

Investigation of Per- and Polyfluoroalkyl Substances (PFAS)
in Fort Gratiot and Burtchville Townships / St. Clair County and
Worth Township / Sanilac County
Surface Water Sampling Update
November 2019

Perfluorinated and polyfluorinated alkyl substances (PFAS) are a very large class of man-made organic chemicals that have been used in numerous industrial processes and consumer products for over 60 years. Validated analytical methods are available for relatively few of the thousands of compounds. Much of the environmental monitoring of PFAS in Michigan has focused on measuring only perfluorinated chemicals.

Many PFAS are persistent, some bioaccumulate in the environment, and several are toxic to mammals and/or birds in laboratory tests. The toxicities of most PFAS have not been evaluated. Two perfluorinated compounds; perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), have been the subject of the most toxicological work and environmental monitoring. Both compounds were manufactured intentionally, but they can also be generated as byproducts when other fluorinated compounds break down. In addition, several PFAS are key ingredients in fire-fighting foams. These foams have been used extensively in fire training exercises at military bases nation-wide; in recent years PFAS have been detected in surface and groundwater near many military facilities. Many products containing PFAS are used in numerous industrial processes including metal plating, textile production and treatment, and specialty paper production. Industrial and domestic waste containing these compounds can enter the environment through municipal or private waste treatment systems, stormwater runoff, venting groundwater, or as deposition after emissions into the atmosphere. Both PFOS and PFOA have been measured in surface waters across the state, and PFOS has been detected in most fish tissue samples from Michigan waters that have been analyzed for PFAS.

The Michigan Department of Environment, Great Lakes, and Energy (EGLE) has generated Rule 57 surface water quality values for the protection of human health and aquatic life for PFOS and PFOA. The Rule 57 Human Non-Cancer Value (HNV) for PFOS is 12 nanograms per liter (ng/L; parts per trillion) in surface waters not used as a source of drinking water, and 11 ng/L for those surface waters used as a drinking water source. The HNVs for PFOA are 420 ng/L and 12,000 ng/L for drinking and non-drinking water sources, respectively. The Aquatic Maximum Value (AMV) is the highest concentration of a substance to which an aquatic community can be exposed briefly without resulting in adverse effects, whereas, the Final Chronic Value (FCV) is the highest concentration of a substance to which an aquatic community can be exposed for a long period of time without experiencing adverse effects. The Rule 57 AMV and FCV for PFOS is 880,000 and 7,700 ng/L, respectively. The Rule 57 AMV and FCV for PFOA is 780,000 and 140,000 ng/L, respectively.

EGLE Water Resources Division (WRD), Surface Water Assessment Section (SWAS) conducted surface water sampling in the Black River and Lake Huron coastal watersheds in September and November 2019. This effort was initiated in part because the Fort Gratiot Landfill in Fort Gratiot Township of St. Clair County was listed as a PFAS site after elevated levels of PFOS and PFOA were measured in landfill leachate/groundwater and surface water samples collected near the landfill in 2018. The Fort Gratiot Landfill in Fort Gratiot Township, St. Clair County, was in operation from 1969 to 1994 and accepted industrial waste including paper pulp waste, paint sludge, and contaminated soil from environmental cleanup projects. PFAS sites are where one or more groundwater sample exceeds the Part 201 cleanup criteria for groundwater used as drinking water, which is 70 parts per trillion for PFOS + PFOA. Additional surface water samples collected by contractors for EGLE in July 2019 indicated that there may be significant PFAS sources upgradient of the landfill.

EGLE WRD SWAS collected samples from surface waters in the vicinity of the former Fort Gratiot Landfill and areas not affected by groundwater from the landfill (Table 1; Figure 1). It was hypothesized that land application of PFAS contaminated biosolids and/or paper sludge on agricultural fields may have contaminated surface waters. During the initial sampling event (September 2019), 23 surface water samples were collected at 21 locations to bracket potential sources of PFAS contamination in the watershed and to repeat sampling at locations that were previously sampled by an EGLE contractor. After receipt and analysis of the results from this sampling effort, an additional 52 surface water samples were collected at 48 locations further upstream in the Black River (St. Clair) and Birch-Willow Creek watersheds to determine the extent of the PFAS contamination (Table 1; Figures 2 - 3). Sampling locations were selected to bracket potential sources of contamination, particularly upstream and downstream of potential stockpiles that were observed via Google Earth imagery circa 2014 (Figure 2).

