

GENERAL PFAS SAMPLING GUIDANCE

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

Michigan
Department of
Environmental
Quality



GENERAL PFAS SAMPLING

Guidance

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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	NZIoC – New Zealand Inventory of Chemicals (New Zealand)
CAS Number – Chemical abstracts service number	PCPs – Personal care products
COC – Chain of Custody	PID – Photoionization detector
DEPA – Danish Environmental Protection Agency (Denmark)	PFAA – Perfluoroalkyl acids
EINECS – European List of Notified Chemical Substances (European Union)	PFAS – Per- and Polyfluoroalkyl Substances
ENCS – Existing and New Chemical Substances Inventory (Japan)	PFC – Polyfluorocarbons
ETFE – Ethylene-tetrafluoroethylene	PFCA – Perfluoroalkyl carboxylic acids
FCMP – Fish Contaminant monitoring program	PFOA – Perfluorooctanoic acid
FCSV – Fish consumption screening values	PFOS – Perfluorooctanesulfonic acid
FDA – Food and Drug Administration (United States of America)	PFPE – Perfluoropolyethers
FEP – Fluorinated ethylene propylene	PFSA – Perfluoroalkyl sulfonic acids
HASP – Health and Safety Plan	PICCS – Philippine Inventory of Chemicals and Chemical Substances (Philippines)
HDPE – High-density polyethylene	ppb – Parts per billion
IECSC – Inventory of Existing Chemical Substances Produced or Imported in China	PPE – Personal protection equipment
ITRC – Interstate Technology & Regulatory Council	ppt – Parts per trillion
KECI – Korea Existing Chemicals Inventory (South Korea)	PTFE – Polytetrafluoroethylene
KEMI – Swedish Chemical Agency (Sweden)	PVC – Polyvinyl chloride
LDPE – Low-density polyethylene	PVDF – Polyvinylidene fluoride
LHA – Lifetime Health Advisory (United States Environmental Protection Agency)	PVF – Polyvinyl fluoride
MDEQ – Michigan Department of Environmental Quality	QA/QC – Quality assurance/quality control
MDHHS – Michigan Department of Health and Human Services	QAPP – Quality Assurance Project Plan
MPART – Michigan PFAS Action Response Team	OECD – Organization for Economic Cooperation and Development
MSDS – Material Safety Data Sheet (former reference)	SDS – Safety Data Sheet
ng/L – Nanograms per liter	SWAS – Surface Water Assessment Section (MDEQ)
	TSCA – Toxic Substances Control Act (United States of America)
	USEPA – United States Environmental Protection Agency
	UV – Ultraviolet
	VOC – Volatile organic compounds
	WRD – Water resources division (MDEQ)

Disclaimer

The Michigan Department of Environmental Quality (MDEQ) 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 (www.michigan.gov/PFASresponse) to access the current version of this document.

1. Introduction

Per- and polyfluoroalkyl Substances (PFAS) are a class of **emerging contaminants** composed of more than 3,000 human-made, fluorinated, organic chemicals (Buck et al., 2011, Wang et al., 2017). The actual number of compounds is continuously changing, as some PFAS are no longer produced due to regulatory and voluntary actions, while new ones are created as alternatives. The carbon-fluorine bond that exists in PFAS is one of the strongest bonds in nature, they are tough to break and are 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 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 1930's and commercially used from the 1940's as non-stick coatings. PFAS continued to be used in many industries and various products as more PFAS were developed with unique chemical properties. Some of the documented PFAS uses are in hydraulic fluids, biocides, construction products, fire-fighting foams, household products, wetting and mist suppressing agents, surfactants for oil and natural gas recovery enhancement, polymerization agents, low-friction bearings and seals, insulators, cables, wires, protective coatings for a wide variety of materials, nonstick coatings, surgical patches, cardiovascular grafts, implants, oil and water repellent coatings for a wide range of materials such as paper and cardboard packaging products, carpets, leather products, and textiles (OECD, 2013). The presence of PFAS in these materials is a potential source of environmental concern and cross-contamination.

The probability of false positives is relatively high during PFAS sample collection due to the potential for many sources of cross-contamination, combined with low laboratory detection limits (nanograms per liter (ng/L) or parts per trillion (ppt)). There are many products that could be found in the sampling environment, that have not been documented to either contain or not contain PFAS, and may come into contact with the samples, introducing causing cross-contamination.

