

Subject: Michigan Proof-of-Concept – Non-Mechanical Rain Evaluation for PFAS

Introduction

In October and November 2021, AECOM and EGLE staff conducted a proof-of-concept rainfall investigation to determine if rain samples could be easily and economically collected and analyzed for PFAS. The samples were collected in PFAS free buckets without the use of mechanical/electronic rain sampling equipment. The rain buckets were installed in open residential areas, free of overhanging vegetation, the influence of roofs and other cover. Samples were taken during a rain event (up to 24 hours of rainfall sampled). This sampling effort was based on work done by the North Carolina Department of Environmental Quality, Air Quality Division. Five locations across the lower peninsula of Michigan were selected for the study. The sampling sites were located at private homes in residential areas of East Kentwood, East Lansing, Ypsilanti, Saginaw Township, and Traverse City.

Project Objectives

The objectives of the project were to determine if valid rain samples could be collected using inexpensive and readily obtainable supplies, and secondarily, if PFAS is present in rainfall in Michigan.

Project Results

Two to four rainfall samples were collected per location based on rainfall events at each site during the testing period (October and November). Samples were collected in PFAS free buckets and transferred to 250 mL bottles supplied by Vista Laboratories, El Dorado Hills, California, and were analyzed for 29 PFAS compounds. Sampling information such as date, time, sample observations, weather, amount of rain collected, etc. was collected on a field data sheet (QAPP September 2021). A map showing the locations of the sampling stations and results was also prepared.

A total of the 15 samples were collected state-wide. Of the 15, 10 samples were found to contain PFAS, and 5 samples were non-detect (ND). Each site had at least one detection of PFAS in a rain event. Perfluorobutanoic Acid (PFBA) was the predominant PFAS compound detected and was found at every site and in every sample with a detection. Four other PFAS compounds were found at the Ypsilanti site during the November 23, 2021 rain event.

Quality Assurance/Quality Control Samples

An equipment blank was taken from the buckets that were used for the study; the results were non-detect for PFAS compounds. A sample of the deionized water that was used to rinse the buckets after cleaning was taken and was also non-detect. A matrix spike sample was run by Vista Labs and was found to be acceptable. Finally, a duplicate sample was taken, and the results (see results table below) were found to be acceptable.

Conclusion

Rain samples can be collected using simple and inexpensive methods using locally obtained supplies. A mechanical/electronic rain collection device is not needed to collect rain samples. One inch of rain (based on an inexpensive rain gauge) yielded over one liter of water which was enough for samples and QA/QC samples (duplicates, matrix spikes, and matrix spike duplicates). As the lab is able to do analysis with as little as 20 mL of rain (with higher detection limits), lower amounts of rain, as little as 0.1 inch, should yield enough rain for a lab sample due to the diameter of the bucket.

The use of Uline shipping containers and ice packs (the same as used by the EGLE Drinking Water lab for PFAS samples) were found to be more convenient and less expensive than using coolers and ice. The shipments to the lab made by AECOM were done using coolers and ice, while the samples from EGLE were sent by the Uline method. Freezing rain samples before shipping helped assure that the sample arrived at the lab in California below the EPA recommended receiving temperature.

Report prepared by: Mike Jury, MPART PFAS Specialist, July 2022

Attachments:

- Rain Bucket QAPP and Standard Operating Procedure
- Rain Bucket Proof of Concept Results

**Investigation of Per- and Polyfluoroalkyl Substances (PFAS)
In Michigan Rainwater, October and November 2021
East Lansing, Grand Rapids, Saginaw Township, Traverse City, Ypsilanti**

**Quality Assurance Project Plan (QAPP)
September 2021**

Background

Per- and polyfluoroalkyl substances (PFAS) are a large class of chemicals in which most or all of the carbon atoms in the molecular backbone are fluorinated. Many products containing PFAS are used in many industrial and consumer applications, along with their use in Aqueous Film Forming Foam (AFFF). Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are two compounds in this class that have been detected in Michigan's soils, ground and surface water, and biota. Industrial and domestic waste containing these compounds can enter the environment through wastewater treatment systems, stormwater runoff, or as deposition after being emitted into the atmosphere.

