Board, 2019. Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidelines.
- Florida Department of Environmental Protection, 2019. Draft Standard Operating Procedure – PFAS Sampling.
- Maine DEP, 2019. Standard Operating Procedure No. RWM-DR-014-ADDENDUM Attachment A PFAS Sampling and Analysis Plan Form Template.
- MA DEP, 2018. Interim Guidance on Sampling and Analysis for PFAS at Disposal Sites Regulated under the Massachusetts Contingency Plan.
- MA DEP, 2017. Draft Fact Sheet: Guidance on Sampling and Analysis for PFAS at Disposal Sites Regulated Under the Massachusetts Contingency Plan.
- Michigan Department of Environmental Quality, 2018. Groundwater PFAS Sampling.
- NHDES, 2019. Laboratory Testing Guidelines for Per- and Polyfluoroalkyl Substances (PFAS) at Waste Sites, 2019
- NHDES, 2018. Master Quality Assurance Project Plan of the Hazardous Waste Remediation Bureau Waste Management Division.

- NHDES, 2017. Frequently Asked Questions (FAQs) for Sampling and Analysis of PFASat Waste Management and Disposal (WMD) Sites.
- Washington Department of Ecology, 2016. Quality Assurance Project Plan, Statewide Survey of Per- and Poly-fluoroalkyl Substances in Washington State Rivers and Lakes.

2. The following guidance document is currently being revised. Are you aware of any PFAS sampling guidelines that are currently being developed or revised?
    - NWGA, 2017. Groundwater and PFAS: State of Knowledge and Practice.

3. Peer-reviewed papers that provide a scientific basis for some aspects of PFAS sampling have been reviewed as part of this study. Please list any relevant unpublished data sets or non-peer-reviewed data summaries (e.g., conference presentations, white papers) and a point of contact for requesting additional information.

4. Please rate the impact or importance of providing a scientific basis for the following PFAS sampling guidelines, using a scale of 1 to 3.

5. The project team would like to communicate study results broadly over the next two years. Please suggest outlets for information including journals, newsletters, conferences, webinars, and other media.

6. Please provide any other feedback on the project topic.

Question:	1	2	3		4					5	6
Response No.					Evaluating common materials/equipment that are in direct contact with the sample	Evaluating common materials/equipment that are not in direct contact with the sample	Evaluating different decontamination procedures	Evaluating PPEand technician-related precautions	Other (please specify below)		
1	None known.	None known.	None known.	n/a	3 - very important	2 - somewhat important	3 - very important	3 - very important	-	Regional associations like NEWMOA; ECOS/ITRC	Thank you for looking at this topic.
2					3 - very important	2 - somewhat important	2 - somewhat important	3 - very important		newsletters, webinars	A more practical sampling protocol, which can be readily implemented in the field in terms of equipment, cautions taken, sampling time, cost based on scientific data and evidence , is recommended.
3					3 - very important	2 - somewhat important	3 - very important	3 - very important	Further elaboration regarding "not in direct contact" should be acknowledged. Some activities conducted during sampling could provide "indirect" mechanisms for cross contamination. One possible example is wind direction and speed while sampling outside that could mobilize airborne PFAS-containing particles and dust, etc.	Instruction sheets for sample collection as provided by qualified analytical laboratories. State agency reachout to the professional community engaged in sampling (e.g., PG's, LSPs, LSRPs, LEPs, etc.)	
4		No.			3 - very important	2 - somewhat important	3 - very important	2 - somewhat important	Materials used in well construction and plumbing		
5	None known	No	None		3 - very important	1 - not very important	3 - very important	3 - very important		ITRC, SERDP/ESTCP, Battel	
6	The State of Michigan has developed PFAS sampling methodologies for: Residential wells, Groundwater, Soil, Wastewater, Surface Water, Fish Tissue, Sediment, Surface Water Foam, and Biosolids and Sludge.	No.	NA	NA	3 - very important	3 - very important	3 - very important	3 - very important		The Great Lakes PFAS Summit will be held October 27-28 in Lansing, Michigan, at the Lansing Center.	
7					3 - very important	2 - somewhat important	3 - very important	3 - very important		Environmental Science and Technology (ACS)	
8					3 - very important	2 - somewhat important	2 - somewhat important	3 - very important			
9	USACE Omaha PFAS Guidance				3 - very important	2 - somewhat important	3 - very important	2 - somewhat important		ITRC, DoD EDQW, ACS ES&T, DoD EMDQ	
10		No			3 - very important	2 - somewhat important	3 - very important	3 - very important		Talking PFAS Podcast (Twitter: @TalkingPFAS); The Green Science Policy Institute PFAS Science and Policy Group (Anna@GreenSciencePolicy.org; www.greensciencepolicy.org)	The USGS has an extensive history of evaluating sampling protocols (i.e., to reduce contamination and obtain representative samples) to develop their ppb protocols for sampling organic contaminants. It may be useful to reach out to them to see if they have insights (and any preliminary research/data) regarding sampling for PFAS. Suggested contact: James Gray (jlgray@usgs.gov) who has been working on method development at the NWQL.
11					3 - very important	3 - very important	3 - very important	3 - very important			
12	I do not know of any additional publicly available guidance documents.	I do not know of any additional publicly available PFAS sampling guidelines that are currently being developed or revised.			3 - very important	2 - somewhat important	3 - very important	2 - somewhat important		I applaud the fact that the Rodowa et al., paper is open access - this has quickly become one of the most important references for understanding the potential for cross contamination from sampling.	Excellent communication - I like the examples where you show how much of a particular material would have to be "in the bottle" to meet the LHA. The complimentary photographs in the presentation provide a tangible and simple explanation for the conclusions from this component of the work.
13					3 - very important	2 - somewhat important	3 - very important	2 - somewhat important		Journal of Hazardous Materials; JHM Letters	
14	NYSDEC, 2020. GUIDELINES FOR SAMPLING and ANALYSIS OF PFAS	No			3 - very important	3 - very important	2 - somewhat important	2 - somewhat important		ECOS, ITRC, NEWMOA	Having a scientific basis to revise future guidelines for sampling will be very helpful. We may be unnecessarily conservative.
15					3 - very important	1 - not very important	2 - somewhat important	1 - not very important			
16					3 - very important	2 - somewhat important	3 - very important	3 - very important			
17	New York Dept. Environmental Conservation, 2020. Guidelines for Sampling and Analysis of PFAS under NYSDECs Part 375 Remedial Programs.				3 - very important	1 - not very important	3 - very important	2 - somewhat important	Filters and equipment used for SPLP or porewater generation.	ES&T, Emerging Contaminants conference	
18	In Minnesota, we are using the MI 2018 guidance currently.	The MPCA is working with ORD on investigation procedures for sampling the SML and foam on surface waters. This may evolve into guidance in the future.	Project 1007 data sets; 3M Settlement, MPCA 2019-2020. These data are available for review and updates on the progress of the data are presented to the public over the course of the investigation.	rebecca.higgins@s	3 - very important	2 - somewhat important	3 - very important	3 - very important	PPE considerations should include personal safety products like bug spray, sunscreen and masks.	Youtube update videos sent via email and shown during webinars.	Keep up the good work!
19	NY DEC Guidance: https://www.dec.ny.gov/docs/remediation_hudson_pdf/pfassampanaly.pdf.	No	None		3 - very important	1 - not very important	3 - very important	2 - somewhat important		A referenceable document on the SERP/ESTCP website would be great, assume that is already planned.	
20		Ohio EPA PFAS Ground Water Sampling Guidance (michael.slattery@epa.ohio.gov)	PFAS: Dispelling Sampling Myths	Dave Kaminski - QE	3 - very important	2 - somewhat important	2 - somewhat important	2 - somewhat important			
21			ASTM 7979-19		3 - very important	2 - somewhat important	3 - very important	2 - somewhat important		ITRC webinars and fact sheets	