The United States Environmental Protection Agency (USEPA) has established a Lifetime Health Advisory (LHA) for Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS), separately or combined, of 70 ppt. The MDEQ cleanup criteria protective of groundwater used for drinking water purposes is also 70 ppt for PFOS and PFOA, individually or combined. The MDEQ has also promulgated a standard under Rule 57 for PFOS of 11 ppt for surface water that is used as a drinking water source and 12 ppt for surface water that is not used as a drinking water source.

● - Prohibited ■ - Allowable ▲ - Needs Screening

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 and/or well installation or well abandonment at PFAS sites.

This document is intended to supplement the MDEQ 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 MDEQ staff and contractors.

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 MDEQ staff.

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

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, clean clothing, and clean boots to visit the sampling location. Before arriving at the farm, staff should call the owner of the farm 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 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, staff should always be accompanied by farm personnel.

3.4 After Sampling

Dispose of used disposable boot covers at the facility if possible; otherwise, place in a plastic bag, seal and place 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 MDEQ policy and should include the analyte list, method of analysis, environmental matrices, and reporting limits, which are 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.

The materials associated with sampling that have the potential for PFAS cross-contamination have been divided into three major groups:

- Prohibited (●) identifies items and materials that should not be used when sampling. It is well documented that they contain PFAS or that PFAS are used in their manufacture.
- Allowable (■) identifies items and materials that have been proven not to be sources of PFAS cross contamination and are considered allowable for sampling.
- Needs Screening (▲) identifies items and materials that have the potential for PFAS cross-contamination due to a lack of scientific data or statements from manufacturers to prove otherwise. These items and materials are further sub-divided into two categories:
 - **Category 1:** Items and materials that will come in direct contact with the sample. These should not be used when sampling unless they are known to be PFAS-free, by collecting an equipment blank sample prior to use.
 - **Category 2:** Items and materials that will not come in direct contact with the sample. These should be avoided, if possible, unless they are known to be PFAS-free by collecting an equipment blank sample prior to use.

All of the materials or items discussed in each of the MDEQ's PFAS Sampling Guidance Documents will be divided into ● Prohibited ■ Allowable, or ▲ Needs Screening. Several examples of prohibited and allowable materials and materials that need screening are listed in the **MDEQ PFAS Sampling Quick Reference Field Guide** at the end of this document. Also, materials and items that are 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.

Please note that at this time no published research is available that documents the use of various materials and their effect on sample results. Therefore, a conservative approach is recommended in this guidance based on the evaluation of multiple environmental samples at various PFAS sites. Field sampling occurring during extreme weather (e.g., rainfall, snowfall, or extreme heat) should be conducted while wearing the appropriate clothing that will not pose a risk for cross-contamination but will also ensure the safety of the field personnel.

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, <1/2 the limit of quantitation, or other defined criteria for the specific PFAS compound of interest (ITRC, 2017).

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 purposes if it has been analyzed and shown to be PFAS-free as defined for the project.

4.2.2 Materials Screening

Materials screening should be performed during the Health and Safety Plan (HASP) and QAPP development or the planning phase of sampling programs. The screening should be performed on all of the items and materials that are 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 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 (EINECS), as well as substances pre-registered under the Registration, Evaluation, Authorization, and restriction of Chemicals (REACH) in the European Union.
- Swedish Chemical Agency (KEMI) in Sweden.

● - Prohibited ■ - Allowable ▲ - Needs Screening

- Domestic Substances List (DSL) in Canada.
- Inventory of Existing New Chemical Substances Produced or Imported in China (IECSC)
- Existing and New Chemical Substances Inventory (ENCS) in Japan.
- Korea Existing Chemicals Inventory (KECI) in South Korea.
- New Zealand Inventory of Chemicals (NZIoC) in New Zealand.
- Philippine Inventory of Chemicals and Chemical Substances (PICCS) in the Philippines.

The information available on these lists includes the chemical names and various identity numbers, which is usually the Chemical Abstracts Service number (CAS Number) (KEMI, 2015). The lists may not contain a substantial amount of information because of laws in regards to proprietary information, which gives the suppliers the right to not name newly developed 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 conducted by the Organization for Economic Co-operation and Development (OECD) identified 4,730 PFAS-related CAS numbers (OECD, 2018).

