MICHIGAN DEPARTMENT OF
ENVIRONMENT, GREAT LAKES, AND ENERGY

# GENERAL
# PFAS SAMPLING GUIDANCE

This document contains an introduction to PFAS, biosecurity recommendations, and general recommendations to decrease the possibility of cross-contamination.

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## Acronyms

Acronyms used throughout the **General PFAS Sampling Guidance** document and/or each sampling guidance are as follows:

| | |
|---|---|
| **AFFF** | Aqueous Film Forming Foam |
| **CAS Number** | Chemical Abstracts Service Number |
| **COC** | Chain of Custody |
| **DEPA** | Danish Environmental Protection Agency (Denmark) |
| **EINECS** | European List of Notified Chemical Substances (European Union) |
| **ENCS** | Existing and New Chemical Substances Inventory (Japan) |
| **ETFE** | Ethylene-tetrafluoroethylene |
| **FCMP** | Fish Contaminant Monitoring Program |
| **FCSV** | Fish Consumption Screening Values |
| **FDA** | Food and Drug Administration (United States of America) |
| **FEP** | Fluorinated Ethylene Propylene |
| **HASP** | Health and Safety Plan |
| **HDPE** | High-density Polyethylene |
| **IECSC** | Inventory of Existing Chemical Substances Produced or Imported in China |
| **ITRC** | Interstate Technology & Regulatory Council |
| **KECI** | Korea Existing Chemicals Inventory (South Korea) |
| **KEMI** | Swedish Chemical Agency (Sweden) |
| **LDPE** | Low-density polyethylene |
| **LHA** | Lifetime Health Advisory (United States Environmental Protection Agency) |
| **EGLE** | Michigan Department of Environment, Great Lakes, and Energy |
| **MDHHS** | Michigan Department of Health and Human Services |
| **MPART** | Michigan PFAS Action Response Team |
| **MSDS** | Material Safety Data Sheet (former reference) |
| **ng/L** | Nanograms per liter |
| **NZIoC** | New Zealand Inventory of Chemicals (New Zealand) |
| **PCPs** | Personal Care Products |
| **PID** | Photoionization Detector |
| **PFAA** | Perfluoroalkyl Acids |

| | |
|---|---|
| **PFAS** | Per- and Polyfluoroalkyl Substances |
| **PFC** | Polyfluorocarbons |
| **PFCA** | Perfluoroalkyl Carboxylic Acids |
| **PFOA** | Perfluorooctanoic Acid |
| **PFOS** | Perfluorooctanesulfonic Acid |
| **PFPE** | Perfluoropolyethers |
| **PFSA** | Perfluoroalkyl Sulfonic Acids |
| **PICCS** | Philippine Inventory of Chemicals and Chemical Substances (Philippines) |
| **ppb** | Parts per Billion |
| **PPE** | Personal Protection Equipment |
| **ppt** | Parts per Trillion |
| **PTFE** | Polytetrafluoroethylene |
| **PVC** | Polyvinyl Chloride |
| **PVDF** | Polyvinylidene Fluoride |
| **PVF** | Polyvinyl Fluoride |
| **QA/QC** | Quality Assurance/Quality Control |
| **QAPP** | Quality Assurance Project Plan |
| **OECD** | Organization for Economic Cooperation and Development |
| **SDS** | Safety Data Sheet |
| **SWAS** | Surface Water Assessment Section (EGLE) |
| **TSCA** | Toxic Substances Control Act (United States) |
| **(US)EPA** | United States Environmental Protection Agency |
| **UV** | Ultraviolet |
| **VOC** | Volatile Organic Compounds |
| **WRD** | Water Resources Division (EGLE) |

## Disclaimer

The Michigan Department of Environment, Great Lakes, and Energy (EGLE) intends to update the information contained within this PFAS Sampling Guidance document as new information becomes available. The user of this PFAS Sampling Guidance is encouraged to visit the Michigan PFAS Action Response Team webpage (Michigan.gov/PFASresponse) to access the current version of this document.

## 1. Introduction

Per- and polyfluoroalkyl Substances (PFAS) are a human-made class of chemicals considered **emerging contaminants**. The term PFAS is attributed to a large class of fluorinated chemicals composed of many families that have vastly different physical and chemical properties (Buck et al. 2011, Wang et al. 2017). According to the Centers for Disease Control (CDC), over 9,000 PFAS have been identified (ATSDR, 2021; CDC, 2022). The number of compounds continuously changes, as some PFAS are no longer produced due to regulatory and voluntary actions, while new ones are created as alternatives. The carbon-fluorine bond in PFAS is one of the strongest bonds in nature; they are tough to break and resistant to thermal, chemical, and biological degradation.

**Note: Emerging Contaminants** are chemicals and materials in the environment and present real or potential human health or environmental risks and either

- Do not have peer-reviewed human health standards

  or:

- Standards/regulations are evolving due to new science, new laboratory analytical capabilities, and new knowledge about the chemicals

Due to their unique chemical properties, various PFAS can lower surface tension (act as surfactants), are oil-repelling (oleophobic), and are water-repelling (hydrophobic). Yet, many PFAS with certain functional groups are also relatively water-soluble. They have been used extensively in many industries worldwide for a wide variety of applications. PFAS were first invented in the late 1930s, developed commercially in the 1940s, and started to be more widely used in consumer products from the 1950s as non-stick coatings. Due to their unique chemical properties, PFAS production increased as these chemicals were incorporated into components of inks, varnishes, waxes, firefighting foams, metal plating, cleaning solutions, coating formulations, lubricants, water and oil repellents, paper, and textiles (Paul et al. 2009). Examples of industries using PFAS include automotive, aviation, aerospace and defense, biocides, cable and wiring, construction, electronics, energy, firefighting, food processing, household products, oil and mining production, metal plating, medical articles, paper and cardboard, semiconductors, textiles, leather goods, and apparel (OECD 2013, UNEP 2013). The presence of PFAS in these materials is a potential source of environmental concern.