The Michigan Department of Environment, Great Lakes, and Energy (EGLE) has prepared this QAPP for the sampling of rainwater at five cities in Michigan to measure concentrations of PFAS in rainwater. This project and proof of concept is designed to determine if rainwater samples can be manually and effectively collected without the use of mechanical rain sampling equipment. This sampling effort was based on work done by the North Carolina Department of Environmental Quality, Air Quality Division. Additional sampling may occur based on the results of this project.

Organization and Responsibility

Sampling will be coordinated by Michael Jury of the EGLE Remediation and Redevelopment Division using the attached "Standard Operating Procedure for PFAS in Rainwater Collection Program". Sample collections will be made by AECOM, a State of Michigan contractor, and by EGLE staff at five locations in Michigan's lower peninsula. The analysis of samples for 29 selected PFAS compounds (Michigan recommended list of 28 compounds, plus PFECBS) will be made by Vista Analytical Laboratory, El Dorado Hills, California.

Project Objectives

The objectives of this project are to determine if PFAS is present in rainfall, and if valid samples can be collected using inexpensive and readily obtainable supplies. Rainwater samples will be collected from five sample locations (East Lansing, Grand Rapids, Saginaw Township, Traverse City, and Ypsilanti) with two to four rainfall samples per location. Samples will be collected in PFAS free 250 mL bottles supplied by Vista Laboratories. A map showing the locations of the sampling stations and results will also be prepared.

Associated Sample Parameters and Other Information

Equipment blanks, field blanks, sample duplicates, and matrix spike/matrix spike duplicates will be performed based on the volume of rain collected during the four samples (see attached standard operating procedure). All samples collected will be logged on the lab supplied Chain of Custody and shipped overnight to Vista using FedEx. The samples will be analyzed by Vista's isotope dilution method (also known as EPA 537M) for 29 PFAS compounds including branched and linear compounds for PFOA, PFOS, PFHxS, MeFOSAA, and EtFOSAA.

Expected turn around time for the samples is 21 days. Additionally, sampling information such as date, time, sample observations, weather, etc. will be collected on a field data sheet.

Status Reports

A report summarizing the sampling results, quality assurance analysis and outlining recommended next steps will be produced by EGLE-RRD staff.

Department of Environment, Great Lakes and Energy

**Standard Operating Procedure for the PFAS
in Rainwater Collection Program**

**Preparation, Installation, Collection, and Shipment
of Rainwater Sample Media**

Operator Responsibilities

Prepared by:
Michael Jury, EGLE
Remediation and Redevelopment Division

Approval Sign-Off Sheet

I certify that I have read and approve of the contents of this SOP for the rainwater collection program.

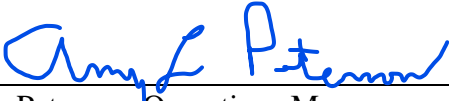


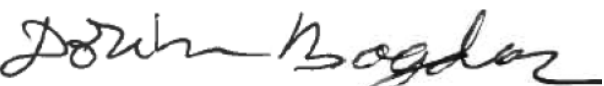
	
Amy Peterson, Operations Manager	Date
	22 March 2022
Michael Jury, Environmental Specialist	Date
	
Dorin Bogdan, AECOM	Date

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1.1 Purpose

The purpose of this Standard Operating Procedure (SOP) is to describe the steps required to setup, collect, process, store, and ship rainwater samples.

