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

STAFF REPORT

INVESTIGATION OF THE OCCURRENCE AND SOURCES OF PERFLUORINATED AND POLYFLUORINATED ALKYL SUBSTANCES (PFAS) IN THE ST. JOSEPH RIVER WATERSHED

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. 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. Many products containing PFAS are used in numerous industrial processes including metal plating, textile production and treatment, and specialty paper production. Industrial and domestic waste containing these compounds can enter the environment through municipal or private waste treatment systems, stormwater runoff, venting groundwater, or as deposition after emissions into the atmosphere. Both PFOS and PFOA have been measured in surface waters across the state, and PFOS has been detected in most fish tissue samples from Michigan waters that have been analyzed for PFAS.

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

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 treatment plant 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 St. Joseph River (HUC 04050001) drains portions of eight counties in southwest Michigan: Berrien, Van Buren, Cass, Kalamazoo, St. Joseph, Calhoun, Branch, and Hillsdale as well as seven counties in northern Indiana. Approximately 42 miles of the entire 210 mile stretch of river are in the State of Indiana (Indiana Department of Natural Resources, 2018). Fifty-eight percent of the St. Joseph River watershed is agricultural production and nearly 20 percent is forested land based on Michigan county data (Wesley and Duffy, 1999). The watershed is divided into five segments: headwaters, upper, middle, lower, and mouth. Major tributaries of the St. Joseph River are Beebe Creek and Soap Creek in the headwaters segment; Hog Creek, Coldwater River, Swan Creek, Nottawa Creek, and Little Portage Creek in the upper segment; Portage River, Rocky River, Prairie River, Fawn River, Mill Creek, Pigeon River, Pine Creek, Little Elkhart River, and Christiana Creek in the middle segment; Baugo Creek, Juday Creek, Brandywin Creek, Dowagiac River, McCoy Creek, and Pipestone Creek in the lower segment; and Paw Paw River and Hickory Creek in the mouth segment (DeGraves, 2005).

In 2001, the Michigan Department of Environmental Quality (MDEQ), Water Resources Division (WRD), sampled surface water from rivers, including the St. Joseph River, in different parts of the state for the presence of PFOA and PFOS. Additional PFAS surface water and fish tissue samples were collected in June 2013 by the MDEQ, WRD, from the St. Joseph River near St. Joseph as part of a statewide PFAS reconnaissance study (Bush et al., 2015). The surface water PFOS geometric mean concentration was 11.3 and 1.6 ng/L in 2001 and 2013, respectively. The surface water PFOA geometric mean concentration was 8.7 and 1.8 ng/L in 2001 and 2013, respectively. While the surface water PFOS and PFOA concentrations are below their respective HNV, the fish tissue sampling from the river indicated the need for a Michigan Department of Health and Human Services (MDHHS) “Eat Safe Fish” advisory due to PFOS.

In April 2016 a gasoline tanker spill occurred near Niles, Michigan, where the local fire department then used fire suppression foam containing PFAS to prevent any fire and explosion hazards. A groundwater sample was collected in September 2017 by Brenner Oil from the source area monitoring well. The sample had a PFOS and PFOA concentration of 16,000 and 13,000 ng/L, respectively. EGLE collected an additional sample from the well in January 2018 and found a PFOS and PFOA concentration of 382,000 and 12,800 ng/L, respectively. The groundwater in this area flows toward a creek that flows into Mud Lake, which eventually connects to the Dowagiac River, a tributary to the St. Joseph River. In May 2018 the Bronson WWTP effluent, which discharges to Swan Creek, a tributary to the St. Joseph River, had a PFOS concentration of 190 ng/L. A wastewater stream from a plater that was being sent to the WWTP had a PFOS concentration of 240,000 ng/L.

For these reasons, EGLE, WRD, decided to monitor the St. Joseph River and select tributaries, including the Dowagiac River and Swan Creek, to try to identify sources of PFAS and to evaluate the potential risk to human health caused by PFAS in area surface waters. After this sampling effort was completed, EGLE was made aware of a groundwater sample collected in October 2018 by the International Automotive Components facility in Mendon, Michigan, with a combined PFOS and PFOA concentration of 1,312 ng/L. Industrial wastes were historically disposed on site, which was formerly operated by a plastics molding facility and later an automotive seating systems company. This site is adjacent to the Little Portage Creek, a tributary to the St. Joseph River, near Mendon. In May 2019 EGLE, WRD, found PFAS-contaminated groundwater at the former Du-Wel Metals Products manufacturing facility near Hartford, Michigan. The highest concentration of PFOS+PFOA in the groundwater was 8,713 ng/L. This site is adjacent to the Paw Paw River, a tributary of the St. Joseph River. Finally, in October 2019 EGLE received notification of off-site migration from Graphic Packaging Incorporated Midwest, LLC (formerly the White Pigeon Paper Company) following the discovery of PFAS-contaminated groundwater in the facility's monitoring wells. This site is adjacent to the Pigeon River, a tributary to the middle segment of the St. Joseph River.

SUMMARY

1. PFOS was detected in 40 of the 55 samples collected throughout the watershed with concentrations ranging from non-detect to 790.0 ng/L.
2. Two locations (SJ-0080; near Niles and a wetland in the Pigeon River watershed) exceeded the PFOS Rule 57 HNV and no samples exceeded the HNV for PFOA.
3. No surface water samples exceeded the Rule 57 aquatic life values for PFOS or PFOA.
4. In the St. Joseph River, slightly elevated (> 3 ng/L) PFOS concentrations were observed near Colon (SJ-0145; 3.2 ng/L), Bristol (SJ-0100; 3.4 ng/L), Buchanan (SJ-0060; 5.7 ng/L); St. Joseph Charter Township (SJ-0030, 10.0 ng/L), Berrien Springs (SJ-0050; 8.4 ng/L, and SJ-0040; 7.4 ng/L), and St. Joseph (SJ-0010; 12.0 ng/L).
5. Slightly elevated PFOS concentrations (> 3 ng/L) were detected in Ox Creek, Paw Paw River, Pigeon River, and Swan Creek tributaries to the St. Joseph River.
6. PFOS was detected in 12 of 13 samples collected from Swan Creek (six sampling locations) ranging from non-detect in the furthest upstream location to 5.8 ng/L downstream of the Bronson WWTP.
7. PFOS would cause an "Eat Safe Fish" consumption advisory in both the Palmer and Long Lake impoundments of Swan Creek; however, mercury causes a more restrictive guidance in these impoundments.
8. The Bronson WWTP discharge of PFOS to the Swan Creek watershed is a likely source for the elevated fish tissue concentrations in the two impoundments.
9. The Bronson Plating Company was identified as a source of PFOS to the Bronson WWTP. In November 2018 the company installed a Granular Activated Carbon pretreatment system, which significantly reduced their discharges of PFOS to the Bronson WWTP.
10. The source of the contamination in the St. Joseph River near Niles remains unknown.
11. PFOS was detected in 8 of 10 samples collected from the Pigeon River and ranged from non-detect to 5.5 ng/L. High water levels at the time of sampling may have resulted in diluted concentrations.

12. The PFOS concentration in a wetland adjected to the former White Pigeon Paper property was 790 ng/L.
13. Two samples collected from wastewater being discharged directly into the Pigeon River at the former White Pigeon Paper Company had concentrations of 130 and 170 ng/L; both of which exceed the PFOS HNV. Further investigations are continuing at the site.
14. Fish collections are planned in the Pigeon River to determine if consumption advisories due to PFOS contamination are warranted.
15. An elevated PFOS concentration (4.3 ng/L) was found in the Paw Paw River near its confluence with the St. Joseph River. Further investigations are being conducted to determine if the contaminated groundwater at the Du-Wells Metals PFAS site in Hartford is impacting the river.
16. The PFOS concentration in the Dowagiac River was non-detect; therefore, based on limited sampling, it does not appear that the M-60 tanker spill contamination site is impacting the St. Joseph River.
17. Additional fish samples have been collected from the Sturgis, Mottville, Niles, and Chapin Lake impoundments of the St. Joseph River and will be analyzed as fillets. The results from those analyses are pending.

