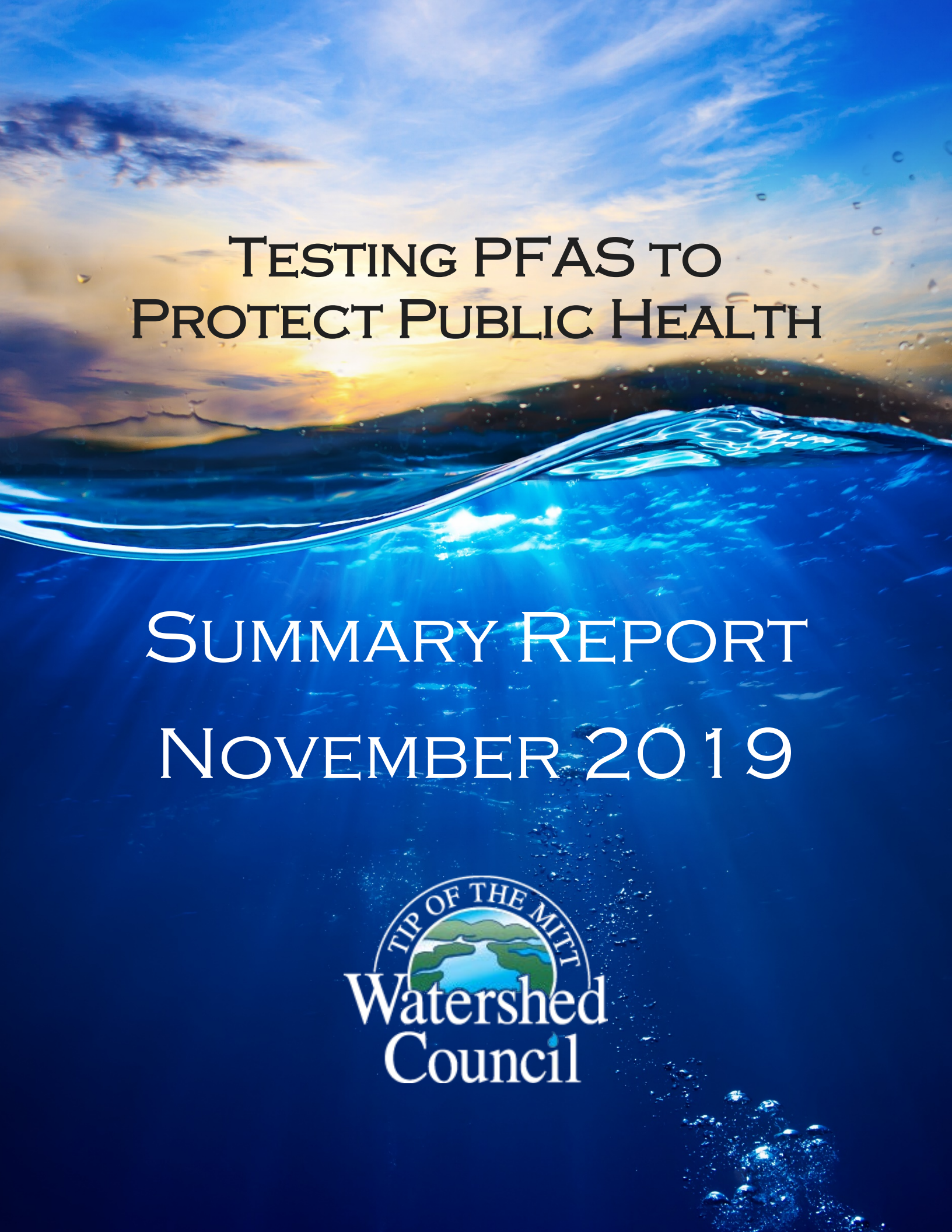


Testing PFAS to Protect Public Health

Summary Report

November 2019

Tip of the Mitt Watershed Council

FUNDERS

CHARLEVOIX COUNTY COMMUNITY FOUNDATION

Giving *Back*. Moving *Forward*.

Petoskey-Harbor Springs Area community foundation

TIP OF THE MITT WATERSHED COUNCIL

FOUNDED IN 1979, THE WATERSHED COUNCIL IS A LEAD ORGANIZATION FOR WATER RESOURCES PROTECTION IN ANTRIM, CHARLEVOIX, CHEBOYGAN, AND EMMET COUNTIES.

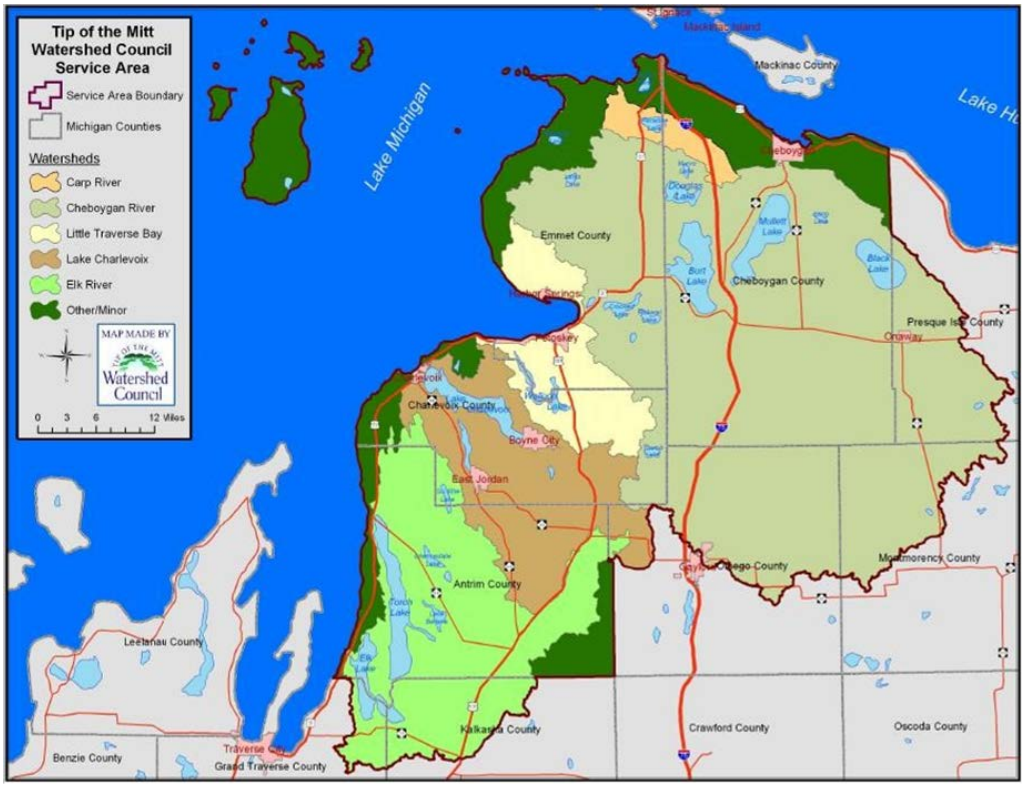
OUR MISSION

The Tip of the Mitt Watershed Council speaks for Northern Michigan's waters. We are dedicated to protecting our lakes, streams, wetlands, and groundwater through respected advocacy, innovative education, technically sound water quality monitoring, thorough research, and restoration actions. We achieve our mission by empowering others and we believe in the capacity to make a positive difference. We work locally, regionally, and throughout the Great Lakes Basin to achieve our goals.

OUR SERVICE AREA

Water resources in our service area include:

- More than 2,500 miles of rivers and streams
- Multiple blue-ribbon trout streams
- 14 lakes larger than 1,000 acres (among the largest in the State)
- 339,000 acres of wetlands (according to 2000 landcover statistics)



PFAS CONTAMINATION

PFAS are man-made chemicals that have been used in industrial and consumer products worldwide since the 1950s. PFAS can be found in everyday consumer products such as:

- Food packaging materials
- Nonstick cookware
- Stain-resistant carpet treatments
- Water-resistant clothing
- Cleaning products
- Paints, varnishes, and sealants
- Firefighting foam

Certain PFAS chemicals, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), are no longer manufactured in the United States as a result of voluntary phase out programs. However, other countries may still manufacture and use them. There are nearly 5,000 different types of PFAS, many of which are still in use today in the United States.

How are we exposed to PFAS?

The most common exposure to PFAS is through drinking contaminated water. At least 1.9 million Michigan residents have been exposed to some level of PFAS in their drinking water. Eating fish caught from water contaminated by PFAS (PFOS, in particular) can also be an exposure pathway. Fish are being collected in Michigan from lakes and rivers and tested for some of the PFAS chemicals. Michigan Department of Human and Health Services releases Eat Safe Fish Guides each spring, and emergency advisories as needed. There are currently no PFOS guidelines for any water bodies in our service area – the watersheds within the Counties of Antrim, Charlevoix, Cheboygan, and Emmet. We recommend that the Eat Safe Fish Guide be checked out annually, as guidelines will be updated if elevated levels of PFOS are found. In water bodies with fish that have a PFOS guideline, touching the fish or water and swimming are not considered a health concern as PFAS do not move easily through the skin.

People can also be exposed to PFAS chemicals contained in consumer products if they are released during normal use, biodegradation, or disposal. This can occur by eating food that was packaged in material that contains PFAS and using products such as non-stick cookware, stain resistant carpeting, and water-repellant clothing.

Why are we concerned about PFAS?

