Investigation of Per- and Polyfluoroalkyl Substances (PFAS) in the Saginaw River Watershed: Surface Water Sampling
October 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.

The Saginaw River watershed (HUC 04080206) is located in Bay, Saginaw, and Tuscola counties. The Cass, Flint, Shiawassee, Tittabawassee, and Chippewa River are the major tributaries to the Saginaw River. The Saginaw River and Saginaw Bay were designated as an Area of Concern under the 1987 Great Lakes Water Quality Agreement due to contaminated sediments, fish consumption advisories, and degraded fisheries and loss of significant recreational values (USEPA 2018).

In 2013, EGLE staff collected three species of fish from the Saginaw River as a part of the State of Michigan Fish Contaminant Monitoring Program. The mean PFOS concentration in fillets of common carp, pumpkinseed, and smallmouth bass was 13.8, 26.9, and 32.6 parts per billion, respectively, all of which exceed MDHHS “Eat Safe Fish” screening values. PFOS causes a four meals per month consumption advisory for Saginaw River sunfish. Mercury, PCBs, and dioxin are the primary causes for the Eat Safe Fish advisories in the other species from this system.

Currently, there are ten PFAS sites located within the Saginaw River watershed. PFAS sites are locations where one or more groundwater samples exceed the Part 201 cleanup criteria for groundwater used as drinking water, which is 70 parts per trillion for PFOS + PFOA.

1. Isabella County Landfill, Deerfield Township, Pine River watershed
2. Roosevelt Refinery, Mt. Pleasant, Pine River watershed
3. MRP (Former Total Petroleum Refinery), Alma, Pine River watershed
4. Diamond Chrome Plating, Howell, Shiawassee River watershed
5. Partz Corporation, Owosso, Shiawassee River watershed
6. Flint Bishop International Airport Landfill, Flint, Flint River watershed
7. RACER Buick City, Flint, Flint River watershed
8. Coldwater Road Landfill, Flint, Flint River watershed
9. Lapeer Plastics & Plating, Lapeer, Flint River watershed
10. Richfield Landfill, Davison, Flint River watershed

Grab samples of ambient surface water from the main flow of the water body were collected on October 29, 2019 by EGLE, WRD-SWAS at 32 locations (Table 1, Figure 1). Surface water sampling locations were selected to bracket potential sources of PFAS contamination in the Saginaw River and in major tributaries near their confluence with the river.

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). 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 selected PFAS listed in Table 2.

Findings:

- The watershed received significant rainfall two days prior to sampling. The discharge at the USGS Stream Gage for the Saginaw River at Holland Ave in Saginaw (USGS 04157005) was approximately 15,000 cubic feet per second (cfs) at the time of sampling which is above the 26-year median discharge of approximately 2,500 cfs for this date and location.
- PFOS was detected in 31 of 32 surface water samples (Table 1, Figure 1). Concentrations greater than the detection limit ranged from 1.1 ng/L in Beaver Creek (BV-0010) to 8.9 ng/L in Dutch Creek (DC-0010).
- 13 of the 32 samples (41 %) were below the PFOS concentration reporting limit (2.0 ng/L).
- No samples exceeded the Rule 57 HNV of 12.0 ng/L for PFOS.
- Elevated PFOS concentrations (>5 ng/L) at or below the Rule 57 HNV were observed in two sampling locations:
    - Dutch Creek @ S. Euclid Rd (DC-0010): 8.9 ng/L
    - Birch Run @ end of Evon Rd (BR-0010): 6.9 ng/L
- PFOA was detected in 31 of the 32 surface water samples (Table 1, Figure 2). Concentrations were all below the Rule 57 HNV and detections ranged from 0.9 ng/L in Beaver Creek (BV-0010) and the Tittabawassee River (TB-0010) to 2.7 ng/L in Birch Run (BR-0010).
- A trip blank and field blank were collected. PFHxS and FOSA were detected in the trip blank at 0.3 ng/L, which is below the laboratory reporting limit of 2.0 ng/L. PFHxS was detected in a laboratory method blank at 0.4 ng/L.
- No PFAS analytes were detected in the field blank.
- PFOS and PFOA were non-detect in the laboratory method blanks analyzed.

