MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY
WATER RESOURCES DIVISION
MARCH 2019

STAFF REPORT

INVESTIGATION OF THE OCCURRENCE AND SOURCES OF PERFLUORINATED AND POLYFLUORINATED ALKYL SUBSTANCES IN THE RIVER RAISIN WATERSHED JUNE-NOVEMBER 2018

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 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 Environmental Quality (MDEQ), Water Resources Division (WRD), has generated Rule 57 surface water quality values for the protection of human health 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. Additionally, the MDEQ has generated Rule 57 surface water quality values for the protection of aquatic life for PFOS and PFOA. 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 PFOA is 780,000 and 140,000 ng/L, respectively. The

Rule 57 AMV and FCV for PFOS is 880,000 and 7,700 ng/L, respectively. The aquatic life values for both PFOS and PFOA are less restrictive than the human health values.

In 2017, the MDEQ, WRD, added PFAS sampling as a part of routine National Pollutant Discharge Elimination System permit compliance sampling inspections. Additionally, in 2018 the MDEQ began a statewide Industrial Pretreatment Program (IPP) PFAS Initiative that required all municipal wastewater treatment plants (WWTP) with required 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, if WWTPs identified significant sources of PFOS, they are required to monitor their WWTP effluent and work with their industrial users to control the discharge of PFOS.

The River Raisin (HUC 04100002) is located in southeast Michigan and drains portions of 5 counties; Hillsdale, Jackson, Lenawee, Monroe, and Washtenaw. Approximately 75% of the River Raisin watershed is agricultural production (River Raisin Watershed Council, 2009). The River Raisin is a primary source of drinking water for 3 municipalities (Adrian, Blissfield, and Deerfield) and is an emergency drinking water source for the city of Monroe. The main tributaries of the River Raisin are Goose Creek near Brooklyn, Evans Creek and Iron Creek near Tecumseh, Wolf Creek and the south branch of the River Raisin near Adrian, Black Creek near Blissfield, and the Little River Raisin, Macon Creek, and Saline River near Dundee.

Previous work by Kannan et al. (2005) found 3.5 ng/L PFOS and 14.7 ng/L PFOA in River Raisin surface water, approximately 1 kilometer (km) upstream of the river mouth. Additionally, PFOS concentrations found in sport fish and forage fish collected from the River Raisin near Monroe in 2016 indicated that sources of PFAS exist in the watershed. For these reasons, the MDEQ, 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.

SUMMARY

1. PFOS was detected in surface water at all 19 sample locations during the June 2018 sampling event (0.7 to 460 ng/L), at 21 of 22 sample locations during the August 2018 sampling event (< 0.5 to 230 ng/L), and at all 5 sample locations during the October 2018 sampling event (0.9 to 3.3 ng/L).
2. The HNV for PFOS was exceeded at 4 (21%), 2 (9%), and 0 sample locations during the June, August, and October 2018 sampling events, respectively.
3. Sample locations that exceeded the PFOS HNV during the June 2018 sampling event did not exceed the HNV during the August 2018 sampling event.
4. PFOA concentrations measured during the June, August, and October 2018 sampling events did not exceed the HNV, with concentrations ranging from non-detect to 1.9 ng/L.
5. None of the PFOS and PFOA surface water samples exceeded their respective AMV and FCV.
6. The concentration of PFOS in fish collected near the mouth of the River Raisin were high enough to warrant a fish consumption advisory.
7. Of the 6 WWTP effluents monitored, only the Saline WWTP effluent exceeded the PFOS HNV at 33 ng/L PFOS.

8. The city of Saline is participating in the IPP PFAS Initiative and has identified 1 source of PFOS and there may be others, potentially including infiltration into the sanitary sewers from contaminated sites.
9. The Saline WWTP is a known PFAS source and, due to confirmed PFAS-contaminated groundwater, the Washtenaw Industrial Facility LLC (former Universal Die Cast) site is a known PFAS source to the Saline River.
10. The former Ford Motor Company site in Saline has confirmed PFAS-contaminated groundwater so is a probable source of PFOS to the Saline River.
11. The sources of the PFOS contamination in the rivers near Tecumseh, Adrian, Deerfield, and Dundee are still unknown.
12. Based on limited sampling, the former Tecumseh Products facility in Tecumseh, Wacker Chemical Company near Adrian, and the Silbond Corporation near Adrian are likely not significant sources of PFAS to the River Raisin watershed.
13. Staff of the MDEQ, WRD, plan to analyze additional fish collected from the River Raisin and Saline River to evaluate water quality due to the variable surface water PFOS concentrations.

METHODS

Surface Water

Surface water grab samples were collected following the MDEQ Surface Water PFAS Sampling Guidance document (MDEQ, 2018a) from the River Raisin and select tributaries on 3 occasions between June and October 2018. All samples were analyzed for 24 PFAS analytes, as described in the Quality Assurance Project Plan (MDEQ, 2018b). To date, a total of 54 surface water samples from 40 locations in the River Raisin watershed were collected by the MDEQ, WRD, and analyzed by TestAmerica-Sacramento.

Sample Collection

Samples were collected in two 250 milliliter (mL) high-density polyethylene (HDPE) bottles (laboratory certified as PFAS-free). Subsurface 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. Samples from nonwadeable locations were collected from either a boat or bridge using a weighted, depth-integrating 1-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 2 sample bottles.

Samples were preserved on ice and shipped via overnight delivery to the TestAmerica Sacramento laboratory at the end of the sample collection event. TestAmerica is a MDEQ contract laboratory and analyzes surface water samples using a modified version of the United States Environmental Protection Agency (USEPA) Method 537 (USEPA, 2009), a process using isotope dilution for analyte quantification. The laboratory provided analytical results for 24 perfluorinated compounds (Table 1) to the MDEQ, WRD, 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).

Table 1. Perfluoroalkyl and polyfluoroalkyl substances (PFAS) analyzed by the TestAmerica Sacramento laboratory.

Compound	Abbreviation
Perfluorotetradecanoic acid	PFTeA
Perfluorotridecanoic acid	PFTriA
Perfluorododecanoic acid	PFDoA
Perfluoroundecanoic acid	PFUnA
Perfluorodecanoic acid	PFDA
Perfluorononanoic acid	PFNA
Perfluorooctanoic acid	PFOA
Perfluoroheptanoic acid	PFHpA
Perfluorohexanoic acid	PFHxA
Perfluoropentanoic acid	PFPeA
Perfluorobutanoic acid	PFBA
Perfluorodecanesulfonic acid	PFDS
Perfluorononanesulfonic acid	PFNS
Perfluorooctanesulfonic acid	PFOS
Perfluoroheptanesulfonic acid	PFHpS
Perfluorohexanesulfonic acid	PFHxS
Perfluoropentanesulfonic acid	PFPeS
Perfluorobutanesulfonic acid	PFBS
Perfluorooctanesulfonamide	PFOSA
Fluorotelomer sulphonic acid 8:2	FtS 8:2
Fluorotelomer sulphonic acid 6:2	FtS 6:2
Fluorotelomer sulphonic acid 4:2	FtS 4:2
2-(N-Ethylperfluorooctanesulfonamido) acetic acid	N-EtFOSAA
2-(N-Methylperfluorooctanesulfonamido) acetic acid	N-MeFOSAA

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 2 sets of samples in succession at the same sample location. Two replicate samples were collected during the June and August 2018 sampling events. Two duplicate samples, each consisting of a 1-liter composite sample dispensed into two sets of two 250 mL HDPE bottles, were collected during the June and August 2018 sampling events. One field blank was collected during all 3 2018 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 3 2018 sampling events and consisted of 1 laboratory prepared bottle of PFAS-free deionized water that was transported unopened to the field and returned to the lab for analysis. Precision of replicate and duplicate results is calculated by the relative percent deviation (RPD) as defined by 100 times the difference (range) of each sample, X1 and X2, divided by the arithmetic mean of the set and calculated from the following equation:

