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 KALAMAZOO RIVER WATERSHED BETWEEN MARSHALL AND ALLEGAN

BACKGROUND

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

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

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

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 Kalamazoo River (HUC 04050003) drains portions of eight counties in southwest Michigan: Hillsdale, Jackson, Calhoun, Eaton, Barry, Kalamazoo, Van Buren, and Allegan. Approximately 47% of the Kalamazoo River watershed is agricultural production and 30% is terrestrial uplands (Kalamazoo River Watershed Council, 2011). The North Branch and South Branch of the Kalamazoo River meet and form the Kalamazoo River near Albion. The main tributaries to the Kalamazoo River are Wilder Creek, Rice Creek, and Bear Creek near Marshall; the Battle Creek River and Wabascon Creek near Battle Creek; Seven Mile Creek, Augusta Creek, and Gull Creek near Augusta; Davis Creek, Portage Creek, and Spring Brook near Kalamazoo; Pine Creek, the Gun River, and Schnable Brook near Otsego; Rossman Creek and Swan Creek near Allegan; and Mann Creek and the Rabbit River near Saugatuck. Approximately 80 miles of the Kalamazoo River in Allegan and Kalamazoo Counties (from Morrow Dam to Lake Michigan) and three miles of Portage Creek are part of the Allied Paper Inc./Portage Creek/Kalamazoo River Superfund Site where soil and sediments are contaminated with polychlorinated biphenyls (PCB). Various cleanups of the soils and sediments at the former paper mill sites, landfills, and along the river have occurred over the years.

Initial PFAS surface water and fish tissue samples were collected in June 2013 by EGLE, Water Resources Division (WRD) from the Kalamazoo River near Allegan, Michigan, as part of a statewide PFAS reconnaissance study (Bush et al., 2015) and found surface water concentrations of PFOS and PFOA between 6.7-7.6 ng/L and 3.4-4.3 ng/L, respectively. The surface water PFOS and PFOA concentrations at all three locations were below their respective HNV, but the concentration of PFOS in the fish indicated the need for a Michigan Department of Health and Human Services (MDHHS) “Eat Safe Fish” advisory. In January 2018 it was discovered that the use of firefighting foam during fire suppression activities at the Kellogg Air National Guard Base (ANGB) near Battle Creek contaminated groundwater with PFAS. The contaminated groundwater is likely to have been venting to nearby Helmer Creek and the Kalamazoo River. In April 2018, under the IPP PFAS Initiative, the city of Kalamazoo sampled the sanitary sewer discharge from the groundwater pumping system at the former location of Production Plated Plastics on North 34th street in Richland. Results showed high concentrations of PFOS in the discharge. Sampling of residential wells in the area by EGLE revealed groundwater concentrations exceeding the United States Environmental Protection Agency (USEPA) health advisory level of 70 ng/L. In June 2018 the Statewide Testing Initiative revealed drinking water PFOS and PFOA concentrations in the city of Parchment’s municipal water supply exceeded the USEPA’s health advisory level. In August 2018 EGLE sampled groundwater monitoring wells at the former Crown Vantage landfill and mill site in Parchment and discovered high levels of PFAS in the groundwater. For these reasons, EGLE, WRD, decided to monitor the river and select tributaries 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, WRD, collected samples at the Nolichucky Industrial Corporation near Kalamazoo and revealed high PFAS concentrations in the groundwater. This

site is adjacent to the Kalamazoo River, is located on a former paper mill property, and is also a former USEPA Superfund site.

SUMMARY

1. No surface water samples exceeded the Rule 57 aquatic life values for PFOS or PFOA.
2. PFOS was detected at all sampling locations with the exception of Harts Lake near Battle Creek. Concentrations at riverine locations ranged from 0.6 ng/L at the furthest upstream location (downstream of Marshall Dam) to 98 ng/L in Helmer Creek near Battle Creek (Sample location HC-0200).
3. The PFOA concentration at the riverine locations was below the Rule 57 HNV at all sample locations and ranged from non-detect (< 0.9 ng/L) to 21 ng/L.
4. The PFOS surface water concentration in the Kalamazoo River exceeded the Rule 57 HNV at two locations immediately downstream of Battle Creek, two locations near Parchment, and one location in Otsego.
5. PFOS would cause a MDHHS “Eat Safe Fish” advisory in largemouth and smallmouth bass, bluegill/sunfish, and common carp downstream of the Morrow Dam to the Kalamazoo River mouth; however, there is a MDHHS “Eat Safe Fish” ‘Do not eat’ advisory for all fish species from this section of the Kalamazoo River due to PCBs.
6. Largemouth bass, rock bass, and common carp collected from the Marshall Dam impoundment in 2013 did not result in a MDHHS “Eat Safe Fish” advisory.
7. The PFOS concentration in surface waters near the Kalamazoo River on the former Crown Vantage site near Parchment ranged from 4,700 to 9,500 ng/L. The PFOS concentration in the sample from the on-site clarifier was 3,100 ng/L.
8. The PFOS surface water concentration was below the Rule 57 HNV in both Gull Lake and the Markin Glen Park fishing ponds.
9. Largemouth bass, rock bass, and bluegill collected from Gull Lake did not result in a MDHHS “Eat Safe Fish” advisory for PFOS. However, mercury is a contaminant of concern and those eating fish from Gull Lake should follow the “Eat Safe Fish” guidance provided by the MDHHS at www.michigan.gov/eatsafefish.
10. Bluegill collected from the large pond at Markin Glen Park near Parchment had detectable levels of PFOS above MDHHS “Eat Safe Fish” screening values. However, mercury causes more restrictive advice and those eating bluegill from this pond should follow the guidance provided by the MDHHS at: www.michigan.gov/eatsafefish.
11. The PFOS surface water concentration exceeded the Rule 57 HNV at five of eight sampling locations in the Helmer Creek watershed near Battle Creek and ranged from non-detect (< 0.4 ng/L) to 98 ng/L.
12. The PFOS surface water concentration in Harts Lake near Battle Creek was below the detection limit (< 0.5 ng/L).
13. Bluegill collected from Beaver Dam Pond in the Helmer Creek watershed resulted in a MDHHS “Eat Safe Fish” ‘Do not eat’ advisory for all fish species in Beaver Dam Pond and Helmer Creek.
14. Bluegill collected from Elks Lodge Pond and Harts Lake in the Helmer Creek watershed did not result in a MDHHS “Eat Safe Fish” advisory for PFOS. However, mercury is a contaminant of concern and those eating fish from these water bodies should follow the “Eat Safe Fish” guidance provided by the MDHHS at www.michigan.gov/eatsafefish.

15. Overall, our sampling results indicate surface water PFAS contamination from contaminated groundwater near the Kellogg ANGB in Battle Creek and at the Crown Vantage site near Parchment.
16. Our limited sampling results suggest that the North 34th street PFAS groundwater contamination is not impacting Gull Lake.
17. Plans for additional sampling in the Kalamazoo River watershed include the collection of fish from Goguac Lake in Battle Creek.
18. The source of surface water contamination in the Kalamazoo River near Otsego has not yet been determined.

METHODS

Surface Water

Surface water grab samples were collected following the EGLE Surface Water PFAS Sampling Guidance document (Michigan Department of Environmental Quality [MDEQ], 2018a) from the Kalamazoo River and select tributaries on three occasions between August 2018 and February 2019. All samples were analyzed for 24 PFAS analytes, as described in the Quality Assurance Project Plan (QAPP; MDEQ, 2018b). To date, a total of 66 samples from 49 locations in the Kalamazoo River watershed were collected by EGLE and analyzed by Eurofins TestAmerica-Sacramento or Eurofins Lancaster Laboratories Environmental in Lancaster, Pennsylvania. These totals include water samples that were collected from ponds and drains on the former Crown Vantage site near the city of Parchment.

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. Stream subsurface samples from non-wadeable 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.