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 actual list of PFAS-containing materials potentially encountered onsite will change based on the specific sampled media and site-specific sampling conditions. Do not use any equipment that contains any known fluoropolymers. Consider all of the following:

- Do not use polytetrafluoroethylene (PTFE) that 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.
- Do not use Polyvinylidene fluoride (PVDF) that 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.
- Do not use Polychlorotrifluoroethylene (PCTFE) that includes the trademark Neoflon®, which can be found in many items, including but not limited to valves, seals, gaskets, and food packaging.
- Do not use Ethylene-tetrafluoroethylene (ETFE) that includes the trademark Tefzel®, which can be found in many items, including but not limited to the wire and cable insulation and covers, films for roofing and siding, liners in pipes, and some cable tie wraps.
- Do not use Fluorinated ethylene propylene (FEP) that includes the trademarks Teflon® FEP and Hostaflon® FEP, and may also include Neoflon®, which can be found in many items, including but not limited to the wire and cable insulation and covers, pipe linings, and some labware.
- Do not use low-density polyethylene (LDPE) for any items that will come into direct contact with the sample media. LDPE can be found in many items, including but not limited to containers and bottles, plastic bags, and tubing.
 - ▲ **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.

● - Prohibited ■ - Allowable ▲ - Needs Screening

- 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 that are either 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 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.
- 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, MDEQ recommends that aluminum foil not is used unless equipment blank samples confirm it is PFAS-free.

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 or a QAPP. Due to the extensive use of PFAS in many industries and products, PPE may contain PFAS. During PFAS investigation, PPE containing PFAS should be avoided to prevent cross-contamination. 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 exposure of staff to PFAS through PPE.

Personal safety is paramount. The safety of staff should not be compromised by fear of PFAS containing materials without any scientific basis. Any deviation from this guidance, including those necessary to ensure the health and safety of sampling personnel, must be recorded in field notes and discussed in the final report.

Globally, protective coatings for textiles are estimated to be about 50 percent of the total use of PFAS (DEPA, 2015). Due to its unique properties of water and oil repellency, 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.

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).

While preparing for sampling, particular focus should be made on clothing that has been 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.

Field Clothing and PPE that should be avoided (●) in the immediate sampling environment include the following:

● - Prohibited ■ - Allowable ▲ - Needs Screening

- Do not use clothing that has been washed with fabric softener which may contain PFAS.
- Do not use clothing that has been made with or washed with water, dirt, and/or stain resistant chemicals.
- Do not use clothing chemically treated for insect resistance and ultraviolet protection (See **Section 4.2.5** on biological hazards).
- Do not use clothing or PPE items that have any of the brand or product names that have been found to contain PFAS by the Danish Ministry of the Environment and presented in **Table 1** below (DEPA, 2015).

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 over-boots may be worn. The overboots must be put on, and hands 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 should be evaluated prior to sampling.

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

- ▲ Latex gloves.
- ▲ Water resistant or stain-treated clothing and PPE.
- ▲ Tyvek suits and clothing that contain Tyvek® (USEPA PFAS sampling guidance from USEPA Region 2 prohibits the use of Tyvek; available product information suggests Tyvek® may be used if required. Coated Tyvek® requires further evaluation; therefore, MDEQ recommends the collection of an Equipment Blank before Tyvek® use).

Table 1 below provides a list of prohibited field clothing (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 during the manufacturing of a particular item.

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

● Prohibited Materials ¹ (DEPA, 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	Unidyne™
Bionic Finish®	RUCO-GUARD®
RUCOSTAR®	RUCO-COAT®
RUCO-PROTECT®	RUCOTEC®
RUCO®	Resist Spills™
Resists Spills and Releases Stains™	Scotchgard™ Fabric Protector

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

4.2.5 Sun and Biological Protection

Because biological hazards (sunburn, mosquitos, ticks, etc.) may be encountered during sampling, the elimination of specific clothing materials or PPE (sunscreens and insect repellants) could pose a health and safety hazard to staff.

The safety of staff should not be compromised by fear of PFAS containing materials without any scientific basis. Personal safety is paramount. Any deviation from this guidance, including those necessary to ensure the health and safety of MDEQ staff, should be recorded in field notes and discussed in the final report.

Prolonged sun exposure will require sunscreens, which may have included PFAS in their manufacture. Protection against insects may require the use of insect repellent. **Table 2** 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.