Surface water samples were collected in accordance with the Michigan Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidance (MDEQ 2018a). QA/QC procedures followed the Michigan Surface Water PFAS Investigation 2019 Quality Assurance Project Plan (QAPP; EGLE 2019). Additionally, surficial sediment samples were collected from 14 locations with known or suspected elevated PFOS surface water contamination during the November 2019 sampling event (Table 2; Figure 4) following the sediment sampling quality assurance manual (MDNR 1994) and sediment PFAS sampling guidance (MDEQ 2018b). All samples were delivered to the Eurofins TestAmerica office in Brighton for shipment to the analytical laboratory by their staff. Surface water samples were analyzed for the PFAS listed in Table 3.

Findings:

- PFOS was detected in 71 of 73 surface water samples (Table 1, Figure 1). Concentrations greater than the detection limit ranged from 0.6 ng/L in a tributary to the Brandymore Drain (BTN-0020) to 11,000 ng/L in another tributary to the Brandymore Drain (UN-0040).
- 17 of the 72 total samples (23.6 %) were below the PFOS concentration reporting limit (2.0 ng/L).
- PFOS concentrations exceeded the Rule 57 HNV of 12.0 ng/L at 25 locations:
 1. An unnamed Tributary to the Brandymore Drain @ North Rd (BMS-0030): 13 ng/L
 2. Carrigan Drain @ 24th Avenue and Lakeshore Dr (CG-0020): 15 ng/L
 3. An unnamed Drain @ Keewahdin Rd (UN-0010): 15 ng/L
 4. An unnamed tributary to Doe Creek @ Brace Rd and State Rd (DCB-0010): 22 ng/L
 5. An unnamed drain east of Howe Drain @ Keewahdin Rd: 25 ng/L
 6. An unnamed drain @ Campbell Rd (UN3-0010): 30 ng/L
 7. The Fort Gratiot Wetland area pond near Parker Rd: 31 ng/L
 8. Birch Creek @ Lakeshore Rd (BI-0010): 38 ng/L
 9. Galbraith Drain @ Lakeshore Rd: 39 ng/L
 10. Brandymore Drain @ Keewahdin Rd (BR-0050): 44 ng/L
 11. An unnamed Tributary to the Brandymore Drain @ North Rd (BTN-0010): 54 ng/L
 12. Burtch Creek @ Jeddo Rd (BH-0010): 66 ng/L
 13. Doe Creek @ Parker Rd (DC-0020): 130 ng/L
 14. An unnamed drain @ Campbell Rd (UN4-0010): 250 ng/L
 15. An unnamed drain north of Beard Rd (UNB-0010): 360 ng/L
 16. Howe Drain west of 24th Ave (HD-0020): 410 ng/L
 17. Howe Drain west of Tamarack Dr (HD-0010): 430 ng/L
 18. Howe Drain @ Keewahdin Rd: 480 ng/L
 19. Howe Drain downstream of Farm Drain (HD-0025): 590 ng/L
 20. Howe Drain @ State Rd: 770 ng/L

21. Doe Creek upstream of Carrigan Rd (DC-0041): 850 ng/L
 22. Doe Creek @ Carrigan Rd (DC-0040): 1,000 ng/L
 23. An unnamed tributary to Doe Creek @ North Rd (DCT-0010): 1,200 ng/L
 24. Doe Creek @ State Rd (DC-0060): 1,500 ng/L
 25. An unnamed drain E. of the Brandymore drain @ Keewahdin Rd (UN-0040): 11,000 ng/L
- Elevated PFOS concentrations (>5 ng/L) at or below the Rule 57 HNV were observed at 5 sampling locations:
 1. Metcalf Drain @ Fort Gratiot County Park (MC-0010): 7.1 ng/L
 2. Carrigan Drain @ Lakeshore Rd (CG-0010): 7.5 ng/L
 3. Milwaukee Creek @ Lakeshore Rd (MK-0010): 8.0 ng/L
 4. Stocks Creek @ Pine Needle Circle (STC-0100): 9.0 ng/L
 5. Brace Drain @ Carrigan Rd (BRD-0030): 12 ng/L
 - PFOA was detected in 69 of the 73 surface water samples. Concentrations were all below the Rule 57 HNV and detections ranged from 0.9 ng/L in a Birch Creek sample (BI-0020) to 1,200 ng/L in an unnamed tributary to the Brandymore drain (UN-0040).
 - PFOS was detected in all 14 sediment sampling locations ranging from 0.3 µg/kg in an unnamed tributary to the Brandymore drain (BMT-0030S) to 60 µg/kg in another unnamed tributary to the Brandymore drain (UN-0040S).
 - PFOA was detected in all 14 sediment sampling locations ranging from 0.05 µg/kg in the BMT-0030S sample to 2.1 µg/kg in the UN-0040S sample.
 - PFOS in the sediment samples was highly correlated with surface water PFOS concentration (Figure 5).
 - Two trip blanks, field blanks, and equipment blanks were collected for the surface water sampling over the two sampling events.
 - No PFAS analytes were detected in the September and November field and equipment blanks.
 - PFOA was detected in the September trip blank at 0.8 ng/L which is below the 2.0 ng/L laboratory reporting limit. No other PFAS analytes were detected.
 - PFOS was non-detect in the November trip blank. PFOA and PFHxA were detected at 1.0 and 1.3 ng/L, respectively, which are both below the 2.0 ng/L laboratory reporting limit. PFHxA (1.3 ng/L) was detected in the November trip blank, however below the laboratory reporting limit. PFPeA was detected above the laboratory reporting limit at 2.2 ng/L; however, this analyte was also detected in the laboratory method blank.
 - PFOS and PFOA were non-detect in the laboratory method blanks analyzed.
 - Three replicate and three duplicate samples were collected over the three sampling events. None of these samples exceeded the 30% relative percent deviation (RPD) quality assurance/quality control objective for PFOS or PFOA. The duplicate sample collected in September (HD-0020) exceeded the RPD for the PFPeS analyte (65.1%). The duplicate samples collected in November (MK-0010) exceeded the RPD for the PFNA analyte (38.8%). No other analytes exceeded the RPD quality assurance/quality control objective.