The presence of PFAS in so many consumer products and commercial materials, combined with low laboratory detection limits (nanograms per liter (ng/L) or parts per trillion (ppt)), has resulted in concerns of potential cross-contamination occurring during the sampling of various environmental matrices. EGLE has promulgated Residential and Nonresidential Drinking Water Criteria under Part 201 for seven PFAS, including perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), perfluorononanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS), perfluorohexanoic acid (PFHxA), perfluorobutane sulfonic acid (PFBS), and hexafluoropropylene oxide dimer acid (HFPO-DA, also known as GenX). EGLE has promulgated Groundwater Surface Water Interface Criteria (GSI) for groundwater under Part 201. A summary of these Part 201 cleanup criteria is provided in the table below and can be found on EGLE's website.

| PFAS | Residential Drinking Water Criteria[1] | Non-residential Drinking Water Criteria[1] | Groundwater Surface Water Interface Criteria[1] |
|---|---|---|---|
| PFOS | 16 | 16 | 12 |
| PFOA | 8 | 8 | 170 |
| PFNA | 6 | 6 | 30 |
| PFHxS | 51 | 51 | 210 |
| PFHxA | 400,000 | 400,000 | NA |
| PFBS | 420 | 420 | 670,000 |
| HFPO-DA | 370 | 370 | NA |

[1] Units are in nanograms per liter (ng/L) or parts per trillion (ppt); NA = a criterion or value is not available.

The Michigan Rule 57 Water Quality Value (WQV) criteria were developed to protect humans, wildlife, and aquatic life. Potentially complete surface water exposure pathways associated with all Sites and corresponding Rule 57 WQV are:

| PFAS | Human Noncancer Value (nondrinking water source) | Human Noncancer Value (drinking water source) | Final Chronic Value | Aquatic Maximum Value | Final Acute Value |
|---|---|---|---|---|---|
| PFOS[1] | 12 | 11 | 140,000 | 780,000 | 1,600,000 |
| PFOA[1] | 170 | 66 | 880,000 | 7,700,000 | 15,000,000 |
| PFBS | 670,000 | 8,300 | 24,000,000 | 120,000,000 | 240,000,000 |
| PFHxS | 210 | 59 | NA | NA | NA |
| PFNA | 30 | 19 | NA | NA | NA |

[1] Units are in nanograms per liter (ng/L) or parts per trillion (ppt); NA = a criterion or value is not available.

## 2. Purpose and Objectives

The purpose of this document is to provide guidance and information to staff who will:

- Collect or handle PFAS environmental samples.
- Perform subsurface activities such as soil borings, well installation, or well abandonment at PFAS sites.

**This document is intended to supplement the EGLE media-specific PFAS sampling guidance documents and is a resource for PFAS sampling.**

**The objectives of this document are as follows:**

- Provide guidance on avoiding PFAS cross-contamination during sampling.
- Improve sampling consistency and data quality.
- Provide guidance to EGLE staff and contractors.

Because PFAS are emerging contaminants and information about their use in various materials is still not readily available, EGLE will update this document as new information becomes available.

**NOTE:** This guidance does not include specific information for sampling environmental media and should not be used to replace specific sampling guidance documents required for use by EGLE staff.

## 3. Farm Biosecurity

In the event PFAS sampling occurs on or near a farm, staff need to follow the requirements in this document when conducting sample collection to reduce the likelihood of transporting animal diseases.

### 3.1 Scheduling

To avoid cross-contamination from previous sampling locations, it is preferable that staff visit only one farm in a day.

### 3.2 Before Sampling

Staff should review Section 4.2.4. Field Clothing and Personal Protective Equipment (PPE) before going into the field.

Staff must have a clean vehicle, clothing, and boots to visit the sampling location. Before arriving at the farm, staff should call the farm owner to indicate they will be arriving shortly and ask if there are any additional biosecurity requirements for their farm. Once at the farm, staff should park away from any animals and barns, preferably in a designated visitor area or on concrete.

Immediately before exiting the vehicle, place disposable PFAS-free boot covers over the boots. (***NOTE***: *Disposable boot covers can be slippery, especially in icy/snowy conditions.*)

### 3.3 While Sampling

Staff should not approach animal areas unless necessary for testing. If access to an animal area is needed, farm personnel should always accompany staff.

### 3.4 After Sampling

Dispose of used disposable boot covers at the facility if possible; otherwise, place them in a plastic bag, seal them, and place them in the vehicle trunk to dispose of properly later.

## 4. General PFAS Sampling

The following sections discuss technical issues such as the need to use PFAS-free water, information about PFAS-free clothing and PPE, and laboratory issues that should be considered when sampling for PFAS.

### 4.1 Sampling Objectives

Before conducting any PFAS sampling, it is recommended that a project-specific Quality Assurance Project Plan (QAPP) should be developed. The QAPP must meet EGLE's policy and should include the analyte list, method of analysis, environmental matrices, and reporting limits based on the project objectives. All of these considerations will be discussed in more detail in this guidance document.

### 4.2 PFAS Cross-Contamination Potential Sources

Potential sources of PFAS cross-contamination in the typical sampling environment include water used during drilling or decontamination, materials used within the sampling environment, sampling equipment, field clothing and personal protective equipment (PPE), sun and biological protection products, personal hygiene, and personal care products (PCPs), food packaging, and the environment itself.

Previous sampling guidance documents and literature to date did not evaluate how the use of sampling materials in the field, when used in accordance with industry-standard sampling procedures, may introduce the potential for PFAS cross-contamination during sampling. Upon further review and evaluation in 2021, two scenarios where cross-contamination during sampling may occur are: direct contact with the sampling supplies and equipment and incidental contamination while a sample container is open. Contact with sampling supplies or equipment is the most likely pathway for potential cross-contamination. Materials associated with sampling that have the potential for PFAS cross-contamination have been divided into two main categories and four groups:

- **Category 1:** Items and materials that are *expected to come in direct contact* with the sample. These should not be used when sampling unless it is known or can be shown that they are PFAS-free by collecting an equipment blank (EB) sample before use.
- **Category 2:** Items and materials that are *not expected to come in direct contact* with

the sample. An EB is recommended only for the items and materials that may still have a very low possibility of producing cross-contamination only in unique sampling or weather conditions (i.e., rain).