NOTE: Sunscreens and insect repellants must be evaluated on a case-by-case basis. Refer to **Section 4.6 Quality Control Samples** for details on collecting equipment blanks.

The MDEQ recommends that additional sunscreens and insect repellents be treated as (▲) Needs Screening and should be evaluated before use.

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

● - Prohibited ■ - Allowable ▲ - Needs Screening

Table 2. Sunscreen and Insect Repellents¹

■ Allowable Insect Repellants	
Photos	Insect Repellent Spray
	<ul style="list-style-type: none"> • OFF Deep Woods • Sawyer Permethrin
■ Allowable Sunscreens	
Photos	Sunscreens
	<ul style="list-style-type: none"> • Banana Boat Sport Performance Sunscreen Lotion Broad Spectrum SPF 30. • Meijer Sunscreen Lotion Broad Spectrum SPF 30. • Neutrogena Ultra-Sheer Dry-Touch Sunscreen Broad Spectrum SPF 30.

■ Allowable Sunscreens
<ul style="list-style-type: none"> • Banana Boat for Men Triple Defense Continuous Spray Sunscreen SPF 30 • Banana Boat Sport Performance Coolzone Broad Spectrum SPF 30 • Banana Boat Sport Performance Sunscreen Lotion Broad Spectrum SPF 30 • Banana Boat Sport Performance Sunscreen Stick SPF 50 • Coppertone Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50 • Coppertone Sport High-Performance AccuSpray Sunscreen SPF 30 • Coppertone Sunscreen Stick Kids SPF 55 • L'Oréal Silky Sheer Face Lotion 50+ • Meijer Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50 • Meijer Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70 • Neutrogena Beach Defense Water + Sun Barrier Lotion SPF 70 • Neutrogena Beach Defense Water + Sun Barrier Spray Broad Spectrum SPF 30 • Neutrogena Pure & Free Baby Sunscreen Broad Spectrum SPF 60+

▲ Materials That Require Screening
<p>Sunscreens: Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss My Face, and baby sunscreens that are “free” or “natural.”</p> <p>Insect Repellents: Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellent, Herbal Armor, California Baby Natural Bug Spray, Baby Ganics.</p> <p>Sunscreen and Insect Repellent: Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion.</p>

¹This table is not considered to be a complete listing of allowable materials and materials that require screening. All materials should be evaluated before use during sampling. Some of the sunscreen and insect repellent testing has been performed using a PFAS screening Method known as Particle Induce Gamma-Ray Emission (PIGE). The use of approved gloves should always be used, and the sample should never come into contact with any of the sunscreen or insect repellent products. An Equipment Blank sample could also be collected to verify the product as PFAS-free.

If an insect repellent has not been approved and staff needs protection against biting insects:

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

- 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 easily see ticks during field activities.
- Light-colored clothing, long sleeves, and large-brimmed hats also prevent sunburn.
- Equipment Blank samples should be collected to verify that the

preferred insect repellent or sunscreen is PFAS-free by using the testing procedures identified in **Section 4.6 Quality Control Samples**.

4.2.6 Personnel Hygiene and Personal Care Products (PCPs)

A number of sampling guidance documents recommend that personal hygiene and personal care products (PCPs) (e.g., cosmetics, shampoo, sunscreens, dental floss, etc.) not be used prior to 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). However, if the MDEQ’s sampling SOPs 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. However, field personnel should be aware of the potential of cross-contamination if the sampling equipment or actual samples would come into contact with these products. The following precautions should be taken when dealing with personal hygiene or PCPs before sampling:

- Do not handle or apply PCPs in the sampling area.
- Do not handle or apply PCPs while wearing PPE that will be present during sampling.
- Move to the staging area and remove PPE if applying personal care products becomes necessary.
- Wash hands thoroughly after the handling or application of 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, food 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 of the use of recycled paper which may contain PFAS. Various studies have found up to 57percent detection frequency in food contact materials such as paper (Trier et al., 2011; Rosenmai et al., 2013; Schaidler et al., 2017).

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

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, food containers, bags, and wraps (OECD, 2002). 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

requires 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.

- Do not handle, consume, or otherwise interact with pre-wrapped food or snacks, carry-out food, fast food, or other food items while on-site during sampling.
- Move to the staging area and remove PPE prior to 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

All bottles used for PFAS sampling should come from the laboratory that will also be performing the PFAS analysis. Commercial laboratories that have demonstrated awareness and elimination of possible PFAS cross-contamination from sample containers and laboratory supplies should be used. Recommended sampling containers will be discussed for each environmental media. Any sampling containers provided by the laboratory should be verified as PFAS-free.