Question:	1	2	3		4					5	6
Response No.					Evaluating common materials/equipment that are in direct contact with the sample	Evaluating common materials/equipment that are not in direct contact with the sample	Evaluating different decontamination procedures	Evaluating PPEand technician-related precautions	Other (please specify below)		
22					3 - very important	2 - somewhat important	3 - very important	2 - somewhat important		A 1 or 2 pager science-based best practices newsletter - ultimately has to be rolled out to project managers in the field / journal, webinar, conferences will miss a large portion of audience	
23	Maine DEP: https://www1.maine.gov/dep/spills/topics/pfas/03222019_Sludge_Memorandum.pdf#page=3; NYSDEC:http://www.dec.ny.gov/docs/remediation_hudson_pdf/pfassampanaly.pdf; MassDEP 2019 document: https://www.mass.gov/doc/interim-guidance-on-sampling-and-analysis-for-pfas-at-disposal-sites-regulated under-the/download; MassDEP sampling video: https://youtu.be/zrwhwSI-R9M	No	PFAS in Sampling Products Paper:https://doi.org/10.1002/rem.21614	Elizabeth Denly; ed	3 - very important	1 - not very important	2 - somewhat important	2 - somewhat important		Remediation Journal, AEHS Soil, Sediment & Groundwater Magazine, AEHS Conferences (East & West), NEWMOA	
24					3 - very important	1 - not very important	3 - very important	1 - not very important			
25					3 - very important	3 - very important	2 - somewhat important	3 - very important		ITRC	Important question: Is there sufficient "risk" of significant sample contamination to support common guidance of not using PFAS-containing materials, even if not in direct contact with sample (e.g., treated jacket or boots)?
26	I do not have knowledge of any additional guidance documents on the subject.	The ITRC PFAS team will be updating their document over this year. Of course it is just doing things similar to what you are doing for this study to come up with standard sampling practices for PFAS.	None that I have		3 - very important	1 - not very important	2 - somewhat important	2 - somewhat important	From the samples that I have collected and my colleagues have collected, it would appear that standard precautions that are used on collecting non-PFAS samples are generally sufficient to prevent/reduce potential biases. Blank samples have remained PFAS free and sampling of wells outside of the PFAS plume have also been non-detect for PFAS. Making sure that nothing comes in contact with the sample and that the sampling equipment is PFAS-free are the essential elements.		
27	none	no			3 - very important	2 - somewhat important	3 - very important	3 - very important	wet ice versus blue ice	ITRC State engagement coordinators, USEPA regions as states meet with them regularly	
28					3 - very important	2 - somewhat important	2 - somewhat important	3 - very important		The SERDP/ESTCP webinars are a great venue. If we ever have conferences again, that would also be effective.	Will this evaluate where water samples should be collected - air/water interface? Depth where samples are normally collected (e.g., a specific depth or fracture)? How does purging a well affect PFAS concentrations?
29			Evaluating PFAS distribution in surface water, sediments and plants near landfills	Lucia Rodriguez-Fr	3 - very important	1 - not very important	3 - very important	2 - somewhat important		AGU and ACS meetings, AEESP meeting in 2021, GRC meeting in 2022, through the AEESP website/communications	I would be very interested in learning about the findings of this project.
30					3 - very important	1 - not very important	2 - somewhat important	1 - not very important	Evaluating the potential for loss of PFAS on the surface of composite sample equipment and tubing.		
31					3 - very important	1 - not very important	3 - very important	3 - very important			