Overall, these results indicate that source(s) of PFAS exist in the Black River and Birch-Willow Creek watersheds. EGLE is currently investigating the stockpiles that may be contributing PFAS to the drains of the Black River and Doe Creek. Sampling and PFAS analysis of soil from these piles and nearby agricultural fields is planned for December 2019. The source of PFAS contamination in Burtch Creek (Sanilac County) is still being investigated.

References

- Michigan Department of Environmental Quality. (2018a). General Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guide.
- Michigan Department of Environmental Quality. (2018b). Sediment PFAS sampling guidance.
- Michigan Department of Environment, Great Lakes, and Energy. (2019). Michigan Surface Water Perfluoroalkyl and Polyfluoroalkyl Compound (PFAS) Investigation: Quality Assurance Project Plan (QAPP).
- Michigan Department of Natural Resources. (1994). Quality Assurance Manual for Water, Sediment, and Biological Sampling. MDNR. Environmental Protection Bureau. Lansing, Michigan.

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Table 1: PFOS and PFOA concentrations measured above their detection limit in surface water samples collected from locations in the Black River and Birch-Willow Creek watersheds in September and November 2019. Concentrations exceeding the Rule 57 HNV are in bold and italicized.

SAMPLE ID	SAMPLE LOCATION DESCRIPTION	LAT	LONG	SAMPLING EVENT	PFOS (NG/L)	PFOA (NG/L)
BH-0010	Burtch Creek @ Jeddo Rd	43.1549	-82.5059	November	66	24
BI-0010	Birch Creek @ Lakeshore Rd	43.1631	-82.5038	November	38	12
BI-0020	Birch Creek @ Fisher Rd	43.1688	-82.5082	November	0.7	0.9
BK-0010	Black River @ Erie St.	42.9764	-82.4276	November	2.7	2.7
BK-0020	Black River @ Scott Ave Boat Ramp	42.9952	-82.4462	November	3.1	2.3
BK-0040	Black River @ Bakersfield Park Docks	43.0140	-82.4507	November	2.6	1.8
BK-0050	Black River @ Bakersfield Park Boat Launch	43.0169	-82.4525	November	1.4	1.8
BK-0100	Black River @ Wadhams Rd	42.9900	-82.5375	November	1.5	1.5
BKT-0010	Black River Trib @ N. River Rd	43.0167	-82.4670	November	1.3	9.6
BMK-0010	Trib to Brandymore Drain @ North Rd; S. of Keyworth Dr	43.0195	-82.5249	November	1.4	ND
BMN-0030	Trib to Brandymore Drain @ North Rd; N. of Maitland Rd	43.0314	-82.5256	November	0.9	2.1
BMS-0030	Trib to Brandymore Drain; S. of Maitland Rd	43.0282	-82.5255	November	13	5.3
BMT-0030	Trib to Brandymore Drain @ North Rd; S. of Keewahdin Rd	43.0359	-82.5260	November	ND	ND
BR-0050	Brandymore Drain @ Keewahdin Rd	43.0382	-82.5082	September	42	45
BR-0060	Brandymore Drain @ Krafft Rd	43.0235	-82.5134	November	44	23
BR-0100	Brandymore Drain @ North Rd	43.0159	-82.5248	September	4.6	5.4
BRC-0020	Black River Canal @ Port Huron N. High	43.0190	-82.4455	November	2.0	12
BRC-0030	Black River Canal @ Pine Grove Ave	43.0165	-82.4506	November ^D	1.7	12
BRD-0030	Brace Drain @ Carrigan Rd	43.0595	-82.5122	November	1.4	1.5
BTN-0010	Trib to Brandymore Drain @ North Rd; S. of Beard Rd	43.0424	-82.5260	November	2.4	1.8
BTN-0020	Trib to Brandymore Drain u/s of BTN-0010	43.0415	-82.5409	November ^R	2.9	2.0
BTS-0010	Trib to Brandymore Drain @ North Rd; N. of Keewahdin Rd	43.0390	-82.5259	November	12	5.2
CG-0010	Carrigan Drain @ Lakeshore Rd	43.0424	-82.5260	September	28	2.6
CG-0020	Carrigan Drain @ 24th Ave / Lakeshore Dr	43.0508	-82.4571	November	54	9.7
BTN-0020	Trib to Brandymore Drain u/s of BTN-0010	43.0415	-82.5409	November	0.6	ND
BTS-0010	Trib to Brandymore Drain @ North Rd; N. of Keewahdin Rd	43.0390	-82.5259	September	2.9	1.2
CG-0010	Carrigan Drain @ Lakeshore Rd	43.0417	-82.4465	November	1.7	1.5
CG-0020	Carrigan Drain @ 24th Ave / Lakeshore Dr	43.0508	-82.4571	September	7.5	12
CG-0020	Carrigan Drain @ 24th Ave / Lakeshore Dr	43.0508	-82.4571	September	15	8.2