**NOTE: Category 1** items and materials that are made of PFAS and come into contact with samples should be prohibited or otherwise avoided if possible. It is recommended for Equipment Blank samples to be collected for all **Category 1** sampling materials. However, the use of **Category 2** items and materials that may also contain PFAS that do not come into direct contact with the samples has a low risk of resulting in cross-contamination if best practices are used to avoid any contact between PFAS-containing materials and the environmental samples. (Denley 2019, Rodowa 2020)

All of the materials or items discussed in each of EGLE's PFAS Sampling Guidance Documents will be divided into the Allowable (🟩), Avoid (◆), Prohibited (●), or Needs Screening (△) groups. At the end of this document, several items and materials that need screening are listed in EGLE's PFAS Sampling Quick Reference Field Guide. Additionally, materials and items specific to a particular environmental media or sampling method will be thoroughly explained in that media's sampling guidance document (such as peristaltic pumps for groundwater sampling).

**NOTE:** If recommended PPE will be used during sampling, **Category 2** materials are not expected to be a source of cross-contamination as long as they do not come into contact with the samples.

- Allowable (🟩) identifies all items and materials (**Category 1** and **Category 2**) that have been proven not to be sources of PFAS cross-contamination and are considered allowable for sampling.

- Avoid (◆) identifies **Category 2** items and materials that should be avoided and, where alternative, PFAS-free materials should be identified and used, if possible. They are items and materials documented to contain PFAS or that PFAS are used in their manufacture. The use of these sampling materials, however, is sometimes necessary for safety reasons.

- Prohibited (●) identifies **Category 1** items and materials that should not be used during sampling. These items are well-documented to contain PFAS or that PFAS are used in their manufacture.

- Needs Screening (△) identifies items and materials that have the potential to contain PFAS or PFAS that may have been used in their manufacture. Many of these items may be produced by industries where PFAS use has been historically documented. Additionally, there may be items for which there is a lack of available scientific data from the manufacturers to show the items are PFAS-free. For **Category 1** items, a materials screening should be conducted to confirm that they are PFAS-free.

To provide a current, scientific-based approach for PFAS sampling, EGLE has used information from multiple sources to revise the initial PFAS General Sampling Guidance from 2018 to incorporate data from sampling efforts completed in Michigan and throughout the United States regarding the likelihood of cross-contamination during sampling. A key point derived from the reviewed information is listed below. A complete summary of information reviewed and considered as part of this revised document is available in Appendix A.

### 4.2.1 PFAS-Free Water

The term PFAS-free water is defined here as water that does not contain significant concentrations of any compound in a specific PFAS analyte list that is being analyzed at a project-defined level. The significant concentrations depend on project data quality objectives and could, for instance, be less than the laboratory reporting limit, <1/3 the limit of quantitation, or other defined criteria for the specific PFAS compound of interest (ITRC 2022).

**NOTE:** The confirmation of PFAS-free water should always be performed prior to the commencement of work. Site or public water supplies have been identified in many instances to contain detectable levels of PFAS.

One important consideration for each project is to identify a PFAS-free water source to use for decontamination of sampling and drilling equipment when applicable. The decontamination of sampling tools or small equipment parts can be performed using laboratory-supplied verified PFAS-free water. Other water can only be used for decontamination if it has been analyzed and shown to be PFAS-free, as defined for the project.

The laboratory used for the PFAS analysis should provide certified PFAS-free reagent water to prepare field blanks. The EGLE Lab can supply PFAS-free water for equipment blanks.

### 4.2.2 Materials Screening

Materials screening should be performed during the Health and Safety Plan (HASP), Sampling Analysis Plan (SAP), QAPP development, or the planning phase of sampling programs. The screening should be performed on all items and materials expected to come into contact with the samples and defined as **Category 1**.

Material screening should include a review of Safety Data Sheets (SDSs; formerly Material SDS [MSDSs]). Make sure the review uses current SDSs because the actual composition of a particular item or material may have changed over time without the manufacturer changing the actual item or material name. All products from the United States or abroad should be screened. Text fragments such as “perfluoro,” “fluoro,” or “fluorosurfactant” may identify the use of PFAS in specific items or materials.

**NOTE:** Manufacturers can change the chemical composition of any product. As a result, equipment blank samples should be collected for all materials that will come into direct contact with the sample media, regardless of what category they might be in, to confirm they are “PFAS-free”, i.e., will not contaminate samples at detectable levels. **There is no guarantee that materials in the ‘Allowable (🟩)’ category will always be PFAS-free.**

Some countries have official national lists of industrial chemicals defined by regulations, such as:

- Toxic Substances Control Act (TSCA) in the United States.
- European List of Notified Chemical Substances and substances pre-registered under the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) in the European Union.
- Swedish Chemical Agency (KEMI) in Sweden.
- Domestic Substances List in Canada.
- Inventory of Existing New Chemical Substances Produced or Imported in China
- Existing and New Chemical Substances Inventory in Japan.
- Korea Existing Chemicals Inventory in South Korea.
- New Zealand Inventory of Chemicals in New Zealand.
- Philippine Inventory of Chemicals and Chemical Substances in the Philippines.

The information on these lists includes the chemical names and various identity numbers, usually the Chemical Abstracts Service number (CAS Number) (KEMI 2015). The lists may not contain substantial information due to laws concerning proprietary information, giving the suppliers the right not to name some chemicals. The information is not always sufficient to identify if the items or materials contain PFAS, as many of the PFAS do not have an assigned CAS Number at this time (KEMI 2015). The most recent summary by the Organization for Economic Co-operation and Development (OECD) identified 4,730 PFAS-related CAS numbers (OECD 2018); however, as stated earlier, there are over 9,000 PFAS. For more information on the chemical structure and categorization of PFAS, see Appendix A.

Sometimes, manufacturers provide information about their products online or upon request, which may indicate if PFAS were used in the manufacturing of a particular item or material.

