MICHIGAN DEPARTMENT OF ENVIRONMENT, GREAT LAKES, AND ENERGY
WATER RESOURCES DIVISION
JULY 2020

STAFF REPORT

INVESTIGATION OF PER- AND POLYFLUOROALKYL SUBSTANCES CONTAMINATION IN THE CLINTON RIVER, LAKE ST. CLAIR, AND SELECTED TRIBUTARIES IN MACOMB COUNTY

BACKGROUND

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. 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, storm water runoff, venting groundwater, or as deposition after emissions into the atmosphere. In addition, several PFAS are key ingredients in fire-fighting foams. These foams have been used extensively in fire training exercises at military bases nationwide; in recent years PFAS have been detected in surface water and groundwater near many military facilities. 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 are 880,000 and 7,700 ng/L, respectively. The Rule 57 AMV and FCV for PFOA are 780,000 and 140,000 ng/L, respectively.

In 2017 EGLE added PFAS sampling to the National Pollutant Discharge Elimination System (NPDES) permit compliance sampling inspections at potential PFAS sources. Additionally, EGLE began a statewide Industrial Pretreatment Program (IPP) PFAS Initiative in 2018 that required all municipal wastewater treatment plants (WWTP) with approved IPPs to determine if they have significant sources of PFOS and/or PFOA discharging to their collection system and potentially passing through the WWTP to surface waters. Under the IPP PFAS Initiative, when WWTPs identify significant sources of PFOS, they are required to monitor their WWTP effluent and work with their sources to reduce the discharge of PFOS from the facility.

The Clinton River (HUC 04090003) drains portions of five counties in southeast Michigan: Oakland, Macomb, Lapeer, St. Clair, and Wayne. Approximately 60% of the Clinton River watershed is agricultural production, 17% is woodland or wetland, and 15% is residential (Clinton River Watershed Council, 2020). The main tributaries of the Clinton River include Sashabaw Creek, Stony Creek, Paint Creek, Red Run, North Branch of the Clinton River, Middle Branch of the Clinton River, Pontiac Creek, Galloway Creek, and the Clinton River Spillway Channel.

Water sampling in Lake St. Clair and the eastern portion of the Clinton River watershed near the Selfridge Air National Guard Base (SANGB) was conducted by EGLE, Water Resources Division (WRD), in a stepwise fashion. Initial limited sampling in August 2017 indicated that there were PFOS concentrations in area surface waters exceeding the HNV. Three subsequent sampling events between November 2017 and July 2019 were then conducted by the WRD in the lower Clinton River watershed to confirm the initial results and to track potential sources of contamination. Additionally, in February 2018 a contractor collected surface water samples from storm water outfalls draining the SANGB and discharging to the Clinton River and Lake St. Clair. Results of that sampling were provided to EGLE. Water samples in the upper Clinton River watershed were also collected at two locations in Stony Creek Lake in August 2019 and from one location in Bear Creek in February 2020.

Lastly, fish tissue samples were collected from three areas in the Clinton River watershed and analyzed for PFAS as well as other contaminants of concern. The analytical results will be used to inform the Michigan Department of Health and Human Services (MDHHS) “Eat Safe Fish” program as well as to provide additional information for contaminant source tracking.

SUMMARY

1. PFOS was detected in 55 of 57 samples collected from the Clinton River watershed or Lake St. Clair and detections ranged from 0.9 ng/L in Stony Creek Lake to 610 ng/L in the Clinton River near its mouth. The duplicate sample collected from the Clinton River mouth sample had a PFOS concentration of 31 ng/L.
2. The following ten sampling locations exceeded the PFOS Rule 57 HNV (no samples exceeded the HNV for PFOA).
    a. Bear Creek near Mound Rd (BC-100): 12.7 ng/L
    b. The Tucker-Jones Drain near Jefferson Ave (TJDr-0010): 13 ng/L

    c. The Clinton River near Riverside Bay Ct. (CR-020): 36 ng/L
    d. The Greiner Drain @ Dunham Rd (GDr-010): 37 ng/L
    e. The Greiner Drain @ N Groesbeck Hwy (GDr-020): 43-71 ng/L
    f. An unnamed drain on the west side of SANGB at Irwin Dr. (Base-0020): 49 ng/L
    g. Lake St. Clair at the Selfridge Public Boat Launch (LSC-001): 180 ng/L
    h. An unnamed drain on the west side of SANGB at Irwin Dr. (Base-0010): 190 ng/L
    i. The Clinton River at Moravian Dr. (CR-090): 470 ng/L
    j. The Clinton River near the mouth (CR-010): 610 ng/L
3. Elevated (> 3 to 12 ng/L) concentrations of PFOS were observed in the following tributaries to the Clinton River:
    a. Middle Branch of the Clinton River d/s Miller Drain (MBC-010): 3.5 ng/L
    b. Canal Drain upstream of its confluence with the river (CDr-010): 3.6 ng/L
    c. North Branch of the Clinton River near Cass Ave (NBC-010): 4.7 ng/L
    d. Miller Drain at Heydenreich Rd (MDr-010): 7.3 ng/L
    e. An unnamed drain on the west side of SANGB at Henry B Joy Blvd (Base-0030): 10 ng/L
    f. Harrington Drain at Harrington St (HDr-010): 12 ng/L
4. No surface water samples exceeded the Rule 57 aquatic life values for PFOS or PFOA.
5. PFAS contaminated storm water near Madison Heights is a source of PFAS to Bear Creek
6. PFAS contamination of the lower Clinton River appears to be influenced by wet weather events.
7. Storm water at the SANGB, which discharges to the Clinton River, had elevated PFOS concentrations of up to 4,540 ng/L.
8. The source of PFAS from Axalta Coating Systems to the Greiner Drain is likely historic releases of PFAS-containing Aqueous Film Forming Foam (AFFF).
9. The Pontiac and Warren WWTP discharge may be a source of PFOS to the upper Clinton River watershed, further investigation in the river near these outfalls is warranted.
10. PFOS was not detected in nine of ten rock bass fillet samples collected from Stony Creek Lake in 2019. The sample with detectable levels of PFOS had a concentration of 12.5 parts per billion (ppb).
11. PFOS was not detected in any of the ten fillet samples of rock bass collected from the Clinton River near Mt. Clemens in 2019.
12. Rock bass were also collected from the Clinton River upstream of the Yates dam; however, these results are still pending.
13. PFOS causes an MDHHS “Eat Safe Fish” consumption advisory of no more than 4 servings per month of bluegill caught from Lake St. Clair.
14. PFOS would also cause a fish consumption advisory for largemouth bass from Lake St. Clair; however, PCBs and mercury cause more restrictive advice.

METHODS

Surface Water

Surface water grab samples were collected from Lake St. Clair, the lower Clinton River, and select tributaries to those water bodies on five occasions between August 2017 and July 2019.

All samples were collected following the EGLE Surface Water PFAS Sampling Guidance document (Michigan Department of Environmental Quality [MDEQ], 2018a) and analyzed for PFAS, as described in the Quality Assurance Project Plan (QAPP; MDEQ, 2018b). To date, a total of 57 samples from 36 locations have been collected by EGLE. In addition, a series of trip, field, and equipment blanks were collected to provide quality control.

Sample Collection

Samples were collected in two 250 milliliter (mL) high-density polyethylene (HDPE) bottles (laboratory certified as PFAS-free). Sub-surface grab samples in wadeable stream sections were taken by hand or by use of a dip pole, directly into bottles. Field personnel used gloved hands, collecting the samples upstream of any sampling equipment or personnel and avoiding the collection of surface scums. Stream samples were taken at or near a point of greatest current, and both sample bottles were filled simultaneously. Subsurface samples from nonwadeable streams were collected using a weighted one-liter HDPE bottle. Samples from locations accessed via a boat were collected using a weighted, depth-integrating one-liter HDPE bottle. The bottle was lowered with a rope swiftly to depth and gradually retrieved to provide a composite sample approximately representative of the water column. The collected water was then dispensed into the two sample bottles.

Samples were preserved on ice and shipped via overnight delivery to the Eurofins TestAmerica Sacramento laboratory at the end of the sample collection event. Eurofins TestAmerica is an EGLE contract laboratory and analyzes surface water samples using a modified version of the United States Environmental Protection Agency (USEPA) Method 537 (USEPA, 2009), a process using isotope dilution for analyte quantification. Samples were analyzed for 19 or 24 PFAS analytes (Table 1). The December 2018 samples were subcontracted out by Eurofins TestAmerica to Eurofins Lancaster Laboratories Env LLC.

Table 1. Perfluoroalkyl and polyfluoroalkyl substances (PFAS) analyzed by the Eurofins TestAmerica Sacramento laboratory. The 19 analytes list was used in 2017 and 2018 whereas, in 2019 and 2020 the 24 analytes list was used.

Compound	Abbreviation	CAS	19	24
Perfluorotetradecanoic acid	PFTeA	376-06-7	X	X
Perfluorotridecanoic acid	PFTriA	72629-94-8	X	X
Perfluorododecanoic acid	PFDoA	307-55-1	X	X
Perfluoroundecanoic acid	PFUnA	2058-94-8	X	X
Perfluorodecanoic acid	PFDA	335-76-2	X	X
Perfluorononanoic acid	PFNA	375-95-1	X	X
Perfluorooctanoic acid	PFOA	335-67-1	X	X
Perfluoroheptanoic acid	PFHpA	375-85-9	X	X
Perfluorohexanoic acid	PFHxA	307-24-4	X	X
Perfluoropentanoic acid	PFPeA	2706-90-3	X	X
Perfluorobutanoic acid	PFBA	375-22-4	X	X
Perfluorodecanesulfonic acid	PFDS	335-77-3	X	X
Perfluorononanesulfonic acid	PFNS	68259-12-1		X
Perfluorooctanesulfonic acid	PFOS	1763-23-1	X	X
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	X	X
Perfluorohexanesulfonic acid	PFHxS	355-46-4	X	X

Compound	Abbreviation	CAS	19	24
Perfluoropentanesulfonic acid	PFPeS	2706-91-4		X
Perfluorobutanesulfonic acid	PFBS	375-73-5	X	X
Perfluorooctanesulfonamide	PFOSA	754-91-6	X	X
Fluorotelomer sulphonic acid 8:2	FtS 8:2	39108-34-4		X
Fluorotelomer sulphonic acid 6:2	FtS 6:2	27619-97-2		X
Fluorotelomer sulphonic acid 4:2	FtS 4:2	757124-72-4		X
2-(N-Ethylperfluorooctanesulfonamido) acetic acid	N-EtFOSAA	2991-50-6		X
2-(N-Methylperfluorooctanesulfonamido) acetic acid	N-MeFOSAA	2355-31-9		X
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5	X	
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6	X	

Quality Assurance/Quality Control (QA/QC)

All quality control objectives and criteria for the PFAS analyses are provided in Table 2. Field sampling and analytical quality were assessed using replicate, duplicate, and blank (trip, field, equipment, and laboratory method) samples. Replicate samples were taken by collecting two samples in succession at the same sample location. One replicate sample was collected during both the November 2017 and February 2018 sampling events, and two replicates were collected during the July 2019 event. One duplicate sample consisting of a one-liter composite sample dispensed into two 250 mL bottles was collected during both the February 2018 and July 2019 sampling events. One field blank was collected during the November 2017, February 2018, and July 2019 sampling events by filling a clean set of sample bottles with PFAS-free deionized water in the field. A trip blank was analyzed for both the February 2018 and July 2019 sampling events and consisted of one laboratory prepared bottle of PFAS-free deionized water that was transported unopened to the field and returned to the lab for analysis.