METHODS

Surface Water

Due to the detection of high PFOS in a waste stream sent to the Bronson WWTP, an initial surface water sampling event for the Swan Creek watershed was conducted on August 21, 2019 (Figure 1). The larger scale St. Joseph River watershed surface water sampling event was then conducted on September 19, 2019 (Figure 2). Following the detection of contaminated groundwater at the former White Pigeon Paper Company in White Pigeon, EGLE, WRD, staff collected samples from the Pigeon River watershed in March 2020 (Figure 3). All samples were collected following the EGLE Surface Water PFAS Sampling Guidance document (MDEQ, 2018a) and analyzed for 24 PFAS analytes (Table 1), as described in the Quality Assurance Project Plan (MDEQ, 2018b). To date, a total of 55 samples from 39 locations in the St. Joseph River watershed were collected by EGLE, WRD, and analyzed by Eurofins TestAmerica.

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 HPDE 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.

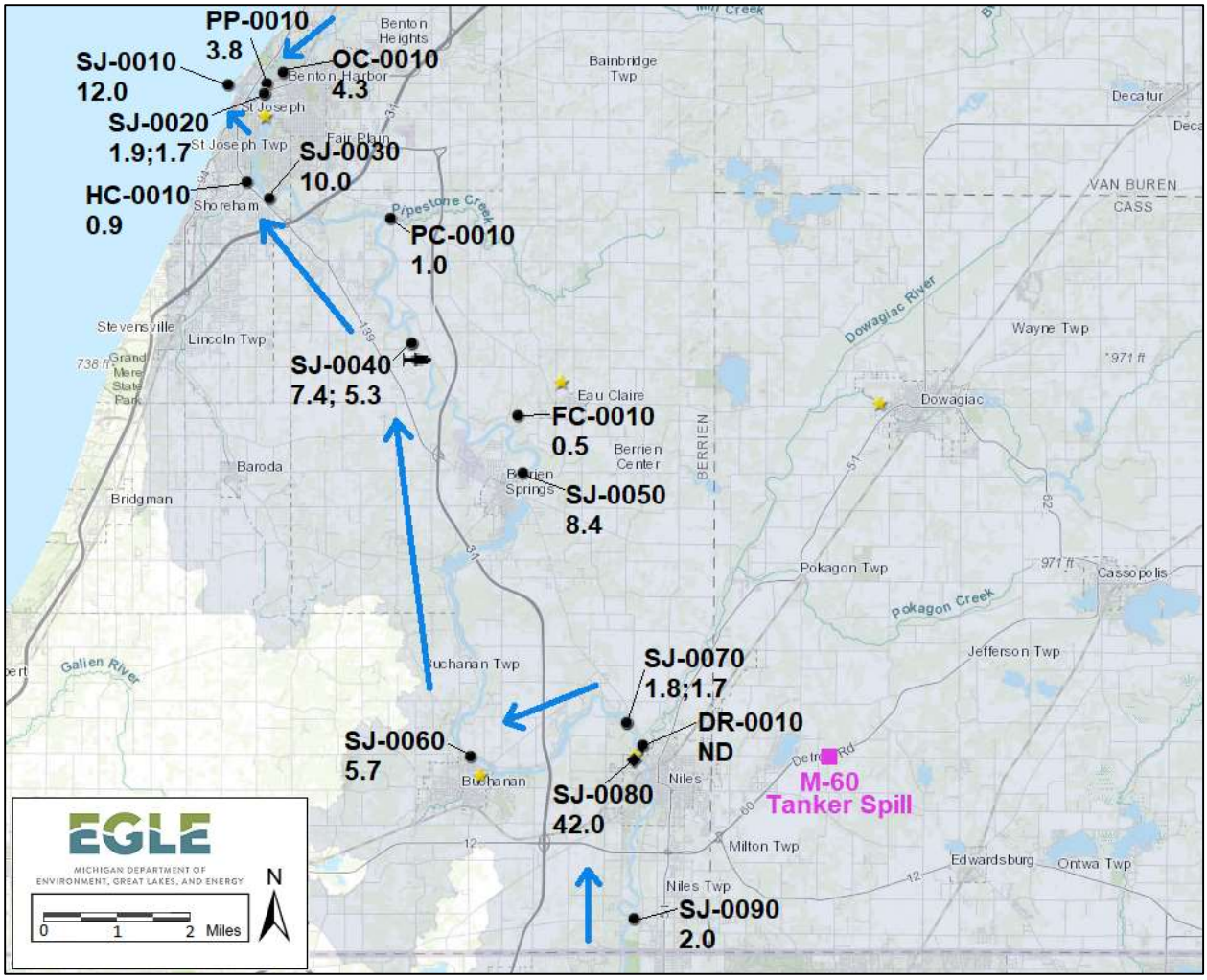

Figure 1. Overview map of the St. Joseph River watershed downstream of Indiana with surface water PFOS concentrations (ng/L) at locations sampled on September 19, 2018. SJ denotes a location on the St. Joseph River; PP is the Paw Paw River; OC is Ox Creek; HC is Hickory Creek; PC is Pipestone Creek; FC is Farmers Creek; DR is the Dowagiac River. The blue arrows indicate general river flow direction. ◆ indicates a sample location with a Part 4, Rule 57 HNV exceedance. ★ indicates approximate location of a wastewater treatment plant or sewage lagoon. ■ indicates approximate location of a known or suspected PFAS site. ➨ indicates approximate location of a fish collection site for the “Eat Safe Fish” guidelines.

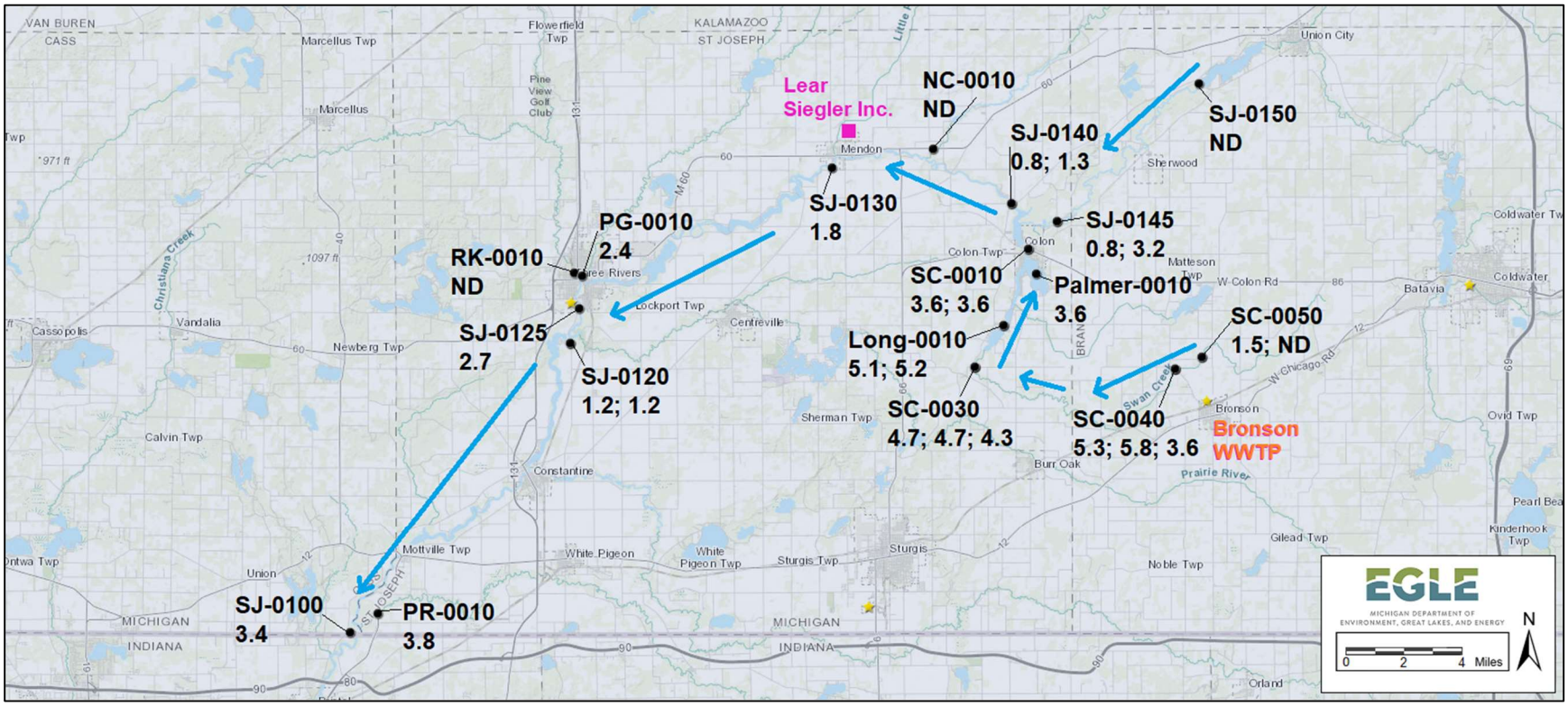

Figure 2. Overview map of the St. Joseph River watershed upstream of Indiana with surface water PFOS concentrations (ng/L) at locations sampled on August 21 and September 19, 2018. SJ denotes a location on the St. Joseph River; RK is the Rocky River; PG is the Portage River; NC is Nottawa Creek; SC is Swan Creek; Palmer and Long are two impoundments of Swan Creek. The blue arrows indicate general river flow direction. ◆ indicates a sample location with a Part 4, Rule 57 HNV exceedance. ★ indicates approximate location of a wastewater treatment plant. ■ indicates approximate location of a known or suspected PFAS site. ➨ indicates approximate location of a fish collection site for the “Eat Safe Fish” guidelines.