### 4.2.3 Sampling Equipment

The list of PFAS-containing materials potentially encountered on the site will change based on the specific sampled media and site-specific sampling conditions.  For additional details, please review each media-specific PFAS sampling guidance document and EGLE’s PFAS Sampling Quick Reference Field Guide. Collection of equipment blanks should also be considered for quality control purposes. In addition to reviewing these documents, please consider the following:

**Category 1** materials made of PFAS, both polymers or non-polymers or that could contain residual concentrations of PFAS, are Prohibited (●) if they are expected to come into direct contact with environmental samples. Category 2 materials that do not come into contact with the environmental samples should be Avoided (◆) if possible. The likelihood of potential cross-contamination from Category 2 materials is considered low. However, during extreme weather conditions (e.g., rain), some of these materials may require extra care to prevent possible cross-contamination. A list of known polymers and some of their uses are presented below. (Denly 2019, Rodowa 2020).

- **Polytetrafluoroethylene** (**PTFE**) includes the trademark Teflon® and Hostaflon®, which can be found in many items, including but not limited to the lining of some hoses and tubing, some wiring, certain kinds of gears, and some objects that require the sliding action of parts.
- **Polyvinylidene fluoride** (**PVDF**) includes the trademark Kynar®, which can be found in many items, including but not limited to tubing, films/coatings on aluminum, galvanized or aluminized steel, wire insulators, and lithium-ion batteries.
- **Polychlorotrifluoroethylene** (**PCTFE**) includes the trademark Neoflon®, which can be found in many items, including but not limited to valves, seals, gaskets, and food packaging.
- **Ethylene-tetrafluoroethylene** (**ETFE**) includes the trademark Tefzel®, which can be found in many items, including but not limited to wire and cable insulation covers, films for roofing and siding, liners in pipes, and some cable tie wraps.
- **Fluorinated ethylene propylene** (**FEP**) includes the trademarks Teflon® FEP and Hostaflon® FEP. It may also include Neoflon®, which can be found in many items, including but not limited to wire and cable insulation and covers, pipe linings, and some labware.
- **Perfluoroalkoxy polymer** (**FAP**), which is known to be used in the food packaging industry.
- **Perfluoropolyethers** (**PFPE**) are used as a surface treatment for natural stone, metal, glass, plastic, textiles, leather, and paper and paperboard treatment for food-contact applications.
- **Side-Chain Fluorinated Polymers** such as **fluorinated acrylates**, **methacrylate**, **urethane**, and **oxetane polymers** have been used in surfactants and surface

protection products. These polymers are useful as water-, stain-, and grease-proofing finishes for textile, leather, and paper surfaces.

- 🟩 Low-density polyethylene (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.
- 🟩 Use materials made of high-density polyethylene (HDPE), polypropylene, silicone, or acetate.
- 🟩 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 time (e.g., stored in a glass container). If the sample comes into direct contact with the glass for a short period of time (e.g., using a glass container to collect the sample, then transferring the sample to a non-glass sample bottle), the adsorption is minimal.

**NOTE:** most analytical methods do not allow the use of glass bottles or the transfer of samples from one container to another.

- 🟩 Powderless nitrile gloves (which can be found at some hardware and major retail outlets).
- △ Latex gloves should be screened before use.
- △ Some sampling guidance documents allow the use of aluminum foil provided the shiny side is placed away from the sample (e.g., fish tissue sampling guidance). As a precaution, EGLE recommends that aluminum foil not be used unless equipment blank samples confirm it is PFAS-free (Denly 2019, Rodowa 2020).
- △ Low-density polyethylene (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.

### 4.2.4 Field Clothing and Personal Protective Equipment (PPE)

Any field planning and mobilization effort should address the physical, chemical, and biological hazards associated with each PFAS site. The mitigation of potential risks may be documented in a site-specific HASP, SAP, or QAPP. Due to the extensive use of PFAS in many industries and products, PPE may contain PFAS. However, all PPE materials are expected to be **Category 2**. During PFAS investigations, PPE containing PFAS should be Avoided (◆), if possible, especially when a PFAS-free alternative is available. Personal safety is paramount, so staff safety should not be compromised due to fear of using PFAS-containing materials. Any deviation from this guidance, including those necessary to ensure the health and safety of sampling personnel, should be recorded in field notes and discussed in the final report. The development of the HASP or QAPP should consider these factors before mobilization in the field. All HASPs or QAPPs need to address the concern of potential staff exposure to PFAS through PPE.

**NOTE:** The Danish Ministry of the Environment identified alternative polymer technology as being PFAS-free. Products treated with this technology are water- resistant, but not oil and dirt repellent to the same extent as products treated with PFAS-based agents (DEPA, 2015).

Globally, textile protective coatings are estimated to be about 50 percent of the total use of PFAS (DEPA 2015). Due to its unique water and oil-repellency properties, PFAS has been used to coat various clothing (i.e., pants, jackets, and t-shirts) and leather products (i.e., boots, shoes, and jackets). Many of these types of clothing and PPE have the potential to be used in the sampling environment.

While preparing for sampling, particular focus should be made on clothing advertised as having waterproof, water-repellant, or dirt and/or stain-resistant characteristics. These types of clothing are most likely to have had PFAS used in their manufacturing. PFAS have been widely used in what is known as durable water repellent (DWR) finish for textiles, and it has been shown that PFAS can be released during washing (Schellenberger 2019).

Field Clothing and PPE that should be Avoided (◆), if possible, as they may contain PFAS, include the following:

◆ Clothing that has been made with or washed with stain-resistant chemicals.

◆ Clothing chemically treated for insect resistance and ultraviolet protection (See **Section 4.2.5** on biological hazards).

◆ Clothing or PPE items with any of the brand or product names found to contain PFAS by the Danish Ministry of the Environment and presented in the following table (DEPA 2015).

**Table 1** provides a list of field clothing to be Avoided (◆) (DEPA, 2015). However, the manufacturer and/or vendor for the field clothing and/or PPE should be contacted to confirm that these brand or product names still contain PFAS. There have been instances where manufacturers have kept the same brand and/or product name but have changed the chemicals used while manufacturing a particular item.

## Table 1. Prohibited Field Clothing and PPE Brand and Product Names

Danish Environmental Protection Agency – **2015**

Advanced Dual Action Teflon® fabric protector.