PFAS bioaccumulate and are incredibly persistent in the environment. This means the amount of PFAS that build up in organisms and in ecosystems over time do not break down in the soil or water environment. Because PFAS are so widespread and persistent, the average person has been exposed to some level of PFAS during their lifetime. As a result, PFAS are found in the bloodstreams of 99% of Americans. However, having PFAS in your blood does not necessarily

mean that you will become ill. Studies indicate that certain PFAS can lead to adverse health problems in humans, including:

- Lowering a woman's chance of getting pregnant
- Increasing the chance of high blood pressure in pregnant women
- Increasing the chance of thyroid disease
- Increasing cholesterol levels
- Changing immune response
- Increasing chance of cancer, especially kidney and testicular cancers

However, the full health impacts from PFAS are not completely understood and research continues to be conducted to understand how the timing, duration, and concentrations of exposure play a role on the effects of PFAS. In addition, new kinds of PFAS are being developed. Some of these may have properties similar to the existing PFAS, and some may be less persistent in the environment. There are very few scientific studies on new PFAS, so more research is necessary to discover whether they may be a health concern.

Is there a safe level of PFAS?

The U.S. Environmental Protection Agency's (EPA) recommended lifetime health advisory limit is set at 70 parts per trillion (ppt) for PFOA and PFOS. Currently, the EPA has not set health advisory levels for the other PFAS chemicals. Michigan has adopted a cleanup standard for contaminated groundwater supplies of 70 ppt for PFOS and PFOA, based on the EPA standard.

However, this number may be too high. A study by the Centers for Disease Control and Prevention (CDC) found that, for certain PFAS, health issues began presenting themselves at significantly lower levels than the current EPA recommendation of 70 ppt.

What is the State of Michigan doing about PFAS?

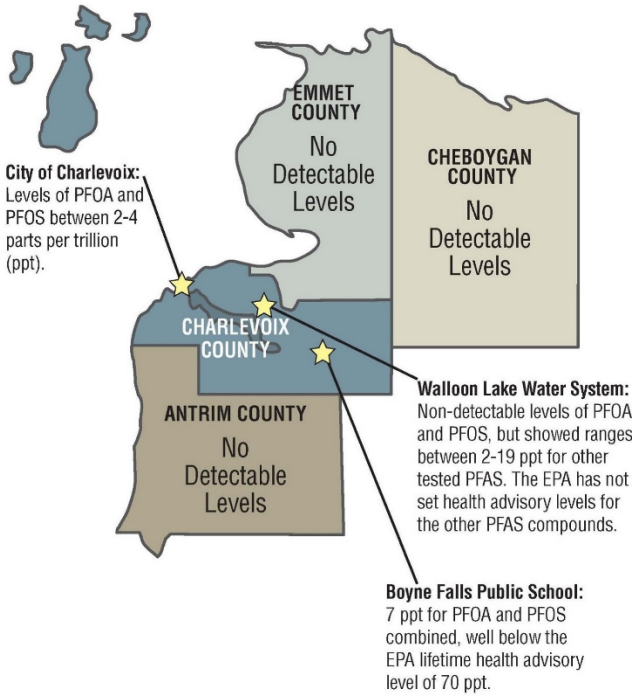
The State of Michigan is taking a proactive approach in identifying areas with PFAS contamination. The State established the Michigan PFAS Action Response Team (MPART) for a rapid and multi-departmental response. MPART is requiring all public water systems and 461 schools to test their water supplies and have asked wastewater treatment plants to test their discharge. Furthermore, Michigan made it labs capable of testing for PFAS, helping to reduce the time it takes to get back certified results. They are also testing different fish and recommending limited or no consumption of certain species due to PFAS contamination.

Michigan is also in the process of developing an enforceable drinking water standard. A final rule with a PFAS Maximum Contaminant Level (MCL) is expected to be in effect in the spring of 2020. All this information is available to the public at www.michigan.gov/pfasresponse

PFAS in Northern Michigan

Public drinking water systems in our service area were tested for PFAS in August of 2018 by the Michigan Department of Environmental Quality (MDEQ), now the Michigan Department of Environment, Great Lakes, and Energy (EGLE). The result of that testing was:

- Antrim County: no detectable levels
- Cheboygan County: no detectable levels
- Emmet County: no detectable levels
- Charlevoix County:
  - City of Charlevoix - levels of PFOA and PFOS between 2-4 parts per trillion (ppt)
  - Walloon Lake Water System- non-detectable levels of PFOA and PFOS, but showed ranges between 2-19 ppt for other tested PFAS. The EPA has not set health advisory levels for the other PFAS compounds.
  - Boyne Falls Public School - 7 ppt for PFOA and PFOS combined, well below the EPA lifetime health advisory level of 70 ppt.



However, this testing was only for communal drinking water systems. Data for lakes, rivers, and individual wells are very limited.

TESTING PFAS TO PROTECT PUBLIC HEALTH

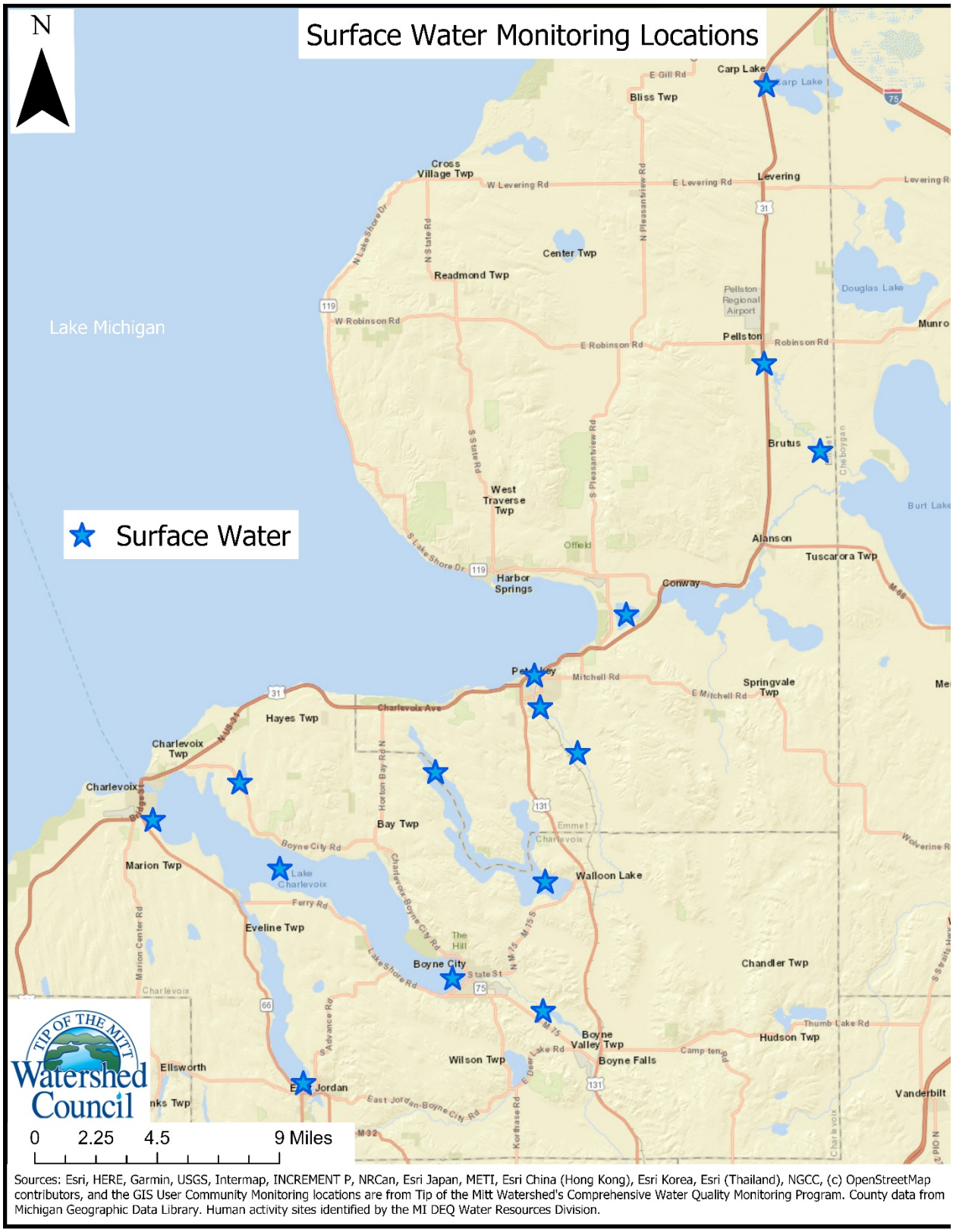
In 2018, the Michigan Department of Environmental Quality (MDEQ) tested municipal water supplies in the State for PFAS. To supplement the work of MDEQ, Tip of the Mitt Watershed Council, with generous funding from the Charlevoix County Community Foundation and Petoskey-Harbor Springs Community Foundation, tested surface water resources for PFAS in our region. The project was intended to protect public health by testing to identify the location of PFAS in Charlevoix and Emmet Counties, if any. It was designed to aid the State of Michigan's response to these emerging contaminants by highlighting potential areas for further investigation within Charlevoix and Emmet Counties.

Tip of the Mitt Watershed Council collected 24 samples from 15 sites within nine water bodies located within Emmet and Charlevoix Counties, including Lake Charlevoix, Boyne River, Susan Lake, Walloon Lake, the Bear River, Round Lake, Paradise Lake, Maple River, and Stover Creek.