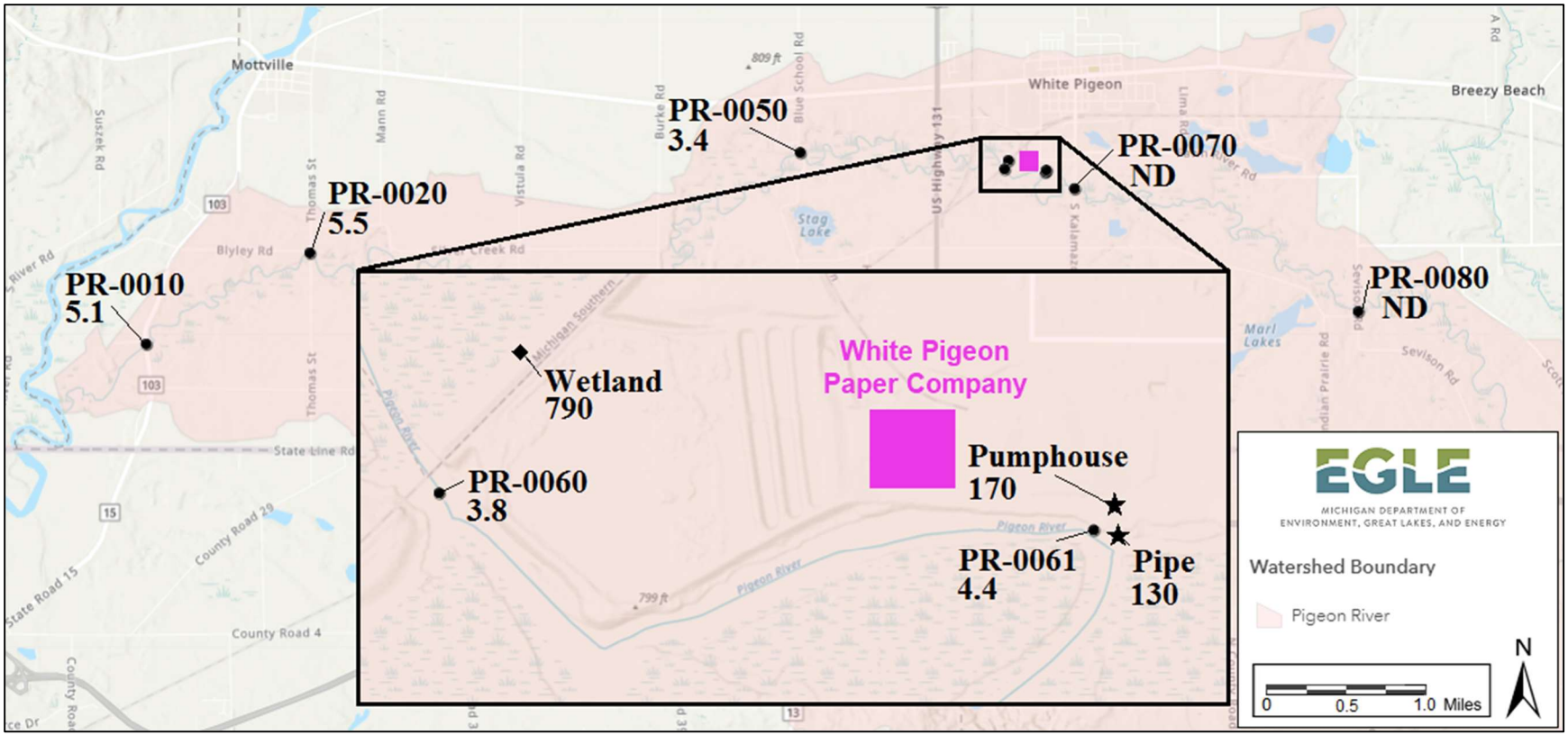

Figure 3. Overview map of the Pigeon River watershed with PFOS concentrations (ng/L) at locations sampled on March 9, 2020. PR denotes a location on the Pigeon River; Wetland is a wetland area adjacent to the former White Pigeon Paper Company property. ◆ indicates a sample location with a Part 4, Rule 57 HNV exceedance. ★ indicates a discharging water sample collected at the former White Pigeon Paper Company property. ■ indicates approximate location of a known or suspected PFAS site.

Samples were preserved on ice and shipped via overnight delivery to the Eurofins TestAmerica 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 (2009), a process using isotope dilution for analyte quantification. The laboratory provided analytical results for 24 perfluorinated compounds to EGLE, WRD, Surface Water Assessment Section (SWAS), in an electronic spreadsheet format as well as in a Level 2 report (a Level 2 report includes a brief narrative, results, and basic quality control results).

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 sets of samples in succession at the same sample location. One replicate sample was collected in August 2018 and March 2020 and three replicates were collected in September 2018. One duplicate, consisting of a one-liter composite sample dispensed into two sets of two 250 mL HDPE bottles, was collected in August 2018 and March 2020 and two duplicates were collected in September 2018. One field blank was collected during all sampling events by filling a clean set of sample bottles with PFAS free deionized water in the field. A trip blank was analyzed for all surface water 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 1. Perfluoroalkyl and polyfluoroalkyl substances (PFAS) analyzed by the Eurofins TestAmerica Sacramento 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
Perfluorooctanoic acid	PFOA	335-67-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorobutanoic acid	PFBA	375-22-4
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorohexanesulfonic acid	PFHxS	355-46-4

Compound	Abbreviation	CAS
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorooctanesulfonamide	PFOSA	754-91-6
Fluorotelomer sulphonic acid 8:2	FtS 8:2	39108-34-4
Fluorotelomer sulphonic acid 6:2	FtS 6:2	27619-97-2
Fluorotelomer sulphonic acid 4:2	FtS 4:2	757124-72-4
2-(N-Ethylperfluorooctanesulfonamido) acetic acid	N-EtFOSAA	2991-50-6
2-(N-Methylperfluorooctanesulfonamido) acetic acid	N-MeFOSAA	2355-31-9

Ambient Water Sampling: Swan Creek Watershed

Initial ambient surface water samples were collected from the Swan Creek watershed for PFAS analysis on August 21, 2018. Sampling locations were selected to determine if the effluent from the Bronson WWTP resulted in elevated PFAS concentrations in Swan Creek and the St. Joseph River. Grab samples of ambient surface water were collected by the SWAS from the main flow of the St. Joseph River at two locations (upstream and downstream of the confluence with Swan Creek), and six locations on Swan Creek, which includes Palmer and Long Lake impoundments of the creek (Table 3; Figure 1).

No United States Geological Survey (USGS) gaging station is located on Swan Creek. However, a USGS gaging station is located on nearby Prairie River near Bronson (USGS 040975299). The river flow on August 21 was 86.4 cubic feet per second (cfs), which is greatest flow over the last five years (median for this date and location is 37 cfs). Heavy precipitation had occurred in the area just prior to when the first sample was collected at 11:55 am near Allegan, Michigan. Following this storm, the river flow increased to ~ 900 cfs at the Battle Creek, Michigan, USGS gaging station. By 3:00 pm on August 6 the river flow reduced to ~ 550 cfs and remained at this level until the sample collection was completed on August 7.