Release Teflon®

Repel Teflon® fabric protector

High-Performance Release Teflon®

High performance Repel Teflon® fabric protector

Ultra Release Teflon®

NK Guard S series

GreenShield®

Tri-Effects Teflon® fabric protector

Lurotex Protector RL ECO®

Oleophobol CP®

Repellan KFC®

Rucostar® EEE6

UnidyneTM

Bionic Finish®

RUCO-GUARD®

RUCOSTAR®

RUCO-COAT®

RUCO-PROTECT®

RUCOTEC®

RUCO®

Resist Spills™

Resists Spills and Releases Stains™

Scotchgard™ Fabric Protector

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[1] This list is not considered to be a complete listing of prohibited materials. All materials should be evaluated before use during sampling.

Field Clothing and PPE that are Allowable (🟩) to wear within the immediate sampling environment include the following:

- 🟩 Powderless nitrile gloves.
- 🟩 Polyvinyl chloride (PVC) or wax-coated fabrics.
- 🟩 Neoprene.
- 🟩 Any boots made of polyurethane and/or PVC. If the HASP requires a specific type of boot, such as (steel-toed), and PFAS-free cannot be purchased, PFAS-free overboots may be worn. The overboots must be put on, and hands must be washed after putting the overboots on before the beginning of sampling activities. Overboots may only be removed in the staging area and after the sampling activities have been completed.
- 🟩 Synthetic and natural fibers (preferably cotton) that are well laundered (more than six times with no fabric softener), clothes, and cotton overalls.

**NOTE**: There could be many PPE materials used during various sampling events, including hard hats and safety glasses. All clothing and PPE are considered **Category 2** materials.

Field Clothing and PPE that must be evaluated (△) before wearing within the immediate sampling environment include the following:

- △ Latex gloves.
- △ Tyvek suits and clothing containing Tyvek® (EPA PFAS sampling guidance from EPA Region 2 prohibits using Tyvek; available product information suggests Tyvek® may be used if required. Coated Tyvek® requires further evaluation; therefore, EGLE recommends the collection of an Equipment Blank before Tyvek® use). EGLE considers these materials as **Category 2**.

### 4.2.5 Sun and Biological Protection

Some PFAS sampling guidance documents either restrict the use of sun and biological protection products, provide very few choices, or recommend, without any supporting scientific data, the use of products containing the words “Natural” and/or “Organic” in the product name as a description of the product. Because biological hazards (sunburn, mosquitos, ticks, etc.) may be encountered during sampling, eliminating specific clothing materials or PPE (sunscreens and insect repellants) could pose a health and safety hazard to staff.

Prolonged sun exposure will require sunscreens, which may have included PFAS in their manufacture. Protection against insects may require the use of insect repellant. **Figure 1** contains a detailed list of sunscreens and insect repellants that have been analyzed and found to be PFAS-free as of the date of this document. Note that this is not a comprehensive list of allowable insect repellants or sunscreens; other products may meet the requirements for use. Listing or omission of any product does not imply endorsement or disapproval. Also, there is no guarantee that these products will always remain PFAS-free.

EGLE considers all sun and biological protection products as **Category 2** materials that are not expected to come into contact with the environmental samples.

- ● Sunscreens and insect repellants should not be applied near the sample collection area.
- ■ Hands should be well washed after applying or handling these products, and afterward, powderless nitrile gloves should be worn.

If an insect repellent is not available and staff needs protection against biting insects:

- Tuck pant legs into socks and/or boots to seal the gap between the boots and the pants to reduce the risk of being bitten by ticks.
- Wear well-washed, light-colored clothing to see ticks during field activities easily.
- Light-colored clothing, long sleeves, and large-brimmed hats also prevent sunburn.

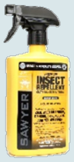
**NOTE:** The words “Natural” and/or “Organic” in the product name or as a descriptor does not mean that it is PFAS-free.

## Figure 1. Sunscreen and Insect Repellents[1]

### 🟩 Allowable Insect Repellents

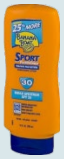
OFF Deep Woods

Sawyer Permethrin



### 🟩 Allowable Sunscreens

Banana Boat –
- Sunscreen for Men Triple Defense Continuous Spray Sunscreen SPF 30
- Sport Performance Coolzone Broad Spectrum SPF 30
- Sport Performance Sunscreen Lotion Broad Spectrum SPF 30
- Sport Performance Sunscreen Stick SPF 50



Coppertone Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50

Coppertone Sport High-Performance AccuSpray Sunscreen SPF 30

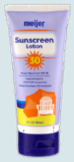
Coppertone Sunscreen Stick Kids SPF 55

L’Oréal Silky Sheer Face Lotion 50+

Meijer Sunscreen Lotion Broad Spectrum SPF 30

Meijer Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50

Meijer Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70



Neutrogena Ultra-Sheer Dry-Touch Sunscreen Broad Spectrum SPF 30

Neutrogena Beach Defense Water + Sun Barrier Lotion SPF 70 & Spray Broad Spectrum SPF 30

Neutrogena Pure & Free Baby Sunscreen Broad Spectrum SPF 60+

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[1] This is not considered a complete listing of allowable materials. Some sunscreen and insect repellent testing has been performed using a PFAS screening Method (Peaslee, University of Notre Dame) known as Particle Induced Gamma-Ray Emission (PIGE). Approved gloves should always be used, and the sample should never come into contact with any sunscreen or insect-repellent products.

### 4.2.6 Personnel Hygiene and Personal Care Products (PCPs)

Several sampling guidance documents recommend that personal hygiene and personal care products (PCPs) (e.g., cosmetics, shampoo, sunscreens, dental floss, etc.) not be used before and on the day(s) of sampling because the presence of PFAS in these products has been documented (OECD 2002, Fujii 2013, Borg and Ivarsson 2017, Denly 2019, Rodowa 2020, Whitehead 2021). However, if EGLE's sampling standard operating procedures (SOP) are followed, these items should not come into contact with the sampling equipment, or the sample being collected. As of the date of this sampling guidance, cross-contamination of samples due to the use of PCPs has not been documented during the collection of thousands of samples. EGLE also considers these materials as **Category 2**, meaning many are used before or within the staging area. However, field personnel should be aware of the potential of cross-contamination if the sampling equipment or samples come into contact with these products. The following precautions should be taken when dealing with personal hygiene or PCPs before sampling:

- 🟩 Move to the staging area and remove PPE if applying personal care products becomes necessary.
- 🟩 Wash hands thoroughly after handling or applying PCPs and, when finished, put on a fresh pair of powderless nitrile gloves.