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

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

Data Quality Indicator	Measurement	Data Quality Objective	Results
Precision	1 Matrix Spike/Matrix Spike (MS/MSD) Duplicate per preparation batch	%RPD < 30%	RPD ranged from 0 to 19 % for all analytes over all three sampling events
Precision	Field Sample Replication/Duplication	%RPD < 30%	RPD < 30 % except 1. RR-0210 (June) PFOS = 30.3 % 2. SR-0210 (June) PFOS = 184.6 % 3. SR-0210 (June) PFHxS = 52.6 % 4. SR-0210 (August) PFOS = 118.2 % 5. SR-0210 (August) PFHxS = 30.9 % 6. SB-0020 (August) PFHpA = 32.9 %
Accuracy/Bias	1 Lab Control Spike (LCS) and 1 MS/MSD per preparation batch	60 to 140 % recovery	Analyte recovery ranged from 81 to 111 % over all three sampling events
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
Accuracy/Bias	Every sample (spiked, standard or method blank) will receive an internal standard	25 to 150 % recovery	Analyte recovery ranged from 37 to 140 % over all three sampling events
Comparability	LC/MS Analytical work to be conducted by the TestAmerica LCMS West Sacramento Laboratory	Laboratory will provide verification that methods were properly implemented, and results meet QA/QC standards	All samples analyses were conducted by TestAmerica LCMS West Sacramento Laboratory and met QA/QC standards
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	$\frac{50}{54} * 100 = 92.6\%$
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 TestAmerica

June 2018 Ambient Surface Water Sampling

Initial ambient surface water samples were collected for PFAS analysis on June 14 and June 15, 2018. Sampling locations were selected near drinking water intakes and to bracket potential sources of PFAS contamination in the watershed. Grab samples of ambient surface water were collected by the MDEQ, WRD, at 13 locations from the main flow of the River Raisin, 2 locations on the south branch of the River Raisin, 2 locations on Wolf Creek near Adrian, Michigan, and 2 locations on the Saline River (Table 3, Figure 1). According to the United States Geological Survey (USGS) stream gaging station on the River Raisin near Manchester, Michigan (USGS 04175600), the river flow during this sampling event was near the 45-year median for this date and location (~ 105 cubic feet per second [cfs]). Significant precipitation did not occur up to 4 days prior to sample collection.

Reconnaissance Meeting

Following the receipt and analysis of the June 2018 surface water sample data in July 2018, staff of the MDEQ, WRD; Remediation and Redevelopment Division (RRD); and Waste Management and Radiological Protection Division (WMRPD) met to discuss additional sampling. Participants at the meeting concluded that the sampling of finished drinking water from 5 water treatment plants should be expedited via the Statewide Testing Initiative due to HNV exceedances for PFOS in surface water samples collected upstream of the drinking water intakes. The MDEQ also discussed the former Tecumseh Products site as a potential source of PFAS in the River Raisin watershed due to known or suspected use of PFAS compounds in their operations. Groundwater sampling was planned by the MDEQ, WMRPD, to determine if this facility was a source to the River Raisin and groundwater used as a drinking water source.

August 2018 Ambient Surface Water Sampling

A follow-up sampling event occurred on August 16, 2018 (Table 3; Figure 2). Sampling locations were selected to bracket potential sources of PFAS contamination near areas where PFOS concentrations in samples collected during the June 2018 sampling event had exceeded the HNV. Grab ambient surface water samples were collected by the MDEQ, WRD, from the main flow of the River Raisin at 14 locations, including 4 revisit sample locations from the initial June 2018 sampling event. More intensive sampling occurred near the city of Tecumseh (Figure 2 inset) because 460 ng/L PFOS was detected in a sample collected in June 2018 near the city. Samples were also collected at 4 locations on the south branch of the River Raisin, including 1 revisit location, and 4 locations on the Saline River, including 1 revisit location. According to the USGS stream gaging station on the River Raisin near Manchester, Michigan (USGS 04175600), the river flow (~ 24 cfs) during this sampling event was below the 45-year median (~ 30 cfs) for this date and location at the start of sample collection. Precipitation occurred during this sampling event and resulted in a 6 cfs increase in flow at this station between the start and end of sample collection.

Table 3. PFOS and PFOA concentrations measured in surface water samples collected from the River Raisin watershed on June 14 and June 15, 2018, and/or August 16, 2018. Revisited sample locations are in bold; Concentrations exceeding the Rule 57 HNV are bolded and italicized. ND denotes a Non-Detect.

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	PFOS (ng/L)	PFOA (ng/L)
RR-0500	River Raisin d/s of Wamplers Lake Road	42.100028	-84.224611	June	0.7†	1.6†
RR-0400	River Raisin d/s of East Austin Road	42.148565	-84.01799	June	0.9†	1.5†
RR-0350	River Raisin d/s of Staib Road	42.042831	-83.964029	June	0.8†	1.5†
RR-0300	Globe Mill Pond	42.005953	-83.9349	August	0.9†	0.9†
RR-0290	River Raisin at East Monroe Road	42.003968	-83.9317	August	0.7†	0.9†
RR-0270	**River Raisin d/s of Tecumseh Wastewater Treatment Plant**	42.001022	-83.931162	June	***460.0***	1.6†
RR-0270	**River Raisin d/s of Tecumseh Wastewater Treatment Plant**	42.001022	-83.931162	August	0.8†	1.4†
RR-0270	**River Raisin d/s of Tecumseh Wastewater Treatment Plant**	42.001022	-83.931162	August[R]	0.7†	1.7†
RD-0010	Drain to the River Raisin adjacent to RR-270	42.00092	-83.931521	October	3.0	1.3†
RR-0269	River Raisin d/s of Tecumseh Landfill	41.999853	-83.930613	October	0.9†	1.1†
RR-0260	River Raisin at Blood Road End	41.994947	-83.9316	August	0.9†	1.7†
RR-0250	River Raisin at Russel Road	41.992222	-83.9305	August	0.6†	1.7†
RR-0250	River Raisin at Russel Road	41.992222	-83.9305	August[D]	0.8†	1.7†
RR-0240	River Raisin at Comford Road End	41.986817	-83.9323	August	0.8†	1.6†
RR-0230	River Raisin at Sutton Road	41.949146	-83.9415	August	0.6†	1.4†
RR-0220	River Raisin at North Raisin Center Highway	41.943368	-83.9451	August	0.6†	1.3†
RR-0210	**River Raisin at North Wilmoth Highway**	41.935687	-83.964511	June	1.0†	1.4†
RR-0210	**River Raisin at North Wilmoth Highway**	41.935687	-83.964511	June[R]	ND	1.3†
RR-0210	**River Raisin at North Wilmoth Highway**	41.935687	-83.964511	August	0.7†	1.4†
RR-0200	River Raisin at Laberdee Road	41.919528	-83.9743	August	1.5†	1.3†
WC-0030	Wolf Creek at Saw Mill Court	41.919103	-84.043464	June	2.6	1.4†
WC-0010	Wolf Creek d/s of Bent Oak Avenue	41.910417	-84.034334	June	1.0†	1.3†
SB-0100	South Branch River Raisin at Carleton Road	41.860191	-84.052808	August	ND	ND
SB-0040	South Branch of River Raisin d/s of Bent Oak Avenue	41.908379	-84.03321	June	1.2†	ND
SB-0030	South Branch River Raisin at North Main Street	41.909518	-84.029571	August	2.5	1.2†

† indicates a concentration at a level that was above the method detection limit but below the laboratory reporting limit.
[R] Replicate Sample
[D] Duplicate Sample