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, have the potential of being treated with PFAS. However, these are considered **Category 2** materials and the field personnel should be aware of the possible PFAS use. Sample containers and equipment that will be used for sampling should not be stored on or come into contact with materials suspected to contain PFAS.

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. The sample container must be kept sealed at all times 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 various materials used in sampling and handling can be found in the **MDEQ Quick Reference Field Guide** located at the end of this document.

In the absence of formal USEPA guidance for PFAS sample storage, the documentation in EPA Method 537 Rev. 1.1 should be used as a guide for thermal preservation (holding temperature), and holding times for other environmental media samples (with the exception of biota – in order 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 Rev. 1.1 are used, follow the guidelines or requirements in those methods for sample storage, preservation, and hold times. Otherwise EPA Method 537 Rev. 1.1 requires that samples must be chilled during storage and shipment, and must 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. The following procedures should be used for sample shipment:

- - Prohibited
- - Allowable
- ▲ - Needs Screening

- 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 and it is absolutely 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, if needed, double bagged in LDPE resealable storage bags if needed.
- Fish and other wildlife samples should be placed on dry ice and frozen before the shipment to the lab. If fish is 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 should be shipped as soon as possible (e.g. overnight) to ensure the samples arrive within the analytical holding time specified by the lab.

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 least contaminated, to areas anticipated or identified to be most contaminated. If analytical results from past sampling events are available, the sampling sequence can be readily determined.

For many PFAS investigation sites, no PFAS sampling has been conducted. 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.

If 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, samples that are known to be upgradient from the impacted area should be sampled first, followed by those that are 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 is not known, and it is unclear how the equipment was handled, especially rental equipment, the equipment should be decontaminated.

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

Throughout the sampling guidance documents, information will be provided about any media-specific decontamination procedures. For non-dedicated **Category 1** sampling equipment, there are many decontamination methods, 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 polyvinylchloride (PVC) brush to remove particulates.
- Decontamination procedures should include triple rinsing with PFAS-free water.
- Do decontaminate sampling equipment after sampling at each location, or at 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, if washed and rinsed, the second bucket (bucket #2).
4. For decontamination of additional equipment, change the decontamination water between cleanings.

4.5 Laboratory Considerations

The PFAS analytical list is available on the MPART website (www.michigan.gov/PFASresponse) under Testing and Treatment. This list includes the 14 analytes required to be analyzed for drinking water samples when using USEPA Method 537 Rev. 1.1, and the 24 analytes the MDEQ recommends be analyzed for 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 QAPP.

Drinking Water Samples

USEPA Method 537 Revision 1.1 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 USEPA does not recognize isotope dilution as an acceptable modification of USEPA Method 537 Rev. 1.1 for drinking water analysis. USEPA 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: USEPA Method 537 Rev. 1.1 was developed to be used only for finished drinking water samples, and contains specific requirements for sample preservation, shipping storage, and holding times.

USEPA Method 537 Rev. 1.1 was designed for finished drinking water and chemical preservation using Trizma® to buffer the sample and remove free chlorine. Non-chlorinated finished drinking water may also be analyzed using USEPA Method 537 Rev. 1.1.

Other Environmental Media Samples

There are currently no published USEPA methods using isotope dilution for determining PFAS in non-drinking water matrices or other sample media. There are USEPA methods for analyzing PFAS in additional matrices going through the development and validation process and may be available as early as fall of 2018. 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. A review of the laboratory's procedure and certifications should be done to ensure that the laboratory is capable of providing data that meet the data quality objectives of the project. MDEQ is implementing a laboratory SOP review process. Staff should refer to the MDEQ internal shared drive to see whether SOPs have been reviewed for the lab they are considering.

The following non-USEPA 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 (ASTM, 2017) - 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 investigated for use with surface water, sludge, and wastewater for selected PFAS. This method has not been evaluated on drinking water matrices. Some commercial laboratories have modified this method and are using isotope dilution.
- ASTM D7968 (ASTM, 2017) - Standard Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography-Tandem Mass Spectrometry (LC/MS/MS). This procedure utilizes a quick extraction and is not intended to generate an exhaustive accounting of the content of PFAS in difficult soil matrices.