Samples were preserved on ice and shipped via overnight delivery to the Eurofins TestAmerica Sacramento laboratory at the end of the sample collection event. Eurofins TestAmerica is an EGLE contract laboratory and analyzes surface water samples using a modified version of USEPA Method 537 (USEPA, 2009), a process using isotope dilution for analyte quantification. The December 2018 samples were subcontracted out by Eurofins TestAmerica to Eurofins Lancaster Laboratories Env LLC. The laboratory provided analytical results for 24 perfluorinated compounds
Table 1) 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 Control / Quality Assurance

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. Two replicate samples were collected in August 2018 and one replicate was collected in December 2018. Two duplicate samples, each consisting of a one-liter composite sample dispensed into two sets of two 250 mL HDPE bottles, were collected in August 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
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

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 20 %
Precision	Field Sample Replication/Duplication	%RPD < 30%	RPD < 30 % except KR-0130 (August) PFBA = 31.3 %; KR-0030 (August) FOSA = 165.7 %; KR-0030 (August) FtS 6:2 = 165.7 %; KR-0090 (August) FtS 6:2 = 59.2 %
Accuracy/Bias	1 Lab Control Spike (LCS) and 1 MS/MSD per preparation batch	60 to 140 % recovery	Analyte recovery ranged from 74 to 113 %
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

Data Quality Indicator	Measurement	Data Quality Objective	Results
Accuracy/Bias	Every sample (spiked, standard or method blank) received an internal standard	25 to 150 % recovery	Analyte recovery < 150 % except for 1. FtS 4:2 HC-0200 (372 %); BD-0010 (369 %); HC-0300 (361 %); HC-0400 (410 %); UN-0010 (418 %); HL-0010 (336 %); HL-0020 (151 %); 2. FtS 6:2 KR-0010 (161 %); KR-0060 (151 %); KR-0090 (162 %); KR-0140 (156 %); BC-0010 (152 %); KR-0200 (154 %); KR-0200D (155 %); DC-0010 (169 %); HC-0200 (289 %); BD-0010 (298 %); HC-0300 (345 %); HC-0400 (377 %); UN-0010 (289 %); HL-0010 (235 %) 3. FtS 8:2 BD-0010 (189 %); HC-0400 (185 %); UN-0010 (214 %) 4. PFBS Clarifier-001 (164 %); HC-0200 (177 %); BD-0010 (207 %); HC-0300 (192 %); HC-0400 (242 %); UN-0010 (213 %); HL-0010 (175 %) 5. NMeFOSAA HC-0200 (151 %); BD-0010 (162 %); HC-0400 (152 %); UN-0010 (173 %); HL-0010 (137 %) 6. NEtFOSAA HC-0200 (158 %); BD-0010 (186 %); HC-0300 (159 %); HC-0400 (171 %); UN-0010 (194 %); HL-0010 (169 %) 7. PFPeA HC-0400 (173 %)
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	$\frac{47}{66} * 100 = 71.2$ % for all analytes $\frac{66}{66} * 100 = 100$ % for PFOS/PFOA

Ambient Water Sampling: Kalamazoo River Watershed

Initial ambient surface water samples were collected for PFAS analysis on August 6-7, 2018. Sampling locations were selected to bracket potential sources of PFAS contamination in the watershed. Grab samples of ambient surface water were collected by EGLE, WRD, SWAS, from the main flow of the Kalamazoo River at 23 locations, three locations on Gull Lake, two ponds at Markin Glen Park, and a location on Davis Creek, Portage Creek, and the Battle Creek River (Table 3; Figure 1). Relatively intensive sampling occurred near the city of Parchment (Figure 1 inset) due to the discovery of PFAS contamination in the city's drinking water supply. In addition to surface water samples, opportunistic samples of four storm water outfalls near the city of Parchment were collected. Lastly, EGLE personnel from the Kalamazoo District Office collected five water samples from ponds, stormwater drains, and abandoned water treatment facilities on the site of the former Crown Vantage paper mill in Parchment. Finally, to obtain a better understanding of spatial differences in PFAS concentrations within the water column additional samples were collected at two select locations along the Kalamazoo River near Parchment (Table 3). At these locations, the following samples were collected: a surface sample, sub-surface sample, mid-depth sample, bottom sample, and depth composite sample.

According to the United States Geological Survey (USGS) gaging station on the Kalamazoo River near Battle Creek, Michigan (USGS 04105500), the river flow on August 6, 2018, was ~ 400 cubic feet per second (cfs), which is at the 80-year median for this date and location. However, heavy precipitation occurred just prior to when the first sample was collected at 11:55 a.m. near Allegan, Michigan. Following this storm, the river flow increased to ~ 900 cfs at the Battle Creek, Michigan USGS gaging station. By 3:00 p.m. on August 6 the river flow reduced to ~ 550 cfs and remained at this level until the sample collection was completed on August 7.

As a part of a separate sampling effort, surface water samples were collected from three locations on Gull Lake, which eventually drains into the Kalamazoo River via Gull Creek, on July 26, 2018.

Ambient Water Sampling: Helmer Creek Watershed

Additional samples were collected from the Kalamazoo River watershed on December 20, 2018, near Battle Creek to investigate the potential contamination of surface water following the detection of PFAS in groundwater near the Kellogg ANGB. Grab samples of surface water were collected by EGLE, WRD, SWAS, from the main flow of the Kalamazoo River at two locations and in the Helmer Creek watershed at seven locations (Table 3, Figure 2).

According to the USGS gaging station on the Kalamazoo River near Battle Creek, Michigan (USGS 04105500), the river flow on this date was ~ 650 cfs, which is above the 80-year median for this date and location (~ 560 cfs). Significant precipitation did not occur up to four days prior to sample collection. A sample from Harts Lake was collected on February 13, 2019, following the detection of PFOS exceeding the HNV in a sample collected from the Harts Lake drain in December 2018.

Table 3. PFOS and PFOA concentrations measured in surface water samples collected from the Kalamazoo River watershed on August 6-7 and December 20, 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)
KR-0010	Kalamazoo River at Lincoln Rd	42.545175	-85.878503	August	9.6	4.6
KR-0020	Kalamazoo River at Grand Street	42.531169	-85.848104	August	9.1	4.4
KR-0030	Kalamazoo River at Williams Bridge Road	42.504603	-85.844237	August	9.3	4.3
KR-0030[R]	Kalamazoo River at Williams Bridge Road	42.504603	-85.844237	August	9.3	4.7
KR-0050	Kalamazoo River at Lincoln Road	42.45989	-85.722541	August	9.2	4.7
KR-0060	Kalamazoo River at N North St	42.462798	-85.701605	August	***49.0***	4.9
KR-0070	Kalamazoo River near US-131	42.453445	-85.65322	August	10.0	4.8
KR-0090	Kalamazoo River at D Avenue	42.376337	-85.578576	August	12.0	5.3
KR-0090[D]	Kalamazoo River at D Avenue	42.376337	-85.578576	August	12.0	5.5
KR-0095	Kalamazoo River d/s of Parchment wells	42.35452	-85.577334	August	7.9	4.1
UC-0010	Unnamed creek at confluence with Kalamazoo	42.346888	-85.576715	August	***13.0***	15.0
KR-0100[T]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	***14.0***	6.0
KR-0100[S]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	***17.0***	7.3
KR-0100[M]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	11.0	5.6
KR-0100[B]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	***19.0***	9.2
KR-0100[C]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	***14.0***	6.8
MG-001	Markin Glen Park small pond	42.339139	-85.584552	August	3.1	2.7
MG-002	Markin Glen Park large pond	42.335816	-85.585472	August	4.2	3.6
KR-0110	Kalamazoo River u/s of old landfill	42.334293	-85.583273	August	4.2	2.2
KR-0110[R]	Kalamazoo River u/s of old landfill	42.334293	-85.583273	August	4.5	2.0
PD-0010	Parchment drain at Kalamazoo River [flowing]	42.332438	-85.579839	August	***5200.0***	1600.0
Culvert-001	Parchment Paper Mill Culvert	42.3325	-85.5791	August	***4700.0***	1300.0
Drain-001	Parchment Paper Mill Drain	42.3325	-85.5791	August	***7000.0***	2400.0

[R] Replicate Site
[D] Duplicate Site
[T] Water Column Investigation Site; Result is a traditional subsurface sample
[S] Surface Sample
[M] Mid-depth Sample
[B] Bottom Sample
[C] Depth Composite Sample

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	PFOS (ng/L)	PFOA (ng/L)
Pond-0010	Pond near Parchment Drain	42.331955	-85.579484	August	***9500.0***	2000.0
Clarifier-001	Parchment Paper Mill Clarifier	42.333166	-85.577696	August	***3100.0***	7700.0
Lagoon-001	Parchment Paper Mill Lagoon	42.332487	-85.578199	August	***5600.0***	1600.0
KR-0120[T]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	4.6	2.3
KR-0120[S]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	***15.0***	3.6
KR-0120[M]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	3.9	2.3
KR-0120[B]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	4.3	2.0
KR-0120[C]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	4.0	2.2
PD-0030	Parchment storm water outfall 3; underwater [flowing]	42.324586	-85.575719	August	4.1	2.2
PD-0040	Parchment storm water outfall 4 [flowing]	42.32399	-85.572968	August	4.4	3.0
PD-0050	Parchment storm water outfall 5; [stagnant]	42.323288	-85.572529	August	10.0	4.7
KR-0130	Kalamazoo River u/s of Parchment stormwater outfalls	42.321904	-85.575512	August	3.8	2.1
KR-0130[D]	Kalamazoo River u/s of Parchment stormwater outfalls	42.321904	-85.575512	August	3.9	2.2
KR-0140	Kalamazoo River at E Mosel	42.317827	-85.573064	August	6.0	2.3
KR-0150	Kalamazoo River at E Paterson Street	42.303268	-85.571038	August	3.2	2.0
PC-0010	Portage Creek at E. Michigan Avenue	42.29459	-85.573515	August	4.1	2.7
PC-0010[R]	Portage Creek at E. Michigan Avenue	42.29459	-85.573515	August	4.1	2.8
KR-0160	Kalamazoo River at Michigan Avenue	42.294787	-85.571884	August	4.0	1.8[†]
DC-0010	Davis Creek at Olmstead Road	42.274299	-85.537982	August	6.3	3.0
KR-0180	Kalamazoo River at E Michigan Avenue	42.288644	-85.40175	August	2.6	1.3[†]
KR-0200	Kalamazoo River at Custer Drive	42.350827	-85.275847	August	***13.0***	4.4
KR-0200[D]	Kalamazoo River at Custer Drive	42.350827	-85.275847	August	***14.0***	4.3
KR-0210	Kalamazoo River at Battle Creek Linear Park	42.345420	-85.255755	August	***47.0***	7.4
KR-0210	Kalamazoo River at Battle Creek Linear Park	42.345420	-85.255755	December	5.7	2.6
KR-0210[R]	Kalamazoo River at Battle Creek Linear Park	42.345420	-85.255755	December	6.6	2.5
HC-0010	Helmer Creek at Battle Creek Linear Park	42.33875	-85.2369	December	***61***	21

[T] Water Column Investigation Site; Result is a traditional subsurface sample
[S] Surface Sample
[M] Mid-depth Sample
[B] Bottom Sample
[C] Depth Composite Sample
[D] Duplicate Site
[R] Replicate Site
[†] Concentration is above the method detection limit but below the laboratory reporting limit.