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	PFOS (ng/L)	PFOA (ng/L)
SB-0020	South Branch River at Howell Highway	41.917652	-84.01	August	3.0	1.8†
SB-0020	South Branch River at Howell Highway	41.917652	-84.01	August[R]	2.9	1.8†
SB-0010	**South Branch of River Raisin u/s of Confluence with Main Branch**	41.924289	-83.977368	June	***26.0***	1.3†
SB-0010	**South Branch of River Raisin u/s of Confluence with Main Branch**	41.924289	-83.977368	August	5.8	1.6†
RR-0130	**River Raisin at East Gorman Road**	41.828526	-83.879853	June	4.7	1.3†
RR-0130	**River Raisin at East Gorman Road**	41.828526	-83.879853	August	***15.0***	1.5†
RR-0120	River Raisin at North Monroe Street	41.838509	-83.867639	June	1.0†	1.5†
RR-0120	River Raisin at North Monroe Street	41.838509	-83.867639	June[D]	1.0†	1.4†
RR-0110	River Raisin at Iffland Road	41.854663	-83.85	August	5.2	1.4†
RR-0100	**River Raisin at Witts End**	41.881945	-83.7858	June	***160.0***	1.4†
RR-0100	**River Raisin at Witts End**	41.881945	-83.7858	August	5.1	1.7†
RR-0090	River Raisin at Taft Road	41.889649	-83.744788	June	2.7	1.3†
RR-0070	River Raisin at East Monroe Street	41.952986	-83.647311	June	1.4†	1.5†
MC-0010	Macon Creek at Stowell Road	41.979554	-83.625083	October	1.0†	1.2†
SR-0230	Saline River at W. Michigan Avenue	42.163305	-83.789	August	0.7†	ND
SR-0215	Saline River u/s Monroe Street	42.159332	-83.78414	October	1.6†	0.9†
SR-0210	**Saline River at Crestwood Circle**	42.158417	-83.780978	June	5.2	1.0†
SR-0210	**Saline River at Crestwood Circle**	42.158417	-83.780978	June[R]	***130.0***	1.0†
SR-0210	**Saline River at Crestwood Circle**	42.158417	-83.780978	August	1.8†	1.7†
SR-0210	**Saline River at Crestwood Circle**	42.158417	-83.780978	August[D]	7.0	1.7†
SR-0200	Saline River at Hartman Road End	42.144046	-83.782	August	1.5†	1.2†
SR-0150	Saline River at Gump Lake Road	42.078017	-83.677679	August	2.0	1.8†
SR-0100	Saline River at Sherman Road	42.062962	-83.653876	June	1.8†	1.4†
SR-0010	Saline River at Bigelow Road	41.98031	-83.616326	October	3.3	1.6†
RR-0060	River Raisin at Plank Road	41.975439	-83.601303	August	***230.0***	1.9
RR-0050	River Raisin at Ida-Maybee Road Launch	41.963911	-83.546834	June	1.0†	1.4†
RR-0020	River Raisin at North Macomb Street	41.91632	-83.393954	June	1.2†	1.6†
RR-0010	River Raisin d/s Riverview Marina	41.900735	-83.355405	June	1.5†	1.6†
RR-0010	River Raisin d/s Riverview Marina	41.900735	-83.355405	June[D]	1.4†	1.5†

† indicates a concentration at a level that was above the method detection limit but below the laboratory reporting limit.
[R] Replicate Sample
[D] Duplicate Sample

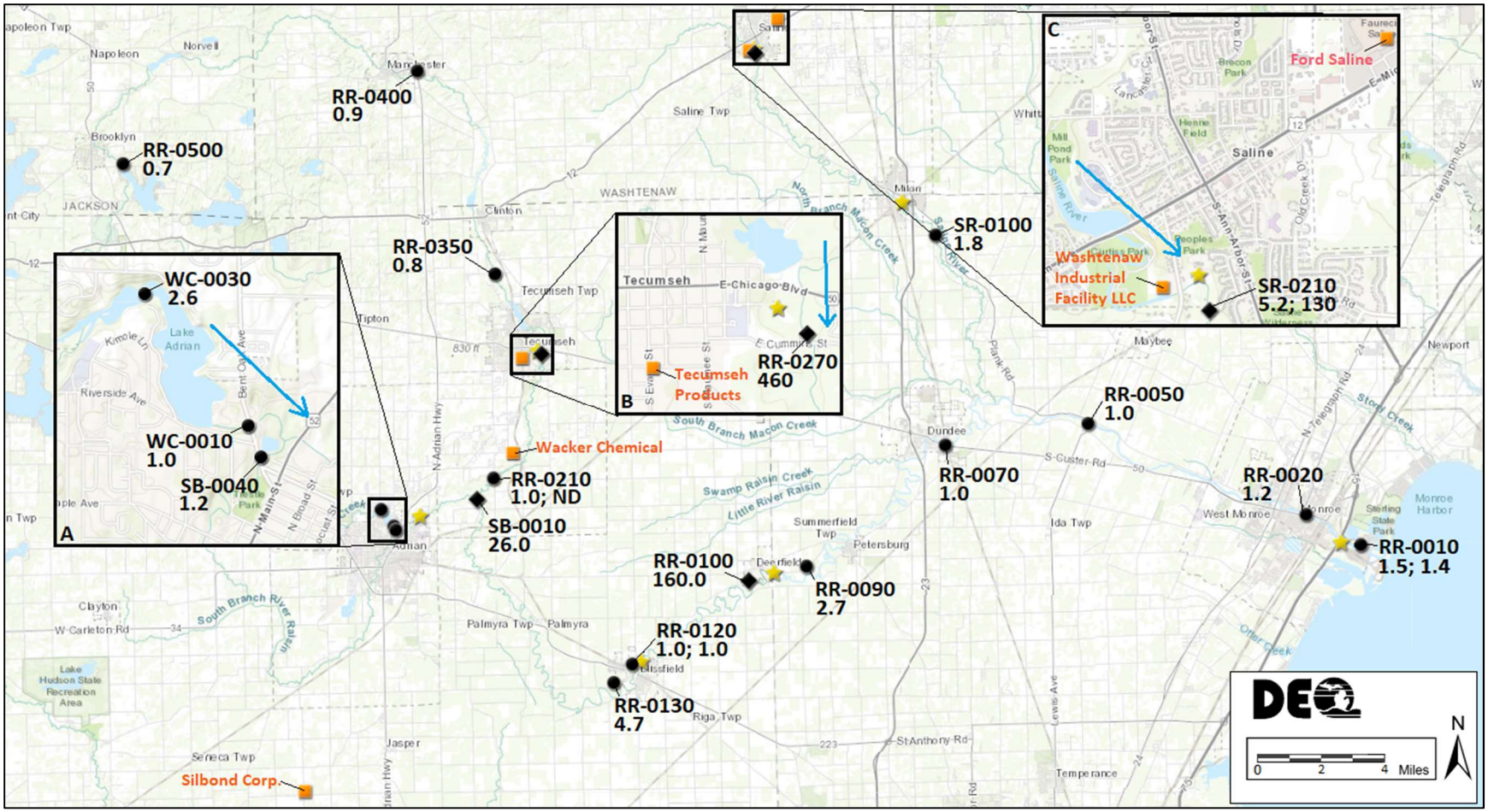

Figure 1. Overview map of the River Raisin with surface water PFOS concentrations (ng/L) at locations sampled on June 14 and June 15, 2018. Inset A provides details for the 2 sample collections near Adrian. Inset B provides details for the sample collected near Tecumseh. Inset C provides details for the sample collections near Saline. The blue arrows indicate general river flow direction. RR denotes a location on the main branch of the River Raisin; SB is the south branch of the River Raisin; WC is Wolf Creek; SR is the Saline River. ◆ 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 facility investigation site.