Precision of replicate and duplicate results is calculated by the relative percent deviation (RPD) as defined by 100 times the difference (range) of each sample, X1 and X2, divided by the arithmetic mean of the set and calculated from the following equation:

$$RPD = 100 * \frac{X1 - X2}{(\frac{(X1 + X2)}{2})}$$

Table 2. Quality objectives and criteria for water measurement data.

Data Quality Indicator	Measurement	Data Quality Objective	Results
Precision	1 Matrix Spike/Matrix Spike (MS/MSD) Duplicate per preparation batch	%RPD < 30%	RPD ranged from 0 to 14%
Precision	Field Sample Replication/Duplication	%RPD < 30%	RPD < 30% except GDr-020 (8:2 FtS = 32.6%; NEtFOSAA = 80.0%; NMeFOSAA = 61.4%; PFDoA = 100%; PFUnA = 62.8%) CR-010R (PFHpS = 127.9%; PFOS = 180.7%)
Accuracy/Bias	1 Lab Control Spike (LCS) and 1 MS/MSD per preparation batch	60 to 140% recovery	Analyte recovery ranged from 72 to 140% except: PFBA in July 2019 LCS (140/141%) PFDA in August 2017 LCS (151/164%)
Accuracy/Bias	1 method blank per preparation batch	No target analytes greater than or equal to the laboratory reporting limit	Analyte detection in all method blanks below reporting limits
Comparability	LC/MS Analytical work was conducted by the Eurofins TestAmerica LCMS West Sacramento Laboratory	The laboratory will provide verification that methods were properly implemented, and results meet QA/QC standards	All samples analyses were conducted by Eurofins TestAmerica LCMS West Sacramento Laboratory and met QA/QC standards
Sensitivity	LC/MS/MS is tested daily or as needed following WS-LC-0025 SOP	Each analyte will pass continuing calibration verification (CCV) criteria of 40 or 50% difference (analyte specific)	Not requested from or provided by Eurofins TestAmerica
Accuracy/Bias	Every sample (spiked, standard or method blank) received an internal standard	25 to 150% recovery	Analyte recovery > 25 and < 150% except for 1. FOSA: CR-020 (3%); LSC-001 (3%) 2. PFPeS: BC-100 (159%) 3. PFBS: BC-100 (159%) 4. 4:2 FTS: BC-100 (156%)
Completeness	[Total number of samples analyzed found to meet or exceed quality control criteria / total number of samples analyzed] * 100	90% samples should pass quality control criteria	$\frac{52}{57} * 100 = 91.0\%$ for all analytes $\frac{56}{57} * 100 = 98.2\%$ for PFOS/PFOA

Ambient Water Sampling: Clinton River Watershed

On August 31, 2017, a single ambient surface water grab sample was collected from both the Clinton River and Lake St. Clair (Table 3; Figure 1). According to the United States Geological Survey (USGS) gaging station on the Clinton River near Mt. Clemens (USGS 04165500), the river flow on August 31 was ~ 300 cubic feet per second (cfs), which is slightly above the 86-year median for this date and location (~ 200 cfs). Significant rainfall had occurred on the evening of August 28, resulting in a 2,850 cfs increase in discharge. After it was determined that PFAS contamination was present in these water bodies, 12 additional samples from 11 locations were collected and analyzed for PFAS in November 2017. Grab samples of ambient surface water were collected between November 7 and 8, 2017, by the WRD, Surface Water Assessment Section (SWAS), from six locations in western Lake St. Clair, four locations from the main branch of the Clinton River; and one location from the Tucker-Jones drain (Table 3; Figure 1). According to the USGS 04165500 gaging station, the river flow on November 7 was ~ 500 cfs, which is slightly above the 86-year median for this date and location (~ 300 cfs). Significant rainfall had occurred on the evening of November 4, resulting in a 700 cfs increase in discharge.

Surface water samples were collected by AECOM, contractors for the SANGB, on February 8, 2018, and analyzed for PFAS using USEPA Method 537 Rev 1.1 Modified. Samples were collected from five storm water compliance sampling points (Figure 2), two of which (Outfalls 001A and 002A) discharge to the Clinton River between EGLE sampling points CR-010 and CR-040.

Source tracking was conducted by EGLE on February 13 and 14, 2018, where 22 samples at 20 locations were collected from the Clinton River watershed. This sampling was conducted after an eight-day period of below freezing air temperatures, and presumably melt/storm water discharge to the river was minimal. According to the USGS 04165500 gaging station, the river flow on February 13 was ~ 350 cfs, which is below the 85-year median for this date and location (~ 400 cfs). Grab samples of ambient surface water were collected from 7 locations on the main branch of the Clinton River, 3 locations from the north branch of the Clinton River, two locations from the middle branch of the Clinton River, two locations from the Clinton River spillway, one location from Lake St. Clair, and one location from each of the Canal, Greiner, Miller, Harrington, and Tucker-Jones drains (Table 3; Figure 3).

Additional source tracking was conducted on July 26, 2019, where 18 samples at 15 locations were collected from the Clinton River watershed. Grab samples of ambient surface water were collected from four locations from the main branch of the Clinton River, three locations from the north branch of the Clinton River, two locations from the Greiner and Tucker-Jones Drains, one location from the Harrington drain, and three unnamed tributaries that drain the SANGB (Table ***3***; Figure 4). According to the USGS 04165500 gaging station, the river flow on July 26 was ~ 200 cfs, which is at the 86-year median for this date and location. Additional samples were collected from Stony Creek Lake on August 28, 2019 (Table 3; Figure 4).

Table 3. PFOS and PFOA concentrations measured in surface water samples collected from the Clinton River watershed and Lake St. Clair between 2017 and 2019. Concentrations exceeding the Part 4, Rule 57 HNV are bolded and italicized. ND denotes a Non-Detect. Revisited sample locations are in bold.

Sample ID	Sample Location	Latitude	Longitude	Sampling Event	PFOS (ng/L)	PFOA (ng/L)
SCL-01	Stony Creek Lake south end of lake	42.7216	-83.0874	Aug 2019	1.0	1.7
SCL-02	Stony Creek Lake north end of lake	42.7306	-83.0767	Aug 2019	1.0	2
BC-100	Bear Creek near Mound Rd	42.4966	-83.0455	Feb 2020	***12.7***	5.7
CR-110	Clinton River u/s of confluence w/Canal Drain	42.5945	-82.9148	Feb 2018	5.6	4.3
CDr-010	Canal Drain u/s of confluence w/Main Branch	42.5986	-82.9268	Feb 2018	3.6	4.1
CR-100	Clinton River u/s confluence w/North Branch, d/s Canal Drain	42.6000	-82.9158	Feb 2018	5.6	3.9
NBC-040	**N. Branch Clinton River near Hall Rd**	42.6260	-82.8954	Feb 2018	ND	1.2
NBC-040	**N. Branch Clinton River near Hall Rd**	42.6260	-82.8954	Jul 2019	1.8	2.1
GDr-010	Greiner Drain @ Dunham Rd	42.6175	-82.8973	Jul 2019	***37***	18
GDr-020	**Greiner Drain @ N Groesbeck Hwy**	42.6128	-82.8908	Feb 2018	***43***	16.0
GDr-020	**Greiner Drain @ N Groesbeck Hwy**	42.6128	-82.8908	Jul 2019	***58***	36
GDr-020[R]	**Greiner Drain @ N Groesbeck Hwy**	42.6128	-82.8908	Jul 2019	***71***	31
NBC-030	**N. Branch Clinton River @ end of Little Rd**	42.6192	-82.9013	Feb 2018	ND	1.4
NBC-030	**N. Branch Clinton River @ end of Little Rd**	42.6192	-82.9013	Jul 2019	1.8	2.2
MBC-020	Middle Branch Clinton River @ Heydenreich Rd	42.6061	-82.9178	Feb 2018	3.2	6.7
MDr-010	Miller Drain @ Heydenreich Rd	42.6090	-82.9173	Feb 2018	7.3	8.4
MBC-010	Middle Branch Clinton River d/s of Miller Drain; u/s of North Branch	42.6067	-82.9142	Feb 2018	3.5	6.9
NBC-010	**N. Branch Clinton River near Cass Ave**	42.6005	-82.9093	Feb 2018	1.6	3.1
NBC-010D[D]	**N. Branch Clinton River near Cass Ave**	42.6005	-82.9093	Feb 2018	1.7	2.8
NBC-010	**N. Branch Clinton River near Cass Ave**	42.6005	-82.9093	Jul 2019	4.7	7
CR-090	**Clinton River @ Moravian Dr**	42.5960	-82.9095	Nov 2017	***470***	5.6
CR-090	**Clinton River @ Moravian Dr**	42.5960	-82.9095	Feb 2018	4.3	4.3
CR-090	**Clinton River @ Moravian Dr**	42.5960	-82.9095	Jul 2019	11	6.8
HDr-010	**Harrington Drain @ Harrington St**	42.5880	-82.9037	Feb 2018	7.9	5.6
HDr-010	**Harrington Drain @ Harrington St**	42.5880	-82.9037	Jul 2019	12	7.5
CR-080	**Clinton River @ Southbound Gratiot Ave**	42.5849	-82.8836	Feb 2018	4.6	4.0
CR-080[R]	**Clinton River @ Southbound Gratiot Ave**	42.5849	-82.8836	Feb 2018	4.9	4.0
CR-080	**Clinton River @ Southbound Gratiot Ave**	42.5849	-82.8836	Jul 2019	12	6.4
SP-020	Clinton River Spillway @ Harper Ave	42.5772	-82.8723	Feb 2018	4.6	5.7