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	PFOS (ng/L)	PFOA (ng/L)
HC-0200	Helmer Creek at Beaver Dam Pond Road	42.3299	-85.2508	December	***98***	17
BD-0010	Beaver Dam Pond at Beaver Dam Pond Road	42.32855	-85.2516	December	***65***	16
HC-0300	Helmer Creek at Avenue A	42.3259	-85.2612	December	5.5	6.6
HC-0400	Helmer Creek at Tecumseh Road	42.32559	-85.2684	December	10	5.2
UN-0010	Unnamed Tributary at End of Reese Road	42.31886	-85.2724	December	***44***	11
HL-0010	Harts Lake Drain at Harts Lake Road	42.31854	-85.2753	December	***54***	18
HL-0020	Harts Lake	42.310992	-85.283991	February	ND	1.2†
KR-0220	Kalamazoo River at S Bedford Road	42.337585	-85.232506	August	2.1	1.0†
KR-0220	Kalamazoo River at S Bedford Road	42.337585	-85.232506	December	0.6†	0.5†
BC-0010	Battle Creek River at pedestrian bridge	42.322434	-85.190396	August	1.9†	1.1†
KR-0230	Kalamazoo River at Hamblin Avenue	42.322304	-85.193415	August	1.1†	ND
KR-0240	Kalamazoo River at 294	42.297318	-85.167823	August	0.9†	ND
KR-0260	Kalamazoo River at 15 Mile Road	42.258397	-84.998239	August	1.0†	1.0†
KR-0270	Kalamazoo River at S Kalamazoo Ave	42.264857	-84.964001	August	0.6†	ND
Gull-01	Gull Lake South	42.378014	-85.401766	August	1.0†	1.4†
Gull-02	Gull Lake Center	42.412516	-85.420696	August	0.9†	1.3†
Gull-03	Gull Lake North	42.424041	-85.429597	August	0.3†	1.2†

† Concentration is above the method detection limit but below the laboratory reporting limit.

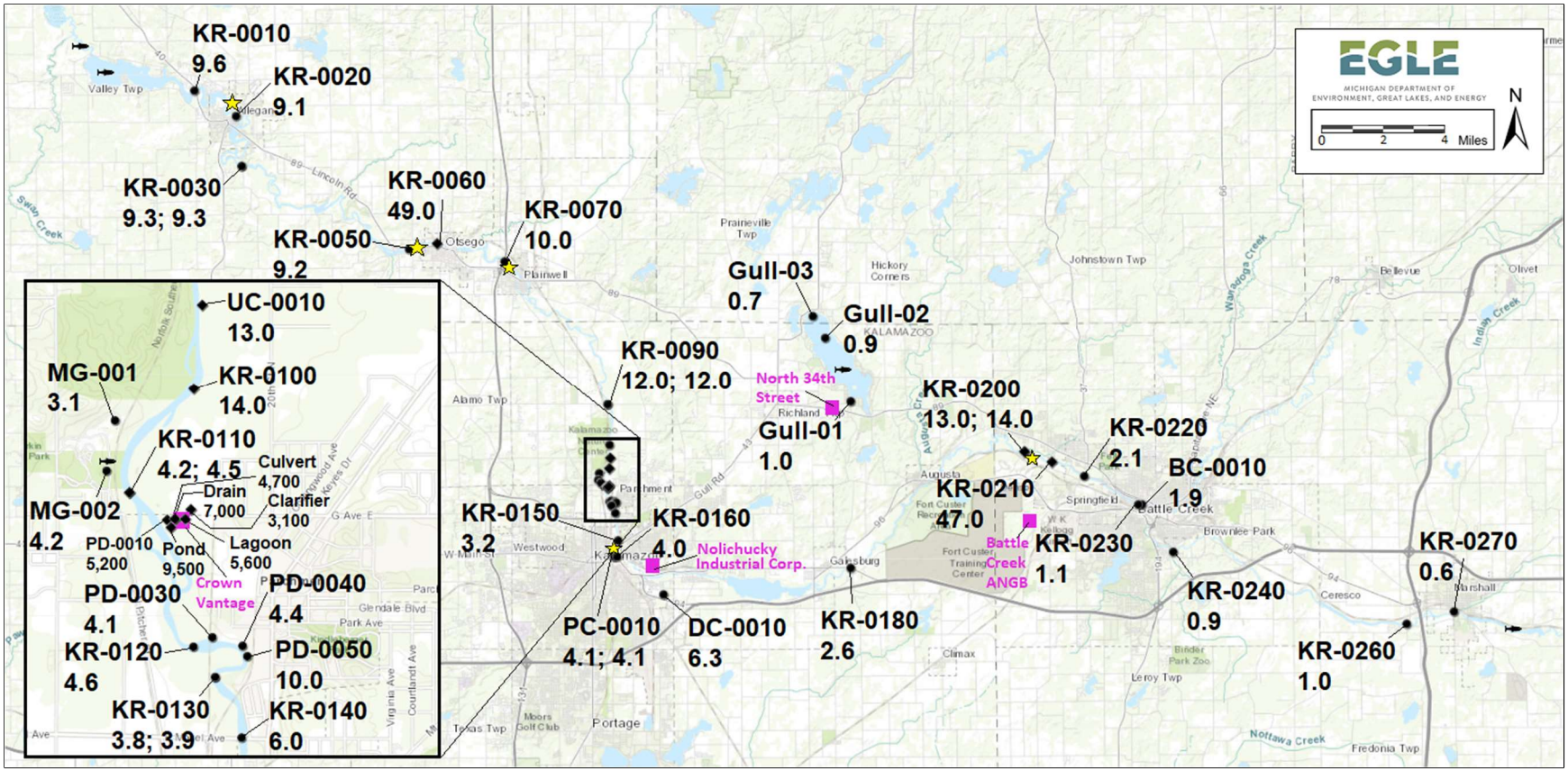

Figure 1. Overview map of the Kalamazoo watershed with surface water PFOS concentrations (ng/L) at locations sampled on August 6-7, 2018. KR denotes a location on the Kalamazoo River; UC is an unnamed creek near Parchment; MG is Markin Glen Park; PD is the Parchment Drain; PC is Parchment Creek; BC is the Battle Creek River; Gull is Gull Lake. Inset represents the relatively intense sampling that occurred near Parchment. ◆ 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.