SAMPLE ID	SAMPLE LOCATION DESCRIPTION	LAT	LONG	SAMPLING EVENT	PFOS (NG/L)	PFOA (NG/L)
DC-0020	Doe Creek @ Parker Rd	43.0678	-82.4782	November	130	27
DC-0040	Doe Creek @ Carrigan Rd	43.0535	-82.4822	September	1000	140
				November	820	140
DC-0041	Doe Creek u/s of Carrigan Rd	43.0516	-82.4829	November	850	150
DC-0060	Doe Creek @ State Rd	43.0489	-82.4967	September	1500	200
				November	1000	170
DCB-0010	Unnamed Drain to Doe Creek @ Intersection of Brace and State Rd	43.0676	-82.4979	November	22	7.0
DCT-0010	Unnamed Drain to Doe Creek @ North Rd	43.0487	-82.5265	November	1200	190
HD-0010	Howe Drain @ Tamarack Dr	43.0209	-82.4485	September	430	64
HD-0020	Howe Drain @ W. of 24th Ave	43.0288	-82.4576	September	410	58
				September ^D	390	59
HD-0025	Howe Drain @ d/s of Farm Drain	43.0344	-82.4688	September	590	74
HD-0030	Howe Drain @ Keewahdin Rd	43.0389	-82.4780	September	480	61
HD-0040	Howe Drain @ State Rd	43.0431	-82.4963	September	730	88
				September ^R	770	90
MC-0010	Metcalf Rd Drain @ Fort Gratiot County park	43.0835	-82.4706	November	7.1	36
MI-0010	Mill Creek @ Lakeshore Rd	43.2217	-82.5281	November	ND	ND
MK-0010	Milwaukee Creek @ Lakeshore Rd	43.1157	-82.4943	November	7.7	5.6
				November ^D	8.0	5.6
ML-0010	Meadow Lawn Drain @ Lakeshore Rd	43.0982	-82.4840	November	1.3	1.9
MOR-0010	Moore Drain @ State Rd	43.0354	-82.4960	November	4.3	70
SCG-0010	Galbraith Drain @ Lakeshore Rd	43.0751	-82.4697	November	39	14
STC-0100	Stocks Creek @ Pine Needle Circle	42.9809	-82.4767	November	9.0	29
TD-0010	Thompson Drain @ Lakeshore Rd	43.0625	-82.4611	September	3.0	9.6
				November	2.5	7.7
UFN-0010	Unnamed Drain @ N. end of Forest Rd	43.2140	-82.5230	November	2.1	2.6
UFS-0010	Unnamed Drain @ S. end of Forest Rd	43.2102	-82.5225	November	1.2	6.3
UHN-0010	Unnamed Drain @ N. end Lakeview Rd	43.2067	-82.5157	November	0.6	6.8
UHS-0010	Unnamed Drain @ Lakeview Rd; S. of Kenmar Ln	43.1976	-82.5112	November	0.7	0.8
UN-0010	Unnamed Drain @ Keewahdin Rd	43.0399	-82.4510	September	15	9.7
UN-0030	Unnamed Drain @ E. of Howe Drain; S. of Keewahdin Rd	43.0390	-82.4716	September	25	15