[R] Replicate Sample
[D] Duplicate Sample

Sample ID	Sample Location	Latitude	Longitude	Sampling Event	PFOS (ng/L)	PFOA (ng/L)
SP-010	Clinton River Spillway @ Jefferson Ave	42.5625	-82.8485	Feb 2018	5.0	6.0
CR-060	**Clinton River d/s Spillway Connect**	42.5841	-82.8742	Nov 2017	6.8	5.6
CR-060	**Clinton River d/s Spillway Connect**	42.5840	-82.8741	Feb 2018	4.7	6.8
CR-040	**Clinton River @ end of Lanse Creuse St**	42.5907	-82.8546	Nov 2017	8.0	6.2
CR-040	**Clinton River @ end of Lanse Creuse St**	42.5907	-82.8546	Feb 2018	5.0	9.6
CR-040	**Clinton River @ end of Lanse Creuse St**	42.5907	-82.8546	Jul 2019	6.0	2.5
CR-040R[R]	**Clinton River @ end of Lanse Creuse St**	42.5907	-82.8546	Jul 2019	6.6	2.5
CR-020	**Clinton River near Riverside Bay Ct.**	42.5928	-82.8171	Aug 2017	***36***	5
CR-020	**Clinton River near Riverside Bay Ct.**	42.5928	-82.8171	Jul 2019	2.8	2.3
CR-010	**Clinton River near mouth**	42.5948	-82.7963	Nov 2017	***610***	6.4
CR-010D[D]	**Clinton River near mouth**	42.5948	-82.7963	Nov 2017	***31***	6.2
CR-010	**Clinton River near mouth**	42.5948	-82.7963	Feb 2018	2.3	4.2
BASE-0010	Unnamed tributary @ Irwin Dr.	42.6017	-82.8518	Jul 2019	***190***	5.2
BASE-0020	Unnamed tributary @ Irwin Dr.	42.6071	-82.8514	Jul 2019	***49***	14
BASE-0030	Unnamed tributary @ Henry B Joy Blvd	42.6097	-82.8534	Jul 2019	10	5.6
TJDr-020	Tucker-Jones Drain @ William P Rosso Hwy	42.6307	-82.8386	Jul 2019	9.2	7.8
TJDr-010	**Tucker-Jones Drain near Jefferson Ave**	42.6302	-82.8239	Nov 2017	***13***	4
TJDr-010	**Tucker-Jones Drain near Jefferson Ave**	42.6302	-82.8239	Feb 2018	3.2	3.6
TJDr-010	**Tucker-Jones Drain near Jefferson Ave**	42.6302	-82.8239	Jul 2019	7.5	6.2
TJDr-010[D]	**Tucker-Jones Drain near Jefferson Ave**	42.6302	-82.8239	Jul 2019	6.5	5.5
LSC-001	**Lake St. Clair @ Selfridge Public Boat Launch**	42.6296	-82.8189	Aug 2017	***180***	4.3
LSC-001	**Lake St. Clair @ Selfridge Public Boat Launch**	42.6296	-82.8189	Feb 2018	1.3	ND
LSC-010	Lake St. Clair @ St. Clair Shores	42.5175	-82.8732	Nov 2017	2.0	1.8
LSC-020	Lake St. Clair @ Cottrell Rd.	42.5510	-82.8434	Nov 2017	2.7	2.1
LSC-030	Lake St. Clair @ Metropark	42.5686	-82.8122	Nov 2017	1.8	1.5
LSC-040	Lake St. Clair @ Selfridge AFB	42.6222	-82.8176	Nov 2017	2.0	2
LSC-050	Lake St. Clair @ New Baltimore	42.6543	-82.7600	Nov 2017	1.4	1.5
LSC-060	Lake St. Clair @ Ira TWP	42.6745	-82.6323	Nov 2017	7.4	1.5

[R] Replicate Sample
[D] Duplicate Sample

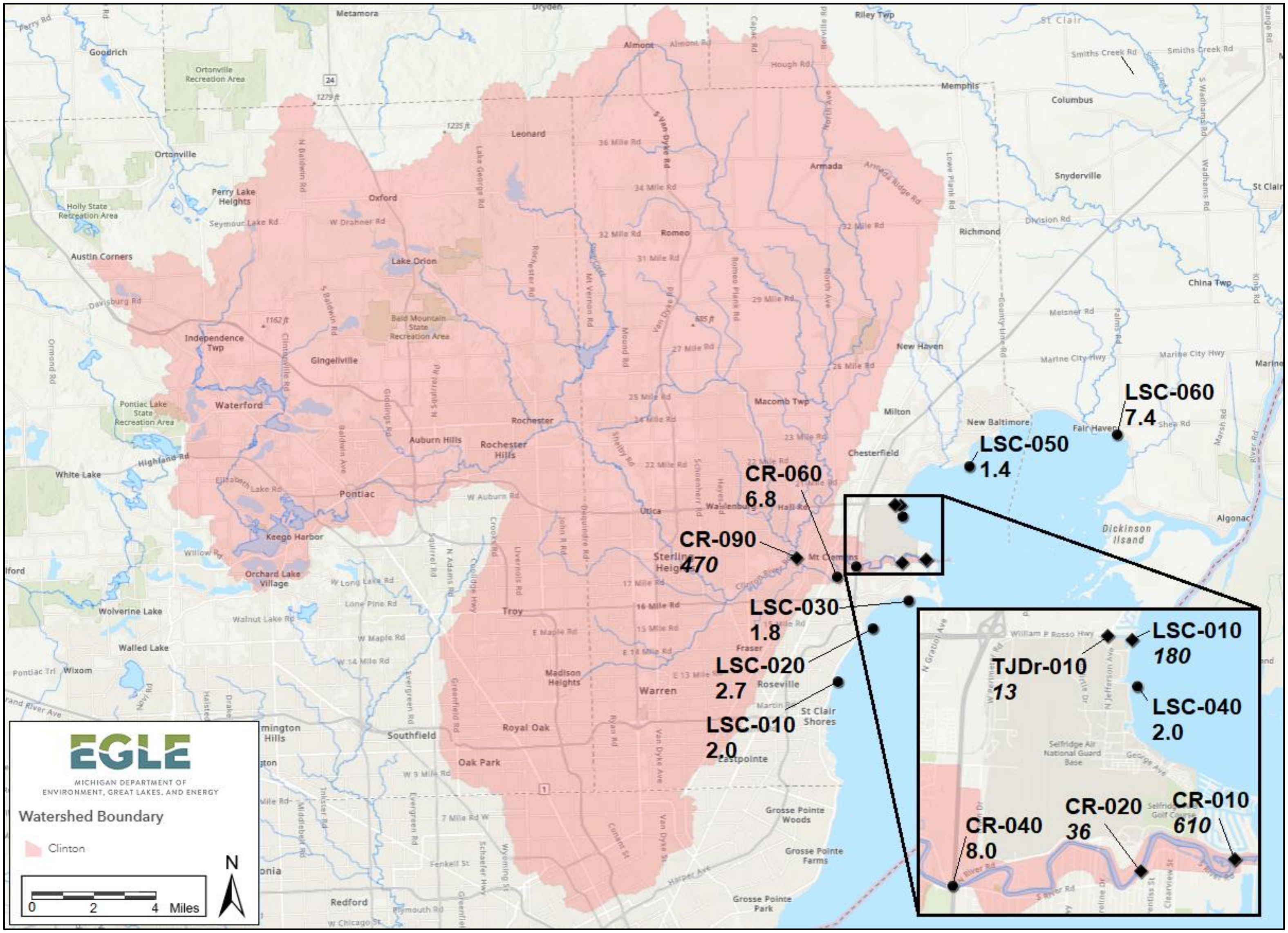

Figure 1. Overview map of the Clinton River watershed with surface water PFOS concentrations (ng/L) at locations sampled on August 31 and November 7, 2017. CR denotes a location on the Clinton River; TJDr is the Tucker-Jones Drain; LSC is Lake St. Clair. ♦ indicates a sample location with a Part 4, Rule 57 HNV exceedance.

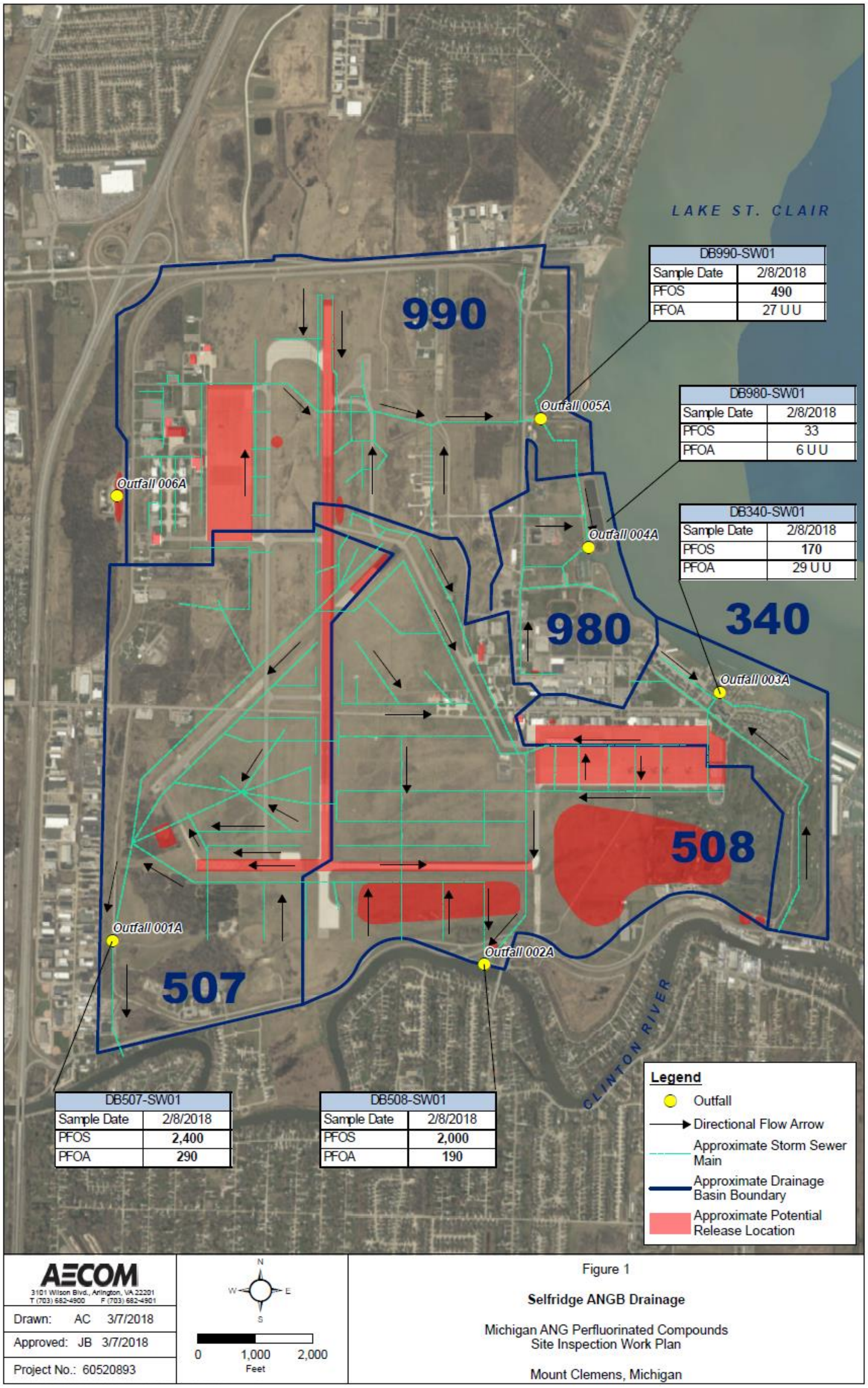

Figure 2. Map depicting PFOS and PFOA concentrations in the outfalls located at the Selfridge Air National Guard Base in Mt. Clemens. Samples were collected on February 8, 2018. Data provided by AECOM.