### 4.2.7 Food Packaging

PFAS has been used by the paper industry as a special protective coating against grease, oil, and water for paper and paperboards, including food packaging, since the late 1950s (Trier et al., 2018). PFAS application for food packaging includes paper products that come into contact with food, such as paper plates, containers, bags, and wraps (OECD, 2002). In January 2016, the Food and Drug Administration (FDA) banned the use of PFAS, which has eight carbon atoms (such as PFOA and PFOS) or more, in food packaging materials. However, PFOA and PFOS or other eight or more carbon chain PFAS may still be detected in food packaging because recycled paper may contain PFAS. Various studies have found up to 57 percent detection frequency in food contact materials such as paper (Trier et al. 2011; Rosenmai et al. 2013; Schaider et al. 2017).

**NOTE:** Short-chain PFAS have not been banned for use in the manufacturing of contact food materials in the United States.

Pre-wrapped food or snacks (such as candy bars, microwave popcorn, etc.) must not be in the sampling and staging areas during sampling due to PFAS contamination of the packaging. When staff require a break to eat or drink, they should remove their gloves, coveralls, and any other PPE, if worn, in the staging area and move to the designated area for food and beverage consumption. When finished, staff should wash their hands and put on a fresh pair of powderless nitrile gloves at the staging area before returning to the sampling area. EGLE does not anticipate food and snacks becoming a source of

PFAS cross-contamination when media-specific sampling guidance is followed, and proper gloves are used.

- ● Do not handle, consume, or otherwise interact with pre-wrapped food or snacks, carry-out food, fast food, or other items while on-site sampling.
- ■ Move to the staging area and remove PPE before leaving the sampling and staging areas if consuming food on-site becomes necessary.

## 4.3 PFAS Sampling Procedures

### 4.3.1 Sample Containers, Handling, and Collection

Any sampling containers provided by the laboratory should be verified as PFAS-free. All bottles used for PFAS sampling must come from the laboratory that will also be performing the PFAS analysis.

Before sampling, staff may come into contact with textiles and fabrics treated with PFAS, such as carpets and car interiors. Staff should be aware that these materials, and any other surfaces that repel water and are stain-resistant, can potentially be treated with PFAS. However, these are considered **Category 2** materials, and field personnel should be aware of their possible PFAS use. Sample containers and equipment used for sampling should not be stored on or come into contact with materials suspected to contain PFAS.

**NOTE:** Head space is allowed and should be used when sampling for PFAS, in order to allow for matrix spike addition or prevent preservatives (i.e., Trizma) from being spilled out. When analyzing for drinking water samples using EPA Method 537.1, Trizma is used as the preservative. EPA Method 533 uses ammonium acetate.

For all environmental media, hands should be well-washed before sampling. Clean, powderless nitrile gloves must be put on before sample collection, handling of sample containers, and handling sampling equipment. Gloves should be changed periodically and always before collecting the next sample. The sample container must be kept sealed and only open during the sample collection. The sampling container cap or lid should never be placed on any surface unless it is PFAS-free. The sampling container cap or lid must never be placed directly on the ground. A list of materials used in sampling and handling can be found in the EGLE Quick Reference Field Guide at the end of this document.

In the absence of formal EPA guidance for PFAS sample storage, the documentation in EPA Method 533 should be used as a guide for thermal preservation (holding temperature) and holding times for other environmental media samples (except for biota). To limit microbial growth, biota samples such as fish and vegetation are recommended to be kept frozen until the sample is prepared.

If published analytical reference methods other than EPA Method 537.1 or EPA Method

533 are used (i.e., EPA Method 8327, Method 1633), follow the guidelines or requirements in those methods for sample storage, preservation, and hold times. Otherwise, EPA Method 537.1 and Method 533 dictate that samples must be chilled during storage and shipment and not exceed 50°F (10°C) during the first 48 hours after collection.

### 4.3.2 Sample Shipment

In general, for all environmental media sampled for PFAS, samples must be kept on ice from the time of sample collection to the arrival at the laboratory. All materials used during sample shipment are **Category 2** and, therefore, are not anticipated to result in cross-contamination. The following procedures should be used for sample shipment:

- 🟩 Regular ice should be used to cool and maintain the sample at or below the proper temperature.
- 🟩 Chemical or blue ice may be used if it is known to be PFAS-free, the blue ice container is not leaking, and it is certain that the sample is cooled and maintained at or below the proper temperature during collection and through transit to the laboratory.
- 🟩 Refresh with regular ice, double bagged in LDPE resealable storage bags if needed.
- 🟩 Fish and other wildlife samples should be placed on dry ice and frozen before shipment to the lab. If fish are frozen, shipping the samples overnight on ice should be acceptable.
- 🟩 The samples, ice, and chain of custody (COC) should always be bagged in polyethylene (i.e., Ziploc®) bags.
- 🟩 Chain of Custody and other forms should be single-bagged in LDPE resealable storage bags and taped to the inside of the cooler lid.
- 🟩 The cooler should be taped closed with a custody seal and shipped by overnight courier.
- 🟩 Samples must be shipped as soon as possible (e.g., overnight) within one day maximum from collection to ensure the samples arrive within the analytical holding time specified by the lab.
- 🟩 It is recommended that unused sample bottles be returned to the laboratory and not stored for long periods for future sampling events.

### 4.3.3 Preferential Sampling Sequence

A preferred sampling sequence should be established before any sampling event to reduce the risk of cross-contamination. In general, the sampling sequence should be such that sampling starts in areas where it is expected or known to be the least contaminated and then move to areas anticipated or identified to be most contaminated. The sampling sequence can be readily determined if analytical results from past sampling events are available.

For many PFAS investigation sites, no PFAS sampling has been conducted before. In these cases, all site information on possible PFAS uses and potential PFAS migration patterns (e.g., upgradient, downgradient) from PFAS sources at the site should be reviewed before the sampling event to help establish the sampling sequence.

Suppose multiple samples (i.e., monitoring wells) will be collected for an area where a particular or potential PFAS release in the environment might have been documented. In that case, samples known to be upgradient from the impacted area should be sampled first, followed by those furthest downgradient from the suspected source. The remaining wells should be progressively sampled from the most distant downgradient to those closer to the known PFAS source.