Ambient Water Sampling: St. Joseph River Watershed

The more intensive watershed scale sampling occurred on September 19, 2018. Sampling locations were selected to bracket potential sources of PFAS contamination. Grab samples of ambient surface water were collected by the SWAS from the main flow of the St. Joseph River at 16 locations including two repeat locations near the Swan Creek confluence. Samples were also collected in Ox Creek, Paw Paw River, Hickory Creek, Pipestone Creek, Farmers Creek, Dowagiac River, Pigeon River, Rocky River, Portage River, and Nottawa Creek near their confluence. Additionally, five locations on Swan Creek were collected to repeat the sampling effort from the August 2018 effort (Table 3; Figure 1). According to the USGS gaging station on the St. Joseph River near Niles (USGS 04101500), the river flow on September 19 was ~ 2,500 cfs, which is slightly above the 88-year median for this date and location (~ 2,000 cfs).

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 25 % except for PFTriA in March 2020 (44 %)
Precision	Field Sample Replication/Duplication	%RPD < 30%	RPD < 30 % except SJ-0020 (PFBS = 32.3 %) SJ-0040 (PFOA = 31.6 %; PFOS = 33.1 %; PFHpA = 65.1 %; PFNA = 121.0 %; PFHxS = 45.2 %; PFPeS = 36.1 %) SJ-0120 (PFPeA = 35.3 %; PFHpA = 72.7 %) Long-0010 (PFBA = 90.5 %; PFPeA = 58.6 %; PFHpA = 33.3 %) SC-0040 (PFOS = 46.8 %)
Accuracy/Bias	1 Lab Control Spike (LCS) and 1 MS/MSD per preparation batch	60 to 140 % recovery	Analyte recovery ranged from 88 to 123 %
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 < 150 % except for 1. FtS 6:2 DR-0010 (157 %); OC-0010 (163 %); PR Wetland (194 %) 2. FtS 4:2 PR Wetland (184 %) 3. FtS 8:2 PR Wetland (180 %)
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	$\frac{47}{55} * 100 = 85.5$ % for all analytes $\frac{53}{55} * 100 = 96.4$ % for PFOS/PFOA

Ambient Water Sampling: Pigeon River

On March 9, 2020, as a part of an inspection at the former White Pigeon Paper Company in White Pigeon, Michigan, the WRD collected ten surface water samples from eight locations in the Pigeon River watershed upstream and downstream of the White Pigeon Paper Company property (Table 3). Two additional samples were collected from water being directly discharged into the Pigeon River (one from an overflowing pumphouse and one from a pipe coming from the pumphouse). According to the USGS gaging station on the Pigeon River near Scott, Indiana (USGS 04099750), the river flow on March 9 was ~ 650 cfs, which is above the 51-year median for this date and location (~ 500 cfs). WRD staff noted that the river was above the banks at the time of sampling and the gaging station listed the water level as being in the flood action stage.

Fish Tissue

Rock bass (*Ambloplites rupestris*), smallmouth bass (*Micropterus dolomieu*), and common carp (*Cyprinus carpio)* were collected by the WRD from the St. Joseph River near surface water sampling site SJ-0040 in Royalton Township on September 11, 2013. Largemouth bass (*M. salmoides*) and bluegill (*Lepomis macrochirus*) were collected by the WRD from the Palmer and Long Lake impoundments on August 21, 2018. Fish were collected using standard electrofishing or netting equipment and were prepared as standard edible portion samples following the SWAS Procedure WRD-SWAS-004 (MDEQ, 1995). Fish tissue samples were analyzed for 11 perfluorinated compounds by the MDHHS Analytical Chemistry Laboratory (Table 4).

Point Source Discharges/Compliance Sampling Inspections

There are seven WWTPs, Water Resource Recovery Facilities (WRRF), or Wastewater Stabilization Lagoons (WWSL) with discharges to the St. Joseph River watershed that were identified for PFAS effluent analysis. Effluent samples from the Benton Harbor-St. Joseph WWTP, Coldwater WRRF, Sturgis WWTP, Eau Claire WWSL, Bronson WWTP, Three Rivers WWTP, and Hillsdale WWTP were collected by EGLE. All of these WWTPs are participating in the statewide IPP PFAS Initiative and have approved IPP programs.

Effluent grab samples were collected by EGLE point source monitoring staff following the Draft 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.

Table 3. PFOS and PFOA concentrations measured in surface water samples collected from the St. Joseph River watershed on August 21 and September 19, 2018. 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 Description	Latitude	Longitude	Sampling Event	PFOS (ng/L)	PFOA (ng/L)
SJ-0010	St. Joseph River near mouth	42.115066	-86.490029	Sep 2018	12.0	2.3
OC-0010	Ox Creek & N 8th St	42.120578	-86.460061	Sep 2018	4.3	2.9
PP-0010	Paw Paw River @ Klock Rd	42.115897	-86.468770	Sep 2018	3.8	4.3
SJ-0020	St. Joseph River @ W Main St	42.111677	-86.470678	Sep 2018	1.9	1.1†
SJ-0020[D]	St. Joseph River @ W Main St	42.111677	-86.470678	Sep 2018	1.7	1.4†
HC-0010	Hickory Creek @ Niles Ave	42.075258	-86.480361	Sep 2018	0.9†	1.4†
SJ-0030	St. Joseph River @ Carronde Park	42.069053	-86.467906	Sep 2018	10.0	1.3†
PC-0010	Pipestone Creek @ River Rd	42.060744	-86.401362	Sep 2018	1.0†	0.9†
SJ-0040	St. Joseph River @ Jasper Dairy Rd	42.009924	-86.389524	Sep 2018	7.4	1.6
SJ-0040[R]	St. Joseph River @ Jasper Dairy Rd	42.009924	-86.389524	Sep 2018	5.3	2.2
FC-0010	Farmers Creek @ Hipps Hollow Rd	41.980209	-86.331366	Sep 2018	0.5†	ND
SJ-0050	St. Joseph River @ Port Rd	41.956392	-86.328618	Sep 2018	8.4	2.7
SJ-0060	St. Joseph River @ E River Rd	41.840853	-86.356906	Sep 2018	5.7	3.2
SJ-0070	St. Joseph River @ Drew Dr	41.854186	-86.271251	Sep 2018	1.8†	1.7†
SJ-0070[D]	St. Joseph River @ Drew Dr	41.854186	-86.271251	Sep 2018	1.7†	1.6†
DR-0010	Dowagiac River @ Front St	41.845138	-86.262451	Sep 2018	ND	1.1†
SJ-0080	St. Joseph River @ Marmont St	41.839110	-86.266948	Sep 2018	***42.0***	1.8
SJ-0090	St. Joseph River @ W Bertrand Rd	41.774290	-86.267168	Sep 2018	2.0	1.6†
SJ-0100	St. Joseph River @ S. River Rd	41.760256	-85.791934	Sep 2018	3.4	1.5†
PR-0010	Pigeon River @ M-103	41.769988	-85.773166	Sep 2018	3.8	1.6†
PR-0010	Pigeon River @ M-103	41.769988	-85.773166	Mar 2020	5.1	1.5†
PR-0020	Pigeon River @ Thomas Rd	41.779686	-85.750322	Mar 2020	5.0	1.6†
PR-0020[R]	Pigeon River @Thomas Rd	41.779686	-85.750322	Mar 2020	5.5	1.7†
PR-0050	Pigeon River @ Blue School Rd	41.790290	-85.681807	Mar 2020	3.4	1.6
PR Wetland	Wetland west of White Pigeon Paper Company	41.789453	-85.652566	Mar 2020	***790***	110
PR-0060	Pigeon River @ White Pigeon Paper Company	41.788567	-85.653063	Mar 2020	3.8	1.8

† Concentration is above the method detection limit but below the laboratory reporting limit.
[D] Duplicate Site
[R] Replicate Site