- Two replicate and two duplicate samples were collected. None of these samples exceeded the 30% relative percent deviation (RPD) quality assurance/quality control objective for PFOS.
    - The SG-0050 replicate sample exceeded the RPD for PFOA (30.3%), PFHpA (60.0%), and PFNA (87.5%).
    - The SG-0060 duplicate sample exceeded the RPD for PFHxA (99.6%), PFHpA (117.4%), PFNA (66.7%), and PFHxS (47.4%).
    - The TB-0035 replicate sample exceeded the RPD for PFPeA (36.6%), PFHxA (69.7%), PFHpA (42.2%), PFNA (59.7%), PFBS (39.5%), and FOSA (43.1%).
    - The SW-0100 duplicate sample exceeded the RPD for PFPeA (40.0%).

Although none of the samples exceeded the Rule 57 surface water quality values for PFOS or PFOA these results do indicate that source(s) of PFAS exist in Saginaw River watershed, particularly in Dutch Creek and Birch Run. Very high river discharge conditions at the time of sample collection likely resulted in low concentrations due to dilution.

EGLE is planning to conduct additional focused source tracking in the watershed in 2020.

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.

Status Update By: Brandon Armstrong, Toxicologist
Joe Bohr, Aquatic Biologist
Surface Water Assessment Section
Water Resources Division
Michigan Department of Environment, Great Lakes, and Energy

Table 1: PFOS and PFOA concentrations measured above their detection limit in surface water samples collected from locations in the Saginaw River watershed on October 29, 2019. No samples exceeded the Rule 57 HNV for PFOS nor PFOA. ND indicates a non-detection.

SAMPLE ID	SAMPLE LOCATION DESCRIPTION	LAT	LONG	PFOS (NG/L)	PFOA (NG/L)
CR-0010	Cass River @ East Rd	43.365	-83.955	1.4	1.3
CP-0010	Chippewa River Near Isabella St	43.611	-84.265	1.9	1.0
FR-0010	Flint River @ end of Curtis Rd	43.321	-84.045	1.7	1.1
MC-0010	Misteguay Creek @ W. Fry Rd	43.292	-83.992	1.6	1.7
PR-0010	Pine River @ E. Prairie Rd	43.597	-84.303	1.5	1.2
CB-0010	Cheboyganing Creek @ end of Ritter Rd	43.508	-83.863	2.0	2.0
DC-0010	Dutch Creek @ S. Euclid Rd	43.557	-83.916	8.9	1.2
SG-0010	Saginaw River @ Sandy Shore Rd Dock	43.645	-83.851	2.1	2.0
SG-0020	Saginaw River @ Wilder Rd Dock	43.625	-83.842	2.2	1.7
SG-0030	Saginaw River @ 3rd St Dock	43.613	-83.854	2.0	1.4
SG-0040	Saginaw River Near N. Johnson St	43.612	-83.874	2.2	1.4
SG-0045	Saginaw River @ Veteran's Memorial Bridge	43.596	-83.894	2.5	1.8
SG-0050	Saginaw River @ Bay City Loop Dock	43.588	-83.897	2.2	1.7
SG-0051	Saginaw River @ Cobblestone Condo Walkway	43.587	-83.896	2.3	1.9
SG-0052	Saginaw River @ Riverwalk Bridge	43.584	-83.900	2.5	1.7
SG-0053	Saginaw River @ Bigelow Park (east side)	43.584	-83.899	2.3	2.0
SG-0055	Saginaw River @ Middleground Trail	43.575	-83.907	2.3	1.9
SG-0055[R]				2.5	1.4
SG-0060	Saginaw River Near Stone Island Rd	43.555	-83.907	2.2	1.6
SG-0060[D]				2.3	1.6
SG-0070	Saginaw River @ I-75 East Service Rd	43.482	-83.912	1.7	1.1
SG-0080	Saginaw River Near Veteran's Memorial Pkwy	43.461	-83.912	2.4	1.8
SG-0085	Saginaw River @ end of Mapleridge Rd	43.455	-83.928	1.8	1.7
SG-0090	Saginaw River @ Johnson St	43.436	-83.940	3.3	1.7
SG-0100	Saginaw River @ Holland St	43.421	-83.951	2.0	1.7
SG-0110	Saginaw River @ W. Center St	43.401	-83.966	2.5	1.9
BD-0010	Bad River @ end of Randolph St	43.303	-84.111	1.6	1.7
BR-0010	Birch Run @ end of Evon Rd	43.358	-83.999	6.9	2.7
BV-0010	Beaver Creek @ E. North St	43.311	-84.142	1.1	0.9
SC-0010	Swan Creek @ end of S. Miller Rd	43.355	-84.072	1.9	1.7
SW-0100	Shiawassee River @ Fergus Rd	43.255	-84.105	1.6	1.6
SW-0100[D]				1.4	1.7
TB-0010	Tittabawassee River @ S. Center Rd	43.393	-84.014	1.7	0.9
TB-0035	Tittabawasee River @ Freeland Rd	43.525	-84.125	1.5	1.3
TB-0035[R]				1.6	1.5
TB-0050	Tittabawassee River @ Currie Pkwy	43.617	-84.253	ND	ND