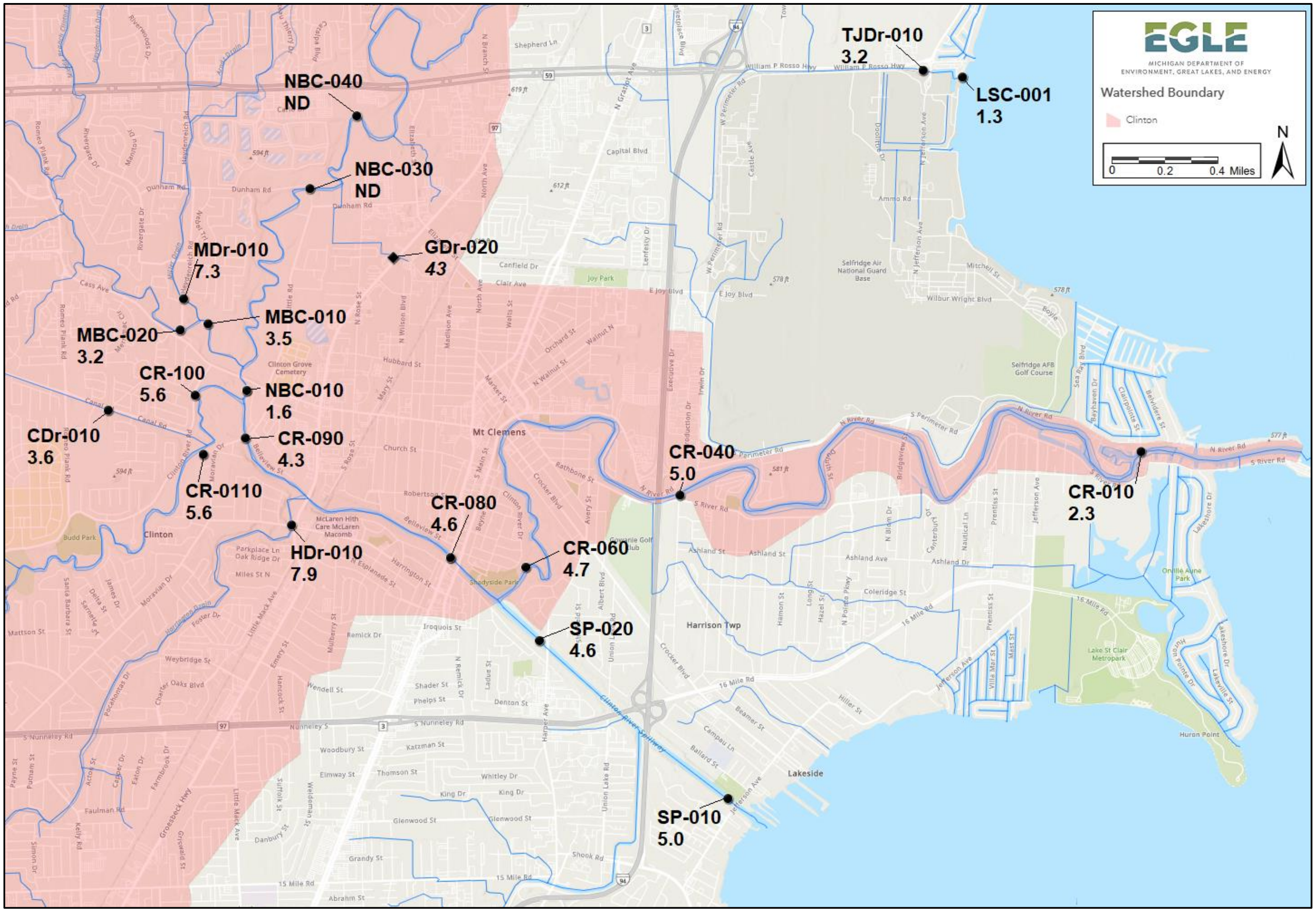

Figure 3. Overview map of the Clinton River watershed with surface water PFOS concentrations (ng/L) at locations sampled on February 13 and 14, 2018. CR denotes a location on the Clinton River; NBC is the North Branch Clinton River; MBC is the Middle Branch Clinton River; MDr is the Miller Drain; TJDr is the Tucker-Jones Drain; HDr is the Harrington Drain; GDr is the Greiner Drain. CDr is the Canal Drain; SP is the Clinton River Spillway; LSC is Lake St. Clair. ♦ indicates a sample location with a Part 4, Rule 57 HNV exceedance.

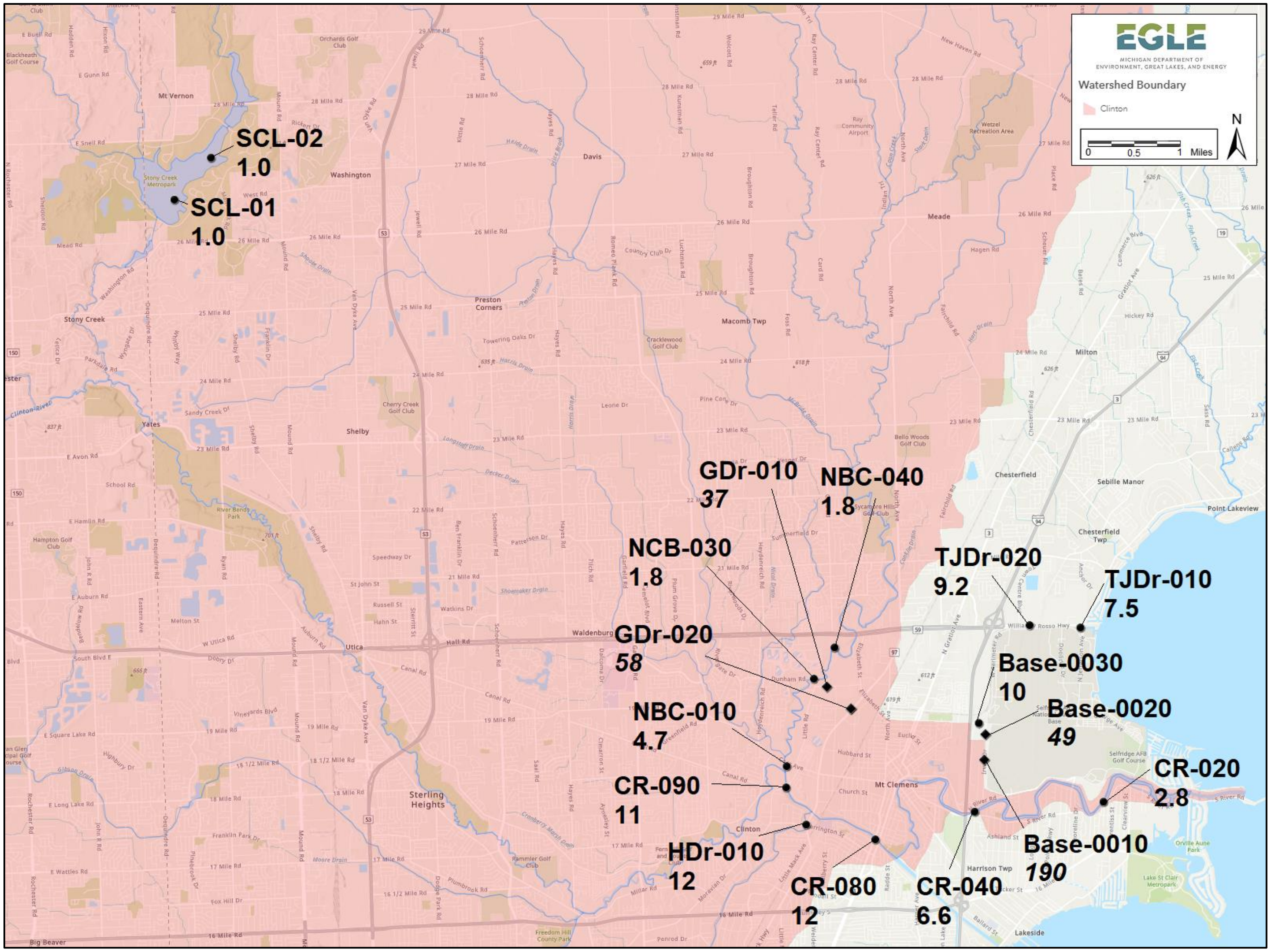

Figure 4. Overview map of the Clinton River watershed with surface water PFOS concentrations (ng/L) at locations sampled on July 26 and August 28, 2019. CR denotes a location on the Clinton River; NBC is the North Branch Clinton River; TJDr is the Tucker-Jones Drain; HDr is the Harrington Drain; GDr is the Greiner Drain; SCL is Stony Creek Lake; BASE are unnamed tributaries draining the Selfridge Air National Guard Base. ♦ indicates a sample location with a Part 4, Rule 57 HNV exceedance.

In December 2019 chromium-contaminated groundwater seeped through a retaining wall onto eastbound I-696 near Madison Heights. EGLE and the USEPA responded to the incident and conducted a source tracking investigation. Samples collected as a part of this investigation revealed PFAS contamination in the groundwater as well as in a pit of the basement at the former Electro-Plating Services facility, which had previously operated from 1967 to 2016. On February 5, 2020, the WRD collected storm water samples near Electroplating-Services as well as a surface water sample from Bear Creek, a tributary to Red Run, which flows into the Clinton River near Clinton Township. The samples were sent to and analyzed by the MDHHS using the 24 PFAS analyte list (Table 1).

Fish Tissue

Bluegill (*Lepomis macrochirus*) and largemouth bass (*Micropterus salmoides*) were collected by the WRD from two areas (Anchor Bay and L'Anse Creuse Bay) in Lake St. Clair on November 7, 2017. Fish were collected using standard electrofishing or netting equipment and were prepared as standard edible portion samples following the WRD, SWAS, Procedure (MDEQ, 1995). Fish tissue samples were analyzed for 11 perfluorinated compounds by the MDHHS Analytical Chemistry Laboratory (Table 4).

Table 4. PFAS compounds analyzed in fish tissue by the MDHHS Analytical Chemistry Laboratory.