APPENDIX B:
Summary of PFAS Sampling Guidance

Table B-1: Summary of Material Prohibitions in PFAS Sampling Guidance that are Consistent across Guidance Documents

Material	Prohibited (Y/N)	Guidance	Relevant Scientific Studies	Notes from Guidance Documents and Scientific Studies
Bentonite (various)	N	ME	Denly et al., 2019	
Excel Purity Paste	Y	ME		
TFW™ Multipurpose Thread sealant	Y	ME		
Vibra-Tite Thread Sealant	Y	ME		
Gasoils NT non-PTFE thread sealant	N	ME		
PVC liners (various)	N	CA (Gen)	Rodowa et al., 2020	Rodowa et al., 2020 demonstrated material had detectable total fluorine by PIGE. Guidance recommends using only under specific controls.
Vinyl end cap	N	ME	Rodowa et al., 2020	Rodowa et al., 2020 demonstrated material had detectable total fluorine by PIGE. Guidance recommends using only under specific controls.
Polyvinyl chloride (PVC) pipe	N	CA (Gen), WA	Denly et al., 2019	
Pump, bladder	N	MI, NH, WA		Evaluate on a case by case basis for gaskets, o-rings, etc.
Pump, peristaltic	N	ITRC, NH, WA		
Pump, inertia	N	MI		Certain types are acceptable (e.g. plastic or stainless steel).
Pump, submersible	N	MI, NH		Certain types are acceptable (e.g. Proactive Stainless Steel with PVC leads and Stainless Steel Geosub pumps).
Pump bladder, Teflon	Y	ITRC, CA (Gen), CA (DW), MI, ME, NAVFC, NH, WA		
Pump bladder, polyethylene	N	MI, NH, WA	Rodowa et al., 2020; Denly et al., 2019	
O-rings, Teflon	Y	ITRC, CA (Gen), CA (DW), MI, ME, NAVFC, NH, WA		
O-Rings, Viton	N	NH		Evaluate on a case by case basis.
Bailer, ethylene propylene (FEP)	Y	ITRC, CA (Gen), MI		
Bailer, polypropylene	N	ITRC, CA(Gen), MI, WA		
Bailer, PVC	N	ITRC, CA(Gen)		
Bailer, Teflon	Y	ITRC, CA (Gen), CA (DW), MI, ME, NAVFC, NH, WA		
Bailer, stainless steel	N	ITRC, CA (Gen), MI, ME, NH		
Bailer twine	N	MI	Denly et al., 2019	Denly et al., 2019 reported PFAS detections after leaching for 24 hours but did not specify material, so cotton or other PFAS-free material is recommended.
Bailer twine, Nylon	N	MI		
Tubing, PTFE lined	Y	ITRC, CA(Gen), CA(DW), MI, NH	Denly et al., 2019	
Tubing, silicone	N	ITRC, CA (Gen), FL, MI, ME, NAVFC, NH, WA	Denly et al., 2019	
HydraSleeve	N	WA		
Sleeves/liners/caps	N	FL, WA		Verify that they don't contain PFAS.
Sleeve/liner, acetate	N	CA (Gen), FL, MI, ME, NAVFC		
Polyvinyl chloride (PVC)	N	ITRC, CA (Gen), FL, MI, WA		
Filters, PTFE	Y	ITRC, CA(Gen), MI		
Filters, Nylon	Y	MI		
Filters, Glass	N	MI		
Soap, Decon 90™	Y	CA(Gen), MI, ME, NAVFC, NH, WA		
Brush	N	CA(Gen), MI, WA		
Water, deionized	N	ITRC, CA(Gen), MI, ME		Confirm PFAS-free.
Marker, Expo	Y	NAVFC		
Ballpoint pen (Various)	N	CA (Gen), CA (DW), FL, MI, ME, NAVFC, NH		
Labels, sampling (various)	N	CA (Gen), CA (DW), FL, ME	Rodowa et al., 2020; Denly et al., 2019	Guidelines vary, but all guidance has standard operating procedures.
Clipboards (aluminum or metal)	N	FL, MI, ME, NAVFC, NH		
Clipboards (cardboard)	N	MI		Guidance recommends verifying that coating is PFAS-free but this is likely unnecessary as long as clipboard does not come into contact with sample.
Clipboards (masonite)	N	MI, ME, NAVFC		
Clipboards (plastic)	Y	CA (Gen), ME, NH		
Clipboards (polypropylene)	N	CA(Gen), MI		
Paper, plain (various)	N	FL,MI, NAVFC, NH, WA		Guidance recommends verifying that coating is PFAS-free but this is likely unnecessary as long as clipboard does not come into contact with sample.
Paper, waterproof/treated	Y	ITRC, CA (Gen), CA (DW), FL, ME, NH, WA	Rodowa et al., 2020	Rodowa et al., 2020 results do not support prohibiting use in field.
Post-it notes, adhesive section	Y	CA (Gen), CA (DW), FL, ME, NAVFC, NH, WA	Rodowa et al., 2020; Denly et al., 2019	Guidance not consistent with scientifically substantiated evidence.
Post-it notes, packaging	Y	CA (Gen), CA (DW), ME, NAVFC, NH, WA		