SAMPLE ID	SAMPLE LOCATION DESCRIPTION	LAT	LONG	SAMPLING EVENT	PFOS (NG/L)	PFOA (NG/L)
UN-0040	Unnamed Drain @ E. of Brandymore Drain	43.0382	-82.5061	September	11000	1200
				November	3200	590
UN-0041	Unnamed Drain u/s of UN-0040	43.0371	-82.5058	November	4.9	2.8
UN2-0010	Unnamed Drain (North) @ Campbell Rd	43.0360	-82.5159	September	0.9	ND
UN3-0010	Unnamed Drain (Middle) @ Campbell Rd	43.0293	-82.5155	September	30	36
UN4-0010	Unnamed Drain (South) @ Campbell Rd	43.0255	-82.5153	September	76	11
				November	250	39
UNB-0010	Unnamed Drain @ N. of Beard Rd	43.0444	-82.5363	November	360	57
WD-0020	Warner Drain @ Keewahdin Rd	43.0386	-82.4860	September	3.1	18
				November	3.3	44
				November ^R	3.6	46
WP-0020	Ft Gratiot Wetland Area Pond @ Parker Rd	43.0430	-82.4773	September	31	11

^D indicates a duplicate sample; ^R indicates a replicate sample

Table 2: PFOS and PFOA concentrations measured above their detection limit in sediment samples collected from locations in the Black River and Birch-Willow Creek watersheds in November 2019.

SAMPLE ID	SAMPLE LOCATION DESCRIPTION	LAT	LONG	PFOS (UG/KG)	PFOA (UG/KG)
DCB-0010S	Unnamed Drain to Doe Creek @ Intersection of Brace and State Rd	43.0676	-82.4979	2.9	0.32
DC-0040S	Doe Creek @ Carrigan Rd	43.05331	-82.48222	24	0.86
DC-0060S	Doe Creek @ State Rd	43.04891	-82.49673	24	0.56
DC-0060S ^D				29	0.71
BTN-0010S	Trib to Brandymore Drain @ North Rd; S. of Beard Rd	43.04246	-82.52604	4.1	0.12
BTS-0010S	Trib to Brandymore Drain @ North Rd; N. of Keewahdin Rd	43.039	-82.52587	0.79	0.16
BMT-0030S	Trib to Brandymore Drain @ North Rd; S. of Keewahdin Rd	43.0359	-82.526	0.27	0.05
BMN-0030S	Trib to Brandymore Drain @ North Rd; N. of Maitland Rd	43.0314	-82.5256	2.7	0.34
BMS-0030S	Trib to Brandymore Drain; S. of Maitland Rd	43.0282	-82.5255	13	1.2
BMK-0010S	Trib to Brandymore Drain @ North Rd; S. of Keyworth Dr	43.0195	-82.5249	0.63	0.26
BR-0050S	Brandymore Drain @ Keewahdin Rd	43.0382	-82.50802	3.4	0.31
BR-0100S	Brandymore Drain @ North Rd	43.0159	-82.5248	0.37	0.16
UN-0040S	Unnamed Drain @ E. of Brandymore Drain	43.03825	-82.50605	60	2.1
UN-0041S	Unnamed Drain u/s of UN-0040	43.0371	-82.5058	3.5	0.22
UN4-0010S	Unnamed Drain (South) @ Campbell Rd	43.02548	-82.51529	10	0.32
UN4-0010S ^D				12	0.37

^D indicates a duplicate sample

Table 3: Perfluoroalkyl and polyfluoroalkyl substances (PFAS) analyzed.

Compound	Abbreviation	CAS #
Perfluorotetradecanoic acid	PFTeA	376-06-7
Perfluorotridecanoic acid	PFTriA	72629-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorobutanoic acid	PFBA	375-22-4
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorooctanesulfonamide	PFOSA	754-91-6
Fluorotelomer sulphonic acid 8:2	FtS 8:2	39108-34-4
Fluorotelomer sulphonic acid 6:2	FtS 6:2	27619-97-2
Fluorotelomer sulphonic acid 4:2	FtS 4:2	757124-72-4
2-(N-Ethylperfluorooctanesulfonamido) acetic acid	N-EtFOSAA	2991-50-6
2-(N-Methylperfluorooctanesulfonamido) acetic acid	N-MeFOSAA	2355-31-9