Compound	Abbreviation	CAS
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorooctane sulfonate	PFOS	1763-23-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorotridecanoic acid	PFTriA	72629-94-8
Perfluorotetradecanoic acid	PFTeA	376-06-7
Perfluorohexane sulfonate	PFHxS	355-46-4
Perfluorodecane sulfonate	PFDS	335-77-3
Perfluorooctane sulfonamide	PFOSA	754-91-6

Point Source Discharges/Compliance Sampling Inspections

There are three WWTPs with discharges to the Clinton River watershed that were identified for PFAS effluent analysis. The Pontiac, Warren, and Mt. Clemens WWTPs are participating in the statewide IPP PFAS Initiative and have approved IPP programs. Effluent samples from these facilities were collected by EGLE in 2018 and/or 2019.

Effluent grab samples were collected by EGLE point source monitoring staff following the EGLE Wastewater PFAS Sampling Guidance document (MDEQ, 2018a). Samples were collected in two 250 mL HDPE bottles (laboratory certified as PFAS-free). Samples were collected directly in bottles by hand or via a dip pole. Field personnel used gloved hands, collecting the samples at the effluent monitoring points for wastewater before discharge. Samples were taken from the cascade in most instances. Sample bottles were filled consecutively and double bagged in Ziploc® bags before storage in a cooler with ice. Sample bottles were delivered to the Eurofins TestAmerica Brighton location and shipped to the Eurofins TestAmerica Sacramento laboratory at the end of the sample collection event.

RESULTS AND DISCUSSION

Ambient Surface Water Sampling QA/QC

All analytes were below detection levels in the field and trip blank samples with the following exceptions: PFHxS was reported at 0.2 ng/L in the field blank sample collected in November 2017. PFHxS was detected at 0.2 ng/L and 0.3 ng/L in the field and the trip blank samples collected during the February 2018 sampling event, respectively. PFHxS was detected in the equipment blank collected in the August 2019 sampling event. This analyte was detected in the each of the laboratory method blanks for these sampling events, indicating the source was most likely within the analytical process. PFOA and PFPeA were in the 2019 trip blank at 0.5 and 1.2 ng/L, respectively, which is below the laboratory reporting limit of 2.0 ng/L.

Surface Water Sampling Overview

A total of 57 ambient surface water samples from 36 sampling locations were collected over the six sampling events. PFOS was detected at all but two sampling locations (NBC-040 and NBC-030 in February 2018; 96.4%) and PFOA was detected at all but one sampling location (LSC-001 in February 2018; 98.2%). PFBS, PFHxS, PFHxA, PFHpA were detected in 100% of the samples. Other detections included PFPeA (98.2%), PFBA (98.2%), PFNA (89.5%), PFDA (59.6%), PFOSA (43.9%), PFPeS (38.1%),6:2 FtS (28.6%), PFHpS (25%), NMeFOSAA (23.8%), NEtFOSAA (23.8%), 8:2 FTS (19%), PFUnA (7.0%), PFDoA (7.0%), and PFHxDA (2.8%). PFTriA, PFTeA, PFNS, PFDS, 4:2 FtS, and PFODA were not detected in any sample.

In August and November 2017 the total (Σ) PFAS arithmetic mean concentration was 142.0 and 122.6 ng/L, respectively, and ranged from 7.8 ng/L in Lake St. Clair near New Baltimore to 657.1 ng/L in the mouth of the Clinton River (Table 5). It is important to note that the 2017 sampling Σ PFAS concentration includes the sum of only 19 PFAS analytes above their detection whereas the 2019 samples were analyzed using the 24-analyte method. PFOS was the most dominant analyte detected across all sampling locations comprising over 40% of an average sample, exceeding 85% of the total PFAS composition at three sampling locations (Figure 5): two locations on the Clinton River (CR-090 and CR-010) and one location on Lake St. Clair (LSC-001).

In February 2018 the Σ PFAS arithmetic mean concentration was 40.8 ng/L and ranged from 6.1 ng/L in Lake St. Clair at the Selfridge Public Boat Launch to 184.6 ng/L in the Greiner Drain (Table 5). For the 2018 samples, the Σ PFAS concentration includes the sum of only 19 PFAS analytes above their detection. PFBA was the most commonly detected analyte during the 2018 sampling comprising over 18.5% of the average sample (Figure 6). Four other analytes (PFHxA: 14.9%; PFOA: 13.3%; PFPeA: 12.9%; and PFBS: 11.7%) had greater percent composition than PFOS (11.5%) in an average sample collected from the watershed in February 2018. However, PFOS was the most dominant analyte in the composition of two sampling locations (Figure 6): the Greiner Drain (GDr-020: 23%) and Lake St. Clair (LSC-001; 21%).

In July 2019 the Σ PFAS arithmetic mean concentration was 114.9 ng/L and ranged from 13.2 ng/L in the Clinton River south of the SANGB to 415.4 ng/L in the Greiner Drain (Table 5). For the 2019 samples, the Σ PFAS concentration includes the sum of all 24 PFAS analytes above their detection. PFOS was again the most common analyte with a composition of 19.1% in an average sample across the watershed (Figure 7). A sample from the SANGB drain (BASE-0010) had a PFOS composition of 82.6%. 6:2 and 8:2 FtS were elevated in the samples collected from the Greiner Drain ranging from 5 to 14.5%. In comparison, these two analytes only made up 1-2% of the total PFAS in an average sample collected in 2019 (Figure 7).

The 2017 samples where PFOS comprised of over 40% of the total PFAS in an average sample were collected following a significant precipitation event with low river flows while no recent precipitation events occurred prior to the 2018 and 2019 sampling events. While a direct comparison of these data cannot be made due to the differences between sampling locations across the sampling events these data suggest that storm water may be an important source of PFOS to the lower Clinton River watershed.

Stony Creek Lake

Two surface water samples were collected from Stony Creek Lake in August 2019. PFOS and PFOA were at or below the laboratory reporting limit of 2.0 ng/L. Rock bass were collected from the lake in 2019 and processed as fillets. PFOS was nondetect in 9 of 10 samples and was 12.5 ppb in the one sample.

Bear Creek

The surface water sample collected from Bear Creek in February 2020 had a PFOS concentration of 12.7 ng/L, which exceeds the HNV. Storm water samples collected near the former Electro-Plating Services facility had PFOS concentrations up to 797 ng/L. Further investigations into additional sources of the contaminated storm water is warranted.

Table 5. Total PFAS concentrations (the sum of PFAS analytes above their detection limit) detected in surface water samples collected from locations in the lower Clinton River watershed, Stony Creek Lake and Bear Creek in the Upper Clinton River watershed, and Lake St. Clair between August 2017 and February 2020. Revisited locations are in bold.

Sample ID	Sample Location	Latitude	Longitude	Sampling Event	ΣPFAS (ng/L)	# Analytes Detected	# Analytes Measured
SCL-01	Stony Creek Lake south end of lake	42.7216	-83.0874	Aug 2019	15.3	10	24
SCL-02	Stony Creek Lake north end of lake	42.7306	-83.0767	Aug 2019	15.9	10	24
BC-100	Bear Creek near Mound Rd	42.4966	-83.0455	Feb 2020	91.1	9	24
CR-110	Clinton River u/s of confluence w/Canal Drain	42.5945	-82.9148	Feb 2018	42.0	10	19
CDr-010	Canal Drain u/s of confluence w/Main Branch	42.5986	-82.9268	Feb 2018	27.9	10	19
CR-100	Clinton River u/s confluence w/North Branch, d/s Canal Drain	42.6000	-82.9158	Feb 2018	39.8	9	19
NBC-040	**N. Branch Clinton River near Hall Rd**	42.6260	-82.8954	Feb 2018	11.1	7	19
NBC-040	**N. Branch Clinton River near Hall Rd**	42.6260	-82.8954	Jul 2019	19.1	9	24
GDr-010	Greiner Drain @ Dunham Rd	42.6175	-82.8973	Jul 2019	193.2	18	24
GDr-020	**Greiner Drain @ N Groesbeck Hwy**	42.6128	-82.8908	Feb 2018	184.6	11	19
GDr-020	**Greiner Drain @ N Groesbeck Hwy**	42.6128	-82.8908	Jul 2019	398.6	19	24
GDr-020[R]	**Greiner Drain @ N Groesbeck Hwy**	42.6128	-82.8908	Jul 2019	415.4	19	24
NBC-030	**N. Branch Clinton River @ end of Little Rd**	42.6192	-82.9013	Feb 2018	12.2	8	19
NBC-030	**N. Branch Clinton River @ end of Little Rd**	42.6192	-82.9013	Jul 2019	20.0	9	24
MBC-020	Middle Branch Clinton River @ Heydenreich Rd	42.6061	-82.9178	Feb 2018	41.2	9	19
MDr-010	Miller Drain @ Heydenreich Rd	42.6090	-82.9173	Feb 2018	78.0	10	19
MBC-010	Middle Branch Clinton River d/s of Miller Drain; u/s of North Branch	42.6067	-82.9142	Feb 2018	44.2	10	19
NBC-010	**N. Branch Clinton River near Cass Ave**	42.6005	-82.9093	Feb 2018	22.1	8	19
NBC-010[D]	**N. Branch Clinton River near Cass Ave**	42.6005	-82.9093	Feb 2018	21.8	8	19
NBC-010	**N. Branch Clinton River near Cass Ave**	42.6005	-82.9093	Jul 2019	56.2	11	24
CR-090	**Clinton River @ Moravian Dr**	42.5960	-82.9095	Nov 2017	508.5	12	19
CR-090	**Clinton River @ Moravian Dr**	42.5960	-82.9095	Feb 2018	35.8	9	19
CR-090	**Clinton River @ Moravian Dr**	42.5960	-82.9095	Jul 2019	70.1	11	24
HDr-010	**Harrington Drain @ Harrington St**	42.5880	-82.9037	Feb 2018	50.7	11	19
HDr-010	**Harrington Drain @ Harrington St**	42.5880	-82.9037	Jul 2019	79.8	15	24
CR-080	**Clinton River @ Southbound Gratiot Ave**	42.5849	-82.8836	Feb 2018	36.4	9	19
CR-080[R]	**Clinton River @ Southbound Gratiot Ave**	42.5849	-82.8836	Feb 2018	38.1	9	19
CR-080	**Clinton River @ Southbound Gratiot Ave**	42.5849	-82.8836	Jul 2019	65.2	12	24