1.2 Recommended Material List

Potential supplies that may be needed for the study:

- ✓ Rainwater Field Data Sheet (FDS) (Appendix A)
- ✓ 1 – Box of powder-free nitrile gloves
- ✓ Lab supplied identification labels for bottles
- ✓ Lab supplied Chain of Custody (COC) forms
- ✓ Pre-cleaned rainwater collection buckets with lids
- ✓ <https://www.lowes.com/pd/United-Solutions-5-Gallon-General-Bucket/1000462835>
- ✓ Ziploc® bags [quart]
- ✓ Ziploc® bags [gallon]
- ✓ 1 – Box of PFAS-free garbage bags, Hefty 33 gallon [Hefty 40-Pack 33-Gallon Black Outdoor Plastic Construction Trash Bag](#)
- ✓ Alconox, Liquinox, or other PFAS free suitable cleaner
- ✓ PFAS-free water -- lab supplied or tested municipal
- ✓ 250 mL pre-cleaned sample bottles with caps (lab supplied) for sampling, blanks, and duplicates
- ✓ Box of Kimwipes
- ✓ 1 – Blue sorbent sheet material for sampling media and sample prep areas
- ✓ Shipping coolers (Coleman style or Uline shipping container with ice packs)
- ✓ [Insulated Foam Shipping Kit - 8 x 6 x 7" S-13391 - Uline](#)
- ✓ Shipping Tape
- ✓ Paper Towels
- ✓ Bubble Wrap
- ✓ Safety Glasses

1.3 Preparation of Rainwater Sampling Media

- 1.3.1 Prepare a clean sink for washing/rinsing and a clean surface for air drying using the provided blue sorbent sheet material or other similar material.
- 1.3.2 Put on new powder-free nitrile gloves.
- 1.3.3 Wash the 5-gallon bucket(s) and lid(s) with Alconox or Liquinox (or another PFAS free cleaner). Rinse the inside, outside, and rim of the 5-gallon bucket(s) and all surfaces of the lid(s) 3 times using PFAS-free water.

- 1.3.4 Allow the 5-gallon bucket(s) and lid(s) to air dry on the blue sorbent sheet material for at least thirty minutes before using the bucket for measuring rainwater or field blank samples.
- 1.3.5 Once the 5-gallon bucket(s) is dry, place the lid(s) onto the 5-gallon bucket and place the bucket(s) into a PFAS-free garbage bag for storage until labeling and use.

1.4 Installation and Removal of Rainwater Sampling Media

- 1.4.1 Sample bucket installation and removal occurs when rain is forecasted. If the sample cannot be collected on the day of expected rainfall (i.e. weekend), then plan on setting out the bucket on Friday, and then collect the sample on Monday. Record the placement and collection date on the Field Data Sheet (FDS). If you are using the Uline box method of shipping samples, make sure the freezer packs are frozen for 24 hours before using.
- 1.4.2 Prepare a new FDS for the sample bucket(s).
- 1.4.3 Put on powder-free nitrile gloves and remove the bucket from the garbage bag.
- 1.4.4 Bring to the installation site the pre-cleaned 5-gallon bucket(s), lid(s), FDS(s), as well as any other field supplies including powder-free nitrile gloves, Kimwipes, and paper towels. The garbage bag used to hold the bucket may be used to carry the supplies.
- 1.4.5 Put on new powder-free nitrile gloves before handling sample bucket(s) and lid(s).
- 1.4.6 When removing any previously installed sample bucket, cover and seal the bucket.
 - 1.4.7 Note the sample removal date, time, site operator, site observations, and sample observations on the corresponding sample ID FDS(s). When recording sample observations on the FDS(s) be sure to add a subjective description about the amount and size of the substances (if any) observed in the sample media. The FDS(s) will go back to the office with the collected sample bucket(s).
 - 1.4.8 At this point, the set of nitrile gloves that are on the operator's hands are "dirty". Put on a new pair of nitrile gloves prior to installing new sample bucket(s).

