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MICHIGAN DEPARTMENT OF ENVIRONMENT, GREAT LAKES, AND ENERGY
WATER RESOURCES DIVISION
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STAFF REPORT

INVESTIGATION OF THE OCCURRENCE AND SOURCES OF PERFLUORINATED AND POLYFLUORINATED ALKYL SUBSTANCES (PFAS) IN THE HURON RIVER WATERSHED USING POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLERS (POCIS)

BACKGROUND

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 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 Huron River drains portions of seven counties in southeast Michigan. The watershed is more than 900 square miles and consists of many tributary creeks, lakes, and the Huron River proper. The concentrations of PFOS in fish fillets collected from Kent Lake were high enough to warrant the Michigan Department of Health and Human Services (MDHHS) to issue a “Do Not Eat” fish advisory to cover Norton Creek and the Huron River from North Wixom Road (Oakland County) to the river mouth. The advisory includes: Norton Creek (Oakland County), Hubbell Pond (Oakland County), Kent Lake (Oakland County), Ore Lake (Livingston County), Strawberry Lake (Livingston County), Zukey Lake (Livingston County), Gallagher Lake (Livingston County), Loon Lake (Livingston County), Whitewood Lakes (Livingston County), Base Line Lake and Portage Lakes (Livingston/Washtenaw County line), Barton Pond (Washtenaw County), Argo Pond (Washtenaw County), Ford Lake (Washtenaw County), Belleville Lake (Wayne County) and the Flat Rock Impoundment (Wayne County).

<u>PFAS Sites</u>
PFAS sites occur where one or more groundwater sample(s) exceed(s) the Part 201 cleanup criteria for groundwater used as drinking water, which is 70 parts per trillion (ppt) PFOS + PFOA. The following three PFAS sites are present within the Huron River watershed:

1. RACER Willow Run began in 1941 as a bomber plant developed by Ford for the Department of the Army. The site has a groundwater collection system that discharges via a sanitary sewer to the Ypsilanti Community Utility Authority (YCUA), which routinely discharges to the Rouge River watershed (and only to the Huron River under emergency situations). In March 2018, as a part of the YCUA Industrial Pre-treatment Program, it was discovered that the groundwater at the RACER site was contaminated with PFAS (up to 428 ppt PFOS + PFOA).
2. The former Chrysler Scio Introl Division facility located in Dexter consisted of several manufacturing operations related to the automobile industry, including plating. PFAS contaminated groundwater (up to 1,700 ppt PFOS + PFOA) was discovered in March 2019 after samples were collected by the facility's consultant.
3. The Thermofil facility located in Green Oaks Township was formerly a metal stamping operation, a plastics molding and painting operation, and a plastic compounding business. In April 2019 PFAS-contaminated groundwater (up to 163 ppt PFOS + PFOA) was discovered in samples collected by a Michigan Department of Environment, Great Lakes, and Energy (EGLE) contractor.

<u>Previous Surface Water PFAS Grab Sampling</u>

Bowman et al. (2020) recently conducted a PFAS monitoring investigation in the Huron River watershed. Grab samples of ambient surface water or storm water were collected from several locations throughout the watershed between July 2018 and December 2019. In July 2018 the EGLE, Water Resources Division (WRD), Surface Water Assessment Section (SWAS), collected 17 surface water samples from the Huron River and select tributaries. Samples from Norton Creek and downstream to Baseline and Portage Lakes equaled or exceeded the Rule 57 Human Non-Cancer Value (HNV) for surface waters used as a drinking water source of 11 nanograms per liter (ng/L; parts per trillion) for PFOS. A sample from Willow Run near Belleville also exceeded the PFOS HNV.

On August 30, 2018, the SWAS collected additional surface water samples from 19 sites on the Huron River, Norton Creek, Pettibone Creek, and Mann Creek. A sample from the west branch of Norton Creek, three samples downstream of the Wixom Wastewater Treatment Plant (WWTP) on Norton Creek, one sample from Mann Creek, one sample from Pettibone Creek, and two samples from the Huron River downstream of Norton Creek all exceeded the PFOS HNV. An industrial user of the Wixom WWTP was identified as a source of PFAS in the watershed.

Additional source investigation occurred in October 2018. Samples from the Huron River, Kent Lake, Hubbell Pond, Mill Pond (Milford), and more intensive sampling of Norton Creek, Mann Creek, Pettibone Creek, and Portage Lake tributaries (Portage River and Honey Creek in Livingston County) occurred. Samples were also collected near the confluence of the Huron River and the following tributaries: Woodruff Creek, Ore Creek, Arms Creek, and Davis Creek. Samples exceeded the PFOS HNV on the main stem of the Huron River at sampling locations from Burns Road to downstream of Base Line and Portage Lakes, in Hubbell Pond, in Kent Lake, and at two sites on Norton Creek downstream from the WWTP.

Another sampling event occurred in April 2019 to continue to track potential sources of PFAS in the Huron River including follow-up sampling in the Huron River main stem, Norton Creek, Willow Run, and Horseshoe Creek. Sampling locations were chosen to bracket potential sources of PFAS contamination in the watershed and to repeat collections at sites previously sampled near and within Norton Creek, Pettibone Creek, and Willow Run. Sampling was also conducted along Horseshoe Creek and Hamburg Lake near the locations where PFAS-containing foam may have been used. Opportunistic sampling of two outfalls also occurred along the main stem of Willow Run. Samples collected from Norton Creek, Willow Run, and one of the outfalls exceeded the PFOS HNV. Additional source investigation is underway in the watershed.

The recent grab sampling by the WRD has shown that PFAS concentrations in surface water can vary both temporally and spatially. Therefore, traditional grab samples may miss episodic releases from point sources and/or intermittent discharge from groundwater seeps and/or storm water runoff. Passive sampling has been utilized as a monitoring tool to determine time-weighted-average PFAS water concentrations and to assess the environmental burden of these compounds within a given watershed (Kaserzon et al., 2019). This approach can detect chemicals occurring at low concentrations in the environment that may show up as non-detect in traditional grab samples (Alvarez et al., 2004). For example, a passive sampling device called Polar Organic Chemical Integrative Samplers (POCIS) had a higher detection frequency of pesticides [median 62 compounds] than grab samples [median 46 compounds] in small streams throughout the Midwest United States (Van Metre et al., 2017). POCIS contains a sorbent medium sandwiched between two microporous membranes (Figure 1A). POCIS have previously been used to monitor PFAS in groundwater (Kaserzon et al., 2019), surface water (Abdel-Moneim et al., 2017, Cerveny et al., 2018), and drinking water (Gobelius et al., 2019).

Figure 1. Polar Organic Contaminant Integrative Samplers (POCIS). A: Each POCIS consisted of an Oasis® HLB sorbent sandwiched between two polyethersulfone membranes and two stainless steel rings. B: Six POCIS were deployed at each location and housed in a stainless-steel canister. C: POCIS canisters were secured inside stainless-steel fish cages to stabilize them in the stream and locked to trees along the streambank to prevent theft.

OBJECTIVES

The main objective of this study was to identify intermittent sources of PFAS contamination in the Huron River watershed by deploying POCIS both upstream and downstream of known or suspected sources. Beyond the source tracking aspect of this work, this study provided baseline data to assess whether existing programs are effectively reducing PFAS concentrations in the aquatic environment as well as for future trend monitoring of PFAS in the Huron River watershed.

SUMMARY

1. Concentrations in POCIS extracts should not be compared to Rule 57 surface water quality values. The data in this report are presented as a concentrated sample extracted from a POCIS following a 28-day deployment in the river. In addition, flow rate, temperature, and the buildup of suspended solids or biofilms can all impact the sampling rate of individual POCIS.
2. PFOS, PFOA, PFHxS, PFHxA, PFHpA, PFBS, PFNA, and 6:2 FTS were detected at all sampling locations.

3. PFPrS, PFMPA, 3:3 FTCA, PFMBA, PFEESA, NFDHA, HFPO-DA, ADONA, 7:3 FTCA, 9Cl-PF3ONS, PFNS, PFDS, PFUnA, PFOSA, 11Cl-PF3OUds, PFDoA, PFTriA, and PFTeA were not detected in any sample. Future work focusing on these compounds using POCIS may need to composite individual samples to increase their likelihood of detection.
4. Mean PFOS ranged from 5.1 nanograms per POCIS (ng/POCIS) in the Huron River downstream of Proud Lake to 70.8 ng/POCIS in Willow Run.
5. Significantly higher PFOS concentrations were observed in the POCIS deployed in Norton Creek and Willow Run.
6. Mean PFOA ranged from 8.7 ng/POCIS in Norton Creek to 18.1 ng/POCIS in the Huron River downstream of Willow Run.
7. PFECHS, which is used as an erosion inhibitor in aircraft hydraulic fluid, was detected in Willow Run and averaged 15 ng/POCIS.
8. 5:3 FTCA was detected in Norton Creek POCIS samples and averaged 3.5 ng/POCIS.
9. 6:2 FTS averaged 7704 and 599 ng/POCIS in the Norton Creek and Willow Run POCIS samples, respectively. Effluent samples and surface water grab samples suggest this analyte is being discharged from the Wixom WWTP and in storm water from the Willow Run Airport (data from Bowman et al., 2020).
10. There were no significant differences in PFOS concentration between replicate POCIS deployed within individual sampling locations. Therefore, future PFAS investigations by the WRD using POCIS can deploy a single set of POCIS at each location to adequately characterize surface water PFAS (both sets will still need to be used for the quality assurance/quality control (QA/QC) replicate samples).
11. Overall, these results support the use of POCIS as an additional monitoring tool for PFAS surface water investigations particularly in watersheds that have shown variable temporal PFOS concentrations (e.g., the River Raisin watershed).
12. Future POCIS studies should be conducted to monitor temporal trends of PFAS and to show improvements following the ongoing remediation efforts to mitigate PFAS contamination in the Huron River watershed and other watersheds across the state.

METHODS

<u>POCIS Deployment</u>

POCIS deployment procedures followed the 2019 Michigan Surface Water Sampling with POCIS Quality Assurance Project Plan (QAPP; EGLE, 2019). POCIS were deployed at eight locations in the Huron River watershed (Table 1) for 28 days beginning on September 26, 2019, and ending on October 24, 2019. Sampling location characteristic information is provided in Table 2. Three POCIS were used as a field blank and three additional POCIS were used as a trip blank. Deployment and retrieval procedures for POCIS followed the guidance provided by Alvarez (2010). Briefly, three POCIS were secured to a stainless steel POCIS holder. Two POCIS holders (six total POCIS) were deployed at each location (Figure 1B). At wadeable locations, the POCIS were suspended in the water column off the bottom of the stream using a stainless steel fish cage (Figure 1C). The HR-0198 sampling location was nonwadeable; therefore, this location was used to determine the spatial differences of PFAS within the water column. At this location, POCIS were deployed by stacking three fish cages (each containing six POCIS) on top of one another (Figure 2A). The stack of cages was then suspended in the water column from a bridge (Figure 2B). The first set of six POCIS were approximately 30 centimeters (cm) from the top of the water surface. The next set of six POCIS were approximately 5 cm below the first set. The final set of six POCIS were approximately 5 cm below the second set POCIS and approximately 5 cm above the bottom of the riverbed. The HR-0198 sample was downstream of Kent Lake and originally coded as HR-0200; however, this sampling location was downstream of the HR-0200 grab sampling location in Kent Lake from Bowman et al.

(2020; 42.52845, -83.64574). Therefore, this sampling location was recoded to HR-0198 to avoid confusion between studies.

Figure 2. POCIS deployment setup at the HR-0198 sampling location to investigate distribution of PFAS throughout the water column in the Huron River. Three stainless steel fish cages were stacked on top of one another; each containing six POCIS (A). The stack of cages was then suspended off a bridge (B).

Table 1. Locations selected for POCIS deployment in the Huron River watershed in 2019.

Sample ID	Sample Location	Lat	Long	Rationale
HR-0240	Huron River @ Wixom Rd	42.5743	-83.5599	u/s of Norton Creek
NC-0100	Norton Creek @ E. Buno Rd	42.5526	-83.5623	d/s of Wixom WWTP
HR-0235	Huron River @ Burns Rd	42.5787	-83.5799	d/s of Norton Creek
HR-0198	Huron River @ Kensington Rd	42.5137	-83.6898	d/s of Kent Lake
HR-0140	Huron River @ Deli Rd	42.3380	-83.8092	d/s of SCIO Chrysler
HR-0060	Huron River @ Rawsonville Rd	42.2096	-83.5434	u/s Willow Run, Belleville Lake
WR-0010	Willow Run @ I94 Service Rd	42.2193	-83.5366	d/s potential sources
HR-0050	Huron River @ E. Huron River Dr	42.2108	-83.4347	d/s Willow Run, Belleville Lake

After retrieval, POCIS were removed from their housing, stored on ice, and shipped overnight to the Environmental Sampling Technologies laboratory for extraction. Samples were extracted in 25 milliliters (mL) of methanol (Honeywell Catalog # LC230-4; Lot # DX731-US). Following extraction, they were quantitatively transferred to 50 mL ampules using methanol as the transfer solvent. The extracts were cooled in an isopropanol alcohol/dry ice mixture and flame sealed. Environmental Sampling Technologies laboratory then shipped the extracts to the MDHHS analytical laboratory for PFAS analysis. POCIS extracts were analyzed for selected PFAS (Table 2). The detection limit in the extract was 1.3 ng/POCIS for all PFAS analytes. The laboratory analyzed all six POCIS extracts from each location individually and reported concentrations in the extracted sample (ng/L). In order to compare results across sampling locations and across projects, we converted these results to a 'per sampler' concentration (ng/POCIS) using the following equation:

$$\frac{X\,ng\,PFAS}{L\,extract} * \frac{1\,L}{1000\,mL} * \frac{25\,mL\,extract}{POCIS} = \frac{Y\,ng\,PFAS}{POCIS}$$

The PFAS concentrations in POCIS extracts presented in this report cannot be directly compared to water concentrations determined by grab sampling or compared to surface water quality values. The POCIS extracts represent a time-integrative signal of the water quality at each location whereas grab samples characterize snap-shot water quality information. Water flow rate, temperature, and the buildup of suspended solids and biofilms can all impact the sampling rate of individual POCIS (Alvarez et al., 2004). A performance reference compound would need to be added to the POCIS prior to deployment in order to determine the sampling rate of each individual POCIS. A performance reference compound is a compound that can be added to passive samplers prior to deployment and, with some assumptions, can provide information about the mass transfer kinetics between the sampler and the sampling environment. Estimating a water concentration based on POCIS extract data was not the goal of this project; and therefore, a performance reference compound was not included. POCIS studies provide another line of evidence for source tracking, especially when fish tissue is not available and grab samples are variable.

Table 2. Site characteristics of POCIS sampling locations at time of deployment.

Sample ID	Depth (m)	Velocity (m/s)	pH	Conductivity (uS)	Temperature (°C)	Dissolved Oxygen (mg/L)
HR-0240	0.79	0.19	8.16	770	22.4	9.8
NC-0100	0.95	0.06	7.50	1244	19.6	6.9
HR-0235	1.50	0.15	7.75	875	21.0	7.7
HR-0198	0.61	0.59	8.43	784	22.7	11.9
HR-0140	0.76	0.40	8.14	707	20.8	9.4
HR-0060	2.43	0.37	7.78	800	21.3	9.0
WR-0010	0.15	0.12	7.98	998	16.9	8.4
HR-0050	0.83	0.27	7.97	740	22.5	5.8

Table 3. Perfluoroalkyl and polyfluoroalkyl substances (PFAS) analyzed in POCIS extracts by the MDHHS laboratory.

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
Branched-Perfluorooctanoic acid	B-PFOA	335-67-1
Linear-Perfluorooctanoic acid	L-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
Branched-Perfluorooctanesulfonic acid	B-PFOS	1763-23-1
Linear- Perfluorooctanesulfonic acid	L-PFOS	1763-23-1
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Branched-Perfluorohexanesulfonic acid	B-PFHxS	355-46-4
Linear-Perfluorohexanesulfonic acid	L-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	EtFOSAA	2991-50-6
2-(N-Methylperfluorooctanesulfonamido) acetic acid	MeFOSAA	2355-31-9
11-chloroeicosafluoro-3-oxanonane-1-sulfonate	11Cl-PF3OUdS	763051-92-9
3:3 Fluorotelomer carboxylic acid	3:3 FTCA	356-02-5
5:3 Fluorotelomer carboxylic acid	5:3 FTCA	914637-49-3
7:3 Fluorotelomer carboxylic acid	7:3 FTCA	812-70-4
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	756426-58-1
ammonium 4,8-dioxa-3H-perfluorononanoate	ADONA	919005-14-4
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6
Perfluorobenzenesulfonic acid	PFBSA	30334-69-0
Perfluoroethylcyclohexanesulfonate	PFECHS	67584-42-3
Perfluoro (2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7
Perfluorohexanesulfonamide	PFHxSA	41997-13-1
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5
Perfluoro-3-methoxypropionic acid	PFMPA	377-73-1
Perfluoropropane sulfonate	PFPrS	423-41-6

Statistical Analysis

All statistical analyses were performed on PFOS and PFOA concentrations using the free online statistical package, Program R (version 3.6.2). Data were checked for normality using a Shapiro-Wilks test and variance homogeneity using a Levene's test. Transformed data did not satisfy the assumptions of an analysis of variance (ANOVA); therefore, non-parametric tests were conducted on the untransformed data. A Kruskal-Wallis rank sum test was performed to determine if the PFOS and PFOA concentration differed among sampling locations. Significant differences ($p < 0.05$) between sampling locations were tested using Dunn's non-parametric all-pairs comparison test using the 'kwAllPairsDunnTest' function in the R package 'PMCMRplus'. A Mann-Whitney U test was performed using the 'wilcox.test' function to determine if a significant difference existed between the two POCIS holders (3 POCIS per holder) deployed within a sampling location. Individual POCIS deployed at each location were treated as replicates as they were fixed in one position and exposed to different parts of the water column.

QA/QC

Field sampling and analytical quality were assessed using replicate and blank (trip, field, and laboratory extraction) samples. Replicate samples were assessed at every sampling location by comparing the first set of three POCIS to the second set of three POCIS. One field blank was collected by exposing three POCIS to ambient air at the HR-0050 sampling location during deployment and retrieval. A trip blank was collected from three POCIS that remained in their sealed container, unexposed to the field conditions, during deployment and retrieval. Precision of replicate results was determined by the relative percent deviation (RPD) which is defined as 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:

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

RESULTS AND DISCUSSION

River Conditions

There are three United States Geological Survey (USGS) stream gage stations along the main stem of the Huron River: Ann Arbor, Michigan (04174500), Hamburg, Michigan (04172000), and Milford, Michigan (04170000). Summary discharge data are provided in Table 4 for the 28-day deployment period. During the deployment period, the mean daily discharge was higher than the historical median daily discharge statistic at all three stream gage locations (Figure 10, Figure 11, Figure 12; Table 4). According to the Ann Arbor City Hall rain gauge (Ann Arbor 2020), a total of 8.1 cm of rain fell in the area during the 28-day POCIS deployment period with no more than 1.6 cm of precipitation occurring within a 24-hour period.

Table 4. Summary of daily discharge data (cubic feet per second; cfs) for three USGS stream gages on the Huron River during the period of POCIS deployment. Median daily discharge statistic represents the historical discharge for this period and gage location.

Location (USGS gage number)	Mean Discharge	Median Discharge	Minimum Discharge	Maximum Discharge	Median daily discharge statistic
Ann Arbor, Michigan (04174500)	484	460	304	795	227
Hamburg, Michigan (04172000)	283	259	203	384	143
Milford, Michigan (04170000)	135	131	81	178	78

<u>POCIS Results</u>

PFOS and PFOA were detected at all eight stream sampling locations (Figure 3). Mean PFOS in POCIS (Figure 3 and Figure 4) ranged from 5.1 ng/POCIS at the furthest upstream location on the Huron River (HR-0240) to 70.8 ng/POCIS in Willow Run (WR-0010). There was a significant difference in PFOS concentration among sampling locations (Kruskal Wallis; χ^2 = 60.1, df = 11, $p < 0.001$). Significant differences in PFOS concentrations were observed between several sampling locations (Table 5). The POCIS deployed at NC-0100, HR-0198, HR-0140, WR-0100, and HR-0050 had a significantly higher PFOS concentration compared to the blanks. Mean PFOA ranged (Figure 3) from 8.7 ng/POCIS in Norton Creek (NC-0100) to 18.1 ng/POCIS in the Huron River downstream of Willow Run (HR-0050). There was a significant difference in PFOA concentration among sampling locations (Kruskal Wallis; χ^2 = 51.2, df = 11, $p < 0.001$). Significant differences were observed between several sampling locations (Table 6). The POCIS deployed at HR-0240, HR-0235, WR-0100, and HR-0050 had a significantly higher PFOA concentration compared to the blanks.

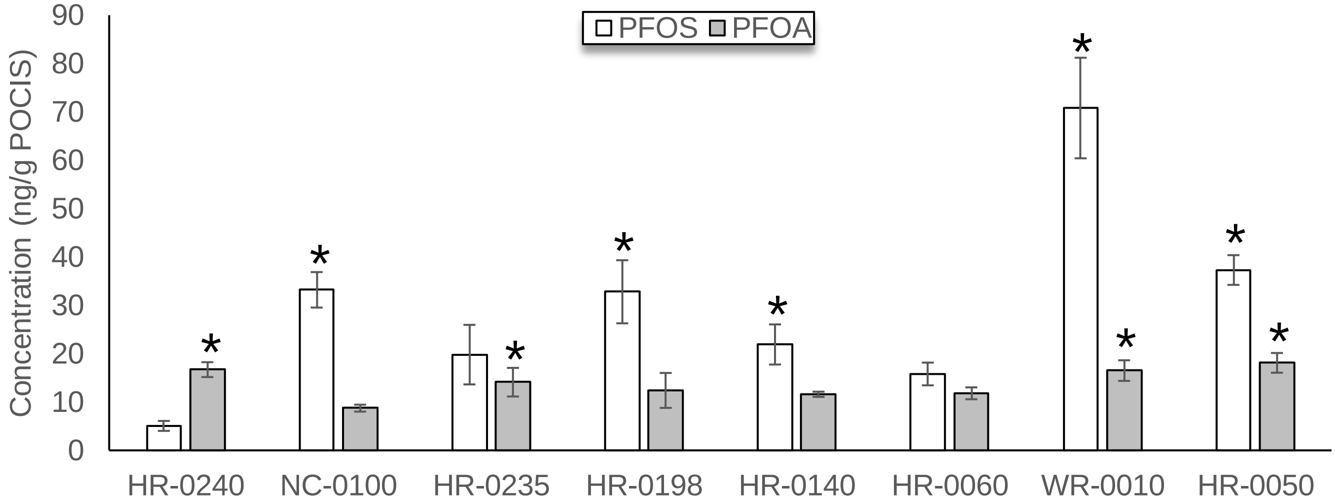

Figure 3. Mean concentration (ng/POCIS) of PFOS and PFOA in six POCIS deployed for 28 days in the Huron River watershed between September 26, 2019, and October 24, 2019. Error bars are ± 1 standard deviation between POCIS pseudoreplicates (N = 6/location). * indicates a significant difference between the sampling location and the field-blank ($p < 0.05$).

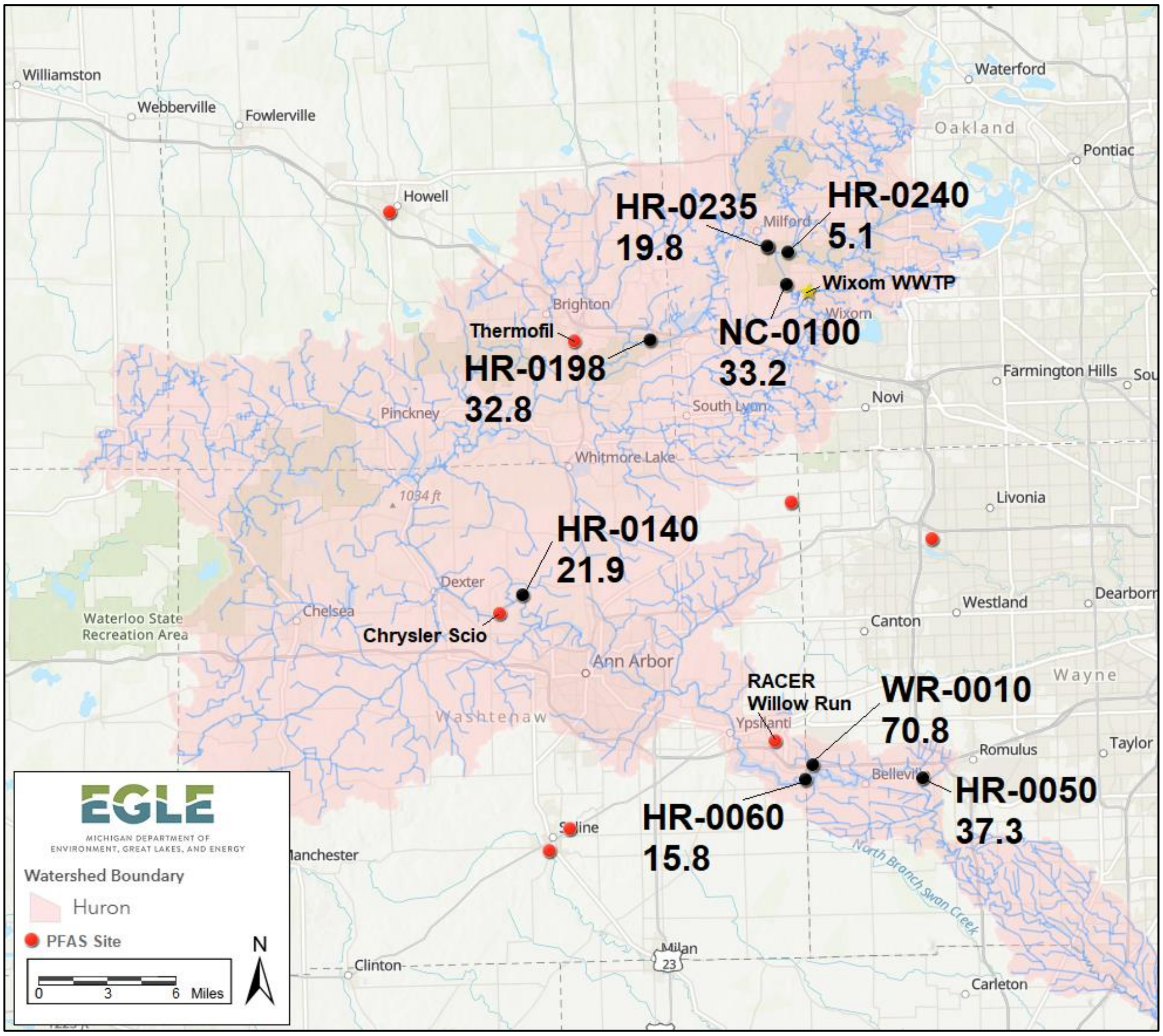

Figure 4. Mean PFOS concentrations (ng/POCIS) of six POCIS deployed at each location for 28 days in the Huron River watershed between September 26, 2019, and October 24, 2019. Known PFAS Sites are displayed as red circles. The yellow star indicates the location of the Wixom Wastewater Treatment Plant.

Table 5. Kruskal Wallis Post Hoc Dunn's Test p-values with Benjamini-Hochberg adjustment. Significant differences in PFOS concentration between sampling locations are italicized.

Sample ID	FB	TB	HR-0240	NC-0100	HR-0235	HR-0198	HR-0140	HR-0060	WR-0010
TB	1.000	-	-	-	-	-	-	-	-
HR-0240	0.690	0.690	-	-	-	-	-	-	-
NC-0100	*0.004*	*0.004*	*0.003*	-	-	-	-	-	-
HR-0235	0.079	0.079	0.085	0.206	-	-	-	-	-
HR-0198	*0.004*	*0.004*	*0.002*	0.967	0.198	-	-	-	-
HR-0140	*0.035*	*0.035*	*0.035*	0.378	0.690	0.351	-	-	-
HR-0060	0.183	0.183	0.214	0.081	0.681	0.077	0.389	-	-
WR-0010	*0.000*	*0.000*	*0.000*	0.286	*0.017*	0.311	*0.048*	*0.004*	-
HR-0050	*0.002*	*0.002*	*0.001*	0.690	0.084	0.690	0.204	*0.030*	0.520

Table 6. Kruskal Wallis Post Hoc Dunn's Test p-values with Benjamini-Hochberg adjustment. Significant differences in PFOA concentration between sampling locations are italicized.

Sample ID	FB	TB	HR-0240	NC-0100	HR-0235	HR-0198	HR-0140	HR-0060	WR-0010
TB	1.000	-	-	-	-	-			
HR-0240	*0.002*	*0.002*	-	-	-	-	-	-	-
NC-0100	0.624	0.624	*0.002*	-	-	-	-	-	-
HR-0235	*0.031*	*0.031*	0.240	*0.042*	-	-	-	-	-
HR-0198	0.081	0.081	0.098	0.144	0.634	-	-	-	-
HR-0140	0.204	0.204	*0.027*	0.334	0.303	0.598	-	-	-
HR-0060	0.167	0.167	*0.036*	0.262	0.380	0.699	0.882	-	-
WR-0010	*0.003*	*0.003*	0.825	*0.003*	0.335	0.167	*0.042*	0.066	-
HR-0050	*0.001*	*0.001*	0.765	*0.001*	0.144	0.042	*0.011*	*0.019*	0.598

Eighteen PFAS were not detected in any of the 60 POCIS samples deployed in the Huron River watershed (PFPrS, PFMPA, 3:3 FTCA, PFMBA, PFEESA, NFDHA, HFPO-DA, ADONA, 7:3 FTCA, 9Cl-PF3ONS, PFNS, PFDS, PFUnA, PFOSA, 11Cl-PF3OUds, PFDoA, PFTriA, and PFTeA). PFOS, PFOA, PFHxS, PFHpA, and PFBS were detected in every sample. PFHxA (96.7% of the 60 samples), PFNA (85.0%), 6:2 FTS (78.3%), PFDA (53.3%), PFBSA (45.0%), 5:3 FTCA (43.3%), PFECHS (11.7%), PFPeS (11.7%), EtFOSAA (10.0%), PFHxsA (10.0%), PFHpS (10.0%), PFPeA (10.0%), 8:2 FTS (5.0%), PFBA (3.3%), MeFOSAA (1.7%), and 4:2 FTS (1.7%) were detected in at least one sample (Figure 5).

Mean total PFAS concentrations (Table 7) ranged from 46.3 ng/POCIS in the POCIS collected from the furthest upstream location on the Huron River (HR-0240) to 7,920 ng/POCIS in the POCIS collected from Norton Creek (NC-0100). In the Norton Creek samples, 6:2 FTS made up 97.3% of the total PFAS (Figure 5). Downstream of Norton Creek at the HR-0235 sampling location, this analyte made up 92.5% of the total PFAS. In Willow Run, 6:2 FTS was 69.9% of the total PFAS.

Table 7. Mean concentrations (ng/POCIS) of six POCIS deployed for 28 days. Σ PFAS is the total concentration of 39 PFAS analytes that were measured above their detection limit (1.3 ng/POCIS).

Sample ID	PFOS	PFOA	PFHxS	PFHxA	PFBS	PFNA	Σ PFAS
HR-0240	5.1	16.7	6.7	1.5	5.8	3.4	46.3
NC-0100	33.2	8.7	4.5	34.0	3.8	0.8	7920.8
HR-0235	19.8	14.1	6.0	9.2	5.5	2.4	1378.7
HR-0198	32.8	12.4	4.5	14.2	5.6	2.0	226.4
HR-0140	21.9	11.6	3.5	6.7	6.8	2.3	84.6
HR-0060	15.8	11.8	3.7	6.8	6.8	2.3	70.6
WR-0010	70.8	16.5	73.1	8.6	8.7	37.7	857.7
HR-0050	37.3	18.1	6.5	6.0	6.8	4.4	116.5

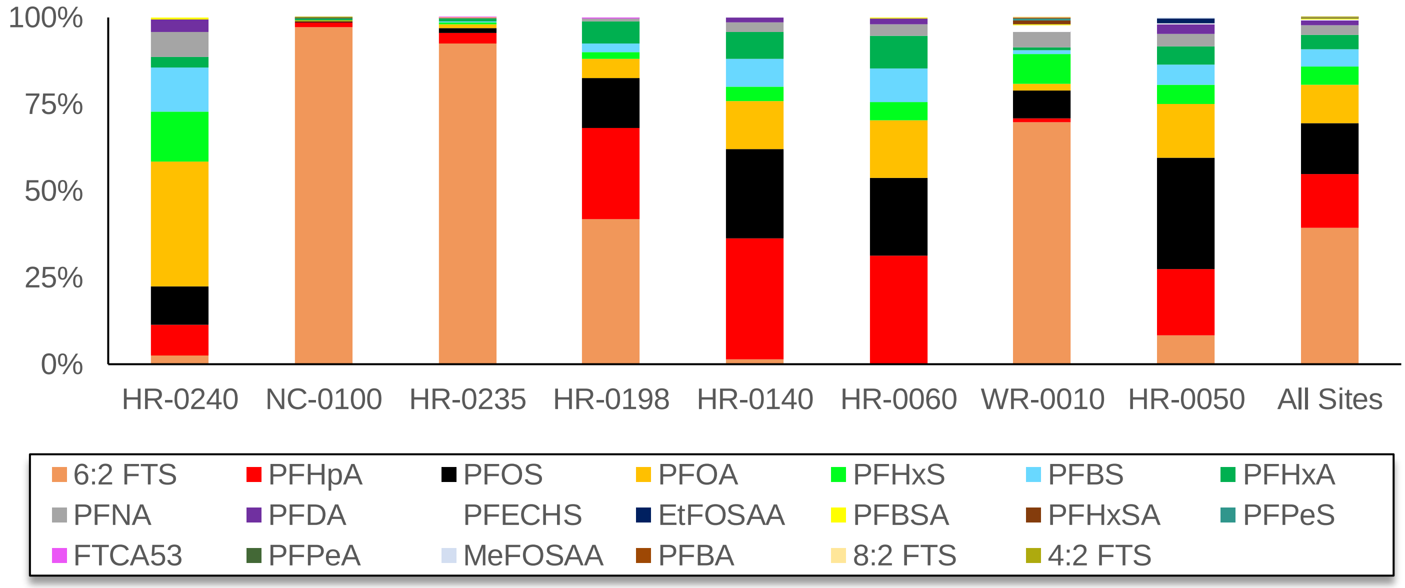

Figure 5. Percent composition of PFAS detected in POCIS samples deployed for 28 days in the Huron River watershed between September 26, 2019, and October 24, 2019. 'All sites' represents the arithmetic mean across all sampling locations.

The Environmental Sampling Technologies laboratory noted that two of the three POCIS from the first holder deployed at the HR-0198 sampling location showed visible signs of damage with several small holes in the membrane. Because there were no significant differences between the three POCIS in the first holder compared to the three POCIS from the second holder (Figure 5), all six membranes were included in our analysis. In fact, there were no significant differences between the two replicate holders deployed at any of the sampling locations (Figure 6) which suggests that only one holder containing three POCIS will be needed for deployments in future PFAS surface water monitoring projects.

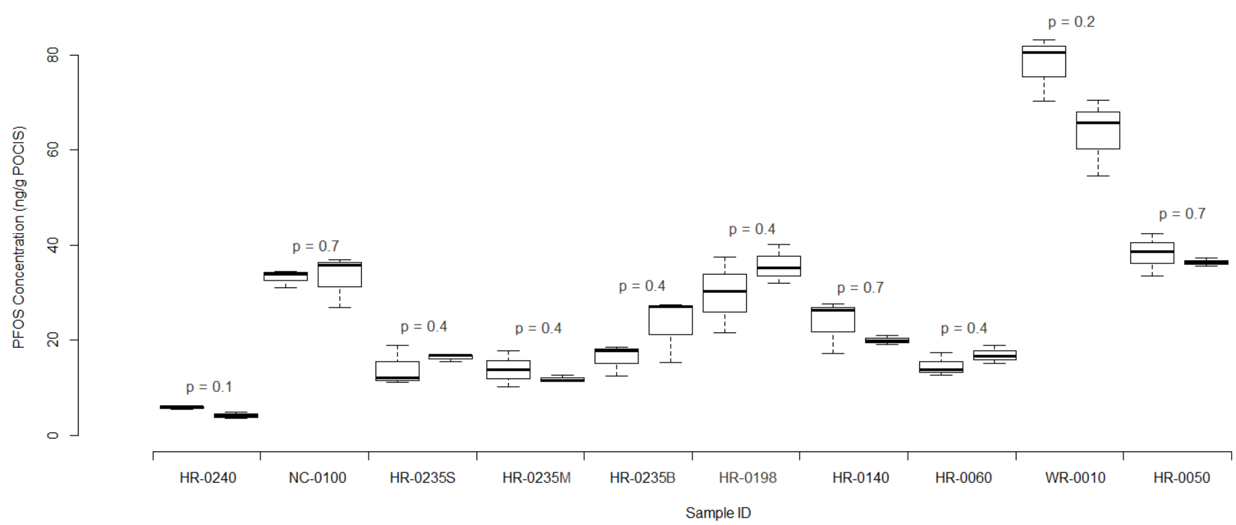

Figure 6. Comparison of the PFOS concentration (ng/POCIS) in two holders containing three individual POCIS that were deployed in the Huron River watershed between September 26, 2019, and October 24, 2019. There were no significant differences between replicate POCIS following a Mann-Whitney U test.

The PFOS concentration was the lowest at the HR-0240 sampling location and was not significantly different from the blanks suggesting that concentrations were low during deployment ($p = 0.690$; Table 5). This sampling location is upstream of known sources of PFAS on the Huron River proper. The concentrations of PFOS measured in previously collected grab samples from this location were consistently low; grab samples were < 2.4 ng/L in July 2018, August 2018, October 2018, and April 2019 (Figure 7; Bowman et al., 2020). In 2019, the WRD collected fish from Proud Lake, which is immediately upstream of the HR-0240 sampling location. The 95% Upper Confidence Limits (UCL) for bluegill, rock bass, and largemouth bass collected in 2019 from Proud Lake were 10, 8.2, and 120 parts per billion (ppb), respectively (Bowman et al., 2020). Interestingly, PFOA in the upstream HR-0240 POCIS (mean 16.7 ng/POCIS) was significantly higher than the blanks ($p = 0.002$; Table 6). Four grab samples collected by Bowman et al. (2020) at this location had low (< 3 ng/L) surface water PFOA concentrations. Furthermore, PFOA was non-detect in fillets of fish collected from Proud Lake in 2019. These data suggest that the PFOA concentration in the POCIS sample at HR-0240 might not be from a specific source but may be attributed to widespread sources (i.e., consumer products). Further investigation at additional areas without known or suspected sources of PFAS is needed to determine the concentration of PFAS in POCIS that can be attributed to widespread sources rather than a specific source.

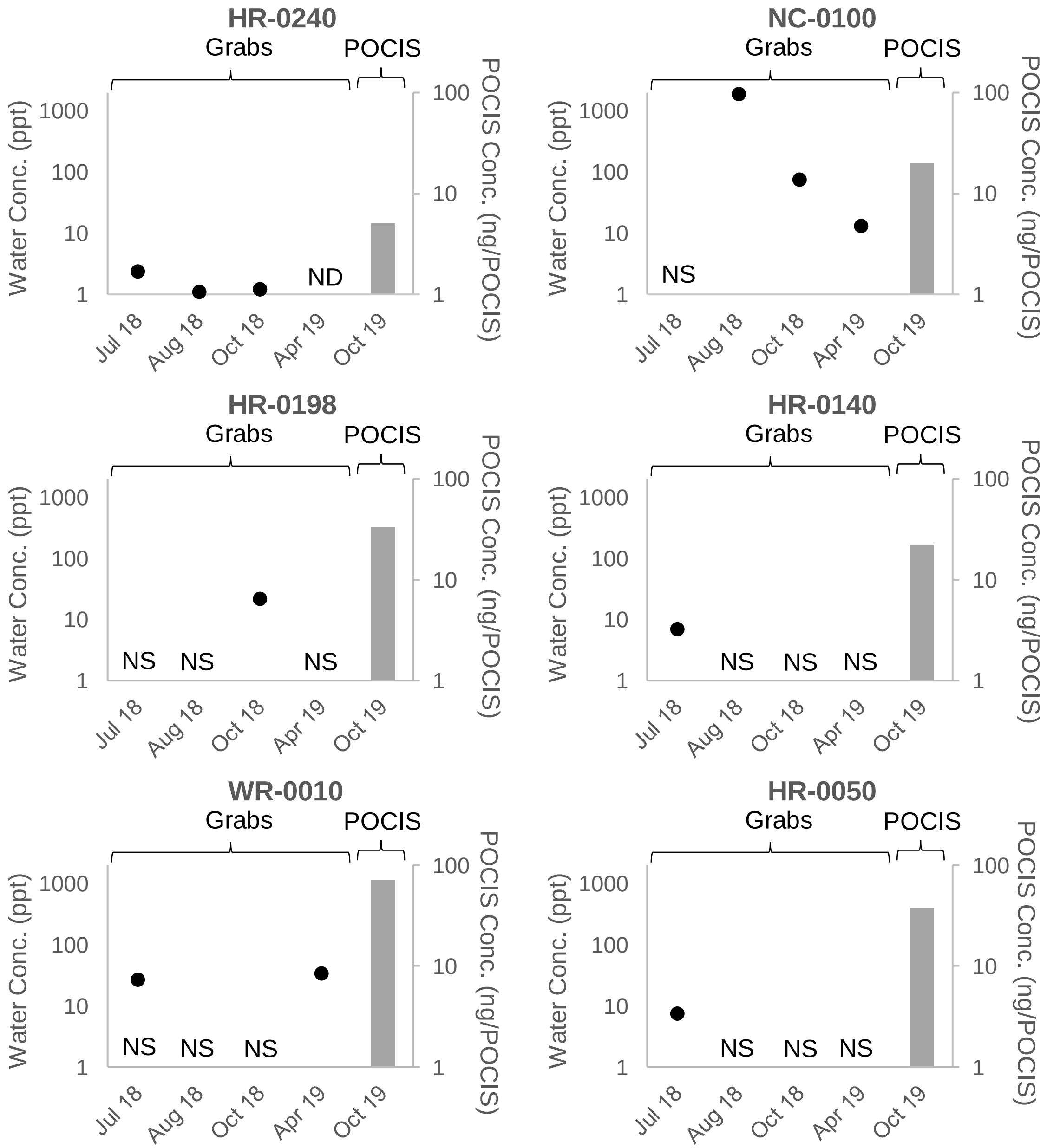

Figure 7. PFOS concentrations in grab samples and POCIS samples collected from the Huron River watershed in 2018 and 2019. ND = Non-Detect; NS = No Sample Collected.

The PFOS concentration in the POCIS deployed in Norton Creek (NC-0100) downstream of the Wixom WWTP averaged 33.2 ng/POCIS and was significantly higher than the blanks and the HR-0240 sampling location ($p = 0.002$; Table 5). The Wixom WWTP conducts PFAS sampling as part of the Industrial Pretreatment Program (IPP) PFAS initiative. In June 2018, effluent from the WWTP had a PFOS concentration of 290 ng/L and total PFAS concentration of 10,927 ng/L. The city of Wixom identified Tribar Manufacturing LLC (Tribar), Plant 4, as a source of the high levels of PFOS to Wixom's sanitary sewer system (Tribar's discharge to the WWTP was 28,000 ng/L PFOS in May 2018). In August and September 2018 the PFOS concentration in the Wixom WWTP effluent was 4,800 and 2,100 ng/L, respectively. In October 2018 Tribar installed a granular activated carbon system to remove PFOS prior to discharge to the Wixom sanitary sewer. Since Tribar installed treatment, Wixom WWTP effluent has decreased from 940 ng/L in October 2018 to 26 ng/L in December 2019 (Bowman et al., 2020). Bowman et al. (2020) reported PFOS surface water concentrations at NC-0100 of 1,850 ng/L in August 2018, 75 ng/L in October 2018, and 13 ng/L in April 2019. The PFOS reduction between 2018 and 2019 at this location is likely due to reduced concentration of PFOS in the Wixom WWTP effluent.

A grab surface water sample collected upstream of the Wixom WWTP (NC-0300) in August 2018 by Bowman et al. (2020) had a PFOS concentration of 26 ng/L (Figure 7). Furthermore, a sample collected on the West Branch of Norton Creek (NCW-0100) had a PFOS concentration of 80 ng/L. This resulted in follow-up sampling at this location in October 2018 (5.2 ng/L PFOS) and April 2019 (non-detect PFOS). The source(s) of PFOS in the August 2018 samples is(are) unknown and may be intermittent.

The U.S. metal plating industry began using 6:2 FTS in their chromium electroplating processes as a response to the U.S. phase out of PFOS (National Association for Surface Finishing, 2019). In addition, 6:2 FTS is a degradation product of PFAS found in fluorotelomer-based aqueous film forming foams (Houtz et al. 2013). 6:2 FTS in the Norton Creek POCIS downstream of the Wixom WWTP (NC-0010) averaged 7,704 ng/POCIS which comprised 97% of the total PFAS detected at this location (Figure 8). 6:2 FTS was non-detect in grab samples collected in April 2019 in the Huron River upstream of Norton Creek (HR-0240) and comprised up to 62% and 74% of the PFAS measured in Norton Creek (NC-0100) and in the Huron River downstream of Norton Creek (HR-0235) sampling locations, respectively (Bowman et al., 2020). This analyte was non-detect in the samples collected by Bowman et al. (2020) upstream of the WWTP on Norton Creek. Effluent from the Wixom WWTP sampled before, during, and after the POCIS deployment was largely comprised of 6:2 FTS and ranged from 60% to 75% of the total PFAS detected in the effluent (Figure 8). Overall, these results suggest that the Wixom WWTP is still a source of PFAS to Norton Creek and the Huron River.

5:3 FTCA averaged 3.5 ng/POCIS in Norton Creek downstream of the WWTP. This analyte averaged 1.9 and 0.4 ng/POCIS in the two Huron River sampling locations downstream of Norton Creek (HR-0235 and HR-0198, respectively). All other POCIS were non-detect for 5:3 FTCA. Lang et al. (2017) reported that 5:3 FTCA was the most dominant PFAS analyzed in U.S. landfill leachate. Biodegradation of fluorotelomer-based compounds can biodegrade in soils and activated sludge with 5:3 FTCA being one of the major metabolites (Abada et al. 2018). This analyte is currently not measured as a part of the IPP initiative so a comparison to the WWTP effluent was not possible.

PFPeA was only detected in the Norton Creek POCIS and averaged 24.2 ng/POCIS. Limited information exists regarding the sources of this PFAS; however, it is reportedly a breakdown product of stain and grease-proof coatings on food packaging and textiles (Dery et al., 2019). Furthermore, PFPeA is the predominant compound formed following the biotransformation of 6:2 fluorotelomer alcohol (6:2 FTOH) in river sediment (Zhao et al., 2013). PFPeA was detected in the WWTP effluent at concentrations as high as 580 ng/L with its composition ranging from 10% to 18% of the total PFAS in the effluent samples (Figure 8).

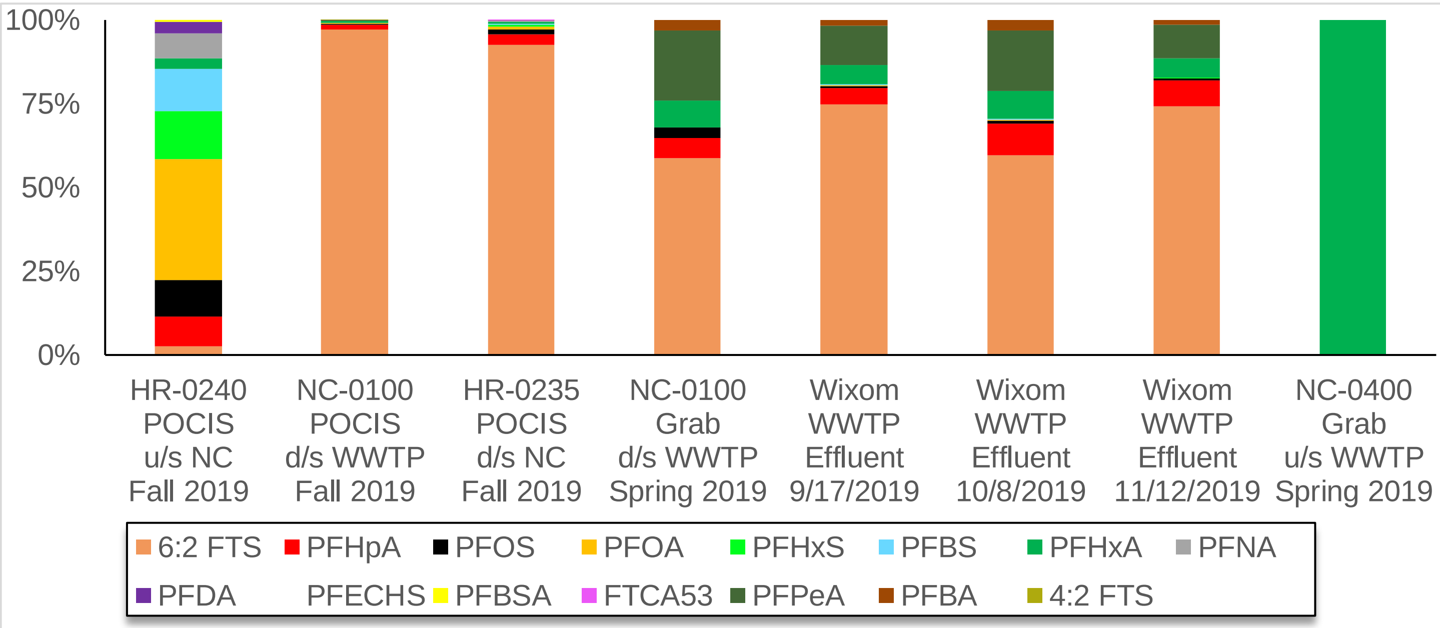

Figure 8. PFAS composition in POCIS and grab surface water samples collected in 2019 from Norton Creek (NC) and the Huron River (HR) and upstream (u/s) and downstream of the Wixom WWTP. Composition of PFAS in the WWTP effluent collected before (September 17, 2019), during (October 8, 2019), and after (November 12, 2019) POCIS deployment are also provided.

Mean PFOS was nominally higher in the POCIS deployed at HR-0198 in comparison to the upstream HR-0235 sampling location; however, the concentrations were not significantly different from one another ($p = 0.634$; Table 5). HR-0198 is immediately downstream of the Kent Lake impoundment of the Huron River. In October 2018, the concentration of PFOS was 22 ng/L in a grab sample collected from Kent Lake at the HR-200 sampling location and was 21 ng/L at the HR-0235 sampling location (Figure 7; Bowman et al., 2020). The difference between PFOS concentrations in the POCIS samples at these two locations may be due to site characteristic differences (i.e., flow) that affect the sampling rates of the individual POCIS (Alvarez et al., 2004). At the time of deployment, stream velocity at the HR-0198 sampling location was 0.59 m/s whereas at the HR-0235 location it was only 0.15 m/s. Alternatively, Jin et al. (2020) reported that the PFAS concentration in surface water or reservoirs depends on the stage of the dam operation (i.e. storage vs discharge period). The concentration of PFOS in the Three Gorges Dam reservoir of the Yangtze River in China was higher during the storage period (mass of 261 kilograms; kg) compared to the discharge period (13.2 kg; Jin et al., 2020). The discharge through the dam of Kent Lake can vary during the fall months depending on the storage operation of the dam (Figure 13S; Hay-Chmielewski et al., 1995).

The 95% UCL in the fillets of pumpkinseed sunfish and largemouth bass collected in 2019 from Kent Lake were 115 and 387 ppb PFOS, respectively (Bowman et al., 2020). These concentrations are much higher than for the bluegill and largemouth bass collected from

Proud Lake, providing additional evidence that the source of PFAS is between the two lakes (i.e., Norton Creek).

The concentration of PFOS at the HR-140 sampling location averaged 21.9 ng/POCIS, which is nominally lower than the HR-0198 location (upstream; 32.8 ng/POCIS) and higher than the downstream location (HR-0060; 15.8 ng/POCIS) on the Huron River. The PFOS concentrations at these locations were not significantly different from one another (Table 5). HR-0140 is downstream of the PFAS Site at the former Chrysler Scio Introl Division facility, located in Dexter, Michigan. The concentration of PFOS in surface water collected at HR-0140 in July 2018 was 7.1 ng/L (Figure 7; Bowman et al., 2020). Based on limited sampling, results are inconclusive as to whether the former Chrysler Scio Introl Division facility is a source of PFAS to the Huron River.

The concentration of PFOS was the highest in the POCIS deployed in Willow Run at the WR-0010 sampling location and averaged 70.8 ng/POCIS. This concentration is significantly higher than the blanks ($p = 0.003$) and the upstream HR-0060 sampling location ($p = p = 0.004$; Table 5). This location is just upstream of Willow Run's confluence with the Belleville Lake impoundment of the Huron River. Grab samples collected at WR-0010 in July 2018 and April 2019 had PFOS concentrations of 26 and 33 ng/L PFOS, respectively. Two outfalls upstream of this location sampled in April 2019 had a PFOS concentration of 5.4 ng/L (WRO-F001) and 92 ng/L (WRO-F002; Bowman et al., 2020). Grab samples collected in April 2019 upstream of these two outfalls in Willow Run had PFOS concentrations ranging from non-detect to 6.1 ng/L.

The concentration of 6:2 FTS averaged 599 ng/POCIS in the WR-0010 POCIS samples and comprised 74% of the total PFAS from this location (**Error! Reference source not found.**). 6:2 FTS comprised up to 47% of the total PFAS in grab samples collected at this sampling location in April 2019 (**Error! Reference source not found.**) (Bowman et al., 2020). In addition, 6:2 FTS comprised 52% of the total PFAS from an outfall on Willow Run (WRO-F002) that discharges airport storm water upstream of WR-0010 (**Error! Reference source not found.**). 6:2 FTS was not detected in the WRO-F001 storm water outfall sample which includes intermittent discharge from the YCUA facility or in a sample collected from an upstream location in Willow Run (WR-0150; Bowman et al., 2020). PFECHS was detected in all six of the WR-0010 (range 12.5 to 17.8 ng/POCIS) and in one of the six HR-0050 (1.5 ng/POCIS) samples. All other POCIS had non-detectable concentrations (< 1.3 ng/POCIS) of this PFAS. PFECHS is a cyclic perfluorinated acid primarily used as an erosion inhibitor in aircraft hydraulic fluid. De Silva et al. (2011) reported PFECHS concentrations in Great Lakes fish up to 3.7 ppb whole body and in surface waters up to 5.7 ppt. PFECHS has also been detected in Great Lakes herring gull (Letcher et al., 2015) and bald eagle (Wu et al., 2020) eggs. Overall, these results suggest that contaminated storm water from the airport is a source of PFAS to Willow Run.

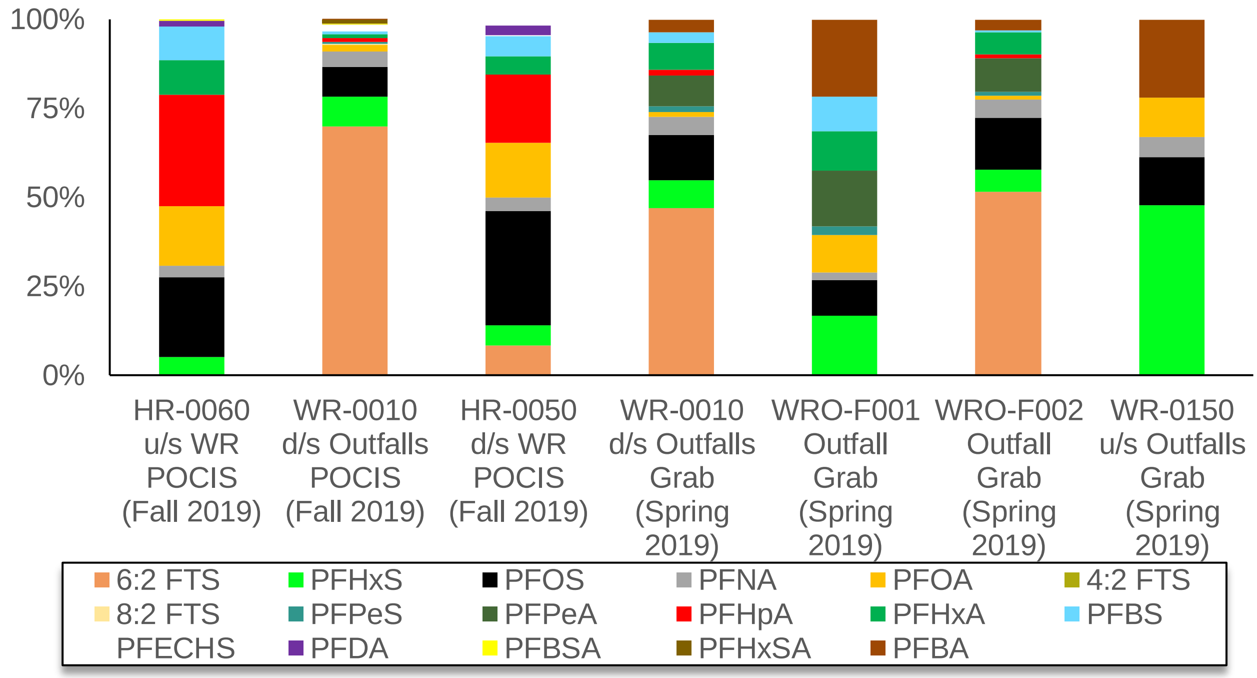

Figure 9. Comparison of the PFAS composition in surface water samples collected in Willow Run (WR) downstream (d/s) and upstream (u/s) of two storm water outfalls (WRO-F001 and WRO-F002). Grab samples were collected in April 2019 (Bowman et al., 2020). The POCIS was deployed between September 26 and October 24, 2019.

HR-0060 is upstream of the Willow Run confluence on the Huron River proper between Ford Lake and Belleville Lake. The POCIS samples collected from this location averaged 15.8 ng/POCIS PFOS, which is significantly lower than the downstream HR-0050 sampling location, which includes input from Willow Run ($p = 0.030$; Table 5). A previous grab sample collected from the HR-0060 sampling location in July 2018 had a PFOS concentration of 7.1 ng/L (Bowman et al., 2020). HR-0050 is located on the Huron River proper downstream of Willow Run and Belleville Lake. The POCIS from this sampling location had an average PFOS concentration of 37.3 ng/POCIS. In 2018, the 95% UCL of PFOS in the fillets of bluegill and smallmouth bass collected from Belleville Lake were 33 and 71 ppb, respectively (Bowman et al., 2020). Overall, these results show that Willow Run is a source of PFAS to Belleville Lake.

<u>Ratios of Select PFAS</u>

Historical production of PFOS and PFOA was done through an electrochemical fluorination (ECF) process which results in a mixture of linear (70 to 80%) and branched isomers (Buck et al., 2011). ECF was phased out in 2002 and replaced by a telomerization process, which produces only linear isomers (Buck et al., 2011). The percentage of the branched isomer of PFOS ranged from 32% to 61% in the POCIS samples (Figure 9A), which is higher than would be expected in an ECF produced product. Karrman et al. (2011) suggest that this may be due to preferential degradation of branched PFOS precursors. The branched isomer of PFOA was only detected in Willow Run where it comprised 9% of the total PFOA (Figure 9B). Overall, these results suggest that contamination of ECF produced PFAS are present in the Huron River watershed. Furthermore, Koch et al. (2019) suggested that the PFHxS to PFOS ratio might be a suitable indicator for different AFFF products. The PFHxS to PFOS ratio at the WR-0010 sample location in Willow Run was 0.51 (Figure 9D), which is higher than typically found in 3M AFFF formulations. Koch et al. (2019) suggests that this may indicate transformation of C_6 precursors found in AFFF.

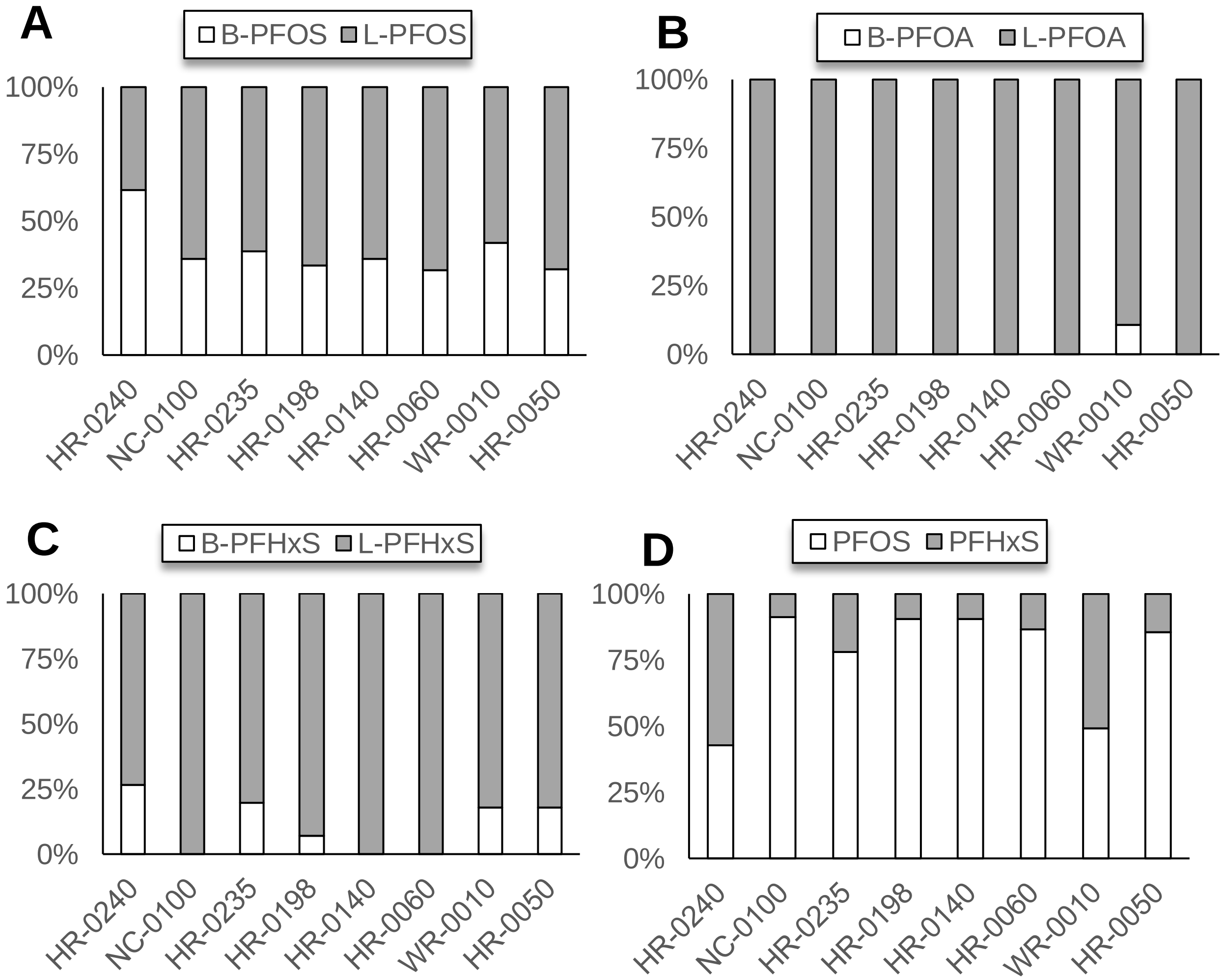

Figure 9. Ratio of branched to linear isomers of PFOS (A), PFOA (B), PFHxS (C), and ratio of total PFOS to total PFHxS (D) in POCIS deployed for 28 days in the Huron River watershed between September 26, 2019, and October 24, 2019.

PFAS Water Column Investigation

Three cages, each containing six POCIS, were deployed at the HR-0235 sampling location to determine the distribution of PFAS throughout the water column in a lotic system. The stream depth at this sampling location was approximately 1.5 meters (Table 2). The PFOS concentration averaged 15.3, 12.9, and 19.8 ng/POCIS in the sub-surface, mid-column, and bottom POCIS respectively (Table 8) and was not significantly different between depths (Table 9). While no conclusions should be drawn from this limited sampling effort, it does lend support for using fish cages secured to the bottom of the river as a POCIS deployment method for surface water PFAS investigations. Future investigations should be conducted at deeper lotic sampling locations as well as in lentic systems to gain a better understanding of PFAS variability in aquatic systems.

Table 8. Mean concentrations (ng/POCIS) of POCIS deployed for 28 days at a non-wadable location on the Huron River to determine the spatial variability within the stream. B = bottom sample; M = middle column sample; and S = surface sample. Σ PFAS is the total concentration of 39 PFAS analytes measured above their detection limit (1.3 ng/POCIS).

Sample ID	PFOS	PFOA	PFHxS	PFHxA	PFBS	PFNA	Σ PFAS
HR-0235S	15.3	14.1	5.3	14.4	7.5	2.5	1,181.0
HR-0235M	12.9	11.0	4.5	16.6	6.6	1.6	910.1
HR-0235B	19.8	14.1	6.0	9.2	5.5	2.4	1378.7

Table 9. Kruskal Wallis Post-hoc Dunn's Test with Benjamini-Hochberg adjustment at the spatial investigation sampling location. There were no significant differences in PFOS concentrations between the three water column samples.

Sample ID	HR-0235S	HR-0235M
HR-0235M	0.690	-
HR-0235B	0.576	0.334

QA/QC

No PFAS analytes were detected in either the trip, field, or laboratory extraction blanks. The mean RPD for linear and branched isomers of PFOS in the river samples were 17.3% and 18.0%, respectively. The average RPD for the linear isomer of PFOA was 8.7% (only 1 location had detectable concentrations of the branched PFOA isomer). Five samples had PFAS RPD exceedances of > 30% between replicate POCIS holders deployed at a single location (Table 10).

Table 10. Relative Percent Differences exceeding 30% in replicate POCIS samples deployed in the Huron River watershed.

Sample ID	Analyte	RPD
HR-0140	PFDA	40.0%
HR-0198	PFBS	46.6%
	PFHxA	41.4%
	PFHpA	38.4%
	6:2FTS	33.9%
HR-0235B	PFBS	35.1%
	PFHxA	36.3%
	PFHpA	41.3%
	L-PFHxS	32.4%
	B-PFHxS	31.6%
	6:2FTS	45.4%
	L-PFOS	34.2%
	B-PFOS	37.0%
	PFNA	33.9%
HR-0240	PFHxA	51.2%
	6:2FTS	86.6%
	B-PFOS	41.0%
WR-0010	PFBA	53.9%
	PFNA	54.3%

CONCLUSIONS

- This study offers support for the use of POCIS as another line of evidence for source tracking of PFAS contamination in watersheds in Michigan.
- This study supports the use of stainless steel fish cages secured to the bottom of the river as a POCIS deployment method for surface water PFAS investigations.
- Previous work by the WRD has determined that caged fish studies are not useful for trend monitoring of PFAS due to a high frequency of non-detections in composited fish samples. This study supports the use of POCIS as a suitable replacement for caged fish trend monitoring and provides baseline results for assessing improvements due to ongoing remediation measures in the Huron River watershed. POCIS should be redeployed periodically at the same locations for trend monitoring of PFAS. Additional samplers should be deployed upstream and downstream of known or potential sources in Norton Creek, Willow Run, and on the Huron River upstream of Chrysler Scio.
- These results point to potential sources of PFAS loading in Norton Creek and Willow Run with significantly higher PFOS concentrations in these two tributaries.
- 5:3 FTCA was detected in Norton Creek.
- 6:2 FTS composition in Norton Creek and Willow Run were similar to the composition of effluent samples collected from the Wixom WWTP and storm water collected from the Willow Run Airport
- PFECHS, a component of aircraft hydraulic fluid, was detected in Willow Run downstream of a storm water outfall of the Willow Run Airport.
- These results also suggest that contamination by PFAS produced by historical electrochemical fluorination is present in the Huron River watershed.
- Further investigations should be conducted at deeper lotic sampling locations as well as in lentic systems to gain a better understanding of PFAS variability in aquatic systems.
- Further investigation at more areas without known or suspected sources of PFAS is needed to determine the background concentration of PFAS in POCIS deployed in Michigan streams.
- POCIS should be used in other watersheds to track improvements through remediation of contaminated sites or source reduction. For example, this could be accomplished by deploying samplers before and after remediation or source reduction.

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APPENDIX

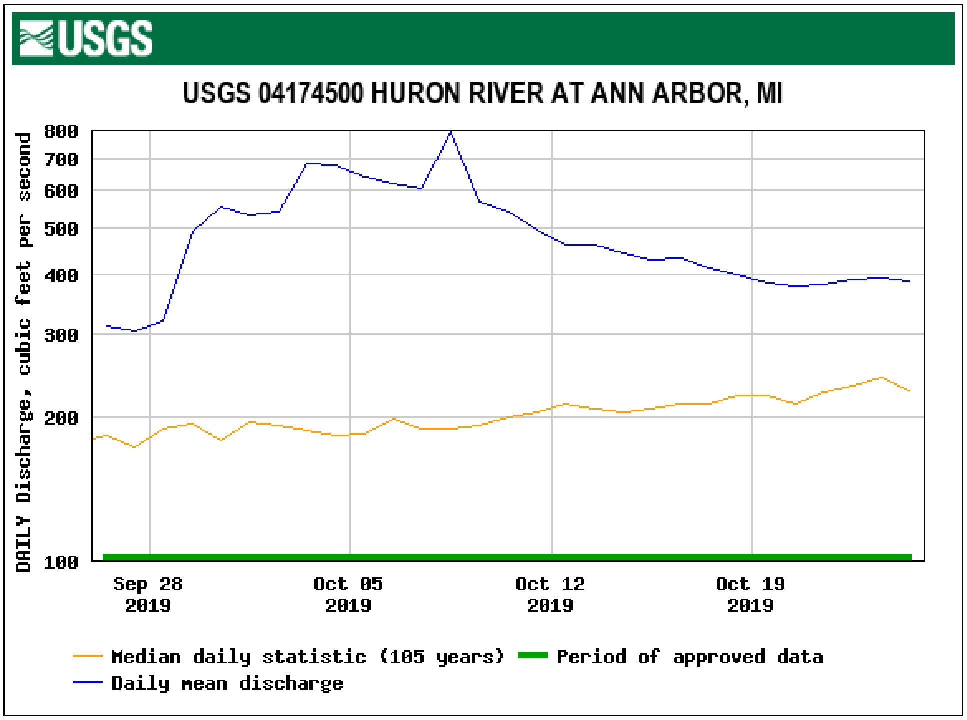

Figure 10. Daily mean discharge of the Huron River in Ann Arbor, Michigan during the 2019 EGLE, WRD, POCIS deployment.

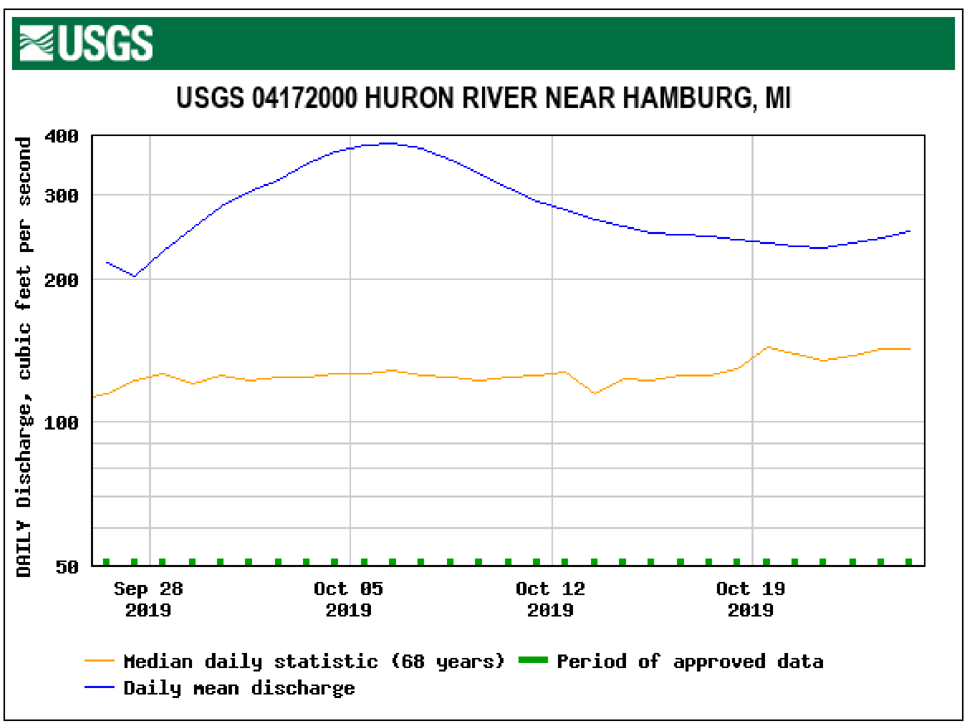

Figure 11. Daily mean discharge of the Huron River in Hamburg, Michigan during the 2019 EGLE, WRD, POCIS deployment.

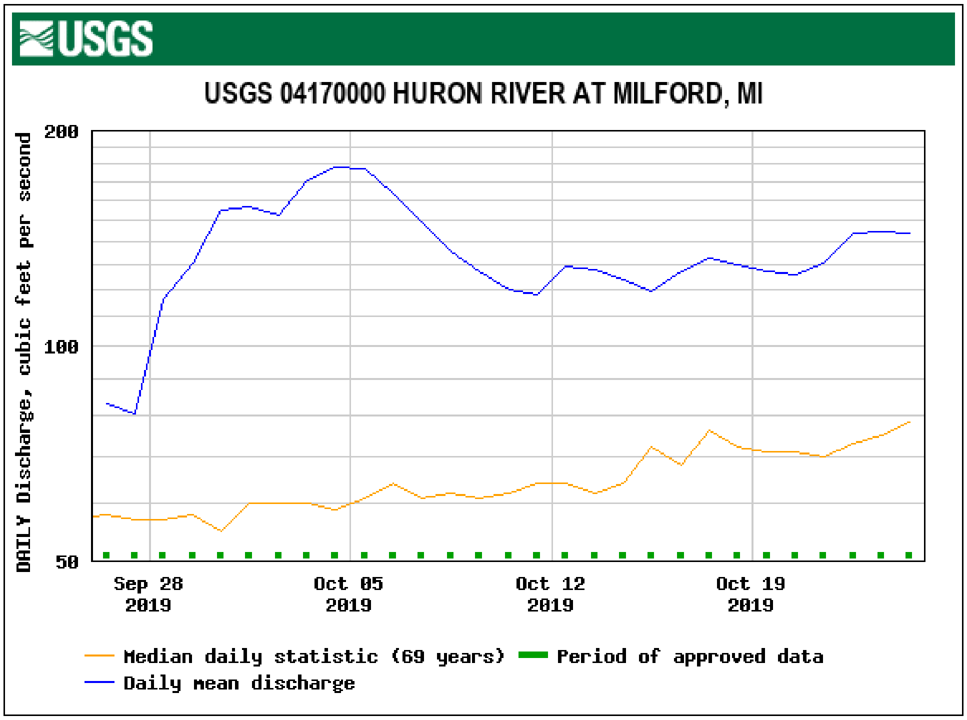

Figure 12. Daily mean discharge of the Huron River in Milford, Michigan during the 2019 EGLE, WRD, POCIS deployment.

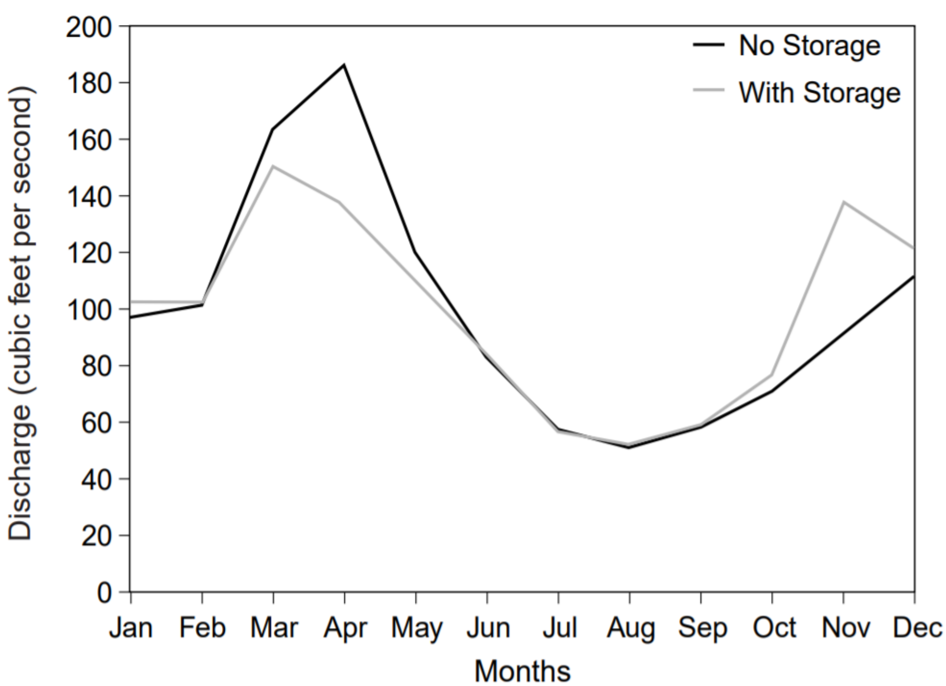

Figure 5.—Median monthly Huron River discharge from Kent Lake, with and without the effect of Kent Lake reservoir.

Figure 13. Median monthly Huron River discharge from Kent Lake, with and without the effect of Kent Lake reservoir (data from Hay-Chmielewski et al., 1995).