Table B-1: Summary of Material Prohibitions in PFAS Sampling Guidance that are Consistent across Guidance Documents

Material	Prohibited (Y/N)	Guidance	Relevant Scientific Studies	Notes from Guidance Documents and Scientific Studies
Post-it notes, paper area	Y	CA (Gen), CA (DW), FL, ME, NAVFC, NH, WA	Rodowa et al., 2020; Denly et al., 2019	Guidance not consistent with scientifically substantiated evidence.
Blue ice	Y	CA (Gen), CA (DW), ME, NAVFC, NH, WA		
Cryopack ice blanket	Y	CA (DW), NH, WA		
Cryopack ice pack	Y	CA (Gen), CA (DW), NH, WA		
Cold Pack	Y	CA (DW), ME	Rodowa et al., 2020	Guidance not consistent with scientifically substantiated evidence.
Freezer Pack	Y	CA (DW), ME	Rodowa et al., 2020	Guidance not consistent with scientifically substantiated evidence.
Loose Ice	N	CA(DW), FL, MI, ME, NAVFC		Must be from PFAS-free water.
Tape, packing	N	CA(DW)		
Bubble wrap	N	MI	Denly et al., 2019	
Clear plastic bags (various)	N	CA(DW), MI	Rodowa et al., 2020	Guidelines vary, but all guidance has standard operating procedures.
Re-sealable plastic storage bags	N	CA(DW), ME	Denly et al., 2019	Guidelines vary, but all guidance has standard operating procedures.
Boot covers (uncoated Tyvek)	Y	CA(DW), NAVFC		
Gore-Tex clothing	Y	ITRC, CA (Gen), CA (DW), MI, ME, NAVFC, NH, WA		
Dryer sheets (various)	Y	CA (Gen)	Rodowa et al., 2020	Guidance not consistent with scientifically substantiated evidence.
Fabric softener (various)	Y	CA (Gen), CA (DW), FL, MI, ME, NH		
Fabric treatment/cleaners/sprays (various)	Y	CA (Gen), CA (DW), MI, ME, WA		
Rain gear, LDPE, vinyl, PVC	N	WA		
Rain gear, Nylon	N	CA (Gen)		
Rain gear, wax-coated	N	MI, NAVFC, NH		
HDPE suits	N	ITRC, CA (Gen), WA		
Nitrile gloves (various)	N	CA (Gen), CA (DW), FL, MI, ME, NAVFC, WA	Rodowa et al., 2020	Rodowa et al., 2020 results do not support prohibiting use in field.
Water or dirt-resistant gloves	Y	ME, NAVFC, WA		
Safety glasses	N	CA (Gen), FL		Review safety data sheets to determine if material contains PFAS.
Tyvek (coated)	Y	ITRC, CA (Gen), CA (DW), NAVFC, WA		
Acetate	N	CA (Gen), FL, MI, ME, NAVFC		
Aluminum foil - Durable	Y	ME, WA	Rodowa et al., 2020; Denly et al., 2019	Rodowa et al., 2020 results do not support prohibiting use in field.
Aluminum foil - Non-stick	Y	ME, WA	Rodowa et al., 2020; Denly et al., 2019	Rodowa et al., 2020 results do not support prohibiting use in field.
Aluminum foil - Reynolds	Y	ME, WA	Rodowa et al., 2020; Denly et al., 2019	Rodowa et al., 2020 results do not support prohibiting use in field.
Cotton	N	CA (Gen)		
Ethylene propylene (FEP)	Y	ITRC, CA (Gen), MI		
Ethylene tetrafluoroethylene (ETFE)	Y	ITRC, CA (Gen), CA (DW), MI		
Gore-TEX	Y	ITRC, CA (DW), ME, WA		
HDPE tubing (various)	N	ITRC, CA (Gen), FL, MI, ME, NAVFC, NH, WA	Denly et al., 2019	Guidance not consistent with scientifically substantiated evidence.
Hostaflon	Y	CA (Gen), MI		
Neoprene	N	CA (Gen), MI		
Polychlorotrifluoroethylene (PCTFE)	Y	CA (Gen), CA (DW), MI		
Polyfluoroalkyl phosphate esters	Y	ITRC, CA (DW), MI		
Polypropylene (PP)	N	ITRC, CA (Gen), CA (DW), FL, MI, NAVFC, WA		
Polyurethane (PU)	N	ITRC, CA (Gen), MI, NAVFC, NH		
Polyvinylidene fluoride (PVDF)	Y	ITRC, CA (Gen), MI		
PTFE tape (various)	Y	ITRC, CA (Gen), MI, NH	Rodowa et al., 2020	Rodowa et al., 2020 results indicate that only extreme field sampling scenarios would results in detectable sample bias from PTFE tape.
PTFE tubing	Y	ITRC, CA (Gen), MI, NH	Denly et al., 2019	Some varieties had no detectable PFAS, so using an equipment blank would be sufficient.
Rubber	N	ITRC, CA (Gen), MI, NH		
Stainless steel	N	ITRC, CA (Gen), FL, MI, ME		
Stain-resistant materials	Y	CA (DW), FL, ME, WA		
Skinny Teflon Tape	Y	ITRC, CA (Gen), CA (DW), MI, ME, NAVFC, NH, WA		
Teflon Tape	Y	ITRC, CA (Gen), CA (DW), MI, ME, NAVFC, NH, WA		
Teflon	Y	ITRC, CA (Gen), CA (DW), FL, MI, ME, NAVFC, NH, WA		
Vinyl	N	CA (DW)	Rodowa et al., 2020	
Wax Coatings	N	CA (Gen), NH		