● - Prohibited ■ - Allowable ▲ - Needs Screening

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. For samples with high concentrations of PFAS, an FD may be warranted. 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 as well as 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:

- EB should be collected by passing laboratory verified PFAS-free water over or through decontaminated field sampling equipment before the collection of 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.
- FB are prepared in the laboratory by placing an aliquot of PFAS-free water 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, 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.
- TB are a bottle of PFAS-free water that should be prepared in the laboratory, should then travel from the laboratory to the site, and then get 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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Decon 90® is a trademark of Decon Laboratories Limited.

Gatorade® is a registered trademark of Stokely-Van Camp, Inc.

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MDEQ PFAS SAMPLING QUICK REFERENCE FIELD GUIDE¹

All Items Used During Sampling Event

● Prohibited

- Items or materials that contain fluoropolymers such as
 - Polytetrafluoroethylene (PTFE), that includes the trademarks Teflon® and Hostaflon®
 - Polyvinylidene fluoride (PVDF), that includes the trademark Kynar®
 - Polychlorotrifluoroethylene (PCTFE), that includes the trademark Neoflon®
 - Ethylene-tetrafluoro-ethylene (ETFE), that includes the trademark Tefzel®
 - Fluorinated ethylene propylene (FEP), that includes the trademarks Teflon® FEP and Hostaflon® FEP
- Items or materials that contain any other fluoropolymer

Pumps, Tubing, and Sampling Equipment

● Prohibited

- Items or materials containing any fluoropolymer (potential items include tubing, valves, or pipe thread seal tape)

■ Allowable

- High-density polyethylene (HDPE)
- Low-density polyethylene (LDPE) tubing
- Polypropylene
- Silicone
- Stainless-steel
- Any items used to secure sampling bottles made from:
 - Natural rubber
 - Nylon (cable ties)
 - Uncoated metal springs
 - Polyethylene

▲ Needs Screening²

- Any items or materials that will come into direct contact with the sample that have **not** been verified to be PFAS-free
 - Do not assume that any sampling items or materials are PFAS-free based on composition alone

Sample Storage and Preservation

● Prohibited

- Polytetrafluoroethylene (PTFE): Teflon® lined bottles or caps

■ Allowable

- Glass jars⁴
- Laboratory-provided PFAS-Free bottles:
 - HDPE or polypropylene
- Regular wet ice
- Thin HDPE sheeting
- LDPE resealable storage bags (i.e. Ziploc®) that will not contact the sample media⁶

▲ Needs Screening²

- Aluminium foil⁴
- Chemical or blue ice⁵
- Plastic storage bags other than those listed as ■ Allowable
- Low-density polyethylene (LDPE) bottles

Field Documentation

● Prohibited

- Clipboards coated with PFAS
- Notebooks made with PFAS treated paper
- PFAS treated loose paper
- PFAS treated adhesive paper products

■ Allowable

- Loose paper (non-waterproof, non-recycled)
- Rite in the Rain® notebooks
- Aluminium, polypropylene, or Masonite field clipboards
- Ballpoint pens, pencils, and Fine or Ultra-Fine Point Sharpie® markers

▲ Needs Screening²

- Plastic clipboards, binders, or spiral hard cover notebooks
- All markers not listed as ■ Allowable
- Post-It® Notes or other adhesive paper products
- Waterproof field books

Decontamination

● Prohibited

- Decon 90®
- PFAS treated paper towel

■ Allowable

- Alconox®, Liquinox®, or Citranox®
- Triple rinse with PFAS-free deionized water
- Cotton cloth or untreated paper towel

▲ Needs Screening²

- Municipal water
- Recycled paper towels or chemically treated paper towels

Clothing, Boots, Rain Gear, and PPE

● Prohibited	■ Allowable	▲ Needs Screening ²
<ul style="list-style-type: none"> • New or unwashed clothing • Anything made of or with: <ul style="list-style-type: none"> ○ Gore-Tex™ or other water-resistant synthetics • Anything applied with or recently washed with: <ul style="list-style-type: none"> ○ Fabric softeners ○ Fabric protectors, including UV protection ○ Insect resistant chemicals ○ Water, dirt, and/or stain resistant chemicals 	<ul style="list-style-type: none"> • Powderless nitrile gloves • Well-laundered synthetic or 100% cotton clothing, with most recent launderings not using fabric softeners • Made of or with: <ul style="list-style-type: none"> ○ Polyurethane ○ Polyvinyl chloride (PVC) ○ Wax coated fabrics ○ Rubber / Neoprene ○ Uncoated Tyvek® 	<ul style="list-style-type: none"> • Latex gloves • Water and/or dirt resistant leather gloves • Any special gloves required by a HASP • Tyvek® suits, clothing that contains Tyvek®, or coated Tyvek®