If no information is available about the site, samples are to be collected in the following order:

1. drinking water (e.g., residential wells)
2. surface water
3. groundwater

## 4.4 Decontamination Procedures

It is customary with sampling that equipment is decontaminated at the conclusion of the sampling event. If the previous user of the equipment/materials is unknown or it is unclear how the equipment was handled especially rental equipment, the equipment should be decontaminated before sampling.

Disposable Category 1 sampling equipment should be used, especially for sample bottles and other materials used where the sample may be in contact with the sampling equipment for an extended period.

Non-disposable sampling equipment used at multiple sites or sampling locations can become highly contaminated with PFAS. Decontamination procedures must be implemented to prevent cross-contamination, especially between individual sample locations. It is customary to decontaminate sampling equipment at the end of the sampling event, whether the event is a single sampling location or several sites that conclude at the end of the workday.

The sampling guidance documents will provide information about any media-specific decontamination procedures. There are many decontamination methods for non-dedicated **Category 1** sampling equipment, two of which are listed below.

**Decontamination Method 1:**

- ● Do not use Decon 90®.
- ● Do not put equipment away without decontaminating it.
- 🟩 Laboratory-supplied PFAS-free deionized water is preferred for decontamination.
- 🟩 Alconox®, Liquinox®, and Citranox® can be used for equipment decontamination.
- 🟩 Sampling equipment can be scrubbed using polyethylene or PVC brushes to remove particulates.
- 🟩 Decontamination procedures should include triple rinsing with PFAS-free water.
- 🟩 Decontaminate sampling equipment after sampling at each location or the end of the workday.
- 🟩 Commercially available deionized water in an HDPE container may be used for decontamination if the water is verified to be PFAS-free, as defined in **Section 4.2.1** of this document.
- △ Municipal drinking water may be used for decontamination purposes if it is known to be PFAS-free.

**Decontamination Method 2:**

1. In a PFAS-free bucket, wash the equipment with a mixture of PFAS-free water and PFAS-free soap (bucket #1).
2. In a second PFAS-free bucket (bucket #2), rinse the equipment with PFAS-free water.
3. A second rinse should be done with PFAS-free water using either a third bucket (bucket #3) or the second bucket (bucket #2) if washed and rinsed.
4. For decontamination of additional equipment, change the decontamination water between cleanings.

## 4.5 Laboratory Considerations

The PFAS analytical list is available on MPART's website, Michigan.gov/PFASresponse, under Investigations and Sites. This list includes the 18 analytes required to be analyzed for in drinking water samples when using EPA Method 537.1, the 25 analytes for EPA Method 533, and the 34 or 40 analytes (depending on method) that EGLE recommends be analyzed for in all other environmental media. The MPART website should be visited to download the most recent document. Laboratories should be able to analyze and report PFAS results that will meet the project-specific data quality objectives identified in the SAP or QAPP.

## Drinking Water Samples

EPA Method 537.1 or Method 533 must be used for testing finished drinking water samples. Other methods are available for non-drinking water samples. Many laboratories refer to the isotope dilution method as ‘modified Method 537’, however, the EPA does not recognize isotope dilution as an acceptable modification of EPA Method 537.1 for drinking water analysis. EPA Method 533 allows for isotope dilution, and laboratories should be certified through Michigan’s Laboratory Certification Program for analysis using Method 537.1 or Method 533. EPA drinking water methods are generally prescriptive, and only limited modifications are allowed because the finished treated drinking water is assumed to be free of significant interferences.

**NOTE:** EPA Method 537.1 and Method 533 were developed to be used only for finished drinking water samples, and contain specific requirements for sample preservation, shipping storage, and holding times.

EPA Method 537.1 and Method 533 were designed for finished drinking water and use chemical preservation using Trizma® (537.1) or ammonium acetate (533) to buffer the sample and remove free chlorine. Non-chlorinated finished drinking water may also be analyzed using EPA Method 537.1 or EPA Method 533.

## Other Environmental Media Samples

EPA Method 1633, 4th Draft is the only published EPA method using isotope dilution for determining PFAS in non-drinking water matrices or other sample media. Other EPA methods, such as Method 8327, may be used. Method 1633, 4th Draft, continues to go through the development and validation process and may be promulgated in 2024. However, EPA recommends using this method, and it is currently the only PFAS method validated for the aqueous matrices of wastewater, surface water, and groundwater. Some commercial laboratories have developed isotope dilution methods based on existing published methods. However, there may be significant differences between SOPs from different commercial laboratories regarding the details of the preparation and analysis of PFAS samples. The laboratory’s procedure and certifications should be reviewed to ensure that the laboratory can provide data that meets the project's data quality objectives. EGLE has implemented a laboratory SOP review process. Staff should refer to the EGLE internal share drive to see whether SOPs have been reviewed for the lab they are considering. Please note that EGLE staff or their contractors must have samples come through the EGLE laboratory first (unless it is an analysis unavailable through the EGLE Lab), with an identified overflow contract lab if necessary.

The following non-EPA analytical methods have been published for use in determining PFAS in various media:

- ISO (International Organization for Standardization) Method 25101 (ISO, 2009) - Water quality Determination of PFOA and PFOS - Method for unfiltered samples of drinking water, groundwater, and surface water, using solid phase extraction and liquid chromatography/mass spectrometry (HPLC/MS/MS.)
- ASTM D7979-20 (ASTM, 2020 - Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography-Tandem Mass Spectrometry (LC/MS/MS). This method has been used for the analysis of surface water, sludge, and wastewater for selected PFAS. However, this method has not been evaluated on drinking water matrices. Some commercial laboratories have modified this method and are using isotope dilution.
- ASTM D7968-17a (ASTM, 2017) - Standard Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography-Tandem Mass Spectrometry (LC/MS/MS). This method utilizes a quick extraction and is not intended to generate an exhaustive accounting of the content of PFAS in difficult soil matrices.