[R] Replicate Sample
[D] Duplicate Sample

Sample ID	Sample Location	Latitude	Longitude	Sampling Event	ΣPFAS (ng/L)	# Analytes Detected	# Analytes Measured
SP-020	Clinton River Spillway @ Harper Ave	42.5772	-82.8723	Feb 2018	38.0	10	19
SP-010	Clinton River Spillway @ Jefferson Ave	42.5625	-82.8485	Feb 2018	38.6	10	19
CR-060	**Clinton River d/s Spillway Connect**	42.5841	-82.8742	Nov 2017	45.5	11	19
CR-060	**Clinton River d/s Spillway Connect**	42.5840	-82.8741	Feb 2018	38.7	10	19
CR-040	**Clinton River @ end of Lanse Creuse St**	42.5907	-82.8546	Nov 2017	52.4	12	19
CR-040	**Clinton River @ end of Lanse Creuse St**	42.5907	-82.8546	Feb 2018	40.8	10	19
CR-040	**Clinton River @ end of Lanse Creuse St**	42.5907	-82.8546	Jul 2019	18.6	10	24
CR-040[R]	**Clinton River @ end of Lanse Creuse St**	42.5907	-82.8546	Jul 2019	19.6	10	24
CR-020	**Clinton River near Riverside Bay Ct.**	42.5928	-82.8171	Aug 2017	72.7	12	19
CR-020	**Clinton River near Riverside Bay Ct.**	42.5928	-82.8171	Jul 2019	13.2	10	24
CR-010	**Clinton River near mouth**	42.5948	-82.7963	Nov 2017	657.1	12	19
CR-010[D]	**Clinton River near mouth**	42.5948	-82.7963	Nov 2017	75.7	12	19
CR-010	**Clinton River near mouth**	42.5948	-82.7963	Feb 2018	13.9	8	19
BASE-0010	Unnamed tributary @ Irwin Dr.	42.6017	-82.8518	Jul 2019	229.9	13	24
BASE-0020	Unnamed tributary @ Irwin Dr.	42.6071	-82.8514	Jul 2019	158.6	18	24
BASE-0030	Unnamed tributary @ Henry B Joy Blvd	42.6097	-82.8534	Jul 2019	115.0	10	24
TJDr-020	Tucker-Jones Drain @ William P Rosso Hwy	42.6307	-82.8386	Jul 2019	72.3	11	24
TJDr-010	**Tucker-Jones Drain near Jefferson Ave**	42.6302	-82.8239	Nov 2017	60.6	12	19
TJDr-010	**Tucker-Jones Drain near Jefferson Ave**	42.6302	-82.8239	Feb 2018	36.6	10	19
TJDr-010	**Tucker-Jones Drain near Jefferson Ave**	42.6302	-82.8239	Jul 2019	65.0	11	24
TJDr-010[D]	**Tucker-Jones Drain near Jefferson Ave**	42.6302	-82.8239	Jul 2019	58.7	11	24
LSC-001	**Lake St. Clair @ Selfridge Public Boat Launch**	42.6296	-82.8189	Aug 2017	211.2	10	19
LSC-001	**Lake St. Clair @ Selfridge Public Boat Launch**	42.6296	-82.8189	Feb 2018	6.1	7	19
LSC-010	Lake St. Clair @ St. Clair Shores	42.5175	-82.8732	Nov 2017	12.1	10	19
LSC-020	Lake St. Clair @ Cottrell Rd.	42.5510	-82.8434	Nov 2017	16.4	10	19
LSC-030	Lake St. Clair @ Metropark	42.5686	-82.8122	Nov 2017	9.1	10	19
LSC-040	Lake St. Clair @ Selfridge AFB	42.6222	-82.8176	Nov 2017	11.7	10	19
LSC-050	Lake St. Clair @ New Baltimore	42.6543	-82.7600	Nov 2017	7.8	10	19
LSC-060	Lake St. Clair @ Ira TWP	42.6745	-82.6323	Nov 2017	14.5	10	19

[R] Replicate Sample
[D] Duplicate Sample

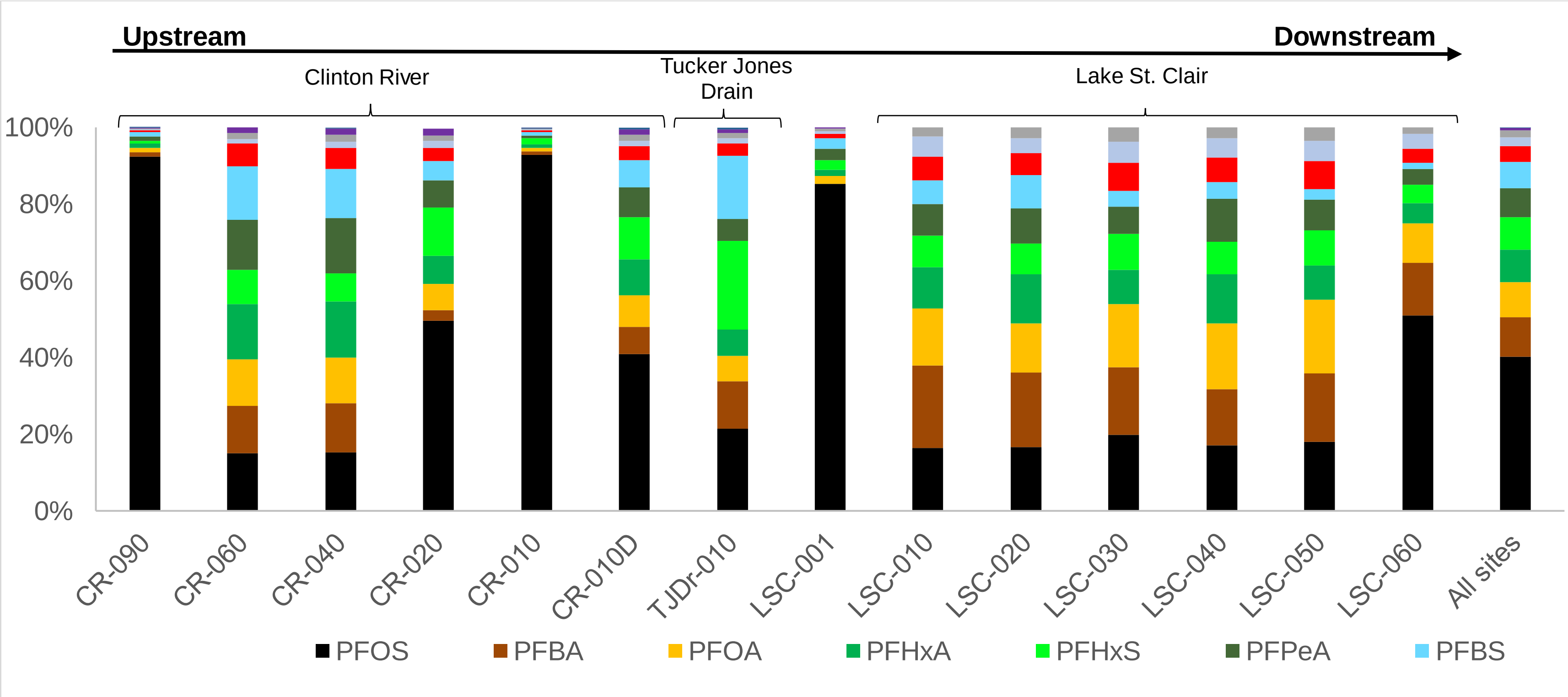

Figure 5. Percentage composition of PFAS measured in surface water collected in the lower Clinton River watershed and Lake St. Clair in 2017. Sample IDs are shown (CR is the Clinton River; TJDr is the Tucker-Jones Drain; LSC is Lake St. Clair). 'All Sites' represents the arithmetic mean percentage of each detected analyte compared to the total PFAS concentration across the entire watershed. A Sample ID followed by the letter 'D' is a duplicate sample.

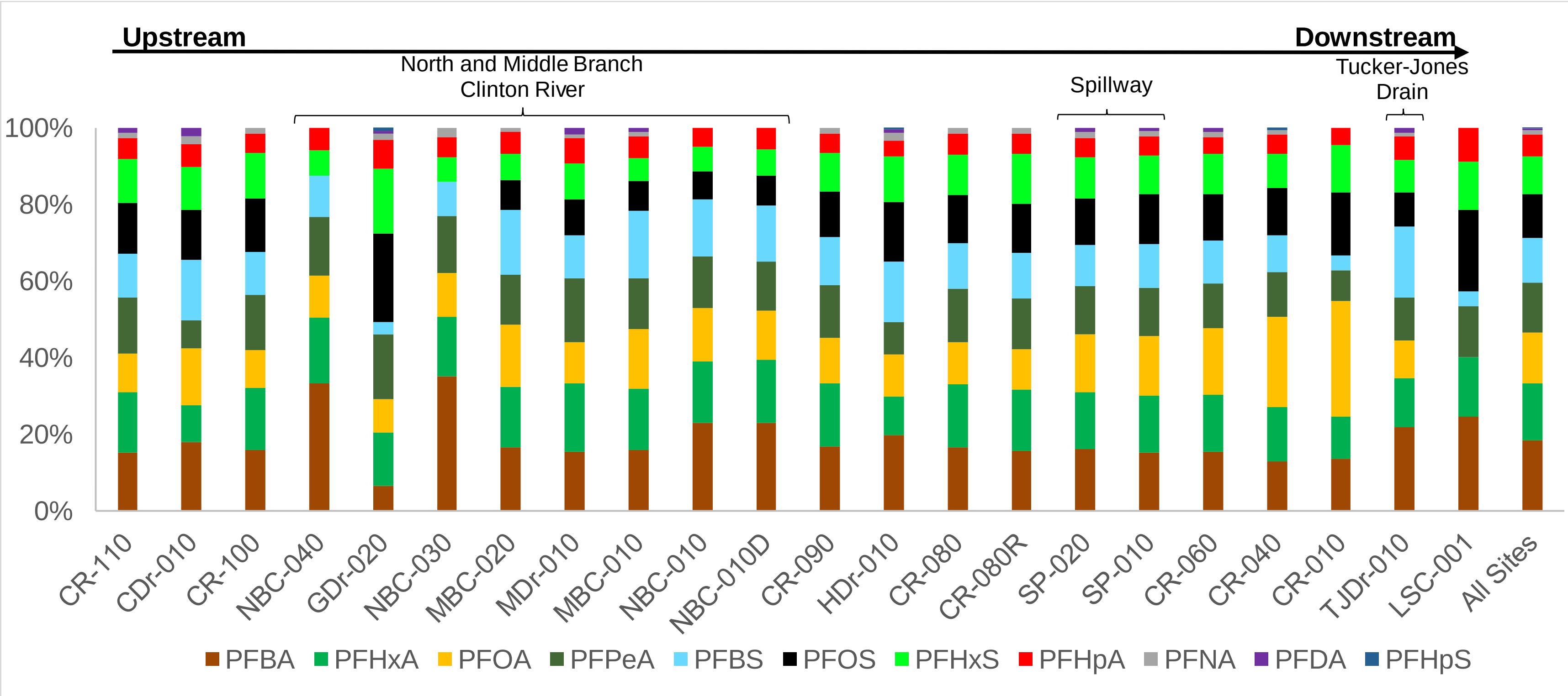

Figure 6. Percentage composition of PFAS measured in surface water collected in the lower Clinton River watershed in 2018. Sample IDs are shown (CR is the Clinton River; NBC is the North Branch Clinton River; MBC is the Middle Branch Clinton River; MDr is the Miller Drain; TJDr is the Tucker-Jones Drain; HDr is the Harrington Drain; GDr is the Greiner Drain. CDr is the Canal Drain; SP is the Clinton River Spillway; LSC is Lake St. Clair). 'All Sites' represents the arithmetic mean percentage of each detected analyte compared to the total PFAS concentration across the entire watershed. A Sample ID followed by the letter 'R' is a replicate sample, and 'D' is a duplicate sample.