The locations were chosen based upon vicinity to nearby potential PFAS use/contamination such as fire departments, landfills, airports, biosolid land application sites, plating and polishing facilities, waste treatment/storage sites, and electroplaters. Samples were collected from the surface, middle, and bottom of the water column and each site was sampled in the spring and fall to account for seasonality.

Two sets of samples were collected in accordance with MDEQ surface water sampling protocols (Appendix C) and tested using United States Environmental Protection Agency (USEPA) Method 537 Rev.1.1. One sample set was collected on May 24th and 25th, while the second set was collected on October 8th and 9th. The samples were analyzed for 14 of the common PFAS chemicals at the University of Michigan Biological Station. The 14 analytes tested for include:

- perfluorooctanoic acid (PFOA)
- perfluorooctanesulfonic acid (PFOS)
- perfluorobutanesulfonic acid (PFBS)
- perflfuorohexanoic acid (PFHxA)
- perfluoroheptanoic acid (PFHpA)
- perfluorononanoic acid (PFNA)
- perfluorodecanoic acid(PFDA)
- perfluoroundecanoic acid(PFUnA)
- perfluorododecanoic acid (PFDoA)
- perfluorotridecanoic acid (PFTriA)
- perfluorotetradecanoic acid (PFTeA)
- N-methylperfluorooctanesulfonamidoacetic acid (N-MeFOSAA)
- N-ethylperfluorooctanesulfonamidoacetic acid (N-EtFOSAA)
- perfluorohexanesulfonic acid (PFHxS)



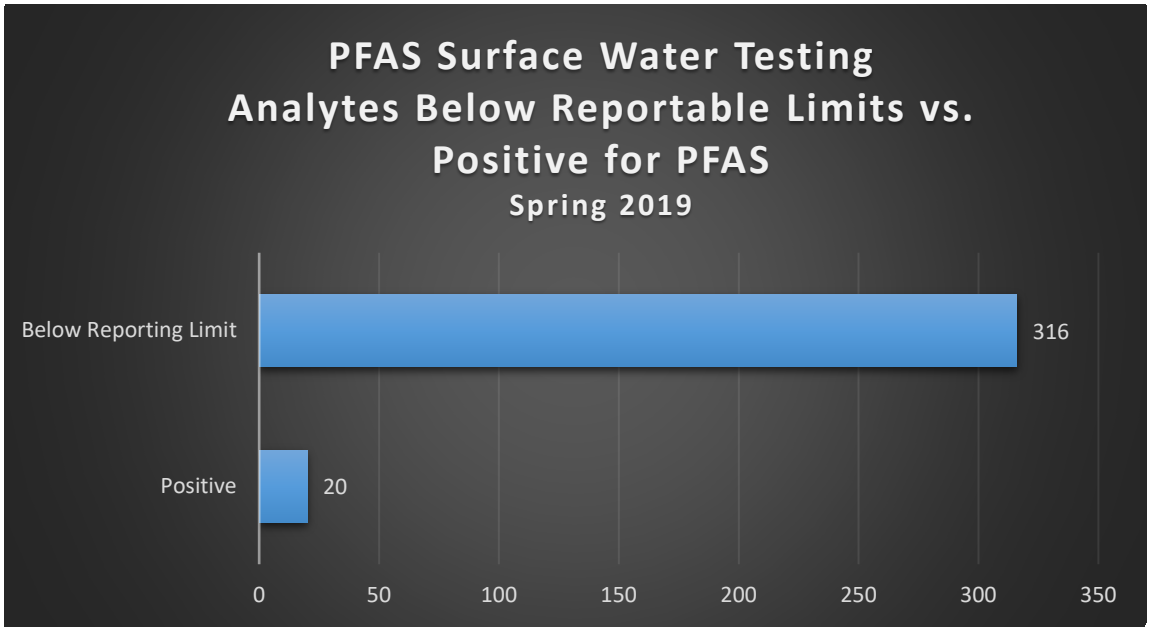
Sources: Esri, HERE, Garmin, USGS, Intermap, INCREMENT P, NRCan, Esri Japan, METI, Esri China (Hong Kong), Esri Korea, Esri (Thailand), NGCC, (c) OpenStreetMap contributors, and the GIS User Community Monitoring locations are from Tip of the Mitt Watershed's Comprehensive Water Quality Monitoring Program. County data from Michigan Geographic Data Library. Human activity sites identified by the MI DEQ Water Resources Division.

SAMPLING RESULTS

SPRING SAMPLING

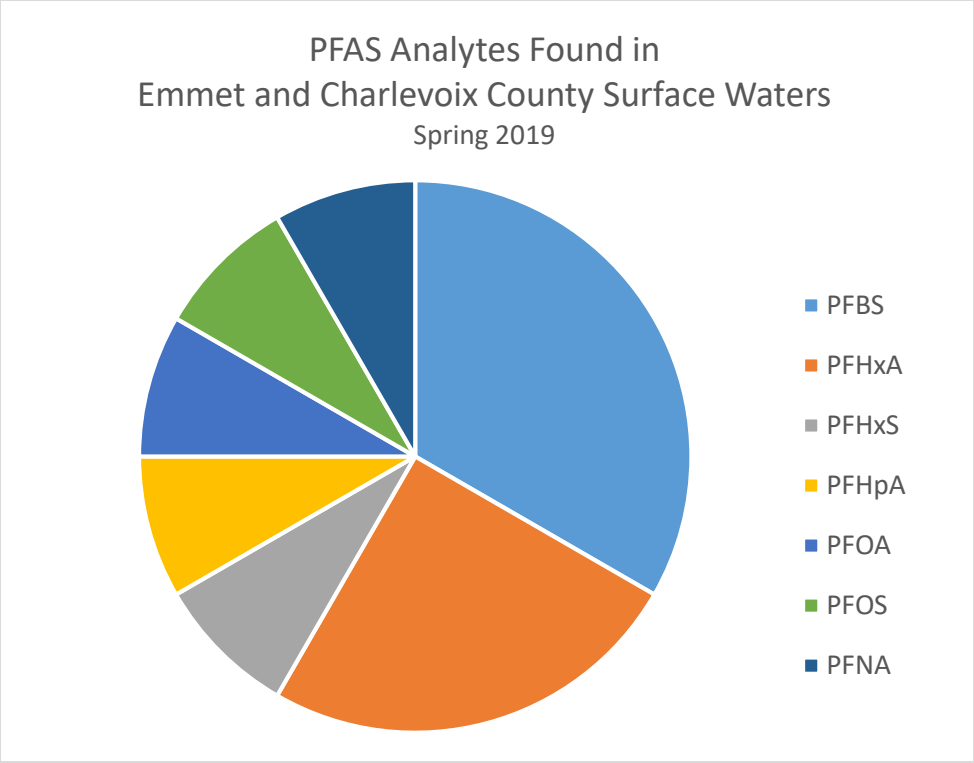
In May of 2019, surface water samples tested positive for PFAS in six different water bodies. Lake Charlevoix, the Maple River, Round Lake, Paradise Lake, Walloon Lake, and Susan Lake all tested positive. No PFAS were found, or they were below detectable limits, for the Bear River, Boyne River, and Stover Creek. Cumulative total PFAS found during the spring sampling was 115.2 ppt.

Of the 14 PFAS tested, seven different types were reported, representing 50% of the PFAS chemicals analyzed. However, given the number of sites sampled (24) and PFAS tested (14), there could have been a total of 336 positive hits. The results showed only 20 positive hits for PFAS, representing .06% of the total testing. The full list of sites sampled and results are provided in Appendix A.



Graph 1.

PFBS, PFHxA, PFHxS, and PFHpA were the most commonly found analytes. Of these, PFBS was found in all six water bodies and reported at nine sample locations.



Graph 2.

Table 1. shows the breakdown of the total concentrations of PFAS chemicals found per water body during the spring sampling. PFBS was not only most commonly found, it was found in the greatest concentrations, with a total of 88.2 parts per trillion (ppt). One part per trillion is equal to a single drop of water in 20 Olympic-sized swimming pools.

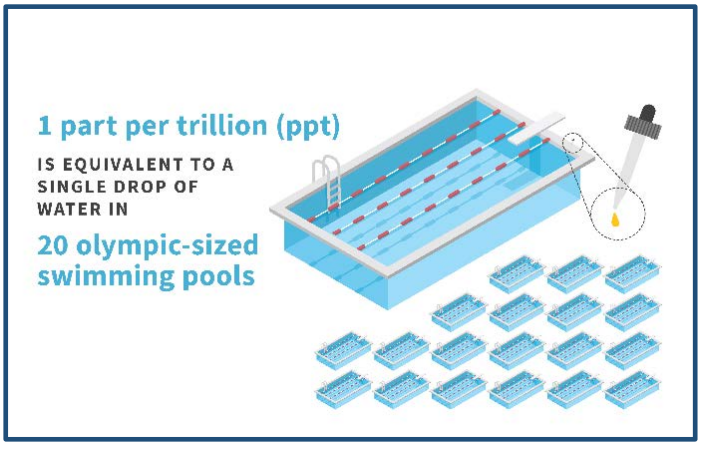


Image: Michigan Department of Environment, Energy, and Great Lakes

Values reported for PFBS ranged from 0 (below the detection limit of 1 ppt) to 26 ppt. The West Basin of Walloon Lake reported the highest levels of PFBS at 26 ppt, which was the highest reading of all samples.