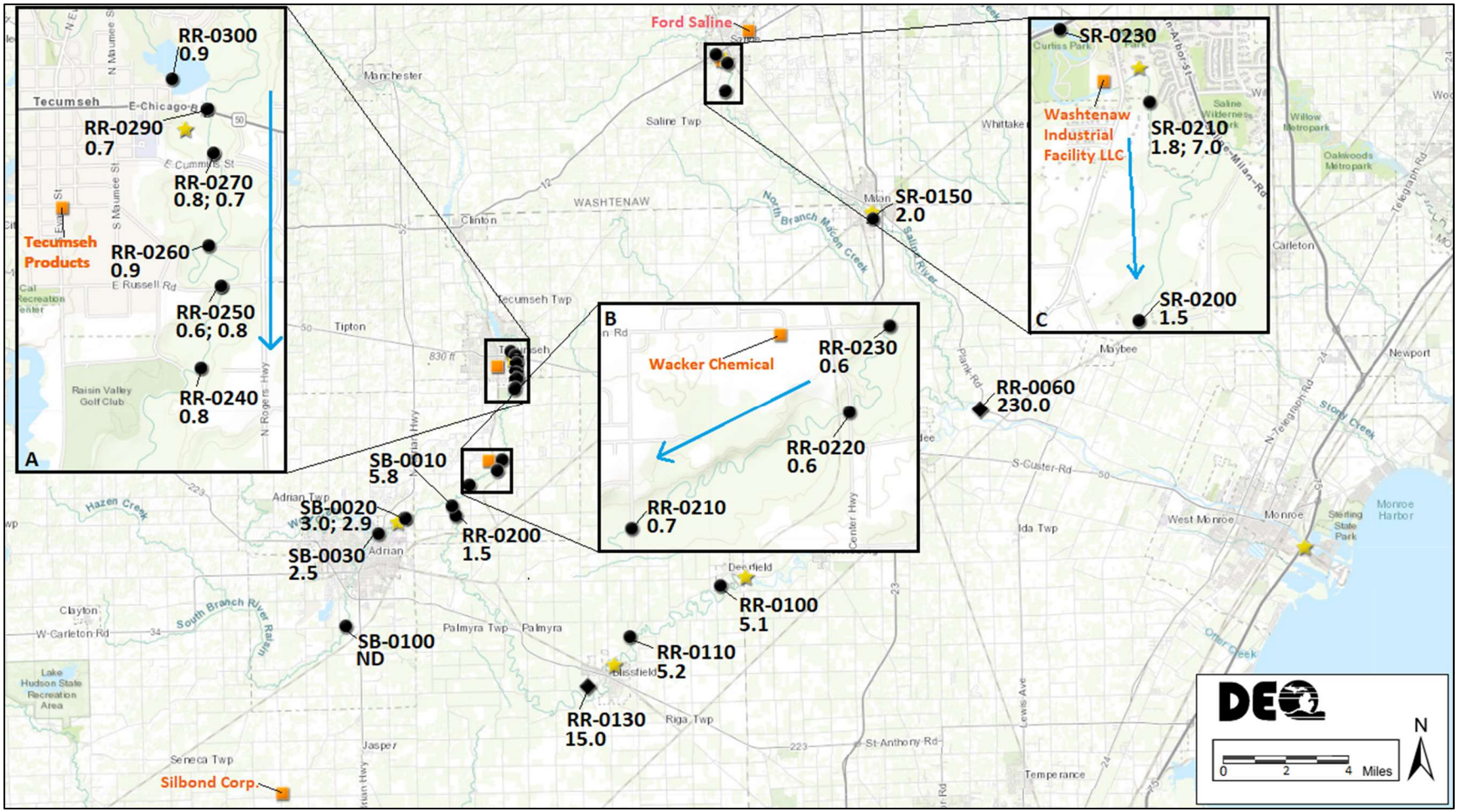

Figure 2. Overview map of the River Raisin with surface water PFOS concentrations (ng/L) at locations sampled on August 16, 2018. Inset A provides details for the sample collections upstream and downstream of Tecumseh Products. Inset B provides details for the samples collected upstream and downstream of Wacker Chemical. Inset C provides details for the samples collected upstream and downstream of Washtenaw Industrial Facility. The blue arrows indicate general river flow direction. RR denotes a location on the main branch of the River Raisin; SB is the south branch of the River Raisin; SR is the Saline River. ◆ indicates a sample location with a Part 4, Rule 57 HNV exceedance. Inset provides detail for the Tecumseh area sample locations. ★ indicates approximate location of a wastewater treatment plant. ■ indicates approximate location of a facility investigation site.

Reconnaissance Meeting

Following the receipt and results of the August 2018 surface water sampling in September 2018, the MDEQ, WRD; RRD; and WMRPD staff met to discuss 3 additional facilities as potential sources of PFAS in the River Raisin watershed because they were known or suspected to have used PFAS compounds in their operations: (1) The Wacker Chemical Company near Adrian; (2) Silbond Corporation near Adrian; and (3) Washtenaw Industrial Facility LLC (former Universal Die Cast) site in Saline. Additionally, a historic landfill near Dundee was discussed as a potential source of PFAS to the River Raisin watershed. Groundwater sampling was planned at these locations to determine potential sources to surface water bodies and groundwater used as a drinking water source.

October 2018 Ambient Surface Water Sampling

A third targeted sampling event initiated by the MDEQ, WMRPD, occurred on October 29, 2018, following the detection of PFOS in groundwater monitoring wells at the Washtenaw Industrial Facility LLC (former Universal Die Cast) site in September 2018. The PFOS concentration in 1 of the monitoring wells had a PFOS concentration of 3,030 ng/L. This site is located adjacent to the Saline River and approximately 0.5 km upstream of the SR-0210 surface water sample location where 130 ng/L PFOS concentration was detected in June 2018. During this sampling event, staff from the MDEQ, WMRPD; WRD; and RRD collected 5 grab ambient surface water samples in the River Raisin watershed (Figure 3). A sample was collected from the Saline River adjacent to the monitoring well at the Washtenaw Industrial Facility LLC (former Universal Die Cast) site. Another surface water sample was collected in the Saline River and Macon Creek near their confluence with the River Raisin and adjacent to an old landfill near Dundee, Michigan, because 230 ng/L PFOS concentration was detected in August 2018 at the RR-0060 sample location downstream of these 2 confluences. A sample was collected from a drain to the River Raisin in Tecumseh adjacent to the RR-0270 sample location where 460 ng/L PFOS concentration was detected in June 2018. The final surface water sample was collected from the River Raisin downstream of the Tecumseh landfill. According to the USGS stream gaging station on the River Raisin near Manchester, Michigan (USGS 04175600), the river flow during this sampling event was near the 45-year median for this date and location (~ 55 cfs). Precipitation occurred the day before this sampling event and resulted in an 18 cfs increase in flow at this station prior to sample collection.

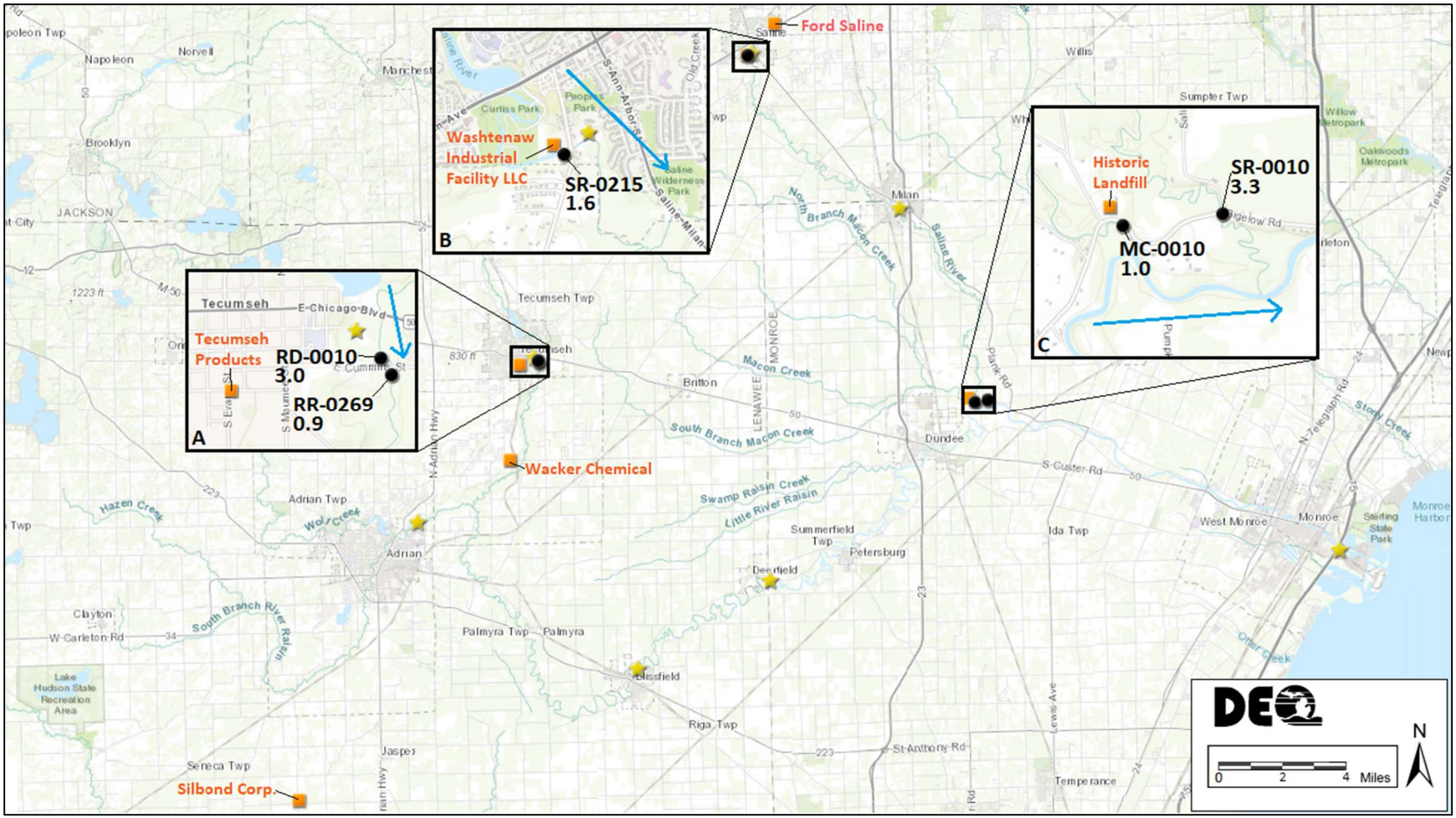

Figure 3. Overview map of the River Raisin with surface water PFOS concentrations (ng/L) at locations sampled on October 29, 2018. Inset A provides details for the 2 samples collected near Tecumseh. Inset B provides details for the 1 sample location collected near Saline. Inset C provides details for the 2 sample locations collected downstream of a historic landfill. The blue arrows indicate general river flow direction. RD denotes a drain to the River Raisin near Tecumseh; RR denotes a location on the main branch of the River Raisin; MC denotes the Macon Creek; SR is the Saline River. ★ indicates approximate location of a wastewater treatment plant. ■ indicates approximate location of a facility investigation site.