## 4.6 Quality Control Samples

### 4.6.1 Laboratory Quality Control Samples

The QAPP should describe what batch quality control (QC) samples – such as method blank (MB), laboratory control sample (LCS), laboratory control sample duplicate (LCSD), field duplicate (FD), matrix spike (MS), and matrix spike duplicate (MSD) – are prepared for each media type. In some cases, depending on the project, additional QC samples may be required. The QAPP should also reference the laboratory SOP.

### 4.6.2 Field Quality Control Samples

Field QC samples can be used to evaluate the field equipment and supplies and assess the possibility of cross-contamination during sampling, transport, and storage of samples. For samples such as equipment rinse blanks (EB), field blanks (FB), and trip blanks (TB), the following is required:

- The EB should be collected by passing laboratory-verified PFAS-free water over or through decontaminated field sampling equipment before collecting samples to assess the adequacy of the decontamination process and/or to evaluate potential contamination from the equipment used during sampling. The recommended frequency should be in the QAPP.

- The FB is prepared in the laboratory by placing an aliquot of PFAS-free reagent water in a sample container and treating it as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, transfer to a clean sample container in the field, storage, preservation, and all analytical procedures. The purpose of the FB is to determine if method analytes or other interferences are present in the field environment. The recommended frequency should be in the QAPP.

- The TB is a bottle of PFAS-free water that should be prepared in the laboratory, travel from the laboratory to the site, and be transported back to the laboratory without having been exposed to any sampling procedures. Typically, a TB is used for volatile compounds, but it may be recommended for PFAS sampling to assess cross-contamination introduced from the laboratory and during shipping procedures. The recommended frequency should be in the QAPP.

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# Appendix A

Many materials that are used during sampling are listed as prohibited in PFAS sampling guidance documents that are published by other federal, state, and civilian organizations, including the United States Navy in 2017, the United States Army in 2018, the Government of Western Australia Department of Environment Regulations in 2016, Cooperative Research Center for Contamination Assessment and Remediation of the Environment in 2017, National Groundwater Association in 2019, and the States of California in 2019, Maine in 2019, and New Hampshire in 2017. Materials prohibited in various sampling guidance documents include reusable ice packs, water-repellent field notebooks, markers, sticky notes, and many others that increase the cost, time, and difficulty of sampling but with no documented benefit or, many times, no analytical data to support the prohibition. Many of the sampling guidance documents are often considered conservative in their approach. EGLE's initial General PFAS Sampling Guidance from 2018 followed a similar, conservative approach since no published research was available that documented the use of various materials and their effect on sample results. However, many prohibited materials included those for which plausible scenarios for the materials to come into direct contact with the environmental samples were difficult to imagine.

Since the publication of many PFAS sampling guidance documents, including Michigan's PFAS Guidance Documents, various states and the Department of Defense have completed extensive sampling programs. In Michigan, for example, extensive PFAS studies, including a statewide sampling of over 1,700 drinking water systems, have been conducted, along with extensive remedial investigations at multiple locations and sampling of thousands of residential wells (MPART, 2020). Samples collected from numerous locations, including drinking water supplies, residential, and monitoring wells, were analyzed for between 14 and 28 PFAS compounds (depending on the analytical method), and many have been reported as non-detect for PFAS. Following a careful review of analytical results for field equipment blanks, field reagent blanks, and laboratory method blanks collected during these sampling events, and after validating a percentage of these samples, EGLE's current conclusion is that there is a low likelihood of systematic PFAS cross-contamination.

Recently, two peer-reviewed publications were published evaluating the potential of cross-contamination from sampling materials due to the potential leaching of PFAS compounds into the samples (Denly, 2019; Rodowa, 2020). Both publications used sampling methods considered worst-case scenarios and more conservative of actual environmentally relevant scenarios. Denly et al., 2019 evaluated a worst-case scenario of water coming into contact with various materials over 24 hours. Rodowa et al., 2020 used heated methanol shaken for 10 minutes. Some of the conclusions that can be taken from these publications are as follows:

1. Not all materials made of PFAS, such as fluorinated polymers (e.g., Teflon), had detectable PFAS compounds.

2. Some materials (e.g., aluminum foil) are not made of PFAS but have a protective layer that could contain PFAS and have shown both detections and no detections.
3. Materials that are often prohibited (e.g., adhesive notepads/notes) in many sampling guidance documents were tested and found to be non-detect in both studies.
4. There were detections and no detections for the same materials (e.g., labels and low-density polyethylene [LDPE] tubing) from different manufacturers. For example, LDPE tubing was non-detect for some samples but had high detections of over 1,000 ppt for other samples.
5. In some cases, materials considered allowable in all PFAS sampling guidance documents (e.g., high-density polyethylene (HDPE)) and not known to be PFAS-containing materials had low, detectable concentrations.
6. When the potential of cross-contamination is evaluated based on actual environmental field conditions, the likelihood of cross-contamination is low, even for materials where PFAS detections were noted and especially for materials that do not come into contact with the samples.
7. The focus should be on the materials that come into direct contact with the environmental samples, such as Category 1. Equipment blank samples should be used to confirm no cross-contamination occurs during sampling. Analysis of field sampling materials, as described in these two publications, should not be used as a substitute for equipment blank samples, which helps verify that sample materials or the combination of materials used in the field have not resulted in cross-contamination.
8. PFAS can be divided into two (2) primary categories: non-polymers and polymers. The non-polymer category includes perfluoroalkyl substances (e.g., compounds in the PFOA and PFOS families) and polyfluoroalkyl substances (PFAS compounds that can partially degrade into other PFAS, like those from the PFOA and PFOS families, often referred to as precursors). The second polymer category includes fluoropolymers, which have a carbon-only polymer backbone with fluorine directly attached to all carbon atoms; perfluoropolyethers, which have a carbon and oxygen polymer backbone with fluorine attached to the carbon; and side-chain fluorinated polymers, which have various components of a non-fluorinated backbone with fluorine side chains attached to the polymer backbone. Polymers generally have very different physical, chemical, and biological properties than non-polymer chemical substances of low molecular weight. PFAS analysis is typically only requested for non-polymer compounds. However, tools have been developed (i.e., particle induced gamma-ray emission [PIGE], combustion ion chromatography) to determine if polymers are present. Commercial laboratories have developed analytical methods for a minimal number of non-polymer PFAS families.