[D] indicates a duplicate sample; [R] indicates a replicate sample

Table 2: Perfluoroalkyl and polyfluoroalkyl substances (PFAS) analyzed in surface water samples

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

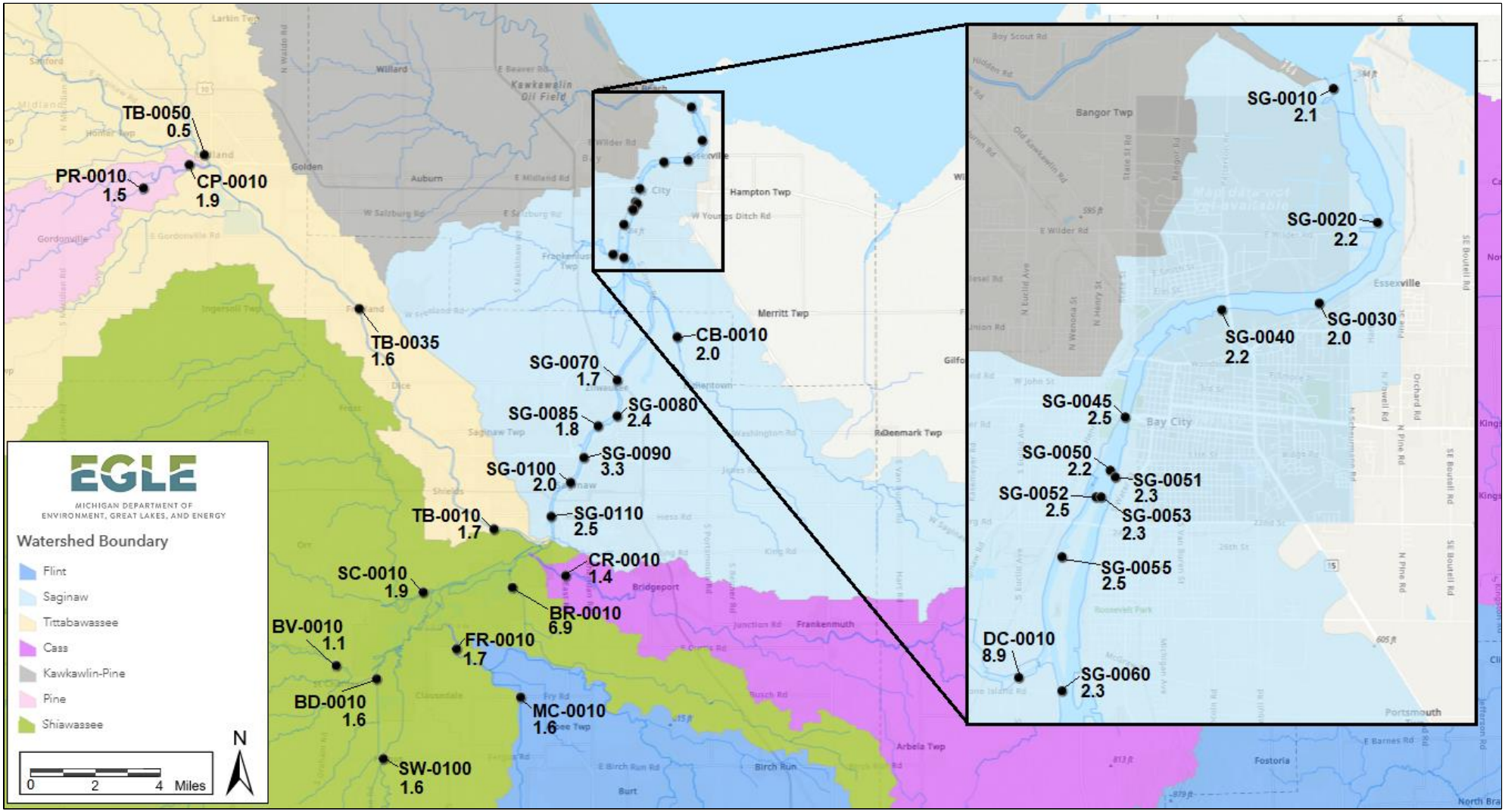

Figure 1: Overview map of surface water PFOS concentrations (ng/L) at locations in the Saginaw River watershed on October 29, 2019. The inset provides more detail for the intensive sampling that occurred around Middle Ground Island. No samples exceeded the Rule 57 Human Non-Cancer Value for PFOS.