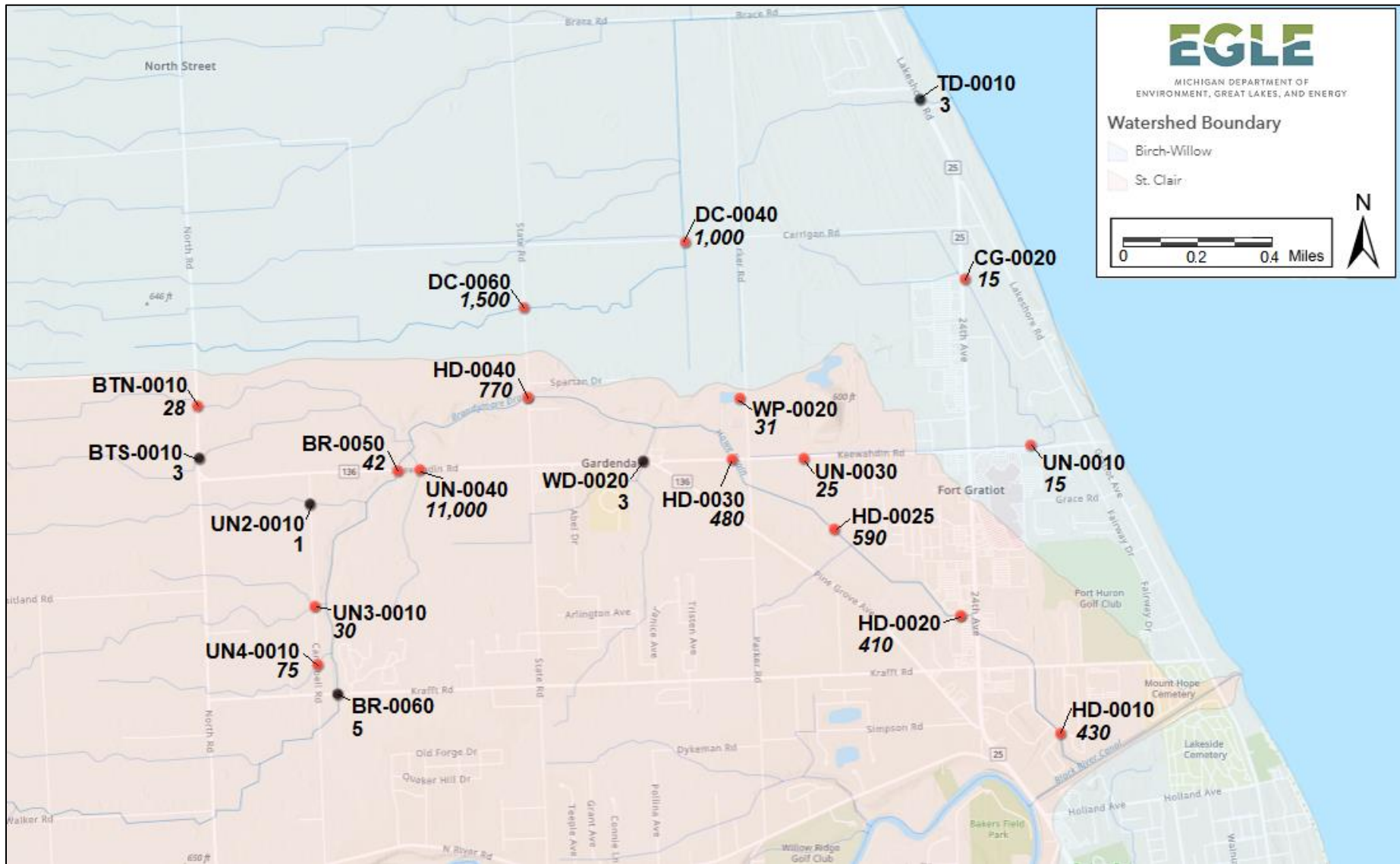


Figure 1: Overview map of surface water PFOS concentrations (ng/L) at locations in the Black River and Birch-Willow Creek watersheds near Fort. Gratiot sampled in September 2019. The blue area is the Birch-Willow Creek watershed whereas the red area is the Black River (St. Clair) watershed. Concentrations exceeding the Rule 57 Human Non-Cancer Value are displayed as red circles.