Fish Tissue

Rock bass (*Ambloplites rupestris*) and largemouth bass (*Micropterus salmoides*) were collected from the River Raisin near the river mouth at Monroe in 2016 using standard electrofishing equipment and were prepared as standard edible portion samples following the MDEQ, WRD, Procedure WRD-SWAS-004 (MDEQ, 2014). Fish tissue samples were analyzed for 11 perfluorinated compounds by the Michigan Department of Health and Human Services (MDHHS), Analytical Chemistry Laboratory (Table 4).

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

Compound	Abbreviation
Perfluorooctanoic acid	PFOA
Perfluorooctane sulfonate	PFOS
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnA
Perfluorododecanoic acid	PFDoA
Perfluorotridecanoic acid	PFTriA
Perfluorotetradecanoic acid	PFTeA
Perfluorohexane sulfonate	PFHxS
Perfluorodecane sulfonate	PFDS
Perfluorooctane sulfonamide	PFOSA

Point Source Discharges/Compliance Sampling Inspections

There are 7 WWTPs with discharges to the River Raisin watershed that were selected for PFAS effluent analysis in 2018. The Tecumseh, Blissfield, and Deerfield WWTPs do not have significant industrial users requiring an IPP. The Adrian, Saline, Milan, and Monroe WWTPs have approved IPP programs and are participating in the statewide IPP PFAS Initiative.

Effluent samples from Tecumseh, Adrian, Blissfield, Deerfield, and Saline WWTPs were collected by the MDEQ, WRD, on July 31, 2018, and the Monroe WWTP effluent was sampled on September 4, 2018. In addition to the MDEQ, WRD, sampling, the cities of Milan and Monroe collected WWTP effluent samples in October 2018. Results of these sampling events are shown below in Table 5 and discussed in context of their river reaches in the Results section of this report.

Table 5. Point Source Discharges/Compliance Sampling Results.

Facility Name	Sampling Date	PFOS (ng/L)	PFOA (ng/L)	Σ PFAS (ng/L)
Saline WWTP	7/31/2018	33.0	6.4	124.8
Tecumseh WWTP	7/31/2018	2.8	14	142.9
Adrian WWTP	7/31/2018	7.1	3.6	64.9
Blissfield WWTP	7/31/2018	5.1	5.7	96.2
Deerfield WWTP	7/31/2018	5.4	5.8	60.8
Milan WWTP	10/16/2018[1]	7.3	7.2	59.9
Monroe WWTP	9/4/2018	8.0	7.0	78.6
Monroe WWTP	10/1/2018[2]	8.3	7.1	76.6
Monroe WWTP	11/20/2018[3]	5.5	5.4	50.3

Effluent grab samples were collected by MDEQ, WRD, following the MDEQ Wastewater PFAS Sampling Guidance document (MDEQ, 2018c; Draft). 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 Ziplocs before storage in a cooler with ice. Sample bottles were delivered to the TestAmerica Brighton location and shipped to the TestAmerica Sacramento laboratory at the end of the sample collection event.

The effluent grab sample at the Milan WWTP was analyzed by RTI Laboratories using test method "EPA Method 537 Modified by Isotope Dilution." Sample protocols to prevent cross contamination followed the MDEQ, WRD's, *PFAS Sampling Guidance for Wastewater*. The effluent grab sample at Monroe WWTP was analyzed by TestAmerica using test Method 537 (modified), which is an isotope dilution method. The Monroe WWTP used the Interstate Technology Regulatory Council's (ITRC) guidance entitled *Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances* to prevent cross contamination.

RESULTS AND DISCUSSION

Finished Drinking Water Samples

The finished drinking water from 5 facilities (Tecumseh, Adrian, Deerfield, Blissfield, and Saline) was collected by the MDEQ, Drinking Water and Municipal Assistance Division on August 2, 2018. PFOS and PFOA were non-detect at all 5 facilities. For further details on the drinking water sampling visit the Michigan PFAS Response Web site.

River Raisin Watershed Sampling

Ambient water sampling in the River Raisin watershed was conducted by the MDEQ, WRD, in a stepwise fashion. The initial ambient surface water samples collected for PFAS analysis on

[1] Sample collected by the City of Milan
[2] Sample collected by the City of Monroe
[3] Sample collected by a MDEQ contractor as part of a statewide PFAS biosolids evaluation

June 14 and June 15, 2018, found that PFOS concentrations at 4 sample locations (21%) exceeded the HNV for PFOS. Follow-up surface water sampling was conducted on August 16, 2018, to begin tracking potential sources of contamination, with 2 of the sample locations (9%) exceeding the HNV for PFOS. Another more targeted sampling event occurred on October 29, 2018, near Tecumseh, Saline, and Dundee. None of the 5 samples collected during this event exceeded the HNV for PFOS.

A total of 54 ambient surface water samples were collected over the 3 sampling events at 40 locations. PFOS and PFOA were detected in 53 and 52 of the 54 collected samples, respectively (Table 3). The analytes (Table 6; Figure 4-6) PFBS, PFHxS, PFBA, and PFHpA were detected in all 54 samples. PFPeA, PFHxA and PFNA were detected in 53, 53, and 45 samples, respectively. PFDA, PFHpS, 6:2 FTS, PFNS, PFTeA, and PFPeS were detected in 6, 3, 2, 2, 2, and 1 sample(s), respectively. The analytes PFTriA, PFDoA, PFUnA, PFDS, FOSA, 8:2 FTS, 4:2 FTS, NMeFOSAA, and NEtFOSAA were not detected in any sample.

The following is a more detailed discussion of the investigations, sampling, and results found for various river reaches in the watershed:

River Raisin (Main Branch)

A total of 34 samples at 25 locations were collected over the 3 sampling events from the main branch of the River Raisin and analyzed for PFAS. No samples collected from the main branch of the river during these sampling events exceeded the HNV for PFOA and all samples were below the PFOA laboratory reporting limit. Only 4 samples collected from the main branch of the River Raisin exceeded the HNV for PFOS over the 3 sampling events: 2 locations in June and 2 different locations in August 2018. In June 2018, PFOS was detected at 460 ng/L downstream of the WWTP near Tecumseh, Michigan (Sampling location RR-0270; Table 3). During the October 2018 surface water sampling, PFOS was detected at 3.0 ng/L in a sample collected from a drain in Tecumseh that empties into the River Raisin adjacent to the RR-0270 sample location. A sample collected from the River Raisin in October 2018 downstream of the Tecumseh landfill and sample location RR-0270 had a PFOS concentration of 0.9 ng/L. This sample location was revisited during the August 2018 sampling and the 0.8 ng/L PFOS concentration did not exceed the HNV for PFOS. Furthermore, none of the 6 samples collected in August 2018 from the river near Tecumseh had reportable levels of PFOS. In July 2018, the Tecumseh WWTP effluent had a PFOS and PFOA concentration of 2.8 and 14.0 ng/L, respectively. Furthermore, the groundwater investigation at the former Tecumseh Products facility determined that this facility is not a significant source of PFAS to the River Raisin watershed.

Table 6. Total PFAS concentrations (the sum of 24 analytes with only concentrations above detection limits included in calculation) detected in surface water samples collected from locations in the River Raisin watershed on June 14 and June 15, 2018, August 16, 2018, or October 29, 2018. Revisited locations are in bold.