- 1.4.9 Remove the lid(s) from the pre-cleaned 5-gallon bucket(s) that are to be installed and place them in a PFAS free garbage bag to be carried back to the office for storage.
- 1.4.10 Install the bucket on the surface of the sampling area. Be sure to pick an area where the bucket will not pick up excessive debris such as leaves, large amounts of dust, water from sprinkler systems, or where it might be disturbed by children or animals. Ensure that the bucket is stable and resting flat. If high winds are expected, place bricks, milk jugs with water, or other items around the bucket to make sure it isn't disturbed by the wind.
- 1.4.11 Note the sample date, time of installation, site operator, site name, and site ID on the corresponding FDS(s). Note any comments and site visit information on the FDS(s).
- 1.4.12 Store the FDS(s) in a Ziploc bag (gallon).
- 1.4.13 Bring the collected sealed bucket(s), current sample bucket lid(s), FDS(s) for the collected sample(s), and any material(s) brought from the office, back to the office for sample processing and shipment to the Lab.

1.5 Preparation, Installation, and Handling of Field Blank

- 1.5.1 If a field blank sample is required (check with your supervisor), prepare a pre-cleaned 5-gallon bucket and lid according to this sample ID format. (FBMMDDYY-Site ID) "FB" for field blank.
- 1.5.2 Using a clean sample bottle or a graduated cylinder on a level surface, measure 600 mL of PFAS-free water and pour the measured volume into a pre-cleaned 5-gallon bucket. Place the sample lid on the 5-gallon bucket.
- 1.5.4 Transport the sealed 5-gallon bucket with 600 mL PFAS-free water to the field site alongside the rainwater sample media for the sampling period. Place the 5-gallon bucket near the sample area. Open the Field Blank bucket while preparing and installing the sample bucket. When the field bucket installation is completed, pour the contents of the Field Blank bucket into the labeled sample bottles. Discard any remaining water. Place the used bucket and lid into the garbage bag.
- 1.5.5 Note the field blank installation information on the corresponding FDS(s). Initial and date all entries.

1.6 Processing and Preparing Rainwater Samples for Shipment to the Laboratory

Preparation of a Trip Blank

- 1.6.1 Label one 250 mL sample bottle with a strip of tape, or lab supplied labels according to this sample ID format (TBMDDYY-Site ID) “TB” for trip blank. The trip blank sample ID should correspond to the date the samples are scheduled to be shipped to the Lab. The trip blank should be created the same day the rainwater samples are scheduled to be shipped to the Lab.
- 1.6.2 Prepare a new FDS for the trip blank. Ensure the sample ID on the sample bottle matches the sample ID on the FDS.
- 1.6.3 The trip blank is created by pouring 250 mL of PFAS-free water into a labeled 250 mL pre-cleaned sample bottle, then sealing the 250 mL bottle in a Ziploc® bag (quart). Remove as much air in the bag as possible then seal the bag shut. Shipment of the trip blank is discussed starting in Step 1.6.15

Measuring and Shipping Rainwater Samples

- 1.6.4 Perform the following steps at the office on a level surface to ensure accurate volume measurements. Remember to change your gloves each time if you are handling more than one rain bucket sample.
- 1.6.5 Label the 250 mL sample bottle(s) with a strip of orange tape or lab-provided labels according to this sample ID format. (TMMDDYY-Site ID) where “T” indicates the sample Type which will be: “W” for wet deposition; “FB” for field blank; “D” for duplicate. Use the provided Sharpie to write on the labels. The number of labels needed will depend upon the type of samples and the volume of samples measured in the following steps.
- 1.6.6 Gently swirl the rainwater collected in the 5-gallon bucket several times to get water droplets off the side of the bucket, and then gently tap the bucket on the countertop to get the rest of the water drops off the sides and/or lid.
- 1.6.7 Remove the lid of the 5-gallon bucket and record any sample observations on the FDS.
- 1.6.8 Carefully pour the sample into the 250 mL sample bottle(s) and measure the amount of rainwater collected in the 5-gallon bucket as you fill the bottles using the scale on the side of the bottle. One inch of rain will produce more than 1,250 mL of sample. Depending on the type of sample and the volume of sample measured go to the following steps to proceed:
 - **Less than 500 mL** go to Step 1.6.9