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	PFOS (ng/L)	PFOA (ng/L)
PR-0061	Pigeon River @ White Pigeon Paper Company d/s Pipe	41.788262	-85.647533	Mar 2020	4.4	2.1
PR-0070	Pigeon River @ Kalamazoo St	41.788271	-85.647366	Mar 2020	ND	ND
PR-0070[D]	Pigeon River @ Kalamazoo St	41.779686	-85.750322	Mar 2020	ND	ND
PR-0080	Pigeon River @ Sevison Rd	41.788380	-85.647302	Mar 2020	ND	ND
SJ-0120	St. Joseph River @ Constantine Rd	41.909626	-85.639525	Sep 2018	1.2†	1.6†
SJ-0120[R]	St. Joseph River @ Constantine Rd	41.909626	-85.639525	Sep 2018	1.2†	1.5†
SJ-0125	St. Joseph River @ 3 Rivers LL	41.927550	-85.633909	Sep 2018	2.7	1.5†
RK-0010	Rocky River @ Moore St	41.945819	-85.637251	Sep 2018	ND	ND
PG-0010	Portage River @ E Michigan Ave	41.944125	-85.631378	Sep 2018	2.4	3.0
SJ-0130	St. Joseph River & S. Railroad St.	41.999943	-85.458781	Sep 2018	1.8	ND
NC-0010	Nottawa Creek @ M-60	42.009414	-85.388227	Sep 2018	ND	0.9†
SJ-0140	St. Joseph River @ N Farrand Rd	41.981423	-85.334367	Aug 2018	0.8†	1.0†
SJ-0140	St. Joseph River @ N Farrand Rd	41.981423	-85.334367	Sep 2018	1.3†	0.9†
SC-0010	Swan Creek @ E. State Rd	41.958217	-85.322660	Aug 2018	3.6	ND
SC-0010	Swan Creek @ E. State Rd	41.958217	-85.322660	Sep 2018	3.6	0.9†
Palmer-0010	Palmer Lake	41.945465	-85.317056	Aug 2018	3.6	ND
Long-0010	Long Lake	41.918707	-85.339424	Aug 2018	5.1	ND
Long-0010[D]	Long Lake	41.918707	-85.339424	Aug 2018	5.2	0.9†
SC-0030	Swan Creek @ Townline rd	41.897427	-85.359635	Aug 2018	4.7	ND
SC-0030[R]	Swan Creek @ Townline rd	41.897427	-85.359635	Aug 2018	4.7	ND
SC-0030	Swan Creek @ Townline rd	41.897427	-85.359635	Sep 2018	4.3	ND
SC-0040	Swan Creek @ Burr Oak Rd	41.896124	-85.220674	Aug 2018	5.3	ND
SC-0040	Swan Creek @ Burr Oak Rd	41.896124	-85.220674	Sep 2018	5.8	ND
SC-0040[R]	Swan Creek @ Burr Oak Rd	41.896124	-85.220674	Sep 2018	3.6	ND
SC-0050	Swan Creek @ Horkey Rd	41.902226	-85.202339	Aug 2018	1.2†	ND
SC-0050	Swan Creek @ Horkey Rd	41.902226	-85.202339	Sep 2018	ND	ND
SJ-0145	St. Joseph River @ Stowell Rd	41.972439	-85.302719	Aug 2018	0.8†	1.1†
SJ-0145	St. Joseph River @ Stowell Rd	41.972439	-85.302719	Sep 2018	3.2	1.1†
SJ-0150	St. Joseph River @ Riley Rd	42.043339	-85.204213	Sep 2018	ND	ND

† Concentration is above the method detection limit but below the laboratory reporting limit.
[D] Duplicate Site
[R] Replicate Site

Table 4. Perfluorinated compounds analyzed in fish tissue by the Michigan Department of Health and Human Services (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

RESULTS AND DISCUSSION

St. Joseph River Watershed Sampling

A total of 45 surface water samples were collected at 32 locations over the course of the two 2018 sampling events. PFOS and PFOA were detected in 40 (88.9 percent) and 30 (66.7 percent) of the total collected samples, respectively (Table 3). The analytes PFHxS, PFBS, and PFBA were detected in all 45 samples (Figure 4). PFPeA, PFHpA, PFHxA, and PFNA were detected in 41, 40, 36, and 20 samples, respectively. FtS 6:2 (seven detections), PFPeS (five detections), PFHpS (three detections), PFTeA (two detections), and FOSA and PFDA (one detection) were also detected in at least one sample. FtS 8:2, FtS 4:2, NEtFOSAA, NmEFOSA, PFNS, PFDS, PFTriA, PFDoA, and PFUnA were not detected in any surface water sample.

St. Joseph River (Main Branch)

The Hillsdale WWTP, Litchfield WWSL, Jonesville WWTP, and North Adams WWSL all discharge treated municipal wastewater to the headwaters of the St. Joseph River in Hillsdale County. Hillsdale WWTP has an IPP and participated in the IPP Initiative. They found no industrial sources of PFAS and WWTP effluent samples were non-detectable for PFOS and PFOA. Litchfield WWSL is developing an IPP and will be required to conduct an evaluation of potential PFAS sources. Jonesville WWTP and North Adams WWSL discharge into the watershed but do not have IPPs and did not participate in the IPP Initiative.

A total of 22 surface water samples at 16 locations were collected over the two 2018 sampling events from the main branch of the St. Joseph River and analyzed for PFAS (Table 5). No samples collected from the St. Joseph River during either sampling event exceeded the HNV for PFOA, ranging from non-detect to 3.2 ng/L. Our furthest downstream sample (SJ-0010) was collected near the mouth of the St. Joseph River and had a PFOS concentration of 12.0 ng/L, which is equivalent to the PFOS HNV. Concentrations of PFOS in fillets of common carp, smallmouth bass, and rock bass near SJ-0040 averaged 21.0, 50.7, and 21.7 µg/kg in fish

collected from the St. Joseph River near SJ-0040 in 2013. The smallmouth bass and carp tissue PFOS concentrations exceed the MDHHS “Eat Safe Fish” screening values and would cause an advisory in these species; however, PCBs cause more restrictive advice. The rock bass PFOS tissue concentration resulted in a MDHHS “Eat Safe Fish” advisory of one meal per month. In October 2018 a sample of the effluent from the Benton Harbor-St. Joseph WWTP had a PFOS and PFOA concentration of 8.2 and 6.1 ng/L, respectively (Table 6). The Benton Harbor-St. Joseph WWTP participated in the IPP PFAS Initiative and identified Tech Nickel Inc as a PFOS source (27.7 ng/L). Additional sampling has been performed as part of the source evaluation. The Buchanan WWTP participated in the IPP PFAS Initiative and identified the Southeast Berrien County Landfill as a source of PFOS (71.9 ng/L) and PFOA (519 ng/L). Individual landfill cells have since been sampled as the evaluation of this source continues. On January 24 and October 16, 2019, the Buchanan WWTP effluent was tested and was non-detect for PFOS; however, PFOA was present in the effluent up to 53 ng/L (Table 6).

PFOS exceeded the HNV and was detected at 45 ng/L in a surface water sample collected from the St. Joseph River near Niles (SJ-0080; Table 3). This was the only sample collected that exceeded the HNV for PFOS. The Niles WWTP also participated in the IPP Initiative and eliminated their only probable source, landfill leachate from the Southeast Berrien County Landfill, which they received periodically. Leachate acceptance was eliminated on February 5, 2019. The Niles WWTP sampled their influent and effluent on January 8, 2019, for PFOS and PFOA and the results were <10 ng/L for both pollutants (Table 6).

The Lear Siegler, Inc. PFAS site where groundwater sampling revealed combined PFOS and PFOA concentrations up to 1,312 ng/L is situated adjacent to the Little Portage Creek. While we did not sample the Little Portage Creek as a part of this effort, the surface water sampling location SJ-0130 near Mendon is approximately 0.8 kilometers downstream of the confluence of Little Portage Creek on the St. Joseph River (Figure 2). The surface water PFOS concentration was 1.8 ng/L and was non-detect for PFOA (Table 3).

Swan Creek Watershed Sampling

A total of 13 samples from six locations were collected from Swan Creek over the two 2018 sampling events. PFOS concentrations ranged from non-detect at the furthest upstream sample to 5.8 ng/L in a sample collected downstream of the Bronson WWTP. The Palmer and Long Lake impoundments had slightly elevated PFOS concentrations of 3.6 and 5.2 ng/L, respectively. PFOS concentrations at revisited sampling locations within the watershed were similar between the August and September 2018 sampling events (3.2 ng/L and 2.6 ng/L, respectively). In May 2018 a sample of the effluent from the Bronson WWTP had a PFOS and PFOA concentration of 190 and 2.8 ng/L, respectively (Table 6). A sample collected by the city of Bronson from the clarifier outfall at the Bronson Plating Company showed that a waste stream being sent to the Bronson WWTP had a PFOS concentration of 240,000 ng/L. Concentrations of PFOS in fillets of bluegill and largemouth bass collected from the Palmer Lake impoundment in 2018 averaged 6.4 and 12.0 micrograms per kilogram (µg/kg), respectively. Concentrations of PFOS in fillets of bluegill and largemouth bass collected from the Long Lake impoundment in 2018 averaged 10.3 and 17.9 µg/kg, respectively. The fish tissue PFOS concentrations from these water bodies exceed the MDHHS “Eat Safe Fish” screening values and would cause an advisory in these species; however, mercury causes more restrictive advice.