Table B-2: Summary of Material Prohibitions in PFAS Sampling Guidancethat lack Consensus across Guidance Documents

Material	Guidance Discrepancies	Relevant Scientific Studies	Notes from Guidance Documents and Scientific Studies
Pump bladder, LDPE	ITRC, CA (Gen) v NH, Gov't of W Australia		
Tubing, LDPE	ITRC, CA (Gen) v MI, NH	Denly et al., 2019	Scientifically demonstrated to leach PFAS in 24 hours of submersion
Soap, Alconox®	CA (Gen), CA(DW), MI, ME, NAVFC, NH v Gov't of W Australia		
Soap, Liquinox®	CA (Gen), CA(DW), MI, ME, NAVFC, NH v Gov't of W Australia		
Soap, Luminox®	FL v Gov't of W Australia		
Soap, Citranox	CA (Gen), MI, FL v Gov't of W Australia		
Markers, permanent (other) - Sharpie	CA (Gen), CA (DW), FL, NAVFC v MI, ME, NH	Rodowa et al., 2020	Scientifically shown that some permanent marker ink contains PFAS
Markers, permanent (Fine and Ultra-Fine) - Sharpie	CA (Gen), CA (DW), FL, NAVFC v MI, ME, NH	Rodowa et al., 2020	Scientifically shown that some permanent marker ink contains PFAS
Markers, permanent (various) - Non-Sharpie	CA (Gen), CA(DW), FL, NAVFC, NH v MI	Rodowa et al., 2020	Scientifically shown that some permanent marker ink contains PFAS
Waterproof field book cover	ITRC, CA (Gen), CA (DW), ME, NH, Gov't of W Australia v MI, FL		
Waterproof field book pages	ITRC, CA (Gen), CA (DW), ME, NH, Gov't of W Australia v MI, FL	Rodowa et al., 2020	Scientifically shown that water-proof paper contains detectable total fluorine
Plastic bagged ice	CA(DW), NH v MI, Gov't of W Australia		
Tyvek (uncoated)	ITRC, CA (Gen), MI, NH v NAVFC, Gov't of W Australia		
Glass	FL v MI, Gov't of W Australia		
Plastic binders	ME	Rodowa et al., 2020	Scientifically shown to not contain PFAS
Spiral hardcover notebooks	ME		
Latex gloves	CA (gen)		

APPENDIX C:

Estimates of PFAS Concentrations Resultingfrom Hypothetical Cross-Contamination Scenarios

Scenarios Describing Quantities of Substances Containing PFAS Needed to Generate Detectable PFOA in PFOA Samples through Cross-Contamination

Scenario 1

PFAS have been detected in cosmetics. For example, PFOA was detected at concentrations up to 2,160 ng/g. [1] Therefore, assuming the detection limit in a sample is greater than 2 ng/L, it would take up to 0.23 mg of makeup (the equivalent weight of 6 eyelashes) of makeup containing PFASto enter a 250 mL sample bottle in order to be detected.

Scenario 2

Concentrations of PFOA up to 5,700 ng/g have been detected in sunscreen.[2] Therefore, at least 0.088 mg of sunscreen, i.e., 1 to 2 drops, of pure sunscreen would need to enter a 250 mL samplein order to result in a detectable concentration of PFOA in the sample, assuming the detection limitin the sample is greater than 2 ng/L.

Scenario 3A:

Rain has been documented to contain PFAS with samples up to 85 ng/L PFOA.[3] If it is raining during sample collection. Assuming a peak rainfall rate of 0.2 inches of rain per hour and a 250- mL sample container with a diameter of 2.5 inches, a sample container would need to be left openfor over 20 minutes in order to detect 2 ng/L of PFOA. Concentrations in rainfall in other areas were less than 6 ng/L, and would therefore need to be open during peak rainfall for much longer to detect 2 ng/L.

Scenario 3B:

Rainfall could have a significant impact on detected PFAS concentrations at sites near active PFASmanufacturing facilities. At a facility which manufactured Gen X, prior to the installation of air filters, Gen X concentrations up to 630 ng/L were detected in rainwater[4]. At these high concentrations, the same sample container described in Scenario 3A that is left open for just 3 minutes for sampling during peak rainfall of 0.2 inches per hour could collect enough rain to detect2 ng/L of Gen X.