Total Concentrations of PFAS Analyte per Lake from Spring Sampling (in parts per trillion) BRL = Below Reportable Limits							
	PFBS	PFHxA	PFHxS	PFHpA	PFOA	PFOS	PFNA
Lake Charlevoix	20.4	11.4	BRL	1.5	BRL	BRL	BRL
Maple River	4.0	2.7	4.7	BRL	2.1	BRL	BRL
Paradise Lake	5.2	BRL	1.7	BRL	BRL	BRL	BRL
Walloon Lake	31	BRL	BRL	BRL	BRL	BRL	1.2
Susan Lake	13	BRL	BRL	BRL	BRL	BRL	BRL
Round Lake	14.6	BRL	BRL	BRL	BRL	1.7	BRL
Total	88.2	14.1	6.4	1.5	2.1	1.7	1.2

Table 1.

PFBS has been used as a surfactant in industrial processes and in water-resistant or stain-resistant coatings on consumer products such as fabrics, carpets, and paper. 3M introduced the four-carbon molecule PFBS in 2003 to replace PFOS in some products, such as Scotchgard. The 3M Company has been a major manufacturer of PFBS and products containing PFBS. In laboratory animal studies, effects of PFBS exposure included developmental effects (e.g., lower body weight, delayed development) and female reproductive effects in offspring of mothers exposed during pregnancy, as well as changes in thyroid hormone levels and cellular changes to the kidneys. Studies of health effects from PFBS exposure in people are lacking.

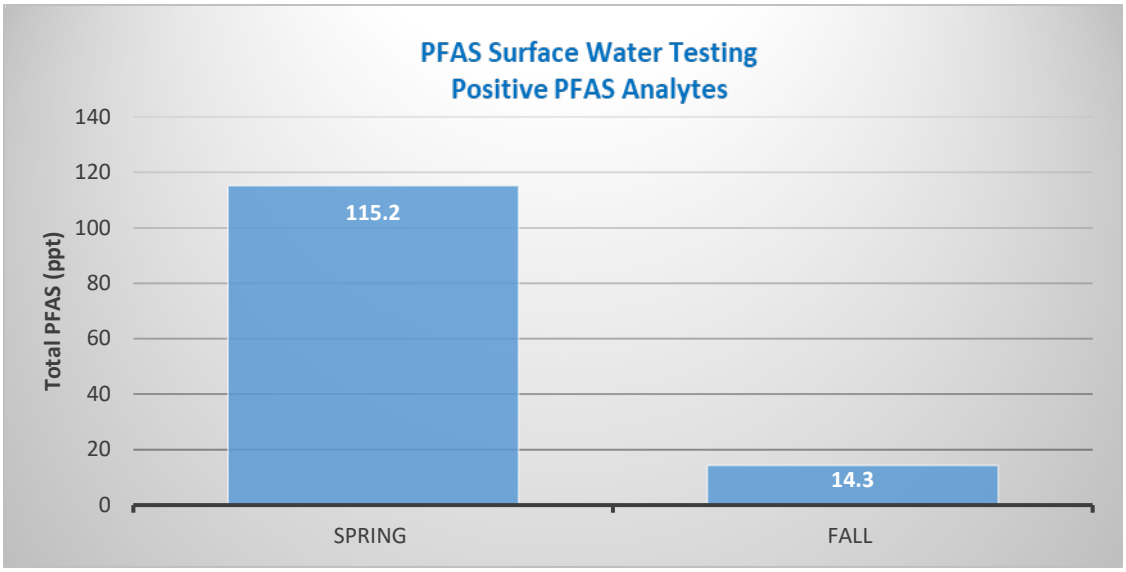
PFOA and PFOS, which represent two of the most commonly used and best studied PFAS compounds, were detected at two locations. The Maple River reported 2.1 ppt for PFOA while the surface of Round Lake reported 1.7 ppt. These values are below the current surface water quality standards for the State of Michigan. Rule 57 has set water quality standards for surface water in the State at the following:

- PFOS:
  - 11 ppt if the surface water is a drinking water source
  - 12 ppt if the surface water is not a drinking water source
- PFOA:
  - 420 ppt if the surface water is a drinking water source
  - 12,000 ppt if the surface water is not a drinking water source

It should be noted that these are the only two PFAS chemicals that currently have surface water standards in Michigan. As the science continues to develop and testing confirms more about the problems associated with PFAS, we are likely to see more PFAS chemicals regulated.

FALL SAMPLING

Overall, significantly lower concentrations of PFAS were detected during the fall sampling than in the spring. A total PFAS of 14.3 ppt was found in October 2019, compared to 115.2 ppt in the spring. However, more water bodies tested positive.

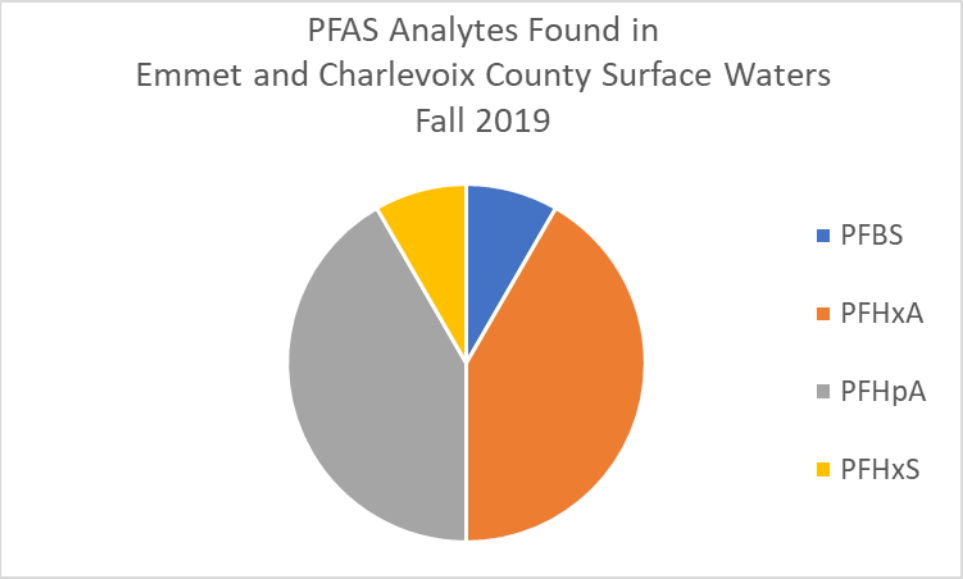


Graph 3.

Surface water samples tested positive for PFAS in seven different water bodies. Lake Charlevoix, the Maple River, Round Lake, Paradise Lake, Walloon Lake, Susan Lake, and the Bear River all tested positive. All of these water bodies tested positive in the spring, with the exception of the Bear River. Once again, no PFAS were detected in the Boyne River or Stover Creek.

Out of a possible total 336 positive hits, there were only 12 positive results, representing .04% positive overall. The full list of sites sampled and results for the fall sampling are provided in Appendix B.

During the fall sampling, fewer types of PFAS were detected, only four out of 14 were found, including, PFBS, PFHxA, PFHxS, and PFHpA. The highest reported value of any location for total PFAS ranged from 0 (below detection limit of 1 ppt) to 2.4 ppt, with the highest individual PFAS reading being 2.0 ppt found at the surface of Round Lake.



Graph 4.

Whereas PFBS was found most during the spring sampling, PFHxA and PFHpA were the two most commonly reported compounds during the fall sampling.

PFHxA is a six-carbon compound once used in firefighting foam and carpet treatment solutions, but was phased out due to U.S. Environmental Protection Agency regulations. It has long-range transport potential and higher bioaccumulation in humans than PFOS.

PFHxS was made by 3M until 2002 and is now found in many sites where firefighting foam was used. PFHxS is considered to be in the “shorter chain” group of the PFAS chemicals, which generally exit the body more quickly. However, PFHxS stays in humans for more than five years. Research has linked PFHxS to liver and thyroid disease, prostate cancer and arthritis, as well as immune and reproductive problems in adults.

Table 2. shows the breakdown of the total concentrations of PFAS chemicals found per water body during the fall sampling.