- **Greater than 500 mL and less than / equal to 1,000 mL** go to Step 1.6.10
 - **Greater than 1,000 mL** go to Step 1.6.11
 - **Field blank** go to Step 1.6.12
- 1.6.9 If the measured rainwater volume is **less than 500 mL** record the measured rainwater volume on the FDS. Gently pour the rain from the bucket into the 250 mL container to the neck, do not fill the bottle to the top. Pour any remaining sample into another 250 mL bottle.
- 1.6.10 If the rainwater volume is **greater than or equal to 500 mL and less than or equal to 1,000 mL** record the rainwater volume on the FDS. Pour all the measured rainwater from the bucket into the labeled 250 mL sample bottles. This procedure will generate between two and four samples in bottles for shipment to the lab. Check with your Manager to determine if you will be collecting duplicate samples from your extra sample volume.
- 1.6.11 If the rainwater volume is **greater than 1,000 mL** measure and record the entire volume of the rainwater collected on the FDS. Using 1000 mL of sample, fill four labeled 250 mL sample bottles from the graduated cylinder for shipment to the lab. This will allow the collection of duplicate or matrix spike/matrix spike (MS/MSD) samples. Check with your Manager to determine if you will be collecting duplicate samples or MS/MSD from your extra sample volume. Discard the remainder of the sample.
- 1.6.12 If the 5-gallon bucket is the **Field Blank**, then measure and record the measured volume under “Volume of PFAS-free water added (mL)” on the FDS. Pour all the measured sample from the bucket into the labeled 250 mL sample bottles. This procedure will generate three samples in bottles for shipment to the Lab.
- 1.6.13 Place each of the 250 mL sample bottles into separate Ziploc® bags (quart). Ensure the label on the sample bottle is visible. Remove as much air in the bag as possible.
- 1.6.14 If rainwater samples will be shipped the day after collection, place the labeled 250 mL sample bottles in a freezer or in a cooler with ice. The rainwater sample should be frozen if possible before shipment. If the samples will be shipped on the collection day, place the labeled 250 mL sample bottles in the provided sample shipment cooler (Coleman style or Uline) as described in the next Step.
- 1.6.15 Cover the bottom and sides of the inside of the sample shipment cooler with bubble wrap, place ice on top of the bubble wrap, and then stand the labeled 250 mL sample bottles on top of the ice. Include a trip blank with each shipment cooler sent to the lab. For the Uline cooler, place a piece of bubble wrap on the bottom of the Styrofoam box and place the 250 mL samples in the box and

arrange the frozen freezer packs in a “H” configuration. With four sample bottles, the fifth freezer pack will go on top of the bottles.

- 1.6.16 Once the labeled 250 mL sample bottles and trip blank are in the sample shipment cooler, then cover them with ice until the cooler is full (around 14 to 21 pounds of ice). Place a sheet of bubble wrap on top of the ice and samples. For the Uline box, also place bubble wrap on top of the samples and place the Styrofoam lid on top of the samples.
- 1.6.17 Copy the FDS form for the project files.
- 1.6.18 Complete the laboratory-supplied Chain of Custody form and place it in a Ziploc® bag (gallon) and place it in the cooler. Tape the cooler closed.
- 1.6.19 Schedule the pickup by UPS or FedEx, or drop off the sample yourself.
- 1.6.20 Record all sample IDs, rainwater volumes, trip blank sample ID, and any additional comments regarding the samples such as tracking numbers and tamper resistant seal number (if used) on the FDS.