Other St. Joseph River Tributaries

In addition to the Swan Creek sampling, samples from 10 other tributaries near their confluence were collected in August 2018 (Table 3). None of these samples exceeded the HNV for PFOS. Pipestone Creek, Hickory Creek, Farmers Creek, Dowagiac River, Rocky River, and Nottawa Creek had either a non-detectable PFOS concentration or it was below the laboratory reporting limit (~ 2 ng/L). The PFOS concentration in the Portage River, Pigeon River, Paw Paw River, and Ox Creek had a PFOS concentration of 2.4, 3.8, 3.8, and 4.3 ng/L, respectively, during the 2018 sampling events (Table 3).

Table 5. Total PFAS concentrations (the sum of 24 analytes above their detection limit) detected in surface water samples collected from locations in the St. Joseph River watershed on August 21 and September 19, 2018. Revisited locations are in bold.

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	Σ PFAS (ng/L)	# Analytes Detected
SJ-0010	St. Joseph River near mouth	42.115066	-86.490029	Sep 2018	27.5	10
OC-0010	Ox Creek & N 8th St	42.120578	-86.460061	Sep 2018	21.3	10
PP-0010	Paw Paw River @ Klock Rd	42.115897	-86.468770	Sep 2018	14.9	9
SJ-0020	St. Joseph River @ W Main St	42.111677	-86.470678	Sep 2018	13.1	9
SJ-0020[D]	St. Joseph River @ W Main St	42.111677	-86.470678	Sep 2018	12.5	9
HC-0010	Hickory Creek @ Niles Ave	42.075258	-86.480361	Sep 2018	10.1	8
SJ-0030	St. Joseph River @ Carronde Park	42.069053	-86.467906	Sep 2018	20.8	9
PC-0010	Pipestone Creek @ River Rd	42.060744	-86.401362	Sep 2018	7.9	8
SJ-0040	St. Joseph River @ Jasper Dairy Rd	42.009924	-86.389524	Sep 2018	18.5	9
SJ-0040[R]	St. Joseph River @ Jasper Dairy Rd	42.009924	-86.389524	Sep 2018	27.5	12
FC-0010	Farmers Creek @ Hipps Hollow Rd	41.980209	-86.331366	Sep 2018	2.5	4
SJ-0050	St. Joseph River @ Port Rd	41.956392	-86.328618	Sep 2018	36.9	12
SJ-0060	St. Joseph River @ E River Rd	41.840853	-86.356906	Sep 2018	40.3	13
SJ-0070	St. Joseph River @ Drew Dr	41.854186	-86.271251	Sep 2018	13.0	9
SJ-0070[D]	St. Joseph River @ Drew Dr	41.854186	-86.271251	Sep 2018	12.2	8
DR-0010	Dowagiac River @ Front St	41.845138	-86.262451	Sep 2018	4.7	6
SJ-0080	St. Joseph River @ Marmont St	41.839110	-86.266948	Sep 2018	57.9	11
SJ-0090	St. Joseph River @ W Bertrand Rd	41.774290	-86.267168	Sep 2018	13.4	9
SJ-0100	St. Joseph River @ S. River Rd	41.760256	-85.791934	Sep 2018	11.3	8
PR-0010	Pigeon River @ M-103	41.769988	-85.773166	Sep 2018	11.1	9
PR-0010	Pigeon River @ M-103	41.769988	-85.773166	Mar 2020	11.4	8
PR-0020	Pigeon River @ Thomas Rd	41.779686	-85.750322	Mar 2020	10.9	8
PR-0020[R]	Pigeon River @Thomas Rd	41.779686	-85.750322	Mar 2020	11.8	8
PR-0050	Pigeon River @ Blue School Rd	41.790290	-85.681807	Mar 2020	10.1	9
PR Wetland	Wetland west of WPP	41.789453	-85.652566	Mar 2020	1729.8	14
PR-0060	Pigeon River @ WPP	41.788567	-85.653063	Mar 2020	11.1	9
PR-0061	Pigeon River @ WPP d/s Pipe	41.788262	-85.647533	Mar 2020	12.0	9
PR-0070	Pigeon River @ Kalamazoo St	41.788271	-85.647366	Mar 2020	4.8	6
PR-0070[D]	Pigeon River @ Kalamazoo St	41.779686	-85.750322	Mar 2020	5.2	7

[D] Duplicate Site
[R] Replicate Site

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	Σ PFAS (ng/L)	# Analytes Detected
PR-0080	Pigeon River @ Sevison Rd	41.788380	-85.647302	Mar 2020	5.3	7
SJ-0120	St. Joseph River @ Constantine Rd	41.909626	-85.639525	Sep 2018	15.6	9
SJ-0120[R]	St. Joseph River @ Constantine Rd	41.909626	-85.639525	Sep 2018	10.3	8
SJ-0125	St. Joseph River @ 3 Rivers LL	41.927550	-85.633909	Sep 2018	11.0	9
RK-0010	Rocky River @ Moore St	41.945819	-85.637251	Sep 2018	3.6	5
PG-0010	Portage River @ E Michigan Ave	41.944125	-85.631378	Sep 2018	13.5	8
SJ-0130	St. Joseph River & S. Railroad St.	41.999943	-85.458781	Sep 2018	7.1	7
NC-0010	Nottawa Creek @ M-60	42.009414	-85.388227	Sep 2018	3.8	5
SJ-0140	St. Joseph River @ N Farrand Rd	41.981423	-85.334367	Aug 2018	8.6	9
SJ-0140	St. Joseph River @ N Farrand Rd	41.981423	-85.334367	Sep 2018	7.9	8
SC-0010	Swan Creek @ E. State Rd	41.958217	-85.322660	Aug 2018	14.4	8
SC-0010	Swan Creek @ E. State Rd	41.958217	-85.322660	Sep 2018	10.7	8
Palmer-0010	Palmer Lake	41.945465	-85.317056	Aug 2018	11.6	6
Long-0010	Long Lake	41.918707	-85.339424	Aug 2018	11.8	8
Long-0010[D]	Long Lake	41.918707	-85.339424	Aug 2018	17.8	10
SC-0030	Swan Creek @ Townline Rd	41.897427	-85.359635	Aug 2018	11.9	6
SC-0030[R]	Swan Creek @ Townline Rd	41.897427	-85.359635	Aug 2018	12.0	7
SC-0030	Swan Creek @ Townline Rd	41.897427	-85.359635	Sep 2018	9.1	7
SC-0040	Swan Creek @ Burr Oak Rd	41.896124	-85.220674	Aug 2018	13.1	7
SC-0040	Swan Creek @ Burr Oak Rd	41.896124	-85.220674	Sep 2018	9.1	5
SC-0040[R]	Swan Creek @ Burr Oak Rd	41.896124	-85.220674	Sep 2018	7.6	6
SC-0050	Swan Creek @ Horkey Rd	41.902226	-85.202339	Aug 2018	7.1	5
SC-0050	Swan Creek @ Horkey Rd	41.902226	-85.202339	Sep 2018	2.6	3
SJ-0145	St. Joseph River @ Stowell Rd	41.972439	-85.302719	Aug 2018	12.1	9
SJ-0145	St. Joseph River @ Stowell Rd	41.972439	-85.302719	Sep 2018	11.0	9
SJ-0150	St. Joseph River @ Riley Rd	42.043339	-85.204213	Sep 2018	9.2	7