Scenario 4:

Volatilization of PFAS products could theoretically provide a potential airborne exposure pathway for PFAS to enter the headspace of a sample bottle. Neutral PFAS that are volatile or semi-volatile have been measured in indoor air environments, as a result of direct outgassing from consumer products or from dust. One study measured concentrations in indoor air up to 1 to 10 ng/m^3 (6:2 FTOH, 8:2 FTOH).[5] Assuming each 250-mL sample bottle is half-full and has aheadspace in the sample bottle that has been impacted with volatile PFAS due to exposure to consumer products during sample collection, outdoor air concentrations would need to be 400times greater than this in order to result in detectable (2 ng/L) concentrations of fluorotelomer alcohols.

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[1] Ministry of Environment and Food of Denmark, 2018. Risk assessment of fluorinated substances in cosmeticproducts. October. ISBN: 978-87-93710-94-8.

[2] Ministry of Environment and Food of Denmark, 2018. Risk assessment of fluorinated substances in cosmeticproducts. October. ISBN: 978-87-93710-94-8.

[3] Scott et al., 2006. Poly and perfluorinated carboxylates in North American precipitation. Environ. Sci. Technol. 40(23): 7167-7174. https://doi.org/10.1021/es061403n.

[4] GenX found in rainwater near Chemours plant, likely source of groundwater contamination. The ProgressivePulse, NC Policy Watch. By Lisa Sorg. Feb 23.

[5] Winkens et al., 2017. Perfluoroalkyl acids and their precursors in indoor air sampled in children's bedrooms.Environmental Pollution 222: 423-432. March. https://doi.org/10.1016/j.envpol.2016.12.010.