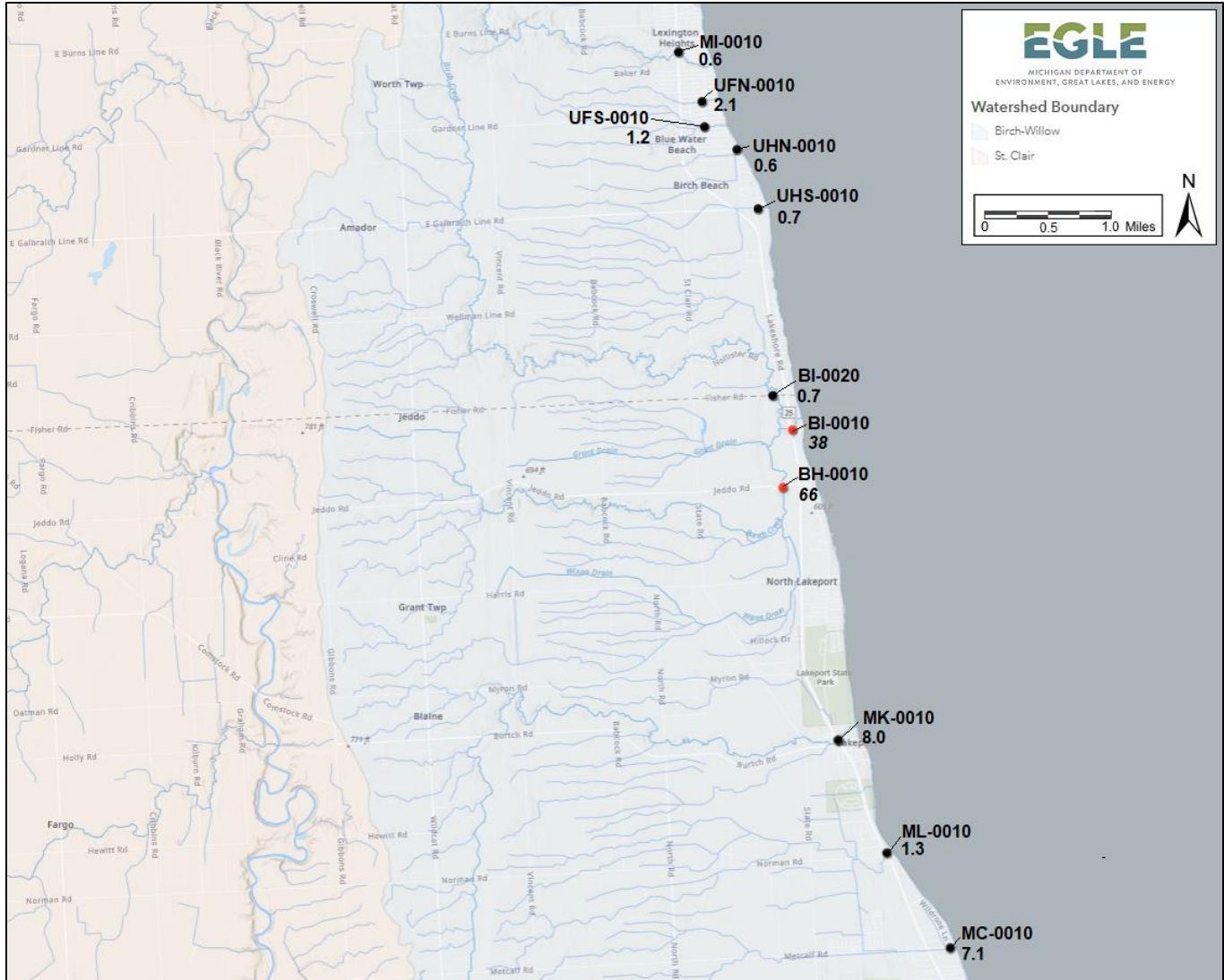


Figure 3: Overview map of surface water PFOS concentrations (ng/L) at locations in Fort Gratiot and Burtchville Townships / St. Clair County and Worth Township / Sanilac County. Samples were collected in November 2019. The blue area is the Birch-Willow Creek watershed whereas the red area is the Black River (St. Clair) watershed. Concentrations exceeding the Rule 57 Human Non-Cancer Value are displayed as red circles.