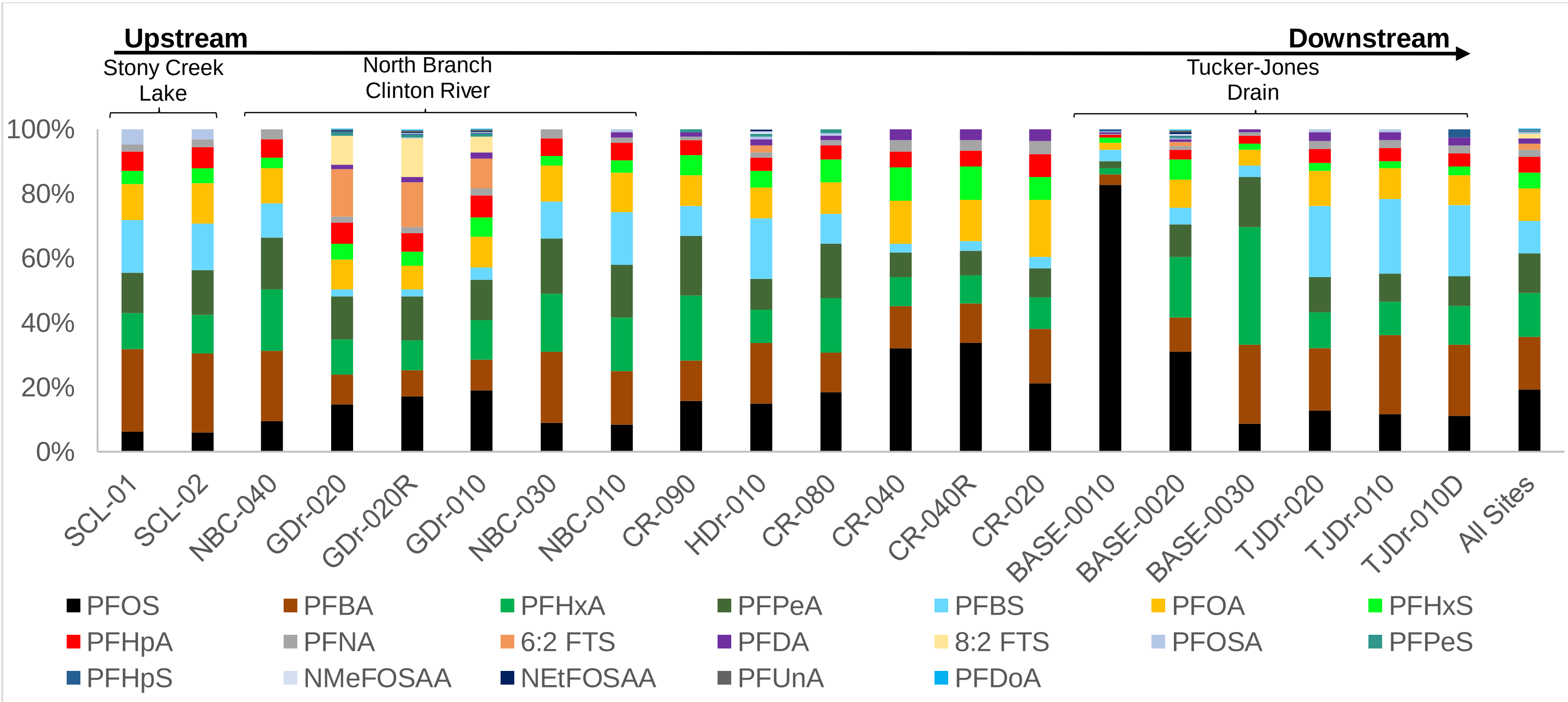

Figure 7. Percentage composition of PFAS measured in surface water collected in the lower Clinton River watershed and Stony Creek Lake in the Upper Clinton River watershed in 2019. Sample IDs are shown (CR is the Clinton River; NBC is the North Branch Clinton River; TJDr is the Tucker-Jones Drain; HDr is the Harrington Drain; GDr is the Greiner Drain; SCL is Stony Creek Lake; BASE are unnamed tributaries draining the Selfridge Air National Guard Base). 'All Sites' represents the arithmetic mean percentage of each detected analyte compared to the total PFAS concentration across the entire watershed. A Sample ID followed by the letter 'R' is a replicate sample, and 'D' is a duplicate sample.

Clinton River Point Source Samples
Between November 2018 and January 2020 samples of the effluent from the Clinton River Water Resource Recovery Facility (CRWRRF), also known as the Pontiac WWTP, had PFOS concentrations ranging from 11 to 48 ng/L (Table 6). Currently, the confirmed sources of PFOS to the CRWRRF include the Oakland County Airport and active and closed Municipal Solid Waste Landfills. The CRWRRF is continuing the efforts to identify additional sources within the collection system. In January 2020 the Warren WWTP effluent had a nondetectable PFOS concentration; however, the reporting limit from the laboratory report was 10 ng/L (Table 6). Effluent samples collected in September and November 2019 from the Warren WWTP had PFOS concentrations of 16 and 12 ng/L. Three effluent samples collected from the Warren WWTP between September 2018 and May 2019 had nondetectable concentrations of PFOS. The primary source of PFOS to the Warren WWTP are metal finishers, specifically chrome platers. There is a secondary source to the collection system from the historical use of AFFF at a United States Military facility. No surface water samples were collected immediately downstream of the outfalls from these WWTPs as the focus of this sampling was to investigate the lower Clinton River PFAS sources that may be influencing Lake St. Clair. Further investigation of potential sources in the upper Clinton River watershed and additional sampling of the Clinton River near the Pontiac and Warren WWTPs may be warranted. In the lower Clinton River watershed, the Mt. Clemens WWTP effluent had a PFOS concentration of 3.4 ng/L in November 2018 (Table 6). Mt. Clemens WWTP did not identify any sources of PFOS and/or PFOA to the collection system.

Table 6. Point Source Discharges/Compliance Sampling Results as of April 17, 2020. Concentrations exceeding the Part 4, Rule 57 HNV are bolded and italicized.

Facility Name	Sampling Date	PFOS (ng/L)	PFOA (ng/L)	Σ PFAS (ng/L)
CRWRRF	1/15/2020	11	13	80.0
CRWRRF	10/2/2019	***45***	63	235.1
CRWRRF	8/9/2019	***48***	52	259.9
CRWRRF	5/17/2019	***41***	37	191.0
CRWRRF	2/27/2019	***24***	33	159.7
CRWRRF	11/14/2018	***20***	38.1	168.6
CRWRRF	11/6/2018	***37***	44	205.7
CRWRRF	10/26/2017	9	13	100
Warren WWTP	1/29/2020	ND[1]	ND[1]	13.7[1]
Warren WWTP	11/15/2019	***12***	ND[1]	39[1]
Warren WWTP	9/16/2019	***16***	ND[1]	54.0[1]
Warren WWTP	5/24/2019	ND[1]	ND[1]	26.0[1]
Warren WWTP	2/14/2019	ND[1]	ND[1]	30.0[1]
Warren WWTP	9/14/2018	ND[1]	ND[1]	70.0[1]
Warren WWTP	10/26/2017	***14***	11	100
Mt. Clemens WWTP	11/15/2018	3.4	9.0	92.2

Clinton River Ambient Samples
A total of 30 surface water samples at 15 locations were collected between 2017 and 2019 from the Clinton River and Clinton River Spillway and analyzed for PFAS (Table 3). Of these, 19 samples (8 locations) were from the main branch; 7 samples (3 locations) were from the north branch, 2 samples (2 locations) were from the middle branch, and 2 samples (2 locations) were from the

[1] Sample had elevated reporting limits (≥ 10 ng/L) for several PFAS including PFOS and PFOA.

spillway. No samples collected from the Clinton River or spillway exceeded the HNV for PFOA, ranging from 1.2 ng/L in the north branch to 9.6 ng/L in the main branch. No samples from the north branch, middle branch, or spillway exceeded the HNV for PFOS ranging from 1.6 ng/L in the north branch to 6.9 ng/L in the middle branch.

Between 2017 and 2019 four samples at three locations exceeded the HNV for PFOS in the main branch of the Clinton River. In August 2017 PFOS was detected at 36 ng/L near the mouth of the river at the CR-020 sampling location (Figure 1). In November 2017 PFOS was detected at 610 ng/L near the mouth of the river at the CR-010 sampling location. A duplicate sample was collected at the CR-010 location and had a PFOS concentration of only 31 ng/L, which results in an RPD QA/QC exceedance. The analytical laboratory reanalyzed the November 2017 CR-010 samples and confirmed the original results. The samples from the nearest upstream sampling locations (CR-040 and CR-060) were below the PFOS HNV; however, elevated (> 3 ng/L) at 8.0 and 6.8 ng/L, respectively. The furthest upstream sampling location during the November 2017 sampling event was CR-090, which had a PFOS concentration of 470 ng/L thus exceeding the HNV.

The CR-010 and CR-090 sampling locations were revisited in February 2018 and the CR-020 was revisited in July 2019. The PFOS concentrations at these sampling locations were 2.3 ng/L, 4.3 ng/L, and 2.8 ng/L, respectively (Figure 2 and Figure 3). Significant rainfall occurred two days prior to the November 2017 sampling event resulting in a 2,000% increase in river discharge. In comparison, the 2018 sampling event was during the winter months when inputs to the stream are minor due to below freezing temperatures and only a minor precipitation event occurred two days prior to the 2019 sampling event which resulted in a 200% increase in discharge.

These results indicate the source(s) of PFOS to the lower Clinton River may be intermittent. There are two storm water outfalls draining the SANGB that discharge to the Clinton River between the river mouth (CR-010) and the CR-040 sampling location. PFOS in these outfalls in samples collected by AECOM in February 2018 had PFOS concentrations of 2,000 and 2,400 ng/L (Figure 2). Furthermore, in 2019 SANGB conducted a short-term storm water characterization study to quantify PFAS discharged from the NPDES permitted storm water outfalls into Lake St. Clair (AECOM, 2019). This effort included sample collection from the six storm water outfalls at SANGB during two qualifying storm “wet” events and two “dry” weather events. PFAS was detected in all storm water samples collected for the study. PFOS concentrations ranged from 17.2 ng/L in monitoring 006A (discharges unnamed tributary, which eventually discharges to Lake St. Clair) to 4,540 ng/L in monitoring point 002A, which discharges to the Clinton River. PFAS concentrations were generally the lowest during the first wet weather event and highest during the second dry and wet weather events.

Therefore, contaminated storm water is a possible cause of the high PFOS concentration measured at CR-010 and CR-020 in 2017. The source of the high PFOS concentration measured at the CR-090 sampling location in November 2017 remains unknown.