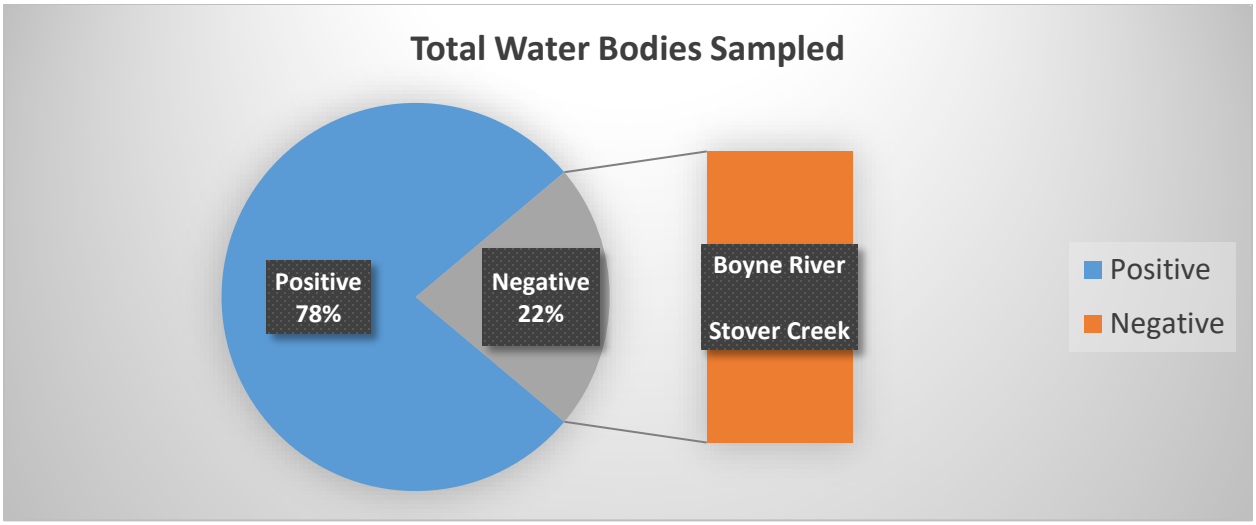
Total Concentrations of PFAS Analyte per Lake from fall sampling (in parts per trillion) BRL = Below Reportable Limits							
	PFBS	PFHxA	PFHxS	PFHpA	PFOA	PFOS	PFNA
Lake Charlevoix	BRL	BRL	1.1	BRL	BRL	BRL	BRL
Maple River	BRL	1	BRL	1.3	BRL	BRL	BRL
Paradise Lake	BRL	BRL	2	BRL	BRL	BRL	BRL
Walloon Lake	BRL	BRL	1	BRL	BRL	BRL	BRL
Susan Lake	1.1	2.3	BRL	BRL	BRL	BRL	BRL
Round Lake	BRL	3.5	BRL	BRL	BRL	BRL	BRL
Bear River	BRL	BRL	1	BRL	BRL	BRL	BRL
Total	1.1	6.8	5.1	1.3	BRL	BRL	BRL

Table 2.

The two most well-known PFAS, PFOA and PFOS, were not detected during the fall sampling.

SUMMARY OF RESULTS

PFAS are ubiquitous, fluorinated, organic compounds found widely in manufactured products, from firefighting foam to stain-resistant carpets. These water- and oil-repellent compounds are known to degrade slowly over time, and have been found in humans, drinking water, and even in Arctic ecosystems. As such, we were not surprised that we found PFAS in 78% of the water bodies sampled. Only two of the 9 water bodies, Boyne River and Stover Creek, did not have detectable levels of PFAS.



Graph 5.

While PFAS were found in the majority of water bodies sampled, they were not found in significant quantities or concentrations. The average concentration of PFAS found was 4.0 ppt. The highest concentration found was 26 ppt, reported from the surface of the West Basin of Walloon Lake during the spring sampling. This was PFBS which currently has no surface water quality standard in the State of Michigan.

For those PFAS compounds that do have surface water quality standards, PFOS and PFOA, the reported quantities were significantly below State surface water quality standards. For PFOS, the only positive sample was in Round Lake at 1.7 ppt, compared to the State standard of 11 ppt or 12 ppt if the surface water is a source of drinking water. The Maple River was the only positive sample for PFOA at 2.1 ppt. The surface water standard is 12,000 ppt or 420 ppt if the surface water is a source of drinking water.

In conclusion, while PFAS were found in the majority of water bodies sampled, the limited findings and low concentrations indicate the PFAS may not be a primary threat to surface waters in Emmet and Charlevoix County. However, it is important to note that this was a preliminary sampling effort. There are nearly 5,000 types of PFAS, some of which have been more widely used. This testing only focused on 14 of the nearly 5,000 types of PFAS. Additionally, not all of the surface waters within Charlevoix and Emmet Counties were tested. Further testing of additional water bodies and PFAS chemicals would provide greater confidence that PFAS do not pose a threat to public health and the environment in Northern Michigan.

As well, the science continues to progress on PFAS. Health-based guidance levels and new regulations are constantly being developed and changed as the impacts of PFAS are better understood. As the research builds toward clearer conclusions on PFAS, public policy will, or

should, follow in order to protect public health and the environment. As a result, what may be deemed “safe” today, may be found to be harmful tomorrow. This is currently happening with drinking water supplies across Michigan. Previously held assumptions that drinking water sources are “safe” are proving false, and communities are left scrambling to provide a treatment solution that restores confidence in the drinking water supply.

Michigan is in the process of establishing limits for certain PFAS compounds in drinking water. Once enacted, the rules will cover seven forms of PFAS, including six that the Watershed Council tested for. The proposed rule is to establish Maximum Contaminant Levels (MCLs) for seven types of PFAS.

Draft Regulations for PFAS MCL

Specific PFAS	Drinking Water MCL
PFNA	6 ng/L (ppt)
PFOA	8 ng/L (ppt)
PFHxA	400,000 ng/L (ppt)
PFOS	16 ng/L (ppt)
PFHxS	51 ng/L (ppt)
PFBS	420 ng/L (ppt)
GenX	370 ng/L (ppt)

Table 3.

The Watershed Council did not test drinking water within Charlevoix and Emmet Counties. However, all surface water sample results found are below the proposed PFAS Drinking Water MCLs.

While PFAS are clearly ubiquitous in the environment, no one knows for sure how many people are affected by PFAS contaminated surface and drinking water, or the long-term health impacts. Tip of the Mitt Watershed Council, thanks to the generous support of the Charlevoix County Community Foundation and the Petoskey-Harbor Springs Community Foundation, initiated research to identify the location of PFAS in Charlevoix and Emmet Counties to protect the health of residents and we will be ready to continue that protection into the future as the science on this topic evolves.

APPENDIX A

SPRING SAMPLING RESULTS

								Concentration (ppt) [Minimum Reporting Limit = 1 ppt]															
Waterbody	Area	Sample	Date Collected	Date Extracted	Date Analyzed	Volume (mL)	PFBS	PFHxA	PFHxS	PFHpA	N-MeFOSAA	N-EtFOSAA	PFOA	PFOS	PFNA	PFDA	PFUdA	PFDoA	PFTrDA	PFTeDA	Total PFAS
Round Lake	Main Basin	Bottom	5/25/19	6/25/19	6/26/19	535.68	3.6	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	3.6
Maple River	West Branch(HW31)	Middle	5/24/19	6/25/19	6/26/19	538.83	4.0	2.7	3.0	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	9.7
Walloon Lake	Foot Basin	Surface	5/25/19	6/25/19	6/26/19	543.14	5.0	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	5.0
Paradise Lake	Main Basin	Bottom	5/25/19	6/25/19	6/26/19	535.92	5.2	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	5.2
Lake Charlevoix	Boyne City	Surface	5/25/19	6/17/19	6/26/19	545.17	9.4	5.2	BRL	1.5	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	16.1
Round Lake	Main Basin	Surface	5/25/19	6/25/19	6/26/19	539.63	11	BRL	BRL	BRL	BRL	BRL	BRL	1.7	BRL	BRL	BRL	BRL	BRL	BRL	12.7
Lake Charlevoix	Main Basin	Surface	5/24/19	6/17/19	6/26/19	535.05	11	2.3	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	13.3
Susan Lake	Main Basin	Surface	5/24/19	6/25/19	6/26/19	535.63	13	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	13
Walloon Lake	West Basin	Surface	5/25/19	6/25/19	6/26/19	539.52	26	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	26
Lake Charlevoix	Main Basin	Middle	5/24/19	6/17/19	6/26/19	541.14	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Lake Charlevoix	Main Basin	Bottom	5/24/19	6/17/19	6/26/19	535.31	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Lake Charlevoix	East Jordan	Surface	5/24/19	6/17/19	6/26/19	542.01	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Lake Charlevoix	East Jordan	Bottom	5/24/19	6/17/19	6/26/19	534.78	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Lake Charlevoix	Boyne City	Bottom	5/25/19	6/17/19	6/26/19	536.33	BRL	3.9	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	3.9
Boyne River	Dam Rd	Middle	5/24/19	6/25/19	6/26/19	533.66	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Susan Lake	Main Basin	Bottom	5/24/19	6/25/19	6/26/19	546.3	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Walloon Lake	West Basin	Bottom	5/25/19	6/25/19	6/26/19	544.2	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Walloon Lake	Foot Basin	Bottom	5/25/19	6/25/19	6/26/19	536.24	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	1.2	BRL	BRL	BRL	BRL	BRL	1.2
Bear River	Quick Road	Middle	5/24/19	6/25/19	6/26/19	540.11	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Bear River	Standish Ave	Middle	5/24/19	6/25/19	6/26/19	531.91	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Bear River	Mouth, Elizabeth	Middle	5/24/19	6/25/19	6/26/19	527.04	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Paradise Lake	Main Basin	Surface	5/25/19	6/25/19	6/26/19	533.26	BRL	BRL	1.7	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	1.7
Maple River	Brutus Road	Middle	5/24/19	6/25/19	6/26/19	542.13	BRL	BRL	1.7	BRL	BRL	BRL	2.1	BRL	BRL	BRL	BRL	BRL	BRL	BRL	3.8
Stover Creek	Ferry Ave	Middle	5/24/19	6/25/19	6/26/19	527.28	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
																					115.2