[D] Duplicate Site
[R] Replicate Site

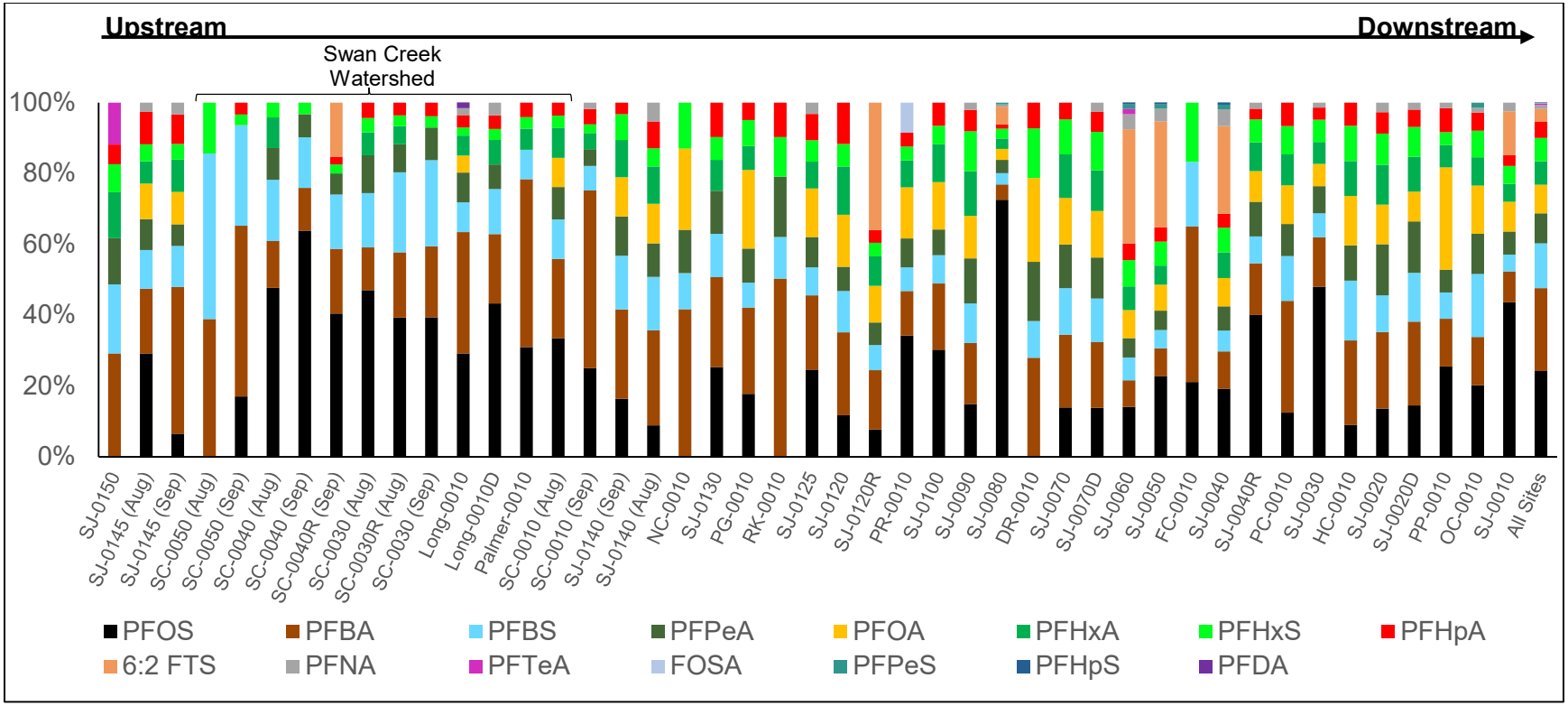

Figure 4. Percentage composition of PFAS measured in surface water collected in the St. Joseph River watershed in August or September 2018. Sample IDs are shown (SJ is the St. Joseph River; SC is Swan Creek; Long and Palmer are impoundments of Swan Creek; NC is Nottawa Creek; PG is the Portage River; RK is the Rocky River; PR is the Pigeon River; DR is the Dowagiac River; FC is Farmers Creek; HC is Hickory Creek; PP is the Paw Paw River; OC is Ox Creek). '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.

2020 Pigeon River Watershed Sampling

At the time of the White Pigeon Paper Company inspection, two samples were collected from water being actively discharged into the Pigeon River. The first sample was collected from a pumphouse that was overflowing onto the ground and into the Pigeon River. The PFOS and PFOA concentration in this sample was 170 and 48 ng/L, respectively. The second sample was collected from a pipe leading out of the pumphouse and was discharging directly into the river. The PFOS and PFOA concentration in this sample was 130 and 34 ng/L, respectively. PFOS and PFOA in the Pigeon River were not detected in the two samples from the Pigeon River collected upstream of the White Pigeon Paper Company in March 2020. In comparison, PFOS and PFOA were detected in all 8 surface water samples near or downstream of White Pigeon Paper Company with concentrations up to 5.5 ng/L and 1.9 ng/L being measured in the river, respectively (Table 3; Figure 5). A wetland directly to the west of the former White Pigeon Paper Company property had PFOS and PFOA concentrations of 790 and 110 ng/L, respectively (Table 3; Figure 5). The PFOS concentration in the wetland exceeds the PFOS HNV of 12 ng/L. High water levels and flooded conditions at the time of sampling likely diluted the PFAS in the river at the time of the 2020 sampling.

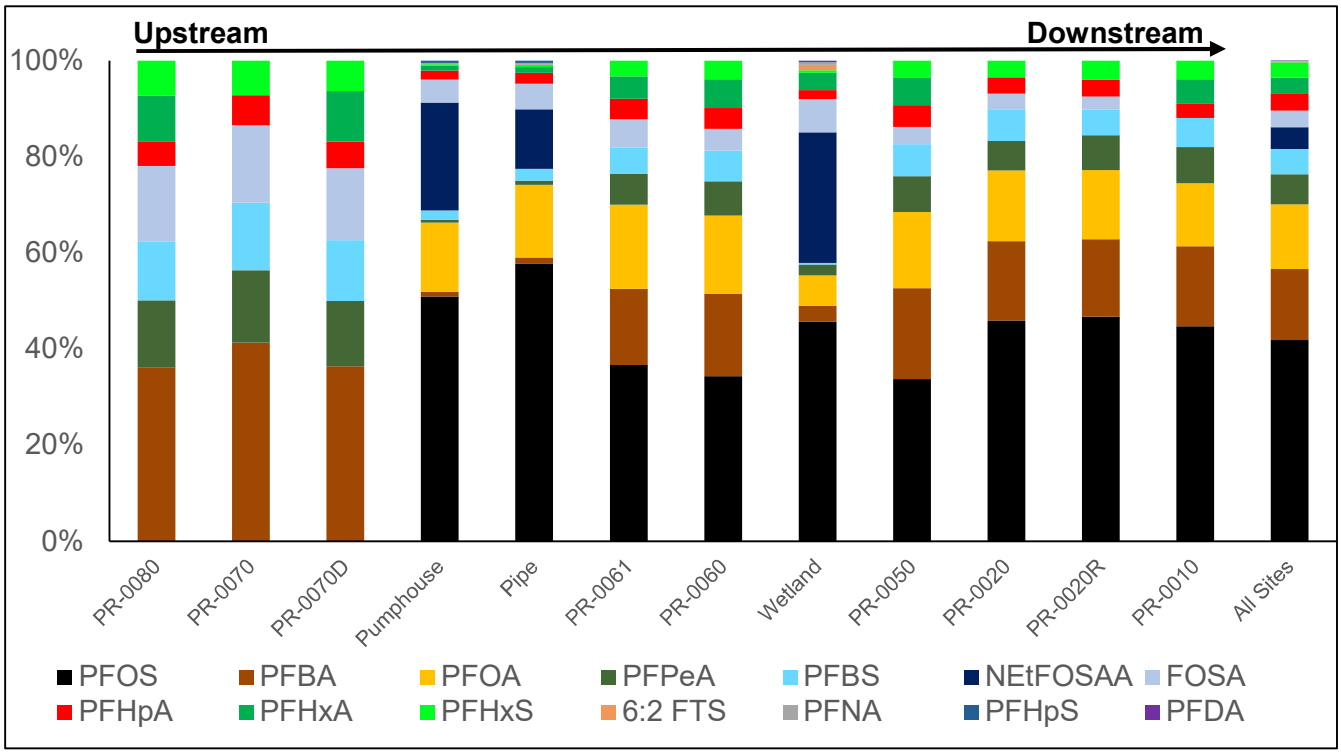

Figure 5. Percentage composition of PFAS measured in surface water collected in the Pigeon River watershed in March 2020. Sample IDs are shown (PR is the Pigeon River; Wetland is a wetland adjacent to the former White Pigeon Paper property; Filter Screen Pipe and Pumphouse are two samples collected from areas of direct discharge to the Pigeon River from the former White Pigeon Paper property). '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.