Samples of rock bass were collected in 2019 from the Clinton River in Mt. Clemens and upstream of the Yates Dam to be analyzed for PFAS and processed as fillets. PFOS was non-detect in all ten rock bass samples from the Clinton River near Mt. Clemens. Results for the samples upstream of Yates Dam are pending.

Drains to the Clinton River and Lake St. Clair
A total of 16 surface water samples at 10 locations were collected from drains that either discharge to the Clinton River or directly into Lake St. Clair. Of these, four samples (two locations) were collected from the Greiner Drain, which discharges into the North Branch of the Clinton River, one sample was from the Miller Drain, which discharges into the Middle Branch of the Clinton River, one sample was collected from the Canal Drain, which discharges into the main branch of the Clinton River upstream of the confluence with the North Branch, two samples (one location) were from the Harrington Drain, which discharges into the main branch of the Clinton River downstream of the confluence with the north branch; five samples (two locations) were from the Tucker-Jones Drain, which discharges directly into Lake St. Clair; and three samples were from three separate unnamed drains on the west side of SANGB.

All four of the Greiner Drain samples had a PFOS concentration exceeding the HNV and ranged from 37 to 41 ng/L. The Greiner Drain's confluence with the Clinton River is approximately 2.6 river miles upstream of the CR-090 sampling location where high PFOS was detected in 2017. No samples from the north branch of the Clinton River downstream of the Greiner drain were collected in 2017. In 2018 and 2019 a sample was collected from the north branch of the Clinton River downstream of the Greiner Drain (sample location NBC-030). The PFOS concentration in the 2018 sample was non-detect and it was below the laboratory reporting limit of 2 ng/L in 2019. Again, the 2018 and 2019 samples were collected when storm water input to the watershed was believed to be low. Also, it is important to highlight that the Greiner Drain samples had an elevated composition of both 6:2 and 8:2 FtS in comparison to the rest of the watershed in 2019 (Figure 7). These analytes were not measured in the 2018 samples as the samples were analyzed using the 19 PFAS analyte method (Table 1).

Samples collected in October 2018 at the storm water outfalls from Axalta Coating Systems, which discharge to the Greiner Drain, showed that runoff from this facility had a PFOS concentration exceeding the HNV at 48 and 61 ng/L. Subsequent dry-weather testing within the Axalta Coating Systems storm sewer system, conducted during May and September 2019, showed that PFOS continued to exceed the HNV at both outfalls (200 and 310 ng/L), and the concentrations within the facility were as high as 580 ng/L. Samples from both outfalls had elevated composition of both 6:2 and 8:2 Fts in comparison to the rest of the watershed, and the sample from the east outfall had elevated composition of both 6:2 and 8:2 Fts in comparison to the samples from the Greiner Drain. In addition, Axalta Coating Systems reported 2 historic releases of PFAS-containing AFFF at the facility, in 2009 and 2013. Direct sampling of groundwater at Axalta Coating Systems is currently pending.

None of the samples from the Harrington, Canal, or Miller Drains exceeded the PFOS or PFOA HNVs. However, elevated PFOS (> 3 ng/L) concentrations were observed in the Canal, Miller, and Harrington Drains. In February 2018, the Canal, Miller, and Harrington Drains had a PFOS concentration of 3.6, 7.3, and 7.9 ng/L, respectively. The second sample from the Harrington Drain collected in September 2019 had a PFOS concentration equivalent to the HNV at 12 ng/L. The sources of PFAS to these drains is still under investigation.

The Tucker-Jones Drain provides an outlet for storm water at the western and northern perimeter of the SANGB, part of northeastern Mt. Clemens, and part of southern Chesterfield Township. The drain empties into Lake St. Clair at the Selfridge Public Boat Launch. Three samples from two locations have been collected from the drain. The first sample was collected near the mouth

(TJDr010) on November 7, 2017, following an extended wet period (precipitation had been recorded at the SANGB each of the previous eight days with a total rainfall of 1.3 inches). The PFOS concentration exceeded the HNV at 13 ng/L (Figure 1), while the PFOA concentration was 4 ng/L. A PFOS concentration of 180 ng/L was collected in Lake St. Clair at the Selfridge Public Boat Launch, which is located at the mouth of the Tucker-Jones drain (Figure 1). Details of this result are discussed in the next section. While the Tucker-Jones Drain does not directly impact the Clinton River, this sampling provides evidence for elevated PFOS in the SANGB storm water, which may explain the relatively high PFOS concentrations measured at the river mouth in August and November 2017 after periods of significant rainfall (Figure 1). As further evidence, on February 8, 2018 AECOM collected five samples from compliance inspection points at the SANGB. All five samples had concentrations with detectable PFOS ranging from 33 ng/L to 2,400 ng/L. Two outfalls with direct discharge to the Clinton River had PFOS concentrations of 2,000 and 2,400 ng/L.

A second sample from the Tucker-Jones Drain near the mouth (TJDr010) was collected through the ice by EGLE on February 13, 2018. Both PFOS and PFOA concentrations in this sample were below their respective HNV, measuring 3.2 and 3.6 ng/L, respectively. Little if any runoff from meltwater was likely to be contributing to the drain discharge since the high temperature had been below freezing for the previous eight days. The elevated PFOS levels in the SANGB storm water samples collected by AECOM in February 2018 did not result in a measurable increase in the February 2018 Clinton River samples collected by EGLE (Figure 3). This may be explained by the overall relatively low river discharge during the winter months and lack of runoff due to below freezing temperatures. Additionally, the SANGB storm water discharge is not continuous as the drainage system includes wet wells with pumps that operate only when the water reaches a designated level within the sump.

A third sample from the Tucker-Jones drain near the mouth (TJDr010) was collected on July 26, 2019. PFOS and PFOA were elevated at 7.5 and 6.2 ng/L, respectively; however, below their respective HNV (Figure 3). A second sample was collected further upstream (TJDr020), which had a PFOS concentration of 9.2 ng/L. Three additional samples were collected from the unnamed drains on the west side of the SANGB that eventually flow into the Tucker-Jones drain. PFOS in these samples ranged from 10 to 190 ng/L. A sample collected from the mouth of the Clinton River had a low PFOS concentration of 2.8 ng/L (Figure 3), which suggests the SANGB storm water at this time was not influencing the Clinton River. This collection event was during a period of low river flow and precipitation had not occurred for several days prior to the sampling.

Lake St. Clair

A total of eight surface water samples at seven locations have been collected from Lake St. Clair and analyzed for PFAS, including two samples nearshore at the Selfridge Public Boat Launch near the discharge of the Tucker-Jones Drain (Table 3). No samples collected from Lake St. Clair exceeded the HNV for PFOA, ranging from 1.5 ng/L in the Metro Park sample (LSC-030) to 4.3 ng/L in the SANGB public boat launch sample (LSC-001). One sample exceeded the HNV for PFOS. PFOS was detected at 180 ng/L in the Lake St. Clair sample collected on August 31, 2017, at the Selfridge Public Boat Launch (LSC-001; Table 3; Figure 1). The sample was taken nearshore near the discharge of the Tucker-Jones Drain three days after a storm event during which nearly 2.3 inches of rainfall was measured at the SANGB. This location was revisited in February 2018 and had a PFOS concentration of 1.3 ng/L, which is below the laboratory reporting limit for PFOS (Table ***3***; Figure 3). PFOS in the offshore samples ranged from 1.4 ng/L near New Baltimore to 7.4 ng/L in Fair Haven. The PFOA concentration in these samples were at or below the laboratory reporting limit of 2.0 ng/L.

Concentrations of PFOS in fillets of bluegill and largemouth bass in Anchor Bay (includes surface water sampling locations LSC-001, LSC-040, LSC-050, and LSC-060) averaged 31.2 and 37.4 micrograms per kilogram (µg/kg), respectively, in 2017. Concentrations of PFOS in fillets of bluegill and largemouth bass in L'Anse Creuse Bay (includes surface water sampling locations LSC-010, LSC-020, and LSC-030) averaged 36.6 and 42.4 µg/kg, respectively, in 2017. These PFOS concentrations exceed the MDHHS "Eat Safe Fish" screening values. PFOS causes an advisory of 4 servings per month for bluegill caught in Lake St. Clair whereas PCBs and mercury cause more restrictive advice in largemouth bass.

CONCLUSIONS AND FUTURE WORK

Concentrations of PFAS in the lower Clinton River and its tributaries have varied both spatially and temporally. PFOS HNV exceedances were observed near the mouth of the Clinton River and downstream of the confluence with the North Branch of the Clinton River. Storm water from the SANGB is a source of the contamination near the mouth of the river as sampling following a significant precipitation event resulted in elevated PFOS concentrations downstream of the base. The generally low concentrations measured in the winter during a period of low storm water runoff also indicates that surface drainage is a likely source of contamination to the river. The source of contamination near the confluence with the North Branch is still unknown; however, surface water and storm water sampling results show that Axalta Coating Systems is a source of PFAS to the Greiner Drain. In addition, the Miller and Harrington Drains had a PFOS concentration between 7 and 8 ng/L; the sources of PFOS to these drains remain unknown.

Effluents from the three major WWTPs in the Clinton River watershed contribute some amount of PFAS to the river, but these systems are further upstream in the watershed where we currently do not have PFAS surface water data. Future investigation should occur, particularly near the Pontiac and Warren WWTPs, where elevated PFOS has been found in the effluent. Rock bass collected from the Clinton River near Mt. Clemens had non-detectable concentrations of PFOS in their fillets. Rock bass were also collected from the Clinton River upstream of Yates dam; however, these results are still pending. Fish tissue analysis can provide a more complete evaluation of water quality when bioaccumulative contaminant concentrations in the surface water are highly variable.

Generally, Lake St. Clair had low levels of PFOS and PFOA with only one sample exceeding the PFOS HNV. In August 2017 a sample collected from the lake near the Tucker-Jones Drain had a PFOS concentration of 180 ng/L. It is likely that contaminated storm water from the SANGB entered the Tucker-Jones Drain as significant rainfall occurred at the base three days prior to the August 2017 sampling event. Five of the six offshore samples ranged from 1.4 to 2.7 ng/L; the sixth sample collected near Fair Haven had an elevated PFOS concentration of 7.4 ng/L. These results are similar to concentrations measured in both the St. Clair River and the Detroit River in 2017 and 2019. PFOS ranged from 1.5 to 2.2 ng/L and PFOA ranged from 1.0 to 1.6 ng/L in those samples taken at the head and mouth of these rivers on four occasions in 2017. PFOS concentrations in largemouth bass and bluegill from Lake St. Clair exceed the MDHHS "Eat Safe Fish" screening values. No more than 4 servings per month of bluegill caught from Lake St. Clair due to PFOS. While PFOS also would cause an advisory in largemouth bass from Lake St. Clair, PCBs and mercury cause more restrictive advice. Additional surface water sampling in Lake St. Clair is not needed at this time.

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