APPENDIX B

FALL SAMPLING RESULTS

Parts Per Trillion (ppt, ng/L) MRL=1 ppt

Waterbody	Area	Sample	Date Collected	Date Received	Date Extracted	Date Analyzed	Volume (mL)	PFBS	PFHxA	PFHpA	PFHxS	PFOA	PFNA	PFOS	PFDA	N-MeFOSAA	N-EtFOSAA	PFUdA	PFDoA	PFTrDA	PFTeDA	Total PFAS
Lake Charlevoix	Main Basin	Surface	10/8/2019	10/11/2019	10/21/2019	11/8/2019	532.2	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Lake Charlevoix	Main Basin	Middle	10/8/2019	10/11/2019	10/21/2019	11/8/2019	536.2	BRL	BRL	1.1	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	1.1
Lake Charlevoix	Main Basin	Bottom	10/8/2019	10/11/2019	10/21/2019	11/8/2019	523.2	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Lake Charlevoix	East Jordan	Surface	10/8/2019	10/11/2019	10/21/2019	11/8/2019	529.7	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Lake Charlevoix	East Jordan	Bottom	10/8/2019	10/11/2019	10/21/2019	11/8/2019	507.5	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Lake Charlevoix	Boyne City	Surface	10/8/2019	10/11/2019	10/21/2019	11/8/2019	530.2	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Lake Charlevoix	Boyne City	Bottom	10/8/2019	10/11/2019	10/21/2019	11/8/2019	531.5	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Boyne River	Dam Rd	Middle	10/8/2019	10/11/2019	10/21/2019	11/8/2019	524	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Susan Lake	Main Basin	Surface	10/8/2019	10/11/2019	10/21/2019	11/8/2019	515.1	1.1	1.3	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	2.4
Susan Lake	Main Basin	Bottom	10/8/2019	10/11/2019	10/21/2019	11/8/2019	519.5	BRL	1.0	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	1.0
Walloon Lake	West Basin	Surface	10/8/2019	10/11/2019	10/21/2019	11/8/2019	530.9	BRL	BRL	1.0	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	1.0
Walloon Lake	West Basin	Bottom	10/8/2019	10/11/2019	10/21/2019	11/8/2019	525.5	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Walloon Lake	Foot Basin	Surface	10/8/2019	10/11/2019	10/21/2019	11/8/2019	529.7	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Walloon Lake	Foot Basin	Bottom	10/8/2019	10/11/2019	10/21/2019	11/8/2019	531.2	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Bear River	Quick Road	Middle	10/8/2019	10/11/2019	10/21/2019	11/8/2019	525.2	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Bear River	Standish Ave	Middle	10/8/2019	10/11/2019	10/21/2019	11/8/2019	532.4	BRL	BRL	1.0	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	1.0
Bear River	Mouth, Elizabeth St.	Middle	10/8/2019	10/11/2019	10/21/2019	11/8/2019	526.2	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Round Lake	Main Basin	Surface	10/8/2019	10/11/2019	10/21/2019	11/8/2019	532.8	BRL	2.0	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	2.0
Round Lake	Main Basin	Bottom	10/8/2019	10/11/2019	10/21/2019	11/8/2019	540.6	BRL	1.5	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	1.5
Paradise lake	Main Basin	Surface	10/8/2019	10/11/2019	10/21/2019	11/8/2019	528.8	BRL	BRL	1.0	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	1.0
Paradise lake	Main Basin	Bottom	10/8/2019	10/11/2019	10/21/2019	11/8/2019	533.6	BRL	BRL	1.0	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	1.0
Maple River	Brutus Rd	Middle	10/8/2019	10/11/2019	10/21/2019	11/8/2019	526.4	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
Maple River	West Branch (HW31'	Middle	10/8/2019	10/11/2019	10/21/2019	11/8/2019	532.2	BRL	1.0	BRL	1.3	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	2.3
Stover Creek	Ferry Ave	Middle	10/8/2019	10/11/2019	10/21/2019	11/8/2019	521.9	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL	BRL
																						14.3

APPENDIX C

SURFACE WATER PFAS SAMPLING GUIDANCE

SURFACE WATER PFAS SAMPLING

Guidance

Introduction

This sampling guidance contains the processes, decontamination procedures, and acceptable items and materials for sampling surface water for Per- and Polyfluoroalkyl Substances (PFAS). This guidance will be used to support the sampling objectives and procedures based on the Quality Assurance Project Plan (QAPP) developed prior to any field activities. This guidance assumes staff has basic familiarity with and/or understanding of basic surface water sampling procedures.

NOTE: Review the **General PFAS Sampling Guidance** prior to reviewing this guidance document.

The Michigan Department of Environmental Quality (MDEQ) intends to update the information contained within this Surface Water PFAS Sampling Guidance document as new information becomes available. The user of this Surface Water 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.

PFAS has been detected in surface water in Michigan at concentrations of over 19,000 parts per trillion (ppt). Because PFAS compounds can be analyzed at concentrations in the parts per trillion (ppt) range, precautions must be taken to prevent cross-contamination. Therefore, there is a high possibility of false positives if decontamination procedures are not followed diligently. This sampling guidance covers both the collection of samples from shallow and deep surface water bodies.

This Surface Water PFAS Sampling Guidance discusses the collection of surface water samples and methods to prevent cross-contamination that can occur from:

- Field clothing and personal protective equipment (PPE)
- Personal care products (PCPs)
- Food packaging
- Sampling equipment
- Equipment decontamination
- Filtering of surface water
- Sample collection and handling
- Sample shipment

Contents

NOTE: Additional information about PFAS testing can be found on the Michigan PFAS Action Response Team (MPART) website: www.michigan.gov/PFASresponse

1. Potential Sources for PFAS Cross-Contamination

Potential sources for PFAS cross-contamination include items and materials used within the sampling environment, such as sampling equipment, field clothing, personal protective equipment (PPE), sun and biological protection products, personal hygiene, personal care products (PCPs), and food packaging. A detailed discussion about potential sources for PFAS cross-contamination is included in the **General PFAS Sampling Guidance**, which should be reviewed before reading this document. However, a high-level summary is presented in this guidance.

All of the items and materials discussed in each of the MDEQ's PFAS Sampling Guidance Documents are 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 acceptable 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.

● - Prohibited ■ – Allowable ▲ - Needs Screening

Please note that at this time no published research is available that documents the use of various materials and effect on sample results. Therefore, a conservative approach is recommended, and the guidance is based on the collection of multiple environmental samples at various PFAS Sites. Sampling staff should take practical and appropriate precautions to avoid items that are likely to contain PFAS at the sampling site as well as avoid specific items during the sampling event.

A general overview of PFAS contamination sources during sampling can be found in **Section 4.2** of the **General PFAS Sampling Guidance**. Any items or materials utilized that are not identified in this guidance or not discussed in **Section 4.2** should be evaluated as described in **Section 4.2.1**.

Sampling staff should take practical and appropriate precautions to avoid items that are likely to contain PFAS at the sampling site as well as avoid specific items during the sampling event (see below).

1.1 Field Clothing and Personal Protection Equipment (PPE)

A general overview of field clothing and PPE can be found in **Section 4** of the **General PFAS Sampling Guidance**.

As with any field mobilization, it is the responsibility of all personnel to be aware of the physical, chemical and biological hazards associated with a particular site. 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, should be recorded in field notes and discussed in the final report.

Depending on the project objectives and sampling plan, the collection of surface water samples could be as simple as a grab sample or as complex as a sample collected using a Van Dorn® sampler from a boat. Generally, for surface water sampling, approved field clothing (discussed in **Section 4** of the **General PFAS Sampling Guidance**) is required. Life jackets made of PFAS-free materials should be used. The coatings used on waders are of particular concern during surface water sampling. Ensure the waders are made from PFAS-free materials before use.

NOTE: Special attention should be given to clothing that has been advertised as having waterproof, water-repellant, or dirt and/or stain characteristics. They are likely to have PFAS in their manufacturing.

NOTE: Life jackets may have protective coatings that contain PFAS.

- ● Do not use waders made of Gore-Tex or other known PFAS containing materials.
- ■ Life jackets made of polyethylene foam and nylon shell fabric may be used.
- ■ Waders made of Neoprene or other PFAS-free materials may be used.

Any field clothing and/or PPE items that might be required for surface water sampling and not discussed in this guidance should be evaluated as described in **Section 4.2.2** of the **General PFAS Sampling Guidance**.

NOTE: Both field clothing and PPE should be kept dust and fiber free. During the sample collection, extra care should be taken so that no dust or fibers can fall into the sample bottle.

Powderless nitrile gloves should frequently be changed any time there is an opportunity for cross-contamination of the sampling including, but not limited to, the following activities:

- Each time sampling equipment is handled.
- Prior to sample collection.

● - Prohibited ■ – Allowable ▲ - Needs Screening

- After handling any sample, including QA/QC samples such as field reagent blanks or equipment rinsate blanks.
- After the handling of any non-dedicated sampling equipment, contact with non-decontaminated surfaces, or when judged necessary by field personnel.
- During and after decontamination of non-dedicated sampling equipment.

1.2 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.

1.3 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). 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.