APPENDIX D:
Summaries of Equipment Blank Datasets

Table D-1: Equipment Blank Results for PFAS at Michigan Sites

Facility	Description	Category	Sample Year	Total PFAS	PFOA+PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFHxDA	PFODA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	FOSA	4:2 FTSA	6:2 FTSA	8:2 FTSA	EtFOSAA	MeFOSAA
Site 1	Hand Auger	Drilling Equipment	2019														---	---													
Site 1	Hand Auger	Drilling Equipment	2019														---	---													
Site 1	Steam Cleaner	Decon Equipment	2019														---	---													
Site 1	Steam Cleaner	Decon Equipment	2019														---	---													
Site 1	Truck Water Tank	Water Tote/Tank	2019														---	---													
Site 1	Truck Water Tank	Water Tote/Tank	2019														---	---													
Site 1	VAS Screen	Sample Equipment - Aqueous	2019														---	---													
Site 1	VAS Screen	Sample Equipment - Aqueous	2019														---	---													
Site 2	Decon Water	Decon Water Source	2019	**1.5**				**1.5**									---	---													
Site 2	Decon Water	Decon Water Source	2019														---	---													
Site 2	Sampler	Sample Equipment - Soil	2019														---	---													
Site 2	Shoe	Drilling Equipment	2019														---	---													
Site 3	Sub Pump	Sample Equipment - Aqueous	2019														---	---													
Site 3	Sub Pump	Sample Equipment - Aqueous	2019														---	---													
Site 3	Sub Pump	Sample Equipment - Aqueous	2019														---	---													
Site 3	Sub Pump	Sample Equipment - Aqueous	2019														---	---													
Site 3	Sub Pump	Sample Equipment - Aqueous	2019														---	---													
Site 3	Sub Pump	Sample Equipment - Aqueous	2019														---	---													
Site 4	Hefty Garbage Bag	Field Supplies	2018														---	---													
Site 5	NU-WELL 100	Well Treatment Additive	2018														---	---													
Site 5	Stainless Steel Dipper	Sample Equipment - Aqueous	2019														---	---													
Site 6	Garden Shears	Field Supplies	2019														---	---													
Site 7	Hefty Garbage Bag	Field Supplies	2018														---	---													
Site 7	Putty Scraper	Field Supplies	2019														---	---													
Site 7	Shovel	Field Supplies	2019														---	---													
Site 7	Soil Sampler	Sample Equipment - Soil	2019														---	---													
Site 7	Stainless Steel Dipper	Sample Equipment - Aqueous	2019														---	---													
Site 7	SW Sampler	Sample Equipment - Aqueous	2019														---	---													
Site 7	Water tote	Water Tote/Tank	2019														---	---													
Site 7	Water tote	Water Tote/Tank	2019														---	---													
Site 7	Water tote	Water Tote/Tank	2019														---	---													
Site 8	Bladder pump	Sample Equipment - Aqueous	2019														---	---													
Site 8	Macro Barrel	Water Tote/Tank	2019														---	---													
Site 9	Bladder pump	Sample Equipment - Aqueous	2019														---	---													
Site 9	Bladder pump	Sample Equipment - Aqueous	2019														---	---													
Site 9	Bladder pump	Sample Equipment - Aqueous	2019														---	---													
Site 9	Bladder pump	Sample Equipment - Aqueous	2019														---	---													
Site 9	Bladder pump	Sample Equipment - Aqueous	2019														---	---													
Site 9	Bladder Pump	Sample Equipment - Aqueous	2018														---	---									---			---	---
Site 9	Bladder Pump	Sample Equipment - Aqueous	2018	**0.5**													---	---			**0.5**										
Site 9	Bladder Pump	Sample Equipment - Aqueous	2018														---	---													
Site 9	Bladder Pump	Sample Equipment - Aqueous	2019														---	---													
Site 9	Bladder Pump	Sample Equipment - Aqueous	2019														---	---													
Site 9	Blade	Field Supplies	2019														---	---									---			---	---
Site 9	Cloth	Sample Equipment - Aqueous	2018														---	---													
Site 9	Cutter	Drilling Equipment	2018														---	---									---			---	---
Site 9	Cutter	Drilling Equipment	2018														---	---									---			---	---
Site 9	Cutting Shoe	Drilling Equipment	2019														---	---									---			---	---
Site 9	Drill Rig	Drilling Equipment	2019														---	---													
Site 9	Drilling Water	Decon Water Source	2018	**2.1**	**2.1**					**2.1**							---	---									---			---	---
Site 9	HDPE Bailer	Sample Equipment - Aqueous	2019														---	---													
Site 9	Monsoon Pump	Sample Equipment - Aqueous	2018														---	---													
Site 9	Monsoon Pump	Sample Equipment - Aqueous	2018														---	---													
Site 9	Sampling Screen	Sample Equipment - Aqueous	2018														---	---													
Site 9	Sleeve	Sample Equipment - Soil	2018	**9.7**	**9.7**												---	---					**9.7**				---			---	---
Site 9	Spoon	Sample Equipment - Soil	2018														---	---									---			---	---
Site 9	Spoon	Sample Equipment - Soil	2019														---	---									---			---	---
Site 9	Spoon	Sample Equipment - Soil	2018														---	---									---			---	---
Site 9	Spoon	Sample Equipment - Soil	2018														---	---									---			---	---
Site 9	Spoon Shoe	Sample Equipment - Soil	2018														---	---									---			---	---
Site 9	Spoon Shoe	Sample Equipment - Soil	2018														---	---									---			---	---
Site 9	Stainless Steel Bailer	Sample Equipment - Aqueous	2019														---	---													
Site 9	Stainless Steel Bailer	Sample Equipment - Aqueous	2019														---	---													
Site 9	Stainless Steel Bailer	Sample Equipment - Aqueous	2019														---	---													
Site 9	Stainless Steel Bailer	Sample Equipment - Aqueous	2018														---	---													
Site 9	Stainless Steel Dipper	Sample Equipment - Aqueous	2018	**9.1**													---	---										**9.1**			
Site 9	Water Bailer	Sample Equipment - Aqueous	2018														---	---													
Site 9	Water Level Meter	Sample Equipment - Aqueous	2018														---	---									---			---	---
Site 9	Water Level Meter	Sample Equipment - Aqueous	2019	**5.1**	**5.1**												---	---					**5.1**				---			---	---
Site 9	Water Level Meter	Sample Equipment - Aqueous	2019														---	---									---			---	---
Site 9	Water Level Meter	Sample Equipment - Aqueous	2018														---	---									---			---	---
Site 9	Water Level Meter	Sample Equipment - Aqueous	2019														---	---									---			---	---
Site 9	Water Level Meter	Sample Equipment - Aqueous	2019														---	---									---			---	---
Site 9	Water Level Meter	Sample Equipment - Aqueous	2019														---	---									---			---	---
Site 9	Water Level Meter	Sample Equipment - Aqueous	2018														---	---													
Site 9	Water Tank	Water Tote/Tank	2018														---	---													
Site 9	Water Tote	Water Tote/Tank	2019														---	---													
Site 9	Water Tote	Water Tote/Tank	2019														---	---													
Site 10	Water Tank	Water Tote/Tank	2019														---	---													
Site 10	Water Tank	Water Tote/Tank	2019														---	---													
Site 10	Water Tank	Water Tote/Tank	2019														---	---													
Site 10	Water Tank	Water Tote/Tank	2019														---	---													