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	Σ PFAS (ng/L)	# Analytes Detected
RR-0500	River Raisin d/s of Wamplers Lake Road	42.100028	-84.224611	June	11.4	10
RR-0400	River Raisin d/s of East Austin Road	42.148565	-84.01799	June	10.7	9
RR-0350	River Raisin d/s of Staib Road	42.042831	-83.964029	June	10.1	9
RR-0300	Globe Mill Pond	42.005953	-83.9349	August	9.1	8
RR-0290	River Raisin at East Monroe Road	42.003968	-83.9317	August	8.0	9
RR-0270	**River Raisin d/s of Tecumseh Wastewater Treatment Plant**	42.001022	-83.931162	June	473.8	12
RR-0270	**River Raisin d/s of Tecumseh Wastewater Treatment Plant**	42.001022	-83.931162	August	12.1	9
RR-0270	**River Raisin d/s of Tecumseh Wastewater Treatment Plant**	42.001022	-83.931162	August[R]	12.4	9
RD-0010	Drain to the River Raisin Adjacent to RR-270	42.00092	-83.931521	October	14.9	12
RR-0269	River Raisin d/s of Tecumseh Landfill	41.999853	-83.930613	October	8.8	8
RR-0260	River Raisin at Blood Road End	41.994947	-83.9316	August	14.4	9
RR-0250	River Raisin at Russel Road	41.992222	-83.9305	August	14.2	9
RR-0250	River Raisin at Russel Road	41.992222	-83.9305	August[D]	14.3	9
RR-0240	River Raisin at Comford Road End	41.986817	-83.9323	August	13.4	9
RR-0230	River Raisin at Sutton Road	41.949146	-83.9415	August	12.0	9
RR-0220	River Raisin at N Raisin Center Highway	41.943368	-83.9451	August	12.4	9
RR-0210	**River Raisin at North Wilmoth Highway**	41.935687	-83.964511	June	10.2	9
RR-0210	**River Raisin at North Wilmoth Highway**	41.935687	-83.964511	June[R]	9.4	8
RR-0210	**River Raisin at North Wilmoth Highway**	41.935687	-83.964511	August	13.5	9
RR-0200	River Raisin at Laberdee Road	41.919528	-83.9743	August	14.6	9
WC-0030	Wolf Creek at Saw Mill Court	41.919103	-84.043464	June	12.8	9
WC-0010	Wolf Creek d/s of Bent Oak Avenue	41.910417	-84.034334	June	11.6	9
SB-0100	South Branch River Raisin at Carleton Road	41.860191	-84.052808	August	4.8	4

[R] Replicate Sample
[D] Duplicate Sample

Sample ID	Sample Location Description	Latitude	Longitude	Sampling Event	Σ PFAS (ng/L)	# Analytes Detected
SB-0040	South Branch of River Raisin d/s of Bent Oak Avenue	41.908379	-84.03321	June	7.5	7
SB-0030	South Branch River Raisin at North Main Street	41.909518	-84.029571	August	14.2	9
SB-0020	South Branch River at Howell Highway	41.917652	-84.01	August	21.1	9
SB-0020	South Branch River at Howell Highway	41.917652	-84.01	August[R]	21.5	9
SB-0010	**South Branch of River Raisin u/s of Confluence with Main Branch**	41.924289	-83.977368	June	37.1	9
SB-0010	**South Branch of River Raisin u/s of Confluence with Main Branch**	41.924289	-83.977368	August	21.4	9
RR-0130	**River Raisin at East Gorman Road**	41.828526	-83.879853	June	14.5	9
RR-0130	**River Raisin at East Gorman Road**	41.828526	-83.879853	August	29.6	9
RR-0120	River Raisin at North Monroe Street	41.838509	-83.867639	June	11.2	9
RR-0120	River Raisin at North Monroe Street	41.838509	-83.867639	June[D]	11.3	9
RR-0110	River Raisin at Iffland Road	41.854663	-83.85	August	19.6	10
RR-0100	**River Raisin at Witts End**	41.881945	-83.7858	June	170.3	10
RR-0100	**River Raisin at Witts End**	41.881945	-83.7858	August	20.1	9
RR-0090	River Raisin at Taft Road	41.889649	-83.744788	June	12.8	9
RR-0070	River Raisin at East Monroe Street	41.952986	-83.647311	June	12.1	9
MC-0010	Macon Creek at Stowell Road	41.979554	-83.625083	October	13.0	8
SR-0230	Saline River at West Michigan Avenue	42.163305	-83.789	August	7.7	8
SR-0215	Saline River u/s Monroe Street	42.159332	-83.78414	October	8.8	8
SR-0210	**Saline River at Crestwood Circle**	42.158417	-83.780978	June	13.2	8
SR-0210	**Saline River at Crestwood Circle**	42.158417	-83.780978	June[R]	137.6	8
SR-0210	**Saline River at Crestwood Circle**	42.158417	-83.780978	August	15.2	10
SR-0210	**Saline River at Crestwood Circle**	42.158417	-83.780978	August[D]	20.6	9
SR-0200	Saline River at Hartman Road End	42.144046	-83.782	August	12.0	9
SR-0150	Saline River at Gump Lake Road	42.078017	-83.677679	August	17.8	10
SR-0100	Saline River at Sherman Road	42.062962	-83.653876	June	12.1	8
SR-0010	Saline River at Bigelow Road	41.98031	-83.616326	October	17.4	9
RR-0060	River Raisin at Plank Road	41.975439	-83.601303	August	252.2	13
RR-0050	River Raisin at Ida-Maybee Road Launch	41.963911	-83.546834	June	12.1	10
RR-0020	River Raisin at North Macomb Street	41.91632	-83.393954	June	12.3	9
RR-0010	River Raisin d/s Riverview Marina	41.900735	-83.355405	June	12.4	9
RR-0010	River Raisin d/s Riverview Marina	41.900735	-83.355405	June[D]	12.1	9