2. Surface Water Sampling Equipment

Surface water sampling equipment that is also used for non-PFAS sampling such as dippers, Kemmerer®, or Van Dorn® samplers, should be decontaminated prior to collecting PFAS samples to avoid cross contamination. This non-dedicated equipment (equipment used for more than one water body or location) should be verified that it is PFAS free at least once prior to use. Surface water sampling equipment can fall into **Category 1** or **Category 2**:

● - Prohibited ■ – Allowable ▲ - Needs Screening

Category 1: Surface water sampling equipment that will come into contact with the surface water sample include sample bottles and various surface water samplers or tubing. Sample bottles should be provided by the laboratory and known to be PFAS free. Any surface water samplers, tubing, or materials that will come into contact with the surface water samples should be screened and known to be PFAS-free. The tubing should always be kept in the original cardboard or bag in which it was shipped. The tubing should always be stored in a clean location free of dust and fibers.

NOTE: As a precautionary action, an equipment rinsate blank should be collected even if the sampling materials are made of materials that are not expected to contain PFAS.

Category 2: Examples of field equipment that do **not** come into contact with the surface water samples include water quality meters, GPS receivers, notebooks, clipboards, and turbidity meters. The surface of some of these pieces of field equipment, or the storage boxes in which they are kept, might contain PFAS.

Do not use any equipment that contains any known fluoropolymers including, but not limited to:

- ● 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-tetrafluoro-ethylene (ETFE), that includes the trademark Tefzel®, which can be found in many items, including but not limited to 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 wire and cable insulation and covers, pipe linings, and some labware.

Note: Manufacturers can change the chemical composition of any product. As a result, all materials that will come into direct contact with the sample media should be tested 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.**

- ● 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.
- ■ 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.
- ■ Use only powderless nitrile gloves (which can be found at some hardware and major retail outlets).
- ■ Keep tubing in the original cardboard or bag in which it was shipped.

●- Prohibited ■ – Allowable ▲- Needs Screening

- ■ Store tubing in a clean location free of dust and fibers.
- ▲ Latex gloves should be screened before use.
- ▲ Post-It® Notes should be screened before use.

NOTE: Depending on the project objectives, boats might be required to be used during surface water sampling. Boats might have various parts that may contain PFAS, including protective water repellent coatings. When boats are used on rivers, samples should always be collected on the upgradient side of the boat.

Depending on the project data quality objectives, water samples can be collected as: a simple grab directly into the sample bottle; a grab sample at a selected depth using any of several collection bottles with subsequent transfer to the sample bottle(s); or as a depth integrated sample. A depth integrated sample can be collected using a simple weighted bottle constructed to allow gradual water inflow (e.g., chlorophyll sampler), or by using a Van Dorn® or Kemmerer® sampler and compositing grab samples from several depths. Composited samples are then transferred to the sample bottle.

Surface water sampling collection can be divided into two method categories as presented in the following Table 1.

Table 1. Surface Water Sampling Methods[1]

Depth to Surface Water Sample	Locations	Sampling Method
0-5 feet	Streams, rivers, creeks, tributaries, lakes, lagoons, ponds, and impoundments.	Direct method, swing, telescoping, and Van Dorn, depth integrating samplers.
Over 5 feet	Large streams, rivers, tributaries, lakes, lagoons, ponds, and impoundments.	Peristaltic pump, swing, telescoping, Van Dorn, Kemmerer, and depth integrating samplers.

[1]This table includes the most frequently used methods for surface water samples.

2.1 Container Immersion

Two types of immersion sampling equipment are available for surface water sampling: extension rods and submersible devices. Extension rods can be used to immerse the actual sample bottle, different types of beakers, or peristaltic pump tubing into the surface water. Submersible devices (i.e., Kemmerer Bottle, Van Dorn Sampler) are fully immersed into the surface water using a rope.

2.1.1 Extension Rods

The most common extension rods are telescoping or swing samplers. Both types of sampling equipment are very similar in design and concept, and both facilitate the immersion of either the sampling bottle or various beakers or scoops. Lists of various extension rod designs are provided below:

- Pendulum or angular beaker.
- Fixed scoop.
- Fix or rotatable head bottle holder.

A peristaltic pump can also be used with extension rods by attaching the tubing to the extension rods and immersing both the rods and the connected tubing to the desired depth in the surface water.

- ■ Use only sample collection equipment, tubing, beakers, and/or scoop materials that are known to be PFAS-free such as stainless steel, glass, HDPE, polyvinyl chloride (PVC), or silicone.
- ■ Extension rods made of materials such as aluminum that has been identified as being PFAS-free can be used.

A specialized extension rod that features a telescoping design for the handle could also be used as a subsurface grab sampler. The sample is collected using a cable from the handle, which has a ring that can be opened for the sample collection after the desired depth has been reached.

2.1.2 Submersible Devices

The most common submersible devices being used are Kemmerer Bottles or Van Dorn Samplers. These devices are primarily used when the samples are collected at depths greater than 5 feet from a boat and/or structure such as a bridge or pier. All submersible devices are submerged in the surface water using a rope.

NOTE: Careful evaluation of all submersible samplers' parts should be done. Any parts that might contain PFAS should be replaced with PFAS-free materials. Equipment rinsate blank samples should be collected to make certain the sampler is PFAS-free.

The Kemmerer Bottle sampler is typically constructed of a stainless-steel tube with polyurethane end seals that can collect a total sample volume of 1.2 liters. The Kemmerer Bottle is not ideal for the collection of samples close to the surface, as the tube is immersed vertically in the water.

The Van Dorn® bottle sampler is typically constructed of 1-liter transparent acrylic tube with two end stoppers. The sampler is suspended horizontally, which is ideal for the sample collection in shallow water bodies as well as sampling at depth.

When submersible samplers are used, the following recommendations should be followed:

- ● Do not use any sampling bottle with Teflon end seals.
- ■ Use a Kemmerer® Bottle made of stainless steel with polyurethane end seals.
- ■ Use a Van Dorn® bottle sampler that uses stoppers made of PFAS-free materials.
- ■ Use nylon line, stainless steel cable, or line or wires made of PFAS-free materials for sample collection.
- ■ Use tubing for the sampling ports made of HDPE, polypropylene, silicone, PVC, or other PFC-free materials.

2.2 Direct Sampling

For surface water samples collected near the shore (e.g., from streams, rivers, lakes, and other surface waters), the direct method can be used to collect the water samples directly into the sample container.

- ● Do not sample without powderless nitrile gloves.

- ● Never place the sample cap directly on the ground or boat deck during sampling.
- ■ Use powderless nitrile gloves
- ■ Hands should be well washed
- ■ Use HDPE sample bottles with Teflon®-free caps, provided by the laboratory.
- ■ If sample bottles that are known to be PFAS-free are not available, the sample container and lid should be rinsed with water that is known to be PFAS-free at least 3 times prior to collecting the sample.
- ■ If samples are collected while wading in the water body, the bottle should be immersed inverted and upstream of the collector.
- ■ If samples are collected from a boat, the bottles should be submerged upstream of the boat.

NOTE: Unless specifically required by the project objectives, surface water samples should ***not*** be taken at the top layer of the water body or of surface scums. PFAS are expected to accumulate at the surface water air interface or be present in the surface runoff, so samples taken at the surface are likely to result in high biased results that are not representative of the bulk surface water.

3. Equipment Decontamination

Field sampling equipment that is used at multiple sites or sampling locations (non-dedicated equipment) could become contaminated with PFAS.

The following should be considered when decontaminating any equipment that contacts the sampling media:

- ● Do not use Decon 90®.
- ■ 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 a polyethylene or Polyvinyl chloride (PVC) brush to remove particulates.
- ■ Decontamination procedures should include triple rinsing with PFAS-free water.
- ■ Commercially available deionized water in an HDPE container may be used for decontamination if the water is verified to be PFAS-free.
- ▲ Municipal drinking water may be used for decontamination purposes if it is known to be PFAS-free.

4. Sample Collection and Handling

A preferred sampling sequence should be established prior to any sampling event to reduce the risk of cross contamination. In general, the sampling sequence should begin in areas expected or known to be least contaminated, proceeding to anticipated areas or identified to be most contaminated. If analytical results from past sampling events are available, the sampling sequence can be readily determined.

However, 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 prior to the sampling event to help establish the sampling sequence.

If multiple samples (i.e., monitoring wells, surface water, residential) will be collected in an area where a PFAS release in the environment has 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 samples should be progressively sampled from the one 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

When collecting and handling surface water samples:

- ● Do not insert or let tubing or any materials inside the sample bottle.
- ● Dust and fibers must be kept out of sample bottles.
- ● The sample cap should never be placed directly on the ground during sampling. If sampling staff must set the sample bottle cap down during sample collection and a second member of the sampling crew (wearing a fresh pair of powderless nitrile gloves) is not available, set the cap on a clean surface (cotton sheeting, HDPE sheeting, triple rinsed cooler lid, etc.).
- ● Regular/thick size markers (Sharpie® or otherwise) are to be avoided; as they may contain PFAS.
- ■ Fine or Ultra-Fine point Sharpies® may be used to label the empty sample bottle while in the staging area provided the lid is on the sample bottle and powderless nitrile gloves are changed following sample bottle labeling.
- ■ Ballpoint pens may be used when labeling sample containers. If ballpoint pens do not write on the sample container labels, preprinted labels from the laboratory may be used.
- ■ Hands should be well washed and gloved.
- ■ Use HDPE, or polypropylene sample bottles with Teflon®-free caps, provided by the laboratory.
- ■ Bottles should only be opened immediately prior to sampling.
- ■ Bottles should be capped immediately after collecting the sample.
- ■ Samples should be double bagged using resealable low density polyethylene (LDPE) bags (e.g., Ziploc®).
- ■ Follow any guidance or requirements in the PFAS analytical reference method that will be used for testing samples, for sample collection, storage, preservation, and holding times.