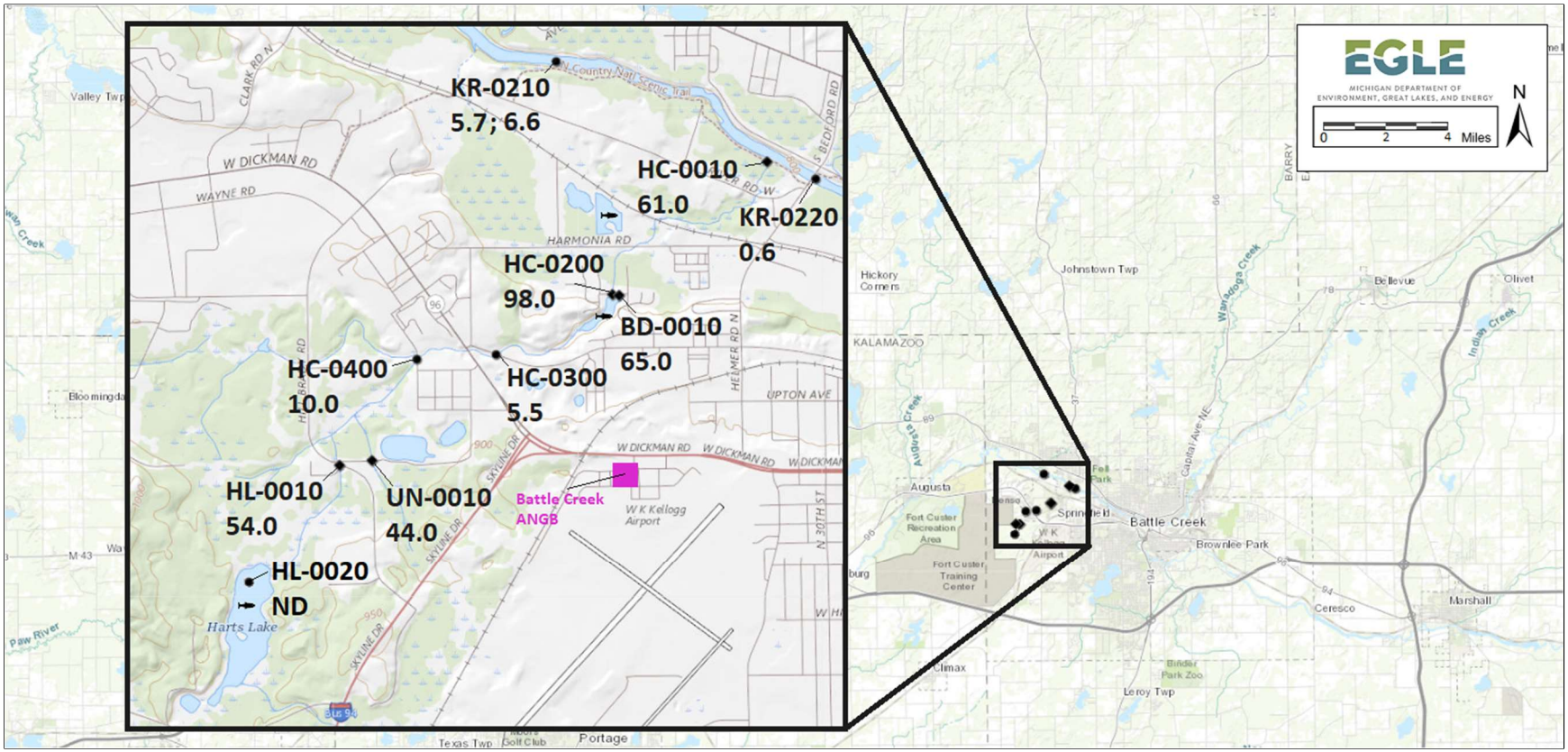

Figure 2. Overview map of the Kalamazoo watershed. Inset represents the surface water PFOS concentrations (ng/L) in the Helmer Creek Watershed sampled on December 20, 2018. The sample from Harts Lake (HL-0020) was collected on February 13, 2019. KR denotes a location on the Kalamazoo River; HC is Helmer Creek; BD is Beaver Dam Pond; UN is an unnamed tributary to Helmer Creek; HL-0010 is the Harts Lake Drain. ◆ indicates a sample location with a Part 4, Rule 57 HNV exceedance. ■ indicates approximate location of a known or suspected PFAS site. ➸ indicates approximate location of a fish collection site for the "Eat Safe Fish" guidelines.

Fish Tissue

Rock bass (*Ambloplites rupestris*), largemouth bass (*Micropterus salmoides*), smallmouth bass (*M. dolomieu*), common carp (*Cyprinus carpio*), and bluegill (*Lepomis macrochirus*) were collected by EGLE, WRD, from the Kalamazoo River in 2013 and 2016. Largemouth bass and rock bass were collected by EGLE, WRD, SWAS, from Gull Lake in July 2018. Bluegill were collected from the fishing ponds at Markin Glen Park by EGLE, WRD, SWAS, in August 2018. Bluegill were collected by EGLE, WRD, SWAS, from Harts Lake in February 2019. In October 2018, the Michigan Department of Natural Resources (MDNR) collected bluegill from Beaver Dam Pond and the Elks Lodge Pond near Battle Creek. Fish were collected using standard electrofishing or netting equipment and/or hook and line and were prepared as standard edible portion samples following EGLE, WRD, SWAS, Procedure (MDEQ, 1995). Fish tissue samples were analyzed for 11 perfluorinated compounds by the MDHHS Analytical Chemistry Laboratory (Table 4).

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

Point Source Discharges/Compliance Sampling Inspections

There are two WWTPs with discharges to the Kalamazoo River watershed that were identified for PFAS effluent analysis in 2018. The Battle Creek and Kalamazoo WWTPs are participating in the statewide IPP PFAS Initiative and have approved IPP programs. Effluent samples from these facilities were collected by EGLE in 2018.

In addition to the IPP initiative sampling, effluent from the WWTPs in Allegan, Otsego, and Plainwell and the Otsego Paper Inc. effluent was tested for PFAS. The effluent from the Otsego WWTP was collected by the city of Otsego in November 2018 and by EGLE, WRD, in May 2019. Due to chromatographic interference in the October sampling, the Otsego Paper Inc collected an additional effluent sample in December. A follow-up sample was collected by EGLE, WRD, in May. Effluent from Allegan and Plainwell WWTPs was also sampled by EGLE, WRD, in May 2019.

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. The Otsego Paper Inc December 2018 sample was analyzed by Pace Analytical (Minneapolis, Minnesota) using the USEPA Method 537 by Isotope Dilution.

RESULTS AND DISCUSSION

Kalamazoo River Watershed Sampling

A total of 49 surface water samples were collected at 40 locations during the two sampling events. The 49 samples do not include the eight additional samples (two locations) collected as part of the water column investigation nor the nine samples (nine locations) collected from the ponds and drains at the Crown Vantage site in Parchment. In August 2018 the Σ PFAS arithmetic mean concentration was 32.1 ng/L and ranged from 7.8 ng/L near Marshall to 133.3 ng/L near Battle Creek (Table 5). It is important to note that the Σ PFAS concentration includes the sum of all 24 PFAS analytes above their detection, including the seven analytes that exceeded the QA/QC recovery threshold (Table 2). In August 2018, PFOS and PFOA were detected in 38 (100%) and 35 (92.1%) of the total collected samples, respectively (Table 3). In addition to PFOS, the analytes PFHxS, PFBS, PFHpA, and PFBA were detected in all 38 samples (Figure 3). PFHxA, PFPeA, and PFNA were detected in 37, 37, and 32 samples, respectively. PFPeS (26 detections), FtS 6:2 (22 detections), PFHpS (13 detections), NEtFOSA (12 detections), FOSA (11 detections), PFTeA (7 detections), PFDA (7 detections), and PFNS (2 detections) were also detected in at least one sample. FtS 8:2, FtS 4:2, NmEFOSA, PFDS, PFTriA, PFDoA, and PFUnA were not detected in any river sample. In December 2018, the Σ PFAS arithmetic mean concentration within the Helmer Creek watershed was 182.7 ng/L. PFOS and PFOA were detected in all 10 samples (Table 3). In addition to PFOS and PFOA, PFHxS, PFHxA, and PFBS were detected in all 10 samples (Figure 4). PFPeA, PFBA, PFHpA, and PFPeS were detected in 9 samples. PFNA, PFHpS, and FtS 6:2 was detected in 8, 7, and 5 samples, respectively. The remaining 12 analytes were not detected during the December 2018 sampling event. In February 2019 the sample collected from Harts Lake had detectable concentrations of PFBA, PFOA, PFPeA, PFHxA, PFHpA, PFNA, PFBS, and PFHxS.

Table 5: Total PFAS concentrations (the sum of 24 analytes above their detection limit) detected in surface water samples collected from locations in the Kalamazoo River watershed on August 6-7 and December 20, 2018. Revisited locations are in bold.

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	Σ PFAS (ng/L)	# Analytes Detected
KR-0010	Kalamazoo River at Lincoln Road	42.545175	-85.878503	August	36.0	14
KR-0020	Kalamazoo River at Grand Street	42.531169	-85.848104	August	31.7	11
KR-0030	Kalamazoo River at Williams Bridge Road	42.504603	-85.844237	August	35.3	15
KR-0030[R]	Kalamazoo River at Williams Bridge Road	42.504603	-85.844237	August	37.4	14
KR-0050	Kalamazoo River at Lincoln Road	42.45989	-85.722541	August	36.6	13
KR-0060	Kalamazoo River at N North Street	42.462798	-85.701605	August	86.2	15
KR-0070	Kalamazoo River near US-131	42.453445	-85.65322	August	42.5	14
KR-0090	Kalamazoo River at D Avenue	42.376337	-85.578576	August	42.9	15
KR-0090[D]	Kalamazoo River at D Avenue	42.376337	-85.578576	August	45.7	14
KR-0095	Kalamazoo River d/s of Parchment wells	42.35452	-85.577334	August	29.7	13
UC-0010	Unnamed creek at confluence with Kalamazoo	42.346888	-85.576715	August	57.4	11
KR-0100[T]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	41.7	13
KR-0100[S]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	47.8	13
KR-0100[M]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	36.1	13
KR-0100[B]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	52.4	13
KR-0100[C]	Kalamazoo River d/s of old landfill	42.341276	-85.57747	August	43.3	13
MG-001	Markin Glen Park small pond	42.339139	-85.584552	August	15.8	9
MG-002	Markin Glen Park large pond	42.335816	-85.585472	August	30.7	11
KR-0110	Kalamazoo River u/s of old landfill	42.334293	-85.583273	August	21.6	10
KR-0110[R]	Kalamazoo River u/s of old landfill	42.334293	-85.583273	August	21.6	10