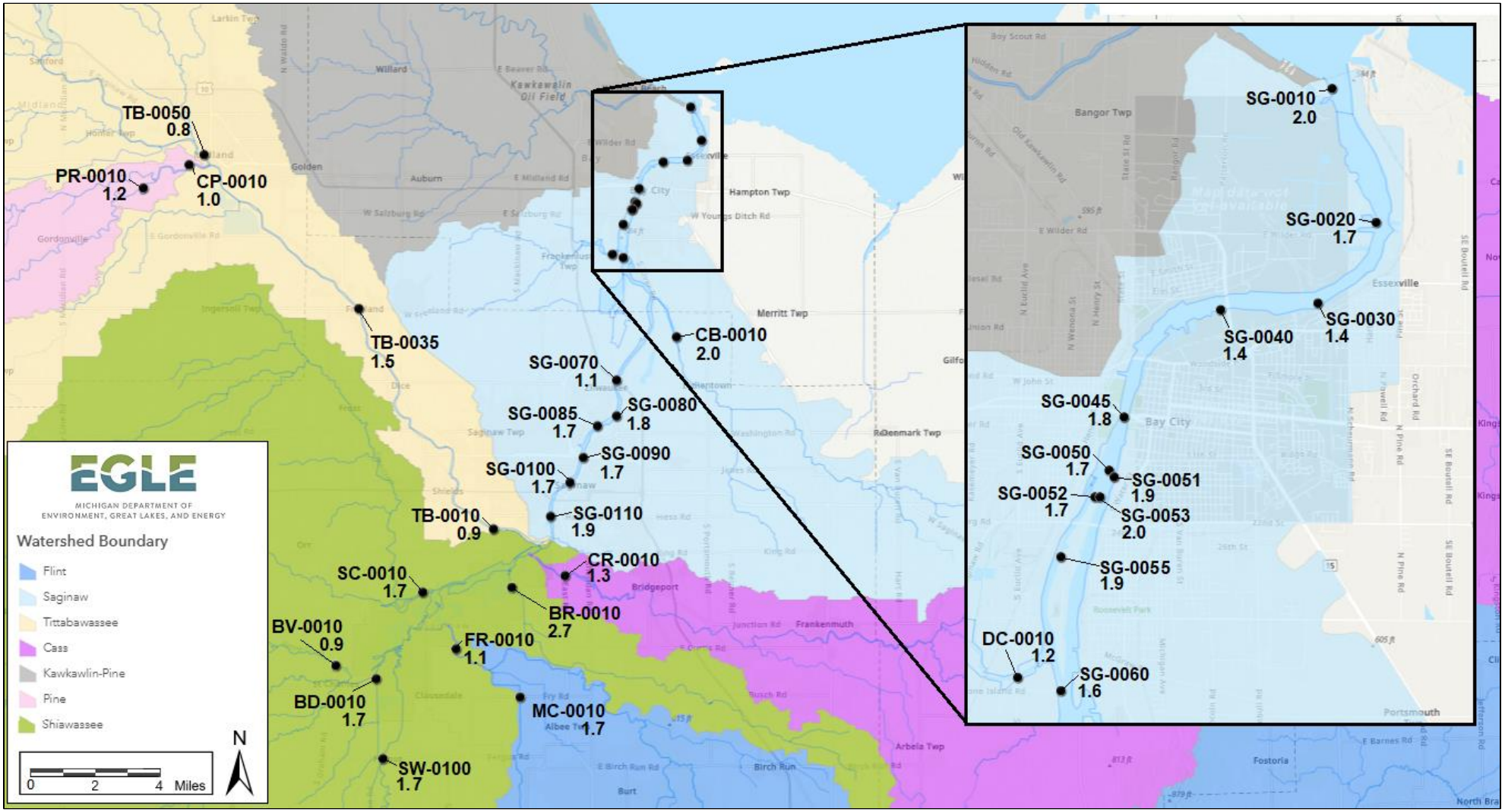

Figure 2: Overview map of surface water PFOA concentrations (ng/L) at locations in the Saginaw River watershed on October 29, 2019. The inset provides more detail for the intensive sampling that occurred around Middle Ground Island. No samples exceeded the Rule 57 Human Non-Cancer Value for PFOA.