Food and Beverages

● Prohibited	■ Allowable
<ul style="list-style-type: none"> • No food should be consumed in the staging or sampling areas, including pre-packaged food or snacks. <ul style="list-style-type: none"> ■ If consuming food on-site becomes necessary, move to the staging area and remove PPE. After eating, wash hands thoroughly and put on new PPE. 	<ul style="list-style-type: none"> • Brought and consumed only outside the vicinity of the sampling area: <ul style="list-style-type: none"> ○ Bottled water ○ Hydration drinks (i.e. Gatorade®, Powerade®)

Personal Care Products (PCPs) - for day of sample collection⁶

● Prohibited	■ Allowable	▲ Needs Screening ²
<ul style="list-style-type: none"> • Any PCPs⁶, sunscreen, and insect repellent applied in the sampling area. 	<p>PCPs⁶, sunscreens, and insect repellents applied in the staging area, away from sampling bottles and equipment followed by thoroughly washing hands:</p> <p>PCPs⁶:</p> <ul style="list-style-type: none"> • Cosmetics, deodorants/antiperspirants, moisturizers, hand creams, and other PCPs⁶ <p>Sunscreens:</p> <ul style="list-style-type: none"> • Banana Boat® for Men Triple Defense Continuous Spray Sunscreen SPF 30 • Banana Boat® Sport Performance Coolzone Broad Spectrum SPF 30 • Banana Boat® Sport Performance Sunscreen Lotion Broad Spectrum SPF 30 • Banana Boat® Sport Performance Sunscreen Stick SPF 50 • Coppertone® Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50 • Coppertone® Sport High Performance AccuSpray Sunscreen SPF 30 • Coppertone® Sunscreen Stick Kids SPF 55 • L'Oréal® Silky Sheer Face Lotion 50 • Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 50 • Meijer® Sunscreen Continuous Spray Broad Spectrum SPF 30 • Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50 • Meijer® Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70 • Neutrogena® Beach Defense Water+Sun Barrier Lotion SPF 70 • Neutrogena® Beach Defense Water+Sun Barrier Spray Broad Spectrum SPF 30 • Neutrogena® Pure & Free Baby Sunscreen Broad Spectrum SPF 60+ • Neutrogena® UltraSheer Dry-Touch Sunscreen Broad Spectrum SPF 30 <p>Insect Repellents:</p> <ul style="list-style-type: none"> • OFF® Deep Woods • Sawyer® Permethrin 	<ul style="list-style-type: none"> • Products other than those listed as <ul style="list-style-type: none"> ■ Allowable

¹ This table is not considered to be a complete listing of prohibited or allowable materials. All materials should be evaluated prior to use during sampling. The manufacturers of various products should be contacted in order to determine if PFAS was used in the production of any particular product.

² Equipment blank samples should be taken to verify these products are PFAS-free prior to use during sampling.

³ **For surface water foam samples:** LDPE storage bags may be used in the sampling of foam on surface waters. In this instance, it is allowable for the LDPE bag to come into direct contact with the sample media.

⁴ **For fish and other wildlife samples:** Depending on the project objectives, glass jars and aluminum foil might be used for PFAS sampling. PFAS has been found to bind to glass and if the sample is stored in a glass jar, a rinse of the jar is required during the sample analysis. PFAS are sometimes used as a protective layer for some aluminum foils. An equipment blank sample should be collected prior to any aluminum foil use.

⁵ Regular ice is recommended as there are concerns that chemical and blue ice may not cool and maintain the sample at or below 42.8°F (6°C) (as determined by EPA 40 CFR 136 – NPDES) during collection and through transit to the laboratory.

⁶ Based on evidence, avoidance of PCPs is considered to be precautionary because none have been documented as having cross-contaminated samples due to their use. However, if used, application of PCPs must be done at the staging area and away from sampling bottles and equipment, and hands must be thoroughly washed after the use of any PCPs prior to sampling.