[R] Replicate Site
[D] Duplicate Site
[T] Water Column Investigation Site; Result is a traditional subsurface sample
[S] Surface Sample
[M] Mid-depth Sample
[B] Bottom Sample
[C] Depth Composite Sample

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	Σ PFAS (ng/L)	# Analytes Detected
PD-0010	Parchment drain at Kalamazoo River [flowing]	42.332438	-85.579839	August	8624.3	16
Culvert-001	Parchment Paper Mill Culvert	42.3325	-85.5791	August	7454.9	16
Drain-001	Parchment Paper Mill Drain	42.3325	-85.5791	August	11958.2	21
Pond-0010	Pond near Parchment Drain	42.331955	-85.579484	August	19003.7	18
Clarifier-001	Parchment Paper Mill Clarifier	42.333166	-85.577696	August	19968.5	18
Lagoon-001	Parchment Paper Mill Lagoon	42.332487	-85.578199	August	13678.0	19
KR-0120[T]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	23.6	10
KR-0120[S]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	41.3	13
KR-0120[M]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	22.1	10
KR-0120[B]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	22.9	10
KR-0120[C]	Kalamazoo River d/s of Parchment stormwater outfalls	42.323955	-85.577425	August	22.9	10
PD-0030	Parchment storm water outfall 3; underwater [flowing]	42.324586	-85.575719	August	23.0	10
PD-0040	Parchment storm water outfall 4 [flowing]	42.32399	-85.572968	August	31.5	9
PD-0050	Parchment storm water outfall 5; not flowing [stagnant]	42.323288	-85.572529	August	34.0	12
KR-0130	Kalamazoo River d/s of Parchment stormwater outfalls	42.321904	-85.575512	August	25.0	11
KR-0130[D]	Kalamazoo River d/s of Parchment stormwater outfalls	42.321904	-85.575512	August	23.0	10
KR-0140	Kalamazoo River at E Mosel	42.317827	-85.573064	August	27.0	11
KR-0150	Kalamazoo River at E Paterson Street	42.303268	-85.571038	August	18.0	11
PC-0010	Portage Creek at E. Michigan Ave	42.29459	-85.573515	August	20.7	10
PC-0010[R]	Portage Creek at E. Michigan Ave	42.29459	-85.573515	August	20.6	11
KR-0160	Kalamazoo River at Michigan Ave	42.294787	-85.571884	August	25.3	12
DC-0010	Davis Creek at Olmstead Rd.	42.274299	-85.537982	August	33.7	12
KR-0180	Kalamazoo River at E Michigan Ave	42.288644	-85.40175	August	22.2	12
KR-0200	Kalamazoo River at Custer Drive	42.350827	-85.275847	August	60.8	13
KR-0200[D]	Kalamazoo River at Custer Drive	42.350827	-85.275847	August	63.0	13
KR-0210	Kalamazoo River at Battle Creek Linear Park	42.345420	-85.255755	August	133.3	13

[T] Water Column Investigation Site; Result is a traditional subsurface sample
[S] Surface Sample
[M] Mid-depth Sample
[B] Bottom Sample
[C] Depth Composite Sample
[D] Duplicate Site
[R] Replicate Site

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	Σ PFAS (ng/L)	# Analytes Detected
KR-0210	Kalamazoo River at Battle Creek Linear Park	42.345420	-85.255755	December	35.9	9
KR-0210^{R}	Kalamazoo River at Battle Creek Linear Park	42.345420	-85.255755	December	38.0	10
HC-0010	Helmer Creek at Battle Creek Linear Park	42.33875	-85.2369	December	346.8	12
HC-0200	Helmer Creek at Beaver Dam Pond Road	42.3299	-85.2508	December	370.8	12
BD-0010	Beaver Dam Pond at Beaver Dam Pond Road	42.32855	-85.2516	December	324.7	12
HC-0300	Helmer Creek at Avenue A	42.3259	-85.2612	December	130.9	11
HC-0400	Helmer Creek at Tecumseh Road	42.32559	-85.2684	December	101.3	11
UN-0010	Unnamed Tributary at End of Reese Road	42.31886	-85.2724	December	200.7	12
HL-0010	Harts Lake Drain at Harts Lake Road	42.31854	-85.2753	December	275.0	12
HL-0020	Harts Lake	42.310992	-85.283991	February	9.9	8
KR-0220	Kalamazoo River at S Bedford Road	42.337585	-85.232506	August	22.7	10
KR-0220	Kalamazoo River at S Bedford Road	42.337585	-85.232506	December	2.9	5
BC-0010	Battle Creek River at pedestrian bridge	42.322434	-85.190396	August	20.7	10
KR-0230	Kalamazoo River at Hamblin Avenue	42.322304	-85.193415	August	10.6	9
KR-0240	Kalamazoo River at 294	42.297318	-85.167823	August	9.1	8
KR-0260	Kalamazoo River at 15 Mile Road	42.258397	-84.998239	August	13.6	9
KR-0270	Kalamazoo River at S Kalamazoo Avenue	42.264857	-84.964001	August	7.8	6
Gull-01	Gull Lake South	42.378014	-85.401766	August	9.5	10
Gull-02	Gull Lake Center	42.412516	-85.420696	August	9.0	9
Gull-03	Gull Lake North	42.424041	-85.429597	August	8.3	9

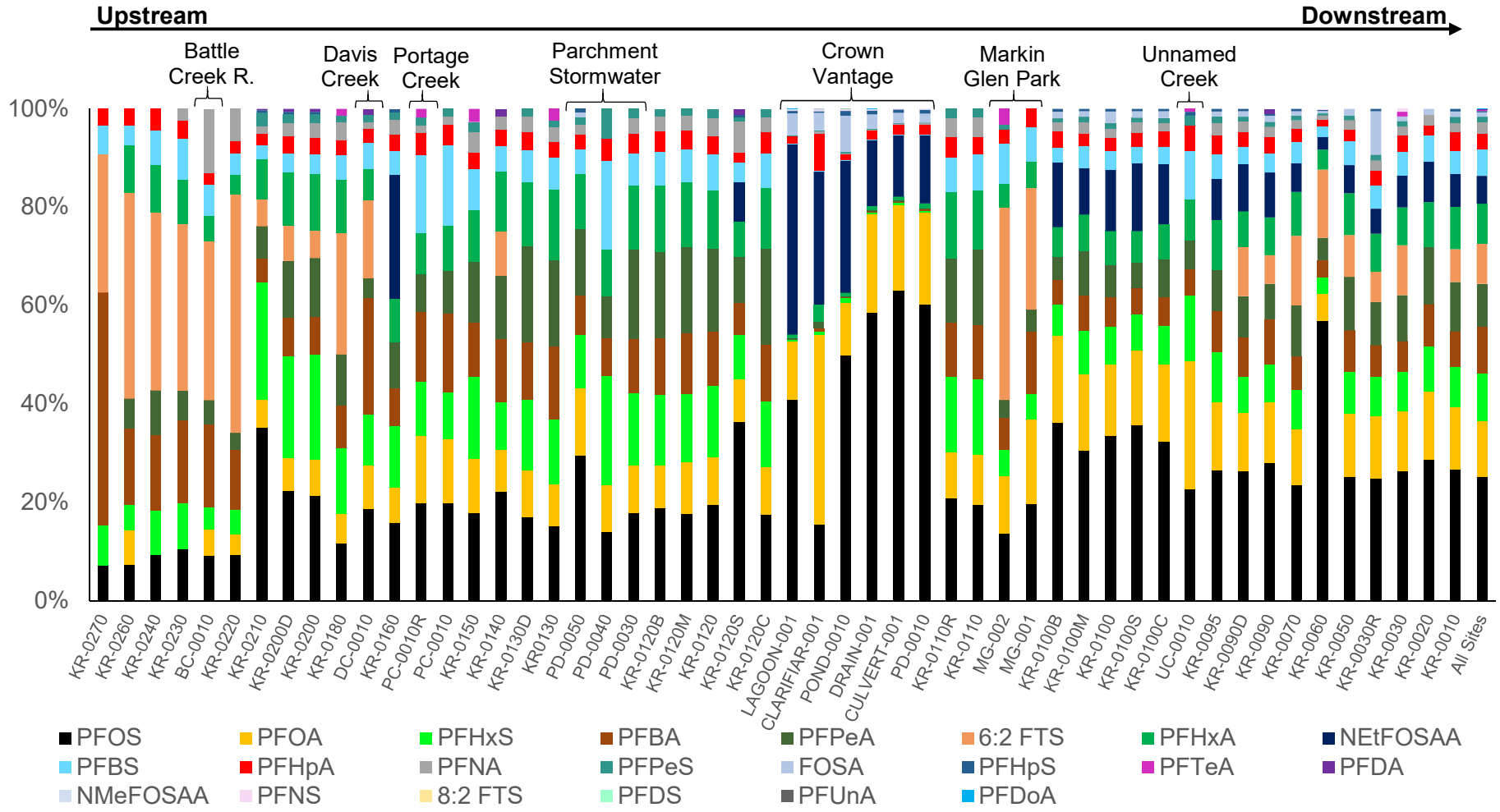

Figure 3. Percentage composition of PFAS measured in surface water collected in the Kalamazoo River watershed in August 2018. Sample IDs are shown (KR is the Kalamazoo River; UC is an unnamed creek near Parchment; MG is Markin Glen Park; PD is the Parchment Drain; PC is Parchment Creek; BC is the Battle Creek River; Gull is Gull Lake). '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 'S' indicates a surface sample, 'C' is a depth composite sample, 'M' is a mid-depth sample, 'B' is a bottom-depth sample, 'R' is a replicate sample, and 'D' is a duplicate sample.