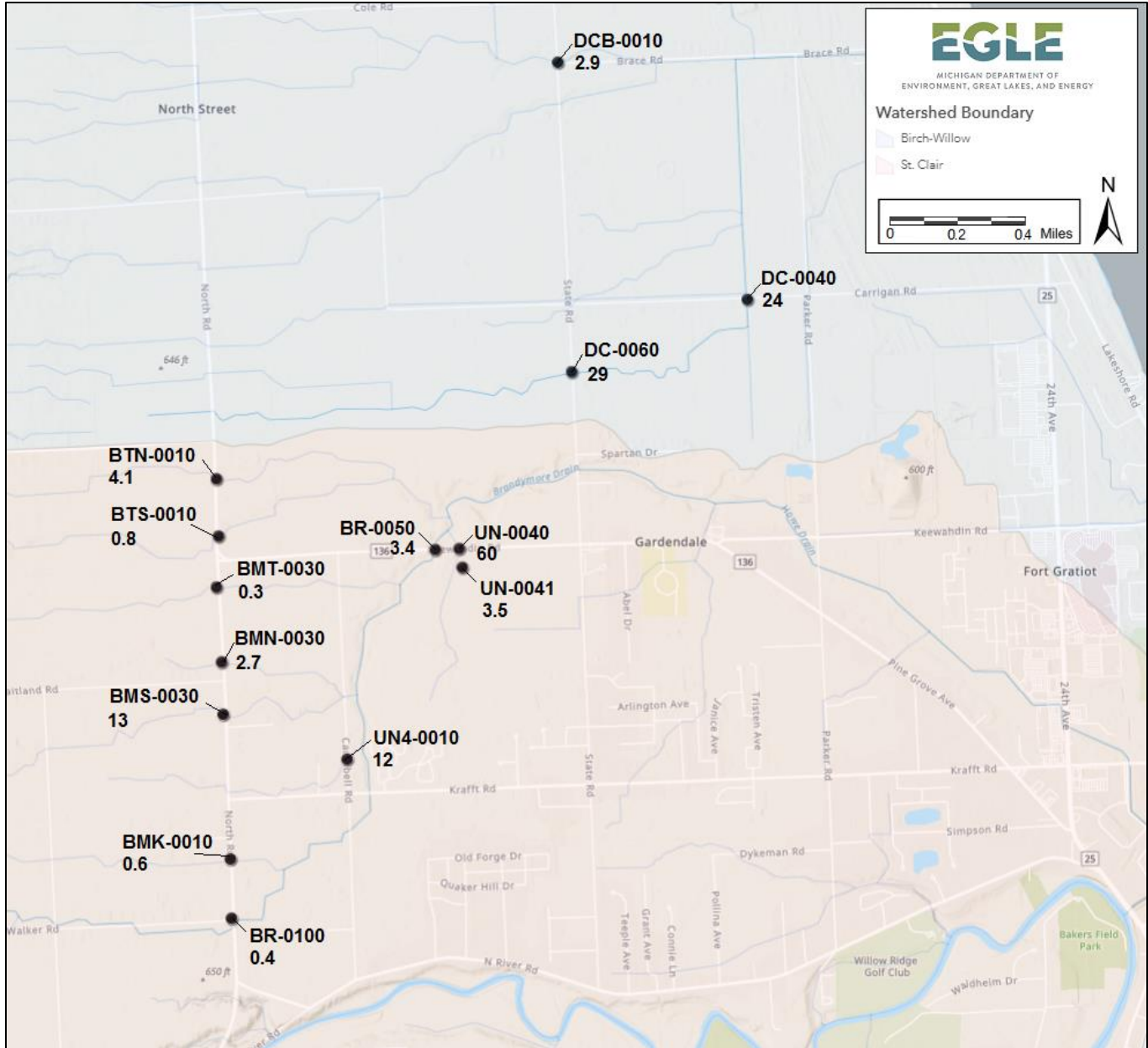


Figure 4: Overview map of sediment PFOS concentrations ($\mu\text{g}/\text{kg}$) at locations in Fort Gratiot and Burtchville Townships / St. Clair County. Samples were collected in November 2019. The blue area is the Birch-Willow Creek watershed whereas the red area is the Black River (St. Clair) watershed.

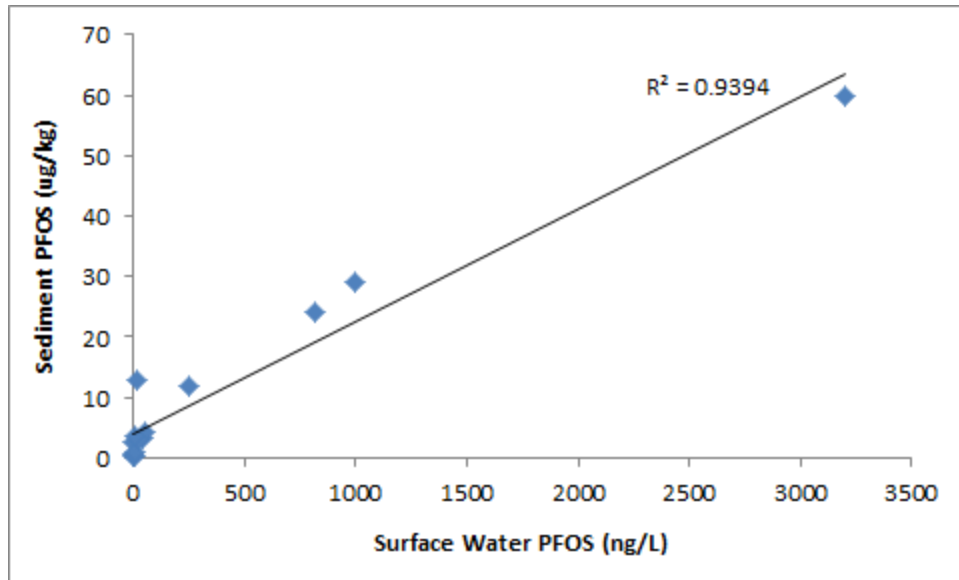


Figure 5: Correlation between surface water and sediment PFOS concentrations in samples collected from locations in Fort Gratiot and Burtchville Townships / St. Clair County in November 2019.