If a published testing method is not used, and in the absence of formal United States Environmental Protection Agency guidance for PFAS sample storage, the documentation in USEPA Method 537 Rev. 1.1 should be used as a guide for thermal preservation (holding temperature), and holding times for surface water or other samples. Samples must be chilled during storage and shipment, and must not exceed 50°F (10º C) during the first 48 hours after collection.

NOTE: USEPA Method 537 Rev. 1.1 was developed for the analysis of finished drinking water samples only. It was not designed for testing surface water or other matrices that could cause significant interferences to the method.

Surface water samples should be extracted as soon as possible but must be extracted within 14 days. Extracts must be stored at room temperature and analyzed within 28 days after extraction (EPA Method 537 Rev. 1.1).

5. Filtering of Surface Water

Since PFAS can adsorb to particulate matter, unfiltered samples may result in high-biased results. PFAS are known to absorb to various filters. As a result, filtering of surface water samples prior to delivery to the lab should be avoided unless called for in the project data quality objectives. To reduce the need for filtering, samples should be collected with as minimal disturbance to sediments as possible.

NOTE: It is recommended that filtering of the samples should **only be performed in the laboratory** in order to reduce the possibility of cross contamination.

If it is known beforehand that samples will need to be filtered the procedure should be discussed with the laboratory and sample handling methods and responsibilities should be described in the sampling workplan and QAPP.

The following recommendations should be used when considering filtering of the samples:

- ● **Field filtration of the sample is generally not advised.**
  - ▲ If filtering is absolutely necessary, if specifically requested by a client or for other reasons:
- ● Do not use any filters that contain any PFAS, such as PTFE filters
- ● Do not use nylon filters.
- ■ Glass filters are recommended to be used.
- ■ Consider use of a centrifuge in the laboratory to reduce the need for sample filtering.

6. Sample Shipment

When prepping samples for shipping:

- ■ Check the cooler periodically to ensure samples are well iced and at the proper temperature.
- ■ Refresh with regular ice, if needed, double bagged in LDPE resealable storage bags if needed.
- ■ 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.
- ■ Chain of Custody and other forms should be double bagged in LDPE (Ziploc®) storage bags and taped to the inside of the cooler lid.
- ■ The cooler should be taped closed with a custody seal and, if shipping, 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.

Michigan Department of Environmental Quality

MDEQ PFAS Sampling Quick Reference Field Guide[1]

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®
  ○ Polycholotrifluoroethylene (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	■ Allowable	▲Needs Screening[2]

• Items or materials containing any fluoropolymer (potential items include tubing, valves, or pipe thread seal tape)	• 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
		• 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	■ Allowable	▲Needs Screening[2]
• Polytetrafluoroethylene (PTFE): Teflon® lined bottles or caps	• Glass jars[4] • 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 media[6]	• Aluminium foil[4] • Chemical or blue ice[5] • Plastic storage bags other than those listed as ■ Allowable • Low-density polyethylene (LDPE) bottles

Field Documentation

● Prohibited	■ Allowable	▲Needs Screening[2]
• Clipboards coated with PFAS • Notebooks made with PFAS treated paper • PFAS treated loose paper • PFAS treated adhesive paper products	• 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	• 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	■ Allowable	▲Needs Screening[2]
• Decon 90® • PFAS treated paper towel	• Alconox®, Liquinox®, or Citranox® • Triple rinse with PFAS-free deionized water • Cotton cloth or untreated paper towel	• Municipal water • Recycled paper towels or chemically treated paper towels

Clothing, Boots, Rain Gear, and PPE

● Prohibited	■ Allowable	▲Needs Screening[2]

• New or unwashed clothing
• Anything made of or with:
  ○ Gore-Tex™ or other water-resistant synthetics
• Anything applied with or recently washed with:
  ○ Fabric softeners
  ○ Fabric protectors, including UV protection
  ○ Insect resistant chemicals
  ○ Water, dirt, and/or stain resistant chemicals
	• Powderless nitrile gloves
	• Well-laundered synthetic or 100% cotton clothing, with most recent launderings not using fabric softeners
	• Made of or with:
	  ○ Polyurethane
	  ○ Polyvinyl chloride (PVC)
	  ○ Wax coated fabrics
	  ○ Rubber / Neoprene
	  ○ Uncoated Tyvek®
		• 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

• No food should be consumed in the staging or sampling areas, including pre-packaged food or snacks.
  ■ 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.
	• Brought and consumed only outside the vicinity of the sampling area:
	  ○ Bottled water
	  ○ Hydration drinks (i.e. Gatorade®, Powerade®)

Personal Care Products (PCPs) - for day of sample collection[6]

● Prohibited	■ Allowable	▲Needs Screening[2]
• Any PCPs[6], sunscreen, and insect repellent applied in the sampling area.	PCPs[6], sunscreens, and insect repellents applied in the staging area, away from sampling bottles and equipment followed by thoroughly washing hands: **PCPs[6]:** • Cosmetics, deodorants/antiperspirants, moisturizers, hand creams, and other PCPs[6] **Sunscreens:** • 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 **Insect Repellents:** • OFF® Deep Woods • Sawyer® Permethrin	• Products other than those listed as ■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.

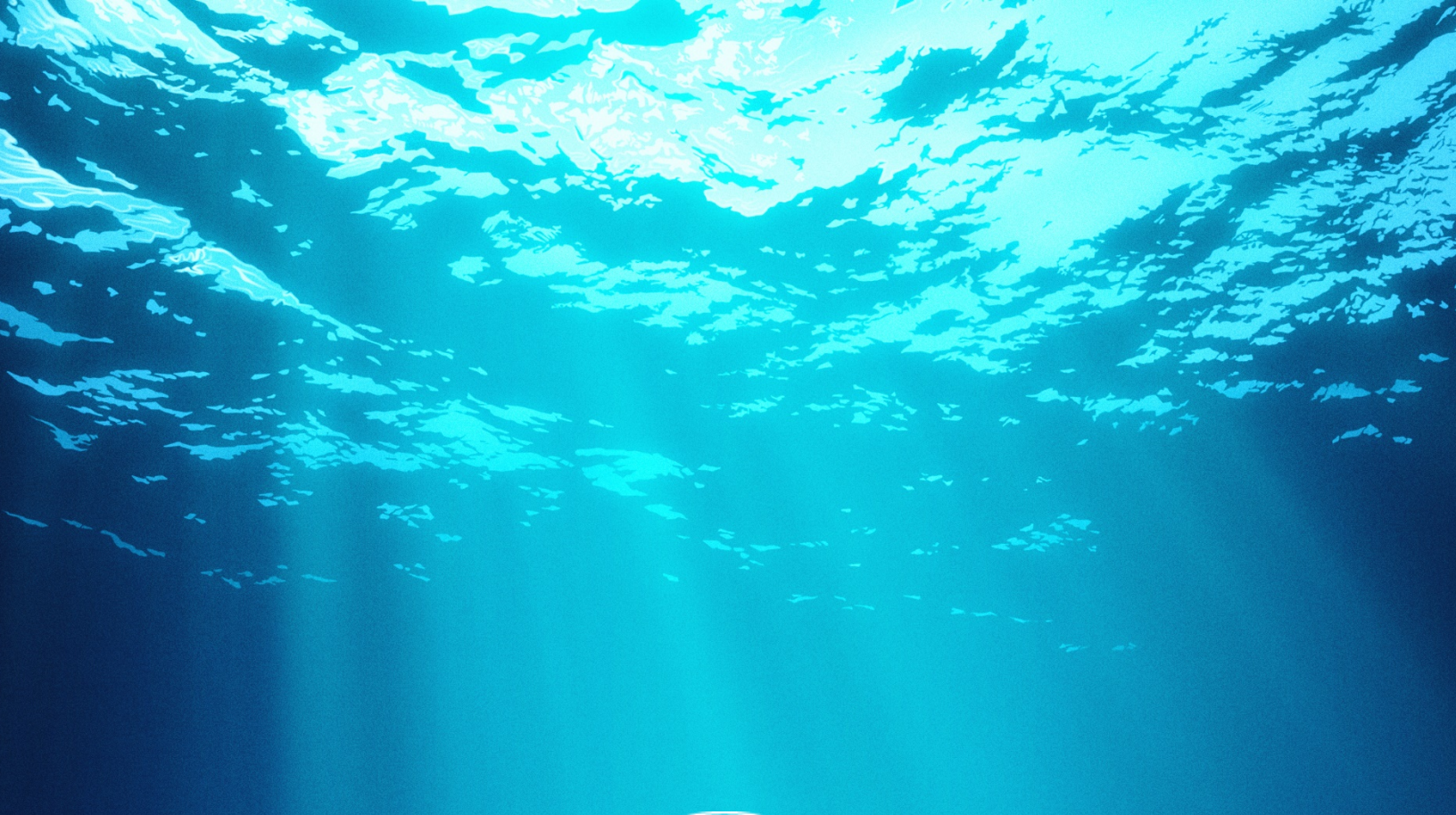
[3] **For surface water foam samples:** LDPE storage bags may be used in the sampling of foam on surface waters. In this instance, it is allowable for the LDPE bag to come into direct contact with the sample media.

[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.

● - Prohibited ■ - Allowable ▲ - Needs Screening



Tip of the Mitt Watershed Council

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