[R] Replicate Sample
[D] Duplicate Sample

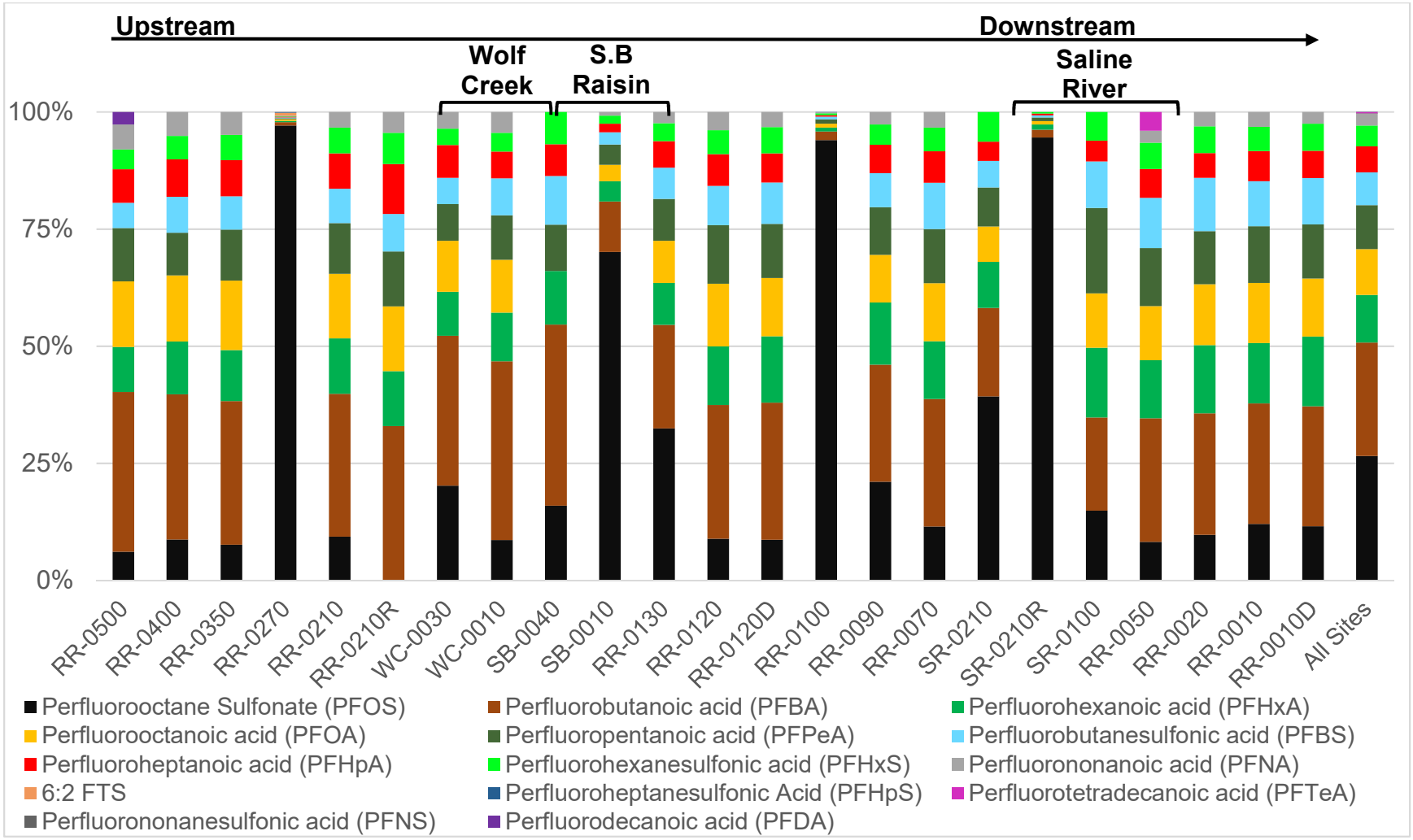

Figure 4. Percentage composition of PFAS measured in surface water collected in the River Raisin watershed in June 2018. Sample IDs are shown (RR denotes a location on the main branch of the River Raisin; SB is the south branch of the River Raisin; WC is Wolf Creek; SR is the Saline River). 'All Sites' represents the arithmetic mean percentage of each detected analyte compared to the total PFAS concentration across the entire watershed. A Sample ID followed by the letter 'D' indicates a duplicate sample and 'R' indicates a replicate sample.

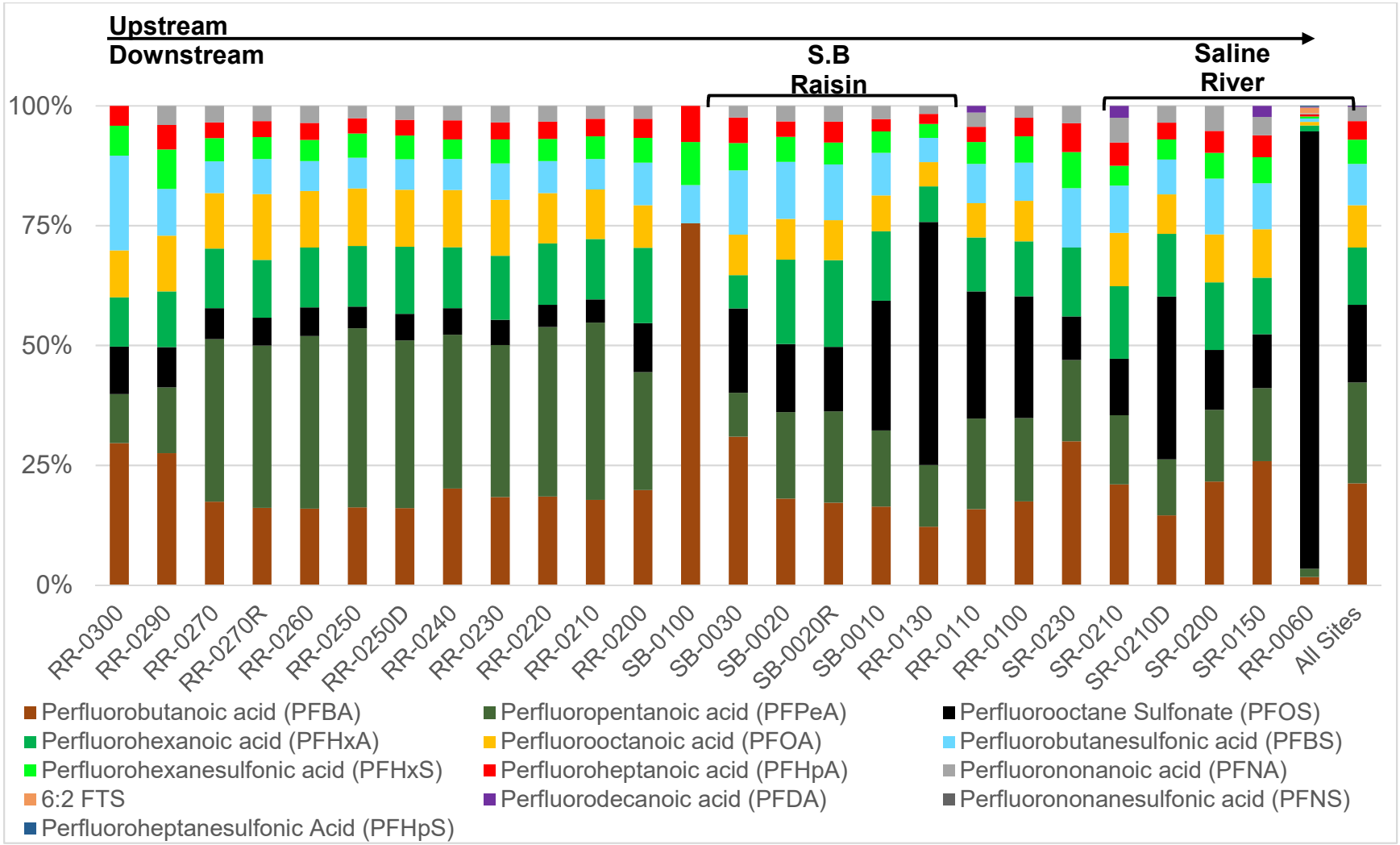

Figure 5. Percentage composition of PFAS measured in surface water collected in the River Raisin watershed in August 2018. Sample IDs are shown (RR denotes a location on the main branch of the River Raisin; SB is the south branch of the River Raisin; SR is the Saline River). ‘‘All Sites’ represents the arithmetic mean percentage of each detected analyte compared to the total PFAS concentration across the entire watershed. A Sample ID followed by the letter ‘D’ indicates a duplicate sample and ‘R’ indicates a replicate sample.