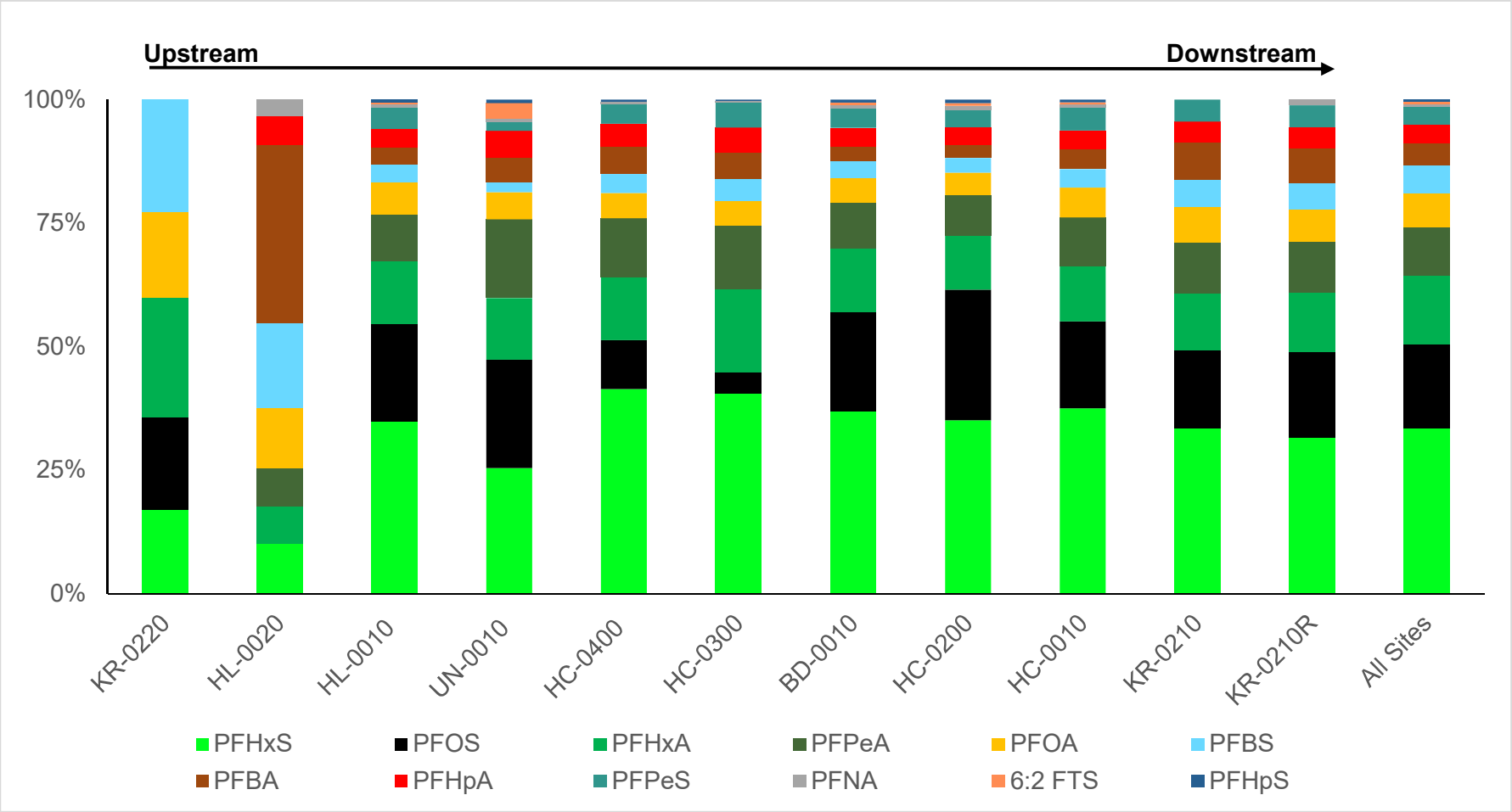

Figure 4. Percentage composition of PFAS measured in surface water collected in the Helmer Creek watershed in December 2018. The HL-0020 sample was collected in February 2019. Sample IDs are shown (KR is the Kalamazoo River; HL is Harts Lake; UN is an unnamed tributary to Helmer Creek; HC is Helmer Creek; BD is Beaver Dam Pond. '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' indicates a replicate sample.

Kalamazoo River (Main Branch)

A total of 25 surface water samples at 23 locations were collected over the two 2018 sampling events from the main branch of the Kalamazoo River and analyzed for PFAS. Six samples (five locations) collected in August 2018 from the Kalamazoo River exceeded the HNV for PFOS. Neither sample collected from the Kalamazoo River near Battle Creek in December 2018 exceeded the PFOS HNV (Table 3). Additionally, no samples collected from the Kalamazoo River during either sampling event exceeded the HNV for PFOA, ranging from non-detect to 9.2 ng/L.

Our furthest downstream site (KR-0010) was just upstream of Lake Allegan and had a PFOS concentration of 9.6 ng/L in August 2018. Concentrations of PFOS in fillets of smallmouth bass, sunfish, and common carp collected in 2013 from Lake Allegan, averaged 82, 37, and 36 micrograms per kilogram (µg/kg; parts per billion). Concentrations of PFOS in fillets of smallmouth bass, bluegill, and common carp collected downstream of Lake Allegan in 2013 averaged 56, 45, and 28 µg/kg. These fish tissue concentrations exceed MDHHS “Eat Safe Fish” screening values and would cause an advisory in these species; however, there is a ‘Do not eat’ advisory for all fish species from this section of the river due to PCBs. In May 2019 a sample of the effluent from the Allegan WWTP had a non-detectable concentration of PFOS (<5.4 ng/L); however, PFOA was detected at 6.9 ng/L (Table 6). The sample required dilution prior to analysis due to abundance of target and/or non-target analytes and therefore had a laboratory reporting limit of 18 ng/L for each of the PFAS analytes.

In August 2018 PFOS was detected at 49 ng/L in a surface water sample collected from the Kalamazoo River (Sample Location KR-0060) near Otsego (Table 3). In October 2018 the Otsego Paper Inc effluent had a PFOS and PFOA concentration of 34 and 30 ng/L, respectively; however, the laboratory reported that there was chromatographic interference in the PFOS analysis, which may have led to a false positive result (Table 6). Follow-up sampling of the effluent in December 2018 revealed non-detectable concentrations of all PFAS analytes. An additional sample of the effluent collected in May 2019 also resulted in a non-detectable concentration for PFOS (<5.1 ng/L); however, PFOA was detected at 41 ng/L. The sample required dilution prior to analysis due to abundance of target and/or non-target analytes and therefore had a laboratory reporting limit of 17 ng/L for each of the PFAS analytes. In November 2018 and May 2019, concentrations of PFOS were not detected in effluent samples collected from the Otsego WWTP (<4.2 ng/L and <2.6 ng/L, respectively Table 6). The effluent had a PFOA detection of 4.1 ng/L in the May 2019 sample; however, this concentration was below the laboratory reporting limit of 8.6 ng/L. This sample had a laboratory reporting limit of 8.6 ng/L for each of the PFAS analytes due to the need for dilution prior to analysis. Additionally, the effluent from the Plainwell WWTP had non-detectable concentrations of PFOS (<5.1 ng/L) and PFOA (<5.3 ng/L) in a sample collected in May 2019 (Table 6). This sample also required dilution prior to analysis and therefore had a laboratory reporting limit of 17 ng/L for each of the PFAS analytes.

PFOS was detected at 19 ng/L (Sample Location KR-0100) and 15 ng/L (Sample Location KR-0120) in the Kalamazoo River near the Crown Vantage site during the August 2018 sampling event. The concentrations at different surface water depths were also assessed at these two locations. The results of the water column sampling were inconsistent. At the first

sample location (KR-0100), PFOS was relatively mixed throughout the water column ranging from 17 ng/L in the surface sample to 11 ng/L in the mid-depth to 19 ng/L in the bottom depth sample (Table 5). The PFOS concentration in the surface, subsurface, and depth composite sample was 17, 14, and 14 ng/L, respectively (Table 3). The Σ PFAS concentration in these samples ranged from 36.1 to 52.4 ng/L with the same 13 analytes detected at each depth (Table 5). At the second sample location (KR-0120), the PFOS concentration was over 3 times higher at the surface (15 ng/L) than anywhere else in the water column (ranging from 3.9 to 4.6 ng/L; Table 3). The total PFAS concentration was also 1.8 times higher at the surface (41.3 ng/L) than the next highest subsurface sample (23.6 ng/L; Table 5). Three PFAS analytes were measurable at the surface that were not detected in the other water column samples at this sample location.