Appendix A: Rainwater Field Data Sheet

Michigan Department of Environment, Great Lakes, and Energy Remediation and Redevelopment Division Rainwater Collection Network Sample Form		Sample ID # (TMMDDYY-Site ID)																																					
		Type (T) W-Wet FB-Field Blank, TB-Trip Blank																																					
Site Name: _____ Site ID: _____		Site Operator (Print/Initial) Name On: _____ Name Off: _____																																					
Sample Container <table style="width: 100%; border-collapse: collapse;"> <tr> <td></td> <td colspan="3" style="text-align: center;">Date</td> <td style="text-align: center;">Time</td> </tr> <tr> <td></td> <td style="text-align: center;">MM</td> <td style="text-align: center;">DD</td> <td style="text-align: center;">YY</td> <td style="text-align: center;">00:01 to 24:00</td> </tr> <tr> <td style="text-align: center;">ON</td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td style="text-align: center;">OFF</td> <td></td> <td></td> <td></td> <td></td> </tr> </table>			Date			Time		MM	DD	YY	00:01 to 24:00	ON					OFF					Analysis Type GenX <input type="checkbox"/> PFAS <input type="checkbox"/> Other <input type="checkbox"/> (Specify) _____																	
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Sample Observations <table border="1" style="width: 100%; border-collapse: collapse; font-size: x-small;"> <tr> <td style="width: 5%;">Y</td> <td style="width: 5%;">N</td> <td style="width: 45%;"></td> <td style="width: 5%;">Y</td> <td style="width: 5%;">N</td> <td style="width: 30%;"></td> </tr> <tr> <td></td> <td></td> <td>Plant matter/Pollen</td> <td></td> <td></td> <td>Bird droppings</td> </tr> <tr> <td></td> <td></td> <td>Particulate matter</td> <td></td> <td></td> <td>Cloudy or <u>Discolored</u></td> </tr> <tr> <td></td> <td></td> <td>Insect/Animal matter</td> <td></td> <td></td> <td>Handling contamination</td> </tr> </table>		Y	N		Y	N				Plant matter/Pollen			Bird droppings			Particulate matter			Cloudy or <u>Discolored</u>			Insect/Animal matter			Handling contamination	Site Observations <table border="1" style="width: 100%; border-collapse: collapse; font-size: x-small;"> <tr> <td style="width: 5%;">Y</td> <td style="width: 5%;">N</td> <td style="width: 90%;"></td> </tr> <tr> <td></td> <td></td> <td>Bucket collector operating correctly</td> </tr> <tr> <td></td> <td></td> <td>Rain gauge data collected and logged (if used)</td> </tr> <tr> <td></td> <td></td> <td>Other Specify _____</td> </tr> </table>		Y	N				Bucket collector operating correctly			Rain gauge data collected and logged (if used)			Other Specify _____
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Field Comments (Include Rain Gauge Data if Collected): 		Post Sampling Processing																																					
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Date Rec'd	Temp Rec'd	Initials/Date																																					
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Rain Bucket Proof of Concept Location and Result (in parts per trillion (ppt))

Date of sample	East Lansing	Grand Rapids	Saginaw Township	Traverse City	Ypsilanti
10/15/2021	not sampled this date	1.19 J PFBA	not sampled this date	not sampled this date	not sampled this date
10/25/2021	not sampled this date	1.74 J PFBA	ND	not sampled this date	not sampled this date
10/26/2021	not sampled this date	not sampled this date	not sampled this date	not sampled this date	ND
10/29/2021	not sampled this date	not sampled this date	1.27 J PFBA	not sampled this date	not sampled this date
11/3/2021	not sampled this date	not sampled this date	not sampled this date	1.8 J PFBA	ND
11/12/2021	not sampled this date	ND	1.20 J PFBA	1.55 J PFBA	not sampled this date
11/14/2021	2.31 J PFBA, 3.09 J Total EtFOSAA	not sampled this date	not sampled this date	not sampled this date	not sampled this date
11/17/2021	ND	1.28 J PFBA	1.14 J PFBA, 1.05 J PFBA (duplicate sample)	not sampled this date	not sampled this date
11/23/2021	not sampled this date	not sampled this date	not sampled this date	not sampled this date	5.78 PFBA, 1.26 J PFPeA, 1.34 J PFBS, 1.30 J PFHxA, 1.16 J PFPHpA
# of samples	2	4	4	2	3

ND = non-detect, which means no PFAS compounds were found above the reporting limit

J = the amount detected is below the Reporting Limit/LOQ but above detection

Not sampled means either there was no rain at the location on that day or the location had not started sampling at that point in time.