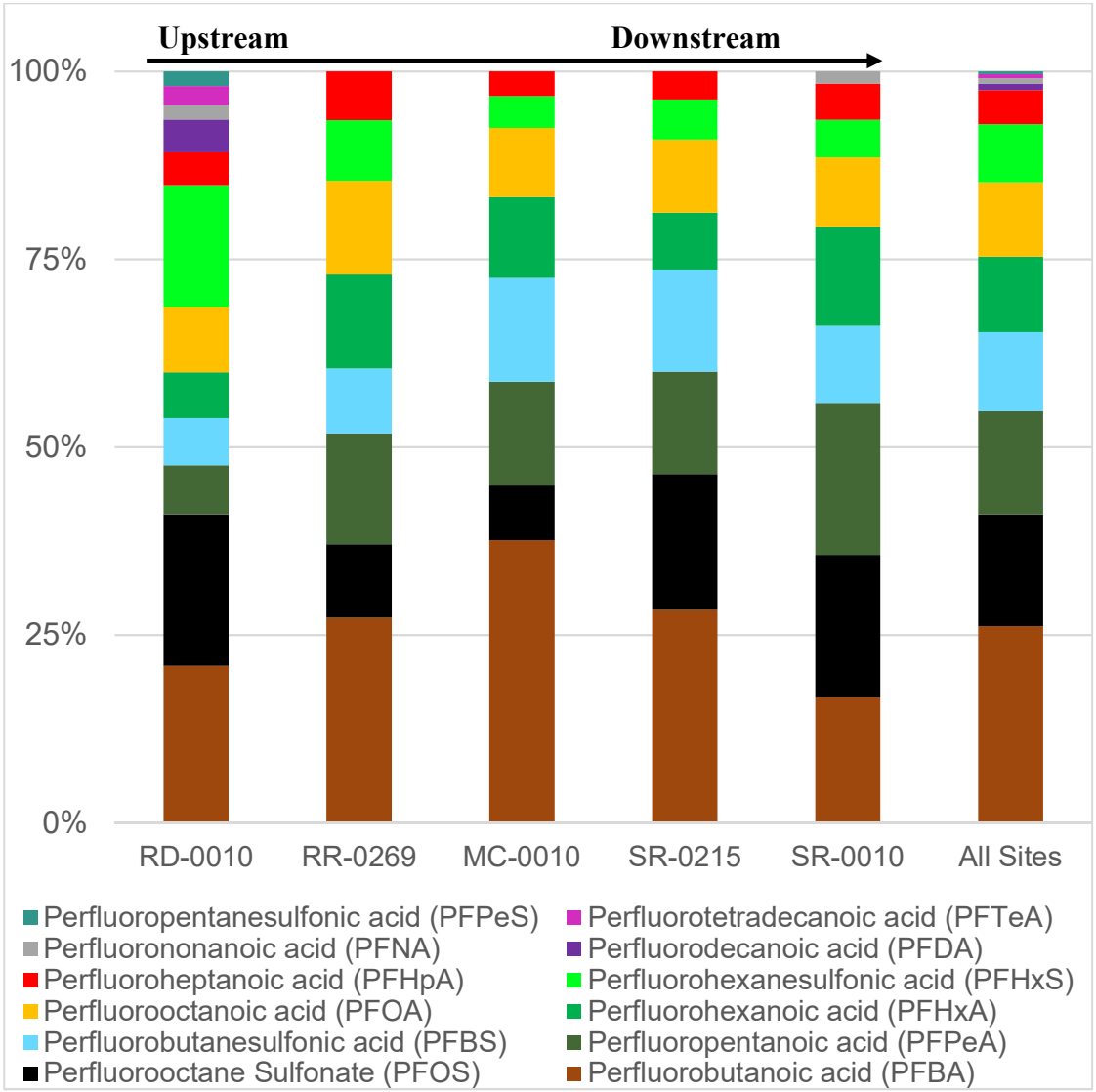

Figure 6. Percentage composition of PFAS measured in surface water collected in the River Raisin watershed in October 2018. Sample IDs are shown (RD denotes a drain to the River Raisin near Tecumseh; RR denotes a location on the main branch of the River Raisin; MC denotes the Macon Creek; SR is the Saline River). ''All Sites' represents the arithmetic mean percentage of each detected analyte compared to the total PFAS concentration across the entire watershed.

PFOS was detected in a surface water sample at 160 ng/L approximately 0.3 km upstream of the drinking water intake near Deerfield, Michigan. This result prompted an accelerated sampling of the finished drinking water for the communities with water intakes in the River Raisin (Adrian, Deerfield, and Blissfield). The surface water at this location was resampled during the August 2018 sampling event and the 5.1 ng/L PFOS concentration did not exceed the HNV for PFOS. In July 2018, the Deerfield WWTP effluent had a PFOS and PFOA concentration of 5.4 and 5.8 ng/L, respectively. In August 2018, PFOS was detected at 15 ng/L in a surface water sample collected approximately 0.1 km upstream of Blissfield, Michigan, drinking water intake (also upstream of Deerfield, Michigan). This sample location was visited in June 2018 and PFOS was found at 4.7 ng/L. In July 2018, the Blissfield WWTP effluent had a PFOS and PFOA concentration of 5.1 and 5.7 ng/L, respectively.

Additionally, during the August 2018 sampling event, PFOS was detected in the main branch of the River Raisin, downstream of the confluence with the Saline River, at 230 ng/L. This surface water sample location was not visited in June 2018; however, a sample location approximately 5.6 km downstream had PFOS levels of 1.0 ng/L in June 2018. The surface water sampling did not find any HNV exceedances further downstream near Monroe. However, the Monroe WWTP tested its effluent monthly from September to November and had a maximum effluent PFOS and PFOA concentration of 8.3 and 7.1 ng/L, respectively. To date, the Monroe WWTP has identified 1 source, a metal finisher, contributing a relatively low PFOS concentration, 6.6 ng/L, to its effluent.

Rock bass (*Ambloplites rupestris*) and largemouth bass (*Micropterus salmoides*) fillets collected from the River Raisin at Monroe in 2016 were analyzed for PFOS and 10 other perfluorinated compounds. Concentrations of PFOS averaged 10 and 21 parts per billion in the rock bass and largemouth bass, respectively. The MDHHS “Eat Safe Fish” advice for the 2 fish populations are based on mercury in rock bass (4 meals per month) or PCBs in largemouth bass (“Limited” consumption). The fish tissue results indicate that PFOS concentrations in the river at the mouth are not extremely high but do indicate a need for a fish consumption advisory based on PFOS. While PFOS is not the primary cause of consumption advisories for these 2 fish populations, it would cause a fish consumption advisory of 12 meals per month of rock bass and 4 meals per month of largemouth bass.

Rock bass from 15 Michigan water bodies have been analyzed for PFAS to-date. Rock bass from the River Raisin at Monroe had PFOS concentrations significantly higher than rock bass from 7 of those water bodies. Largemouth bass or smallmouth bass (*M. dolomieu*) from 29 Michigan water bodies have been analyzed for PFAS to-date (results for the 2 species are combined since contaminant concentrations in both have been found to be equivalent). Largemouth bass from the River Raisin at Monroe had PFOS concentrations significantly higher than 6 of the water bodies sampled.

River Raisin (South Branch)

A total of 7 samples at 4 locations were collected during the June and August sampling events from the south branch of the River Raisin and analyzed for PFAS. No sample locations on this section of the river were visited during the October 2018 sampling event. Only a single sample collected from this branch of the river over the 2 sampling events exceeded the HNV for PFOS. In June 2018, PFOS was detected at 26 ng/L just upstream of the confluence with the main branch of the River Raisin. This sample location was repeated during the August 2018 sampling event and PFOS at this location was 5.8 ng/L, which is below the HNV. No samples collected from the south branch of the River Raisin during either sampling event exceeded the HNV for PFOA and all samples were below the PFOA laboratory reporting limit. In July 2018, the Adrian WWTP effluent had a PFOS and PFOA concentration of 7.1 and 3.6 ng/L, respectively (Table 5). Through its work on the IPP PFAS Initiative,

the Adrian WWTP conducted a thorough investigation and found no sources of PFOS. They sampled 2 industrial users discharging process wastewater to their WWTP as well as 10 contaminated sites with potential to infiltrate contaminated groundwater to sanitary sewers and found no detectable sources of PFOS. Furthermore, limited sampling near the Wacker Chemical Company and the Silbond Corporation northeast of Adrian has shown that these facilities are not significant sources of PFAS to the River Raisin watershed. Ambient river sampling approximately 2.8 km downstream of the Wacker Chemical Company did not show elevated PFAS during either the June or August 2018 sampling events.

Wolf Creek

Samples were collected from 2 locations in Wolf Creek during the June 2018 sampling event and neither PFOS nor PFOA exceeded their respective HNVs. No samples were collected from Wolf Creek in August or October 2018 because the June 2018 sample results suggested that it was not a significant source of PFAS to the south branch of the River Raisin; however, fish were collected from the impoundment on Wolf Creek and the analysis from these samples is pending to confirm this statement.

Macon Creek

A single sample from Macon Creek was collected in October 2018 near the confluence with the River Raisin and adjacent to an old landfill. The confluence is located approximately 2.5 km upstream of the RR-0060 sample location where a PFOS concentration of 230 ng/L was detected in August 2018. The PFOS and PFOA concentration in this sample was 1.0 and 1.2 ng/L, respectively, which are both below the laboratory reporting limit.

Saline River

A total of 10 samples at 7 locations were collected in the Saline River over the course of the 3 2018 sampling events. A single sample collected in June 2018 downstream of the Saline WWTP had a PFOS concentration of 130 ng/L (Sample location SR-0210; Table 3), which exceeds the HNV. However, a replicate sample collected from this location during the same visit had a PFOS concentration of 5.2 ng/L. This location was revisited in August 2018. The duplicate samples collected during this revisit had a PFOS concentration of 1.8 and 7.0 ng/L. In October 2018, a sample location approximately 0.5 km upstream of sample location SR-0210 had a PFOS concentration of 1.6 ng/L. In July 2018, the Saline WWTP effluent had a PFOS and PFOA concentration of 33.0 and 6.4 ng/L, respectively (Table 5). The Saline WWTP has identified 1 source of PFOS contributing 20 ng/L to its effluent and will be investigating their collection system for potential sources such as infiltration into the sanitary sewers from contaminated sites. Furthermore, the groundwater testing at the Washtenaw Industrial Facility LLC (former Universal Die Cast) found contaminated groundwater in the monitoring wells up to 3,030 ng/L, which is likely venting to the River Raisin upstream of the SR-0210 sample location. Finally, PFOS and PFOA were detected up to 730 ng/L and 89 ng/L, respectively, in groundwater monitoring