Table D-1: Equipment Blank Results for PFAS at Michigan Sites

Facility	Description	Category	Sample Year	Total PFAS	PFOA+PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFHxDA	PFODA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	FOSA	4:2 FTSA	6:2 FTSA	8:2 FTSA	EtFOSAA	MeFOSAA
Site 11	Bailer - (checked COC)	Sample Equipment - Aqueous	2019														---	---													
Site 11	Bladder Pump	Sample Equipment - Aqueous	2018														---	---													
Site 11	Bladder Pump	Sample Equipment - Aqueous	2019														---	---													
Site 11	Bladder Pump	Sample Equipment - Aqueous	2019														---	---													
Site 11	Bulb Planter	Sample Equipment - Soil	2019														---	---													
Site 11	Drill Stem	Drilling Equipment	2018	**8.5**		**8.5**											---	---													
Site 11	Drill Stem	Drilling Equipment	2018														---	---													
Site 11	Hand Shears	Field Supplies	2019														---	---													
Site 11	Liner Tube	Sample Equipment - Soil	2018														---	---													
Site 11	Lopper	Sample Equipment-Crops	2019														---	---													
Site 11	Plastic Tube - SIL	Sample Equipment - Soil	2019														---	---													
Site 11	Plastic Tube - SIL	Sample Equipment - Soil	2019														---	---													
Site 11	Stainless Steel Dipper	Sample Equipment - Aqueous	2019														---	---													
Site 11	Steamer / power washer	Decon Water Source	2018														---	---													
Site 11	Water tote	Water Tote/Tank	2018														---	---													
Site 11	Water tote	Water Tote/Tank	2018														---	---													
Site 11	Water tote	Water Tote/Tank	2018														---	---													
Site 13	Control Water	Decon Water Source	2018														---	---		---				---			---			---	---
Site 13	Core Tube	Drilling Equipment	2018														---	---													
Site 13	Dam Stilling Well	Sample Equipment - Aqueous	2018	**1.0**													---	---	**1.0**												
Site 13	Drill Rig Water	Water Tote/Tank	2017	**3.4**	**2.1**	**0.8**								**0.6**						---			**2.1**	---			---			---	---
Site 13	Drill Stem	Drilling Equipment	2018														---	---													
Site 13	Hydrant Water Source	Decon Water Source	2018														---	---													
Site 13	LDPE EB	Field Supplies	2018														---	---													
Site 13	Level Troll	GW Monitoring	2018	**73.0**	**70.5**				**2.5**	**70.5**							---	---		---				---			---			---	---
Site 13	Masterflex	Sample Tubing	2018														---	---													
Site 13	Pipe Dope	Drilling Supplies	2018														---	---													
Site 13	Pipe Dope	Drilling Supplies	2018														---	---													
Site 13	Power Snips	Field Supplies	2018														---	---													
Site 13	Power Washer	Decon Equipment	2018														---	---													
Site 13	Rugged Troll	GW Monitoring	2018	**23.7**	**14.5**	**0.8**				**14.5**							---	---	**8.4**	---				---			---			---	---
Site 13	Suspension Wire	Field Supplies	2018														---	---		---				---			---			---	---
Site 13	Tubing	Sample Tubing	2017																	---				---			---			---	---
Site 13	Water Level Meter	Field Supplies	2018	**0.6**	**0.6**					**0.6**										---				---			---			---	---
Site 13	Water Level Meter	Field Supplies	2018	**0.7**						**0.5**							**0.2**			---				---			---			---	---
Site 13	Water Tote	Water Tote/Tank	2017																	---				---			---			---	---
Site 13	Water Tote	Water Tote/Tank	2018														---	---													
Site 13	Water Tote	Water Tote/Tank	2018														---	---													
Site 13	Water Tote	Water Tote/Tank	2018														---	---													

Table D-2: Equipment Blank Detections in US Navy Facility Samples

Base Where Sample Collected	Sample Date	Associated EB collection	PFOS (ng/L)	PFOA (ng/L)	PFHxS (ng/L)	PFBS (ng/L)	MeFOSAA (ng/L)
PtMugu	9/26/2018	Stainless steel sampling bowl	**10.6**	ND	ND	ND	ND
Port Hueneme	10/2/2018	Geotech Bonded polyethylene tubing	0.24 J	ND	ND	ND	ND
Whidbey Island	12/5/2017	Stainless steel bailer	ND	1.02 JB	ND	ND	ND
Whidbey Island	12/5/2017	Geotech GEO1 Portable PTFE bladder pump	ND	1.9 JB	ND	ND	ND
Whidbey Island	12/6/2017	Geotech GEO1 Portable PTFE bladder pump	ND	1.52 JB	ND	ND	ND
Whidbey Island	12/7/2017	Geotech Bonded polyethylene tubing	ND	2.33 JB	1.03 JB	ND	ND
Whidbey Island	12/7/2017	Geotech GEO1 Portable PTFE bladder pump	ND	2.36 JB	1.18 JB	ND	ND
Whidbey Island	12/8/2017	Geotech GEO1 Portable PTFE bladder pump	ND	1.28 JB	ND	ND	ND
Whidbey Island	12/11/2017	Geotech GEO1 Portable PTFE bladder pump	ND	1.6 JB	ND	ND	**0.975**
Whidbey Island	12/12/2017	Geotech GEO1 Portable PTFE bladder pump	ND	1.55 JB	ND	ND	ND
Whidbey Island	2/20/2018	Geotech GEO1 Portable PTFE bladder pump	ND	1.32 J	ND	ND	ND
Whidbey Island	2/21/2018	Geotech GEO1 Portable PTFE bladder pump	ND	0.931 J	ND	ND	ND
Whidbey Island	1/23/2018	Stainless steel bowls and spoons	ND	0.898 J	ND	ND	ND
Whidbey Island	1/25/2018	Stainless steel bowls and spoons	ND	ND	1.05 J	ND	ND
Whidbey Island	2/17/2018	Geotech Series II Geopump	1.95 J	ND	ND	ND	ND
Whidbey Island	6/25/2018	Grundfos RediFlo 2 impeller pump	**26.3**	ND	ND	5.68 J	ND
Oceana	12/23/2015	Geotech Bonded polyethylene tubing	ND	ND	1.2 J	ND	ND

Cherry Point	8/7/2019	Proactive Monsoon Stainless Steel pump	ND	0.59 J	**1.8**	ND	ND
NAPR	5/22/2019	Sterileware scoop and acetate liner	0.44 J	ND	ND	ND	ND
NAPR	6/26/2019	Geotech Bonded polyethylene tubing	0.16 J	ND	ND	ND	ND
NAPR	6/26/2019	Sterileware scoop andacetate liner	0.19 J	ND	ND	ND	ND