In August 2018 groundwater monitoring wells were sampled by EGLE on or near the Crown Vantage site in Parchment. The maximum combined PFOS and PFOA concentration in the wells was 25,730 ng/L. During the August 2018 surface water sampling event, a total of nine samples were collected from surface waters, old wastewater treatment ponds, and storm water outfalls located off river and on or near the Crown Vantage site adjacent to the Kalamazoo River. PFOS concentrations in these samples ranged from 4,700 ng/L in a drain sample (Sample location Culvert-0010) to 9,500 ng/L in a pond adjacent to the Kalamazoo River (Sample location Pond-0010). PFOA concentrations ranged from 1,300 ng/L in the Culvert-0010 sample to 7,700 ng/L in the wastewater treatment clarifier (Sample location Clarifier-0010). Storm water outfalls located upstream of the Crown Vantage site had detectable levels of PFOS ranging from 4.1 to 10 ng/L and PFOA concentrations ranging from 2.2 to 4.7 ng/L. Between May 21 and August 1, 2018, the Kalamazoo WWTP exceeded the HNV for PFOS nine times. After August 1, 2018, weekly samples from the Kalamazoo WWTP never exceeded the HNV for PFOS (Table 6).

Additionally, PFOS was detected between 13 and 47 ng/L in three surface water samples (two Sample Locations: KR-0200 and KR-210) near Battle Creek in August 2018. In May 2018 PFOS and PFOA concentrations in a sample collected from the Battle Creek WWTP were non-detect (<2.3 ng/L). Samples collected in December 2018 from the Helmer Creek watershed, discussed in further detail in a later section, indicate that Helmer Creek is a source of PFAS to the Kalamazoo River near Battle Creek.

The remaining locations from the Kalamazoo River had PFOS concentrations ranging from non-detect to 12 ng/L. Concentrations of PFOS were not detected in fillets of rock bass and averaged 2.0 µg/kg in fillets of black bass collected in 2013 upstream of Marshall Pond. These concentrations are below the MDHHS “Eat Safe Fish” screening values for PFOS.

Markin Glen Park Fishing Ponds

A surface water sample was collected in August 2018 from both the large and small fishing ponds located at Markin Glen Park. PFOS concentrations in these ponds were 4.2 and 3.1 ng/L, whereas PFOA concentrations were 3.6 and 2.7 ng/L, respectively (Table 3). Neither the PFOS nor PFOA HNV was exceeded in these fishing ponds. Bluegill collected in August 2018 from the large pond at Markin Glen Park had a mean PFOS fillet concentration of 10 µg/kg and would result in a 12 meals per month MDHHS “Eat Safe Fish” consumption advisory. However, this

advisory is superseded by the four bluegill meals per month advisory issued in 2016 due to mercury.

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)
Allegan WWTP	5/14/2019	ND	6.9	797
Battle Creek WWTP	5/8/2018	ND	ND	50
Kalamazoo WWTP	5/21/2018	***38***	15	109.7
Kalamazoo WWTP	5/23/2018	***35***	13	96.7
Kalamazoo WWTP	6/1/2018	***29***	12	98.4
Kalamazoo WWTP	6/27/2018	***28***	19	154.7
Kalamazoo WWTP	6/27/2018	***20***	10	80
Kalamazoo WWTP	7/2/2018	8.4	11	92.7
Kalamazoo WWTP	7/11/2018	12	11	175.7
Kalamazoo WWTP	7/17/2018	***22***	13	108.4
Kalamazoo WWTP	7/25/2018	***40***	ND	130
Kalamazoo WWTP	7/25/2018	***35***	9.8	115.5
Kalamazoo WWTP	8/1/2018	***25***	13	99
Kalamazoo WWTP	8/7/2018	ND	ND	33.7
Kalamazoo WWTP	8/15/2018	12	10	105
Kalamazoo WWTP	8/22/2018	6.8	7.5	68.6
Kalamazoo WWTP	8/29/2018	ND	ND	57
Kalamazoo WWTP	8/29/2018	5.2	ND	31.1
Kalamazoo WWTP	8/29/2018	ND	ND	30
Kalamazoo WWTP	9/5/2018	8.8	9.4	74.3
Kalamazoo WWTP	9/12/2018	ND	ND	35
Kalamazoo WWTP	9/19/2018	ND	ND	51
Kalamazoo WWTP	9/26/2018	ND	ND	50
Kalamazoo WWTP	10/3/2018	ND	ND	ND
Kalamazoo WWTP	10/10/2018	11	ND	79
Kalamazoo WWTP	10/17/2018	11	31	133
Kalamazoo WWTP	10/24/2018	ND	11	58
Kalamazoo WWTP	10/31/2018	ND	ND	45
Kalamazoo WWTP	11/7/2018	ND	ND	61
Kalamazoo WWTP	11/15/2018	ND	ND	36
Kalamazoo WWTP	11/21/2018	ND	ND	88
Kalamazoo WWTP	11/28/2018	ND	ND	83
Kalamazoo WWTP	12/5/2018	ND	ND	79
Kalamazoo WWTP	12/12/2018	ND	ND	95
Kalamazoo WWTP	12/19/2018	ND	ND	58
Kalamazoo WWTP	12/27/2018	ND	ND	41
Kalamazoo WWTP	1/31/2019	3.1	5.8	54.5
Otsego WWTP[1]	11/9/2018	ND	ND	35.9
Otsego WWTP	5/14/2019	ND	ND	49
Otsego Paper Inc.	10/11/2018	***34***[2]	30	150
Otsego Paper Inc.[3]	12/11/2018	ND	ND	ND
Otsego Paper Inc.	5/14/2019	ND	41	83
Plainwell WWTP	5/15/2019	ND	ND	36

[1] Collected by the city of Otsego
[2] Exhibited chromatographic interference that could not be resolved; may be biased high
[3] Collected by the Otsego Paper Inc.

Kalamazoo River Tributaries

A total of five samples at four locations were collected in August 2018 from Kalamazoo River tributaries near their confluence and analyzed for PFAS (Table 3). An unnamed creek near the city of Parchment had a PFOS concentration of 13 ng/L and was the only Kalamazoo River tributary sample in August 2018 with an HNV exceedance for PFOS. Portage Creek had PFOS concentrations ranging from 2.7 to 2.8 ng/L in duplicate samples. PFOS concentrations were 3.0 and 1.1 ng/L in Davis Creek and the Battle Creek River, respectively. No PFOA concentration in these samples exceeded the HNV and ranged from 1.1 to 15 ng/L. In December 2018, samples from Helmer Creek revealed exceedances of the PFOS HNV.

Helmer Creek Watershed

A surface water sample was collected at each of seven locations from the Helmer Creek watershed near Battle Creek in December 2018 and analyzed for PFAS. An additional sample from Harts lake was collected in February 2019. Five samples (5 locations) exceeded the HNV for PFOS with concentrations detected at 44 ng/L in an unnamed tributary to Helmer Creek, 54 ng/L in the Harts Lake drain, 65 ng/L in Beaver Dam Pond, and up to 98 ng/L in Helmer Creek (Table 3). No samples collected from the Helmer Creek watershed exceeded the HNV for PFOA, ranging from 1.9 to 21 ng/L. In May 2018, maximum PFOS and PFOA concentrations from groundwater monitoring wells on the Kellogg ANGB in Battle Creek collected by AECOM were 53,000 and 23,000 ng/L, respectively.

Bluegill collected from Beaver Dam Pond in October 2018 had an average PFOS fillet concentration of 332 µg/kg, which resulted in a MDHHS “Eat Safe Fish” ‘Do not eat’ advisory for all fish species in Helmer Creek, including Beaver Dam Pond. Nine of ten bluegill collected from Elks Lodge Pond in October 2018 had non-detectable fillet concentrations of PFOS. The one bluegill with detectable levels of PFOS had a fillet concentration of 9 µg/kg, below the MDHHS “Eat Safe Fish’ screening values for PFOS. Bluegill collected from Harts Lake also had a mean fillet concentration below the “Eat Safe Fish” screening values. Anglers should be advised to follow the MDHHS guidance due to mercury, however.

Gull Lake

Neither the PFOS nor PFOA HNV was exceeded in any sample collected from Gull Lake. PFOS ranged from 0.7 to 1.0 ng/L, whereas, PFOA ranged from 1.2 to 1.4 ng/L (Table 3). Largemouth bass, rock bass, and bluegill collected from Gull Lake in 2018 had an average PFOS fillet concentration of 2.7, 1.2, and 1.0 µg/kg, respectively, well below the lowest MDHHS “Eat Safe Fish” screening value of 9 µg/kg.

Ambient Water Sampling Quality Control / Quality Assurance

Neither PFOS nor PFOA were measured above their respective detection limit in the August 2018 equipment, field, and trip blanks. All other analytes in the August 2018 blanks were below laboratory detection limits in these blanks with a few exceptions: PFHxS was measured at 0.29, 0.29, 0.23, and 0.23 ng/L in the depth weighed sampling bottle and Van Dorn equipment blanks and the field and trip blanks, respectively, which is above the detection limit (0.15 ng/L) but below the reporting limit. This compound was also detected at a similar level in the laboratory method blanks, indicating the source was most likely within the analytical process. PFBA and PFTeA was measured at 0.39 and 0.33 ng/L, respectively, in the Trip blank; however, was also found at a similar level in the method blank (0.45 and 0.31 ng/L, respectively). FtS 6:2 was detected at 27, 2.6, 5.2 and 2.9 ng/L in the weighed

sampling bottle equipment blank, trip blank, field blank, and laboratory method blank, respectively. No PFAS analytes were detected in the equipment, field, or trip blank collected in December 2018. PFBA, PFOS, PFHxS, and FtS 6:2 were detected below reporting limits in the February 2019 field blank at a concentration of 0.42, 0.89, 0.29, and 4.5 ng/L, respectively. PFBA and PFHxS were detected at a similar level in the laboratory method blank, indicating the source of these analytes was most likely within the analytical process.

Three replicate and two duplicate samples were collected over both sampling events. None of these samples exceeded the RPD threshold of 30% for PFOS or PFOA. The RPD for the KR-0030, KR-0090, KR-0110, KR-0130, PC-0010, KR-0200, and KR-0210 locations for PFOS were 0, 0, 6.9, 2.6, 0, 7.4, and 14.6%, respectively. The PFOA RPD for these locations were 8.9, 3.7, 9.5, 4.7, 3.6, 2.3, and 3.9%, respectively. Three samples exceeded the RPD for at least one other PFAS (Table 2). The KR-0030 replicate sample had an RPD of 165.7 and 44.1% for FOSA and FtS 6:2, respectively. The KR-0090 duplicate sample had an RPD of 59.2% for FtS 6:2. The RPD for the KR-0130 duplicate sample for PFBA was 31.3%. All other data quality control objectives and criteria were met except for the recoveries of seven analytes from several samples which exceeded the 150% upper threshold (Table 2). Seven analytes exceeded the 150% recovery threshold for the spiked internal standards in at least one sample: FtS 4:2 (7 of 66 samples); FtS 6:2 (14 samples); FtS 8:2 (3 samples); PFBS (7 samples); NMeFOSAA (5 samples); NEtFOSAA (6 samples); and PFPeA (1 sample). Due to the number of samples where at least one analyte exceeded the recovery threshold, the QA/QC completeness objective was not met (Table 2). However, no sample exceeded any QA/QC criteria for PFOS or PFOA. Therefore, the failure to meet these data quality objectives did not impact our determination as to whether or not PFAS sources were 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.

CONCLUSIONS AND FUTURE WORK

Samples collected from the following 17 locations in the Kalamazoo River watershed exceeded the HNV for PFOS:

1. KR-0060: Kalamazoo River at N. North Street near Otsego, Michigan.
2. UC-0010: Unnamed Creek near the confluence with the Kalamazoo River in Parchment, Michigan.
3. KR-0100: Kalamazoo River downstream of the old landfill near Parchment, Michigan.
4. PD-0010: The stormwater drain coming off of the Crown Vantage site in Parchment, Michigan, near the confluence with the Kalamazoo River.
5. Culvert-001: The culvert leading to Drain-001.
6. Drain-001: The stormwater drain coming off of the Crown Vantage site in Parchment, Michigan, just downstream of Culvert-001.
7. Pond-0010: A pond located on the Crown Vantage site in Parchment, Michigan, that empties into PD-0010.
8. Clarifier-001: The old clarifier located on the Crown Vantage site in Parchment, Michigan.
9. Lagoon-001: The old wastewater lagoon on the Crown Vantage site in Parchment, Michigan.
10. KR-0120*: Kalamazoo River downstream of the Parchment stormwater drains.
11. KR-0200: Kalamazoo River at Custer Drive near Battle Creek, Michigan.
12. KR-0210: Kalamazoo River at Battle Creek Linear Park.
13. HC-0010: Helmer Creek at Battle Creek Linear Park.
14. HC-0200: Helmer Creek at Beaver Dam Pond Road.
15. BD-0010: Beaver Dam Pond at Beaver Dam Pond Road.

16. UN-0010: Unnamed Tributary to Helmer Creek at the end of Reese Road.
17. HL-0010: Harts Lake Drain at Harts Lake Road.

* This was a water column distribution site, only the surface sample exceeded the HNV. The subsurface, mid-depth, bottom, and depth composite sample were below the HNV.

Fine-scale distributions of chemical plumes can differ between point and nonpoint sources with the former exhibiting a more pulsatile behavior (Lahman and Moore, 2015). Regardless of the source type, average peak concentrations within chemical plumes decrease further downstream away from the source (Lahman and Moore, 2015). The water column sampling displayed a relatively mixed PFOS concentration at the KR-0100 location ranging from 11 ng/L in the mid-depth sample to 19 ng/L in the bottom sample. Furthermore, the PFOS concentration at this location was elevated in comparison to the upstream KR-0110 location (4.5 ng/L) and the downstream KR-0095 location (9.2 ng/L). Additionally, the same 13 PFAS analytes were found throughout the water column at this location, including NEtFOSAA and FOSA. These PFAS analytes were detected in all samples collected from the Crown Vantage site as well as in 16 of 17 samples from the Kalamazoo River downstream. The sole non-detect was at an upstream location in the Kalamazoo River (KR-0110) which is adjacent to the Crown Vantage site. In comparison, the NEtFOSAA analyte was only detected in two out of the 23 surface water samples from the Kalamazoo River collected upstream of the Crown Vantage site. Similarly, the FOSA analyte was only detected once in the upstream samples. It is plausible that the PFAS groundwater contamination at the Crown Vantage site may be influencing the river at or near the KR-0100 sampling location.

In comparison, the other water column investigation sampling location (KR-0120) had 3.3 times higher PFOS concentration on the surface relative to the other water column samples collected at this location. In addition, the sampling revealed three PFAS analytes (PFDA, PFHpS, and NEtFOSAA) were present at the surface that were not detected in the other water column samples at this location. This sample location was downstream of stormwater outfalls with PFOS concentrations up to 10.0 ng/L and was collected following significant rainfall in the watershed. It is plausible that the contamination at the KR-0120 location is still adhered to the surface of the river and not fully mixed in the water column. More sampling would be needed to support these conclusions.

Overall these results indicate that sources are present in the Kalamazoo River watershed near Otsego, Parchment, and Battle Creek. It is likely that the groundwater contamination near the Crown Vantage site in Parchment and the Kellogg ANGB in Battle Creek are sources of surface water contamination in the Kalamazoo River watershed. The source of contamination near Otsego is still unknown and under investigation.

The KR-0160 sampling location is approximately 1.5 kilometer downstream of the Nolichucky Industrial Corporation PFAS site where contaminated groundwater was discovered in May 2019. At the time of our surface water sample collection in 2018, it did not appear the contaminated groundwater at this site was impacting the Kalamazoo River as the KR-0160 location had a PFOS and PFOA concentration of 4.0 and 1.8 ng/L, respectively. However, caution should be taken before making any conclusions regarding this individual sample as our previous PFAS sampling efforts have shown that surface water concentrations can be variable both spatially and temporally.

PFOS concentrations in fish downstream of Morrow Dam to the Kalamazoo River mouth exceed MDHHS “Eat Safe Fish” screening values and would cause varying levels of consumption advice, but they are superseded by the existing “Do not eat” advisory for all species of fish from that reach of river due to PCBs. Bluegill collected from the large fishing pond at Markin Glen Park near Parchment had detectable levels of PFOS that would cause a 12 meals per month advisory; however, this advisory is secondary to the four meals per month mercury advisory for bluegill for this water body.

Fish tissue analysis can provide a more complete evaluation of water quality when bioaccumulative contaminant concentrations in the surface water are highly variable. PFAS groundwater contamination, possibly from the Kellogg ANGB, has impacted Helmer Creek and resulted in a 'Do not eat' advisory for all fish from the creek, including Beaver Dam Pond. Bluegill collected from Harts Lake did not have elevated levels of PFOS. Taken into consideration with the non-detectable PFOS surface water concentration, Harts Lake does not appear to be impacted by the contaminated groundwater. Additionally, Elks Lodge Pond is near Helmer Creek and does not appear to be significantly impacted by the PFAS groundwater contamination as bluegill fillet samples ranged from non-detect to 9 µg/kg PFOS. Lastly, we plan to collect fish from Goguac Lake, a highly developed and popular recreational area within the city of Battle Creek less than two miles southeast of the Kellogg ANGB.

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