Ambient Water Sampling QA/QC

Neither PFOS nor PFOA were measured above their respective detection limit in the equipment, field, and trip blanks with the exception of PFOS, which was detected in one of the Swan Creek equipment blanks. This sample had a PFOS concentration of 0.64 ng/L, which is below the laboratory reporting

limit of 2.0 ng/L. All other analytes in the August 2018 blanks were below laboratory detection limits in these blanks with a few exceptions: PFHxS was measured below the laboratory reporting limit at 0.30, 0.22, and 0.26 ng/L in the St. Joseph River watershed field, trip, and equipment blank, respectively. This analyte was also detected at 0.21, 0.28, and 0.28 ng/L in the 2020 Pigeon River sampling trip, field, and equipment blanks, respectively. PFHxS was also detected below the reporting limit at 0.33 and 0.30 ng/L in the Swan Creek equipment and trip blank. PFHxS was detected at a similar level in the laboratory method blanks, indicating the source was most likely within the analytical process. PFHxA was detected at 0.77 ng/L in the Field Blank during this sampling event. PFBA was detected below the laboratory reporting limit at 0.51 ng/L in the Swan Creek trip blank and at 0.60 ng/L and 0.65 ng/L in the 2020 Pigeon River equipment and field blanks, respectively.

Five replicate and four duplicate samples were collected over all three sampling events. The replicate sample SJ-0040 had an RPD of 33.1 and 31.6 percent for PFOS and PFOA., respectively, which exceeds the RPD threshold of 30 percent. Additionally, the PFOS RPD in the SC-0040R replicate sample exceeded the threshold (46.8 percent). The PFOS RPD at the SJ-0020D, SJ-0070D, Long-0010D, SJ-0120R, and SC-0030R locations was 0, 0, 1.9, 5.7, and 11.1 percent, respectively. The PFOA RPD for these locations was 6.5, 0, 4.8, 5.7, and 24.0 percent, respectively. Five of these QA samples exceeded the RPD for at least one PFAS (Table 2) with the highest RPD exceedance being 121.0 percent for the PFNA analyte in the SJ-0040R sample. All other data quality control objectives and criteria were met except for the recovery of 6:2 FTS (three samples), 4:2 FTS (1 sample), and 8:2 FTS (1 sample) exceeding the 150 percent upper threshold (Table 2). The recovery of 6:2 FTS in the DR-0010, OC-0010, and Wetland samples was 157, 163, and 194 percent, respectively. The recovery of 4:2 FTS and 8:2 FTS in the Wetland sample was 184 and 180 percent, respectively. Therefore, the QA/QC completeness objective (> 90 percent) was not met when considering all 24 PFAS analytes (Table 2). However, the completeness QA/QC criteria for PFOS or PFOA was met (96.4 percent). Therefore, the failure to meet these data quality objectives did not impact our determination as to whether PFAS sources are present in the watershed. In support of this statement, similar RPD exceedances were found in other watersheds (i.e., River Raisin) where a source was later confirmed following the surface water monitoring effort.

Table 6. Point Source Discharges/Compliance Sampling Results. 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)
Benton Harbor – St. Joseph WWTP	10/11/2018	8.2	6.1	54.9
Benton Harbor – St. Joseph WWTP	11/20/2018	3.8	3.2	14.3
Benton Harbor – St. Joseph WWTP	8/29/2019	11	6.4	41.3
Eau Claire WWSL	10/11/2018	4.4	8.9	58.6
Buchanan WWTP	1/24/2019	ND	34.3	397.5
Buchanan WWTP	10/16/2019	ND	53	984
Niles WWTP	1/8/2019	ND	ND	ND
Three Rivers WWTP	6/8/2018	11	52	371.1
Three Rivers WWTP	9/13/2018	10.3	40.6	194.3
Three Rivers WWTP	6/7/2019	***22.3***	38.8	392.5
Three Rivers WWTP	9/13/2019	***13.3***	72.8	436.8
Three Rivers WWTP	12/20/2019	***55.2***	204.7	952.1
Sturgis WWTP	10/11/2018	3.4	3.1	43.7
Bronson WWTP	5/7/2018	***190***	2.8	212.5
Bronson WWTP	7/12/2018	***130***	6.1	221.8
Bronson WWTP	7/18/2018	***140***	13	283.9
Bronson WWTP	7/24/2018	***87***	7.7	159.7
Bronson WWTP	8/2/2018	***70***	5.6	135.2

Facility Name	Sampling Date	PFOS (ng/L)	PFOA (ng/L)	Σ PFAS (ng/L)
Bronson WWTP	9/11/2018	***250***	5.8	338.9
Bronson WWTP	10/17/2018	***360***	3.6	411.6
Bronson WWTP	11/27/2018	***83***	2.3	106.8
Bronson WWTP	12/13/2018	***37***	2.5	59.4
Bronson WWTP	1/11/2019	***16***	6.9	49.7
Bronson WWTP	2/13/2019	***18***	2.4	38.3
Bronson WWTP	3/5/2019	11	2.7	30.9
Bronson WWTP	4/1/2019	12	2.4	
Bronson WWTP	5/7/2019	***25***	2.9	45.9
Bronson WWTP	6/13/2019	***15***	ND	24.9
Bronson WWTP	7/10/2019	***13***	4	70.1
Bronson WWTP	8/5/2019	4.6	ND	16.7
Bronson WWTP	9/3/2019	***21***	4.9	75
Bronson WWTP	10/1/2019	***18***	4.7	72.9
Bronson WWTP	11/4/2019	***16***	2.9	49.1
Bronson WWTP	12/2/2019	9.5	2.0	30.1
Bronson WWTP	1/6/2020	***13***	1.6	30.5
Bronson WWTP	2/3/2020	***13***	2.2	30.4
Bronson WWTP	3/2/2020	7.3	ND	21.2
Bronson WWTP	4/6/2020	6.9	ND	19.2
Coldwater WRRF	3/12/2019	ND	ND	ND
Coldwater WRRF	5/14/2019	ND	ND	29
Coldwater WRRF	10/3/2019	ND	2.6	41.5
Quincy WWSL	11/21/2019	9.4	7.0	42.2
Hillsdale WWTP	6/19/2018	ND	ND	ND

CONCLUSIONS AND FUTURE WORK

Overall these results indicate that PFAS sources are present in the St. Joseph River watershed; however, only two surface water samples from the St. Joseph River watershed exceeded the HNV for PFOS. The source of the PFOS in the St. Joseph River near Niles has not been determined. The source of PFOS contamination in the wetland near White Pigeon is likely the former White Pigeon Paper Company. Limited sampling in the Pigeon River indicates that PFOS is present downstream of this facility; however, at concentrations not exceeding the PFOS HNV. High water levels may have diluted the concentrations at the time of sampling. Fish collections are planned in the Pigeon River to determine if consumption advisories are warranted. In the St. Joseph River, elevated PFOS concentrations were observed near Colon (SJ-0145; 3.2 ng/L), Bristol (SJ-0100; 3.4 ng/L), Buchanan (SJ-0060; 5.7 ng/L); Berrien Springs (SJ-0050; 8.4 ng/L, and SJ-0040; 7.4 ng/L), St. Joseph Charter Township (SJ-0030, 10.0 ng/L), and St. Joseph (SJ-0010; 12.0 ng/L). Elevated (> 3 ng/L) concentrations of PFOS were observed in Ox Creek (OC-0010, 4.3 ng/L) and the Paw Paw River (PP-0010, 3.8 ng/L) near their confluence.

In May 2019 the WRD found PFAS-contaminated groundwater at the former Du-Wel Metals Products manufacturing facility near Hartford. This site is adjacent to a tributary of the Paw Paw River and approximately 30 miles upstream of the PP-0010 sampling location. Further investigations are being conducted to determine if the contaminated groundwater is impacting the river and if other sources are present in the watershed. Additionally, elevated concentrations were also observed in several locations in Swan Creek. The Bronson WWTP discharge of PFOS to Swan Creek is a likely source for

the elevated tissue concentrations in fish collected from the two impoundments and the elevated surface water concentrations in Swan Creek; however, the fish consumption advisory is more restrictive due to mercury contamination. During November 2018 the Bronson Plating Company installed a Granular Activated Carbon pretreatment system, which significantly reduced their discharges of PFOS to the Bronson WWTP. The Bronson WWTP effluent has averaged approximately 16 ng/L PFOS since December 2018. Based on our limited data, the M-60 Tanker spill groundwater contamination does not appear to be impacting the Dowagiac River as PFOS was not detected in the DR-0010 sample and total PFAS was below 5 ng/L. Lastly, we plan to collect fish from the St. Joseph River near areas with elevated PFOS concentrations and the Pigeon River as fish tissue analysis can provide a more complete evaluation of water quality when bioaccumulative contaminant concentrations in the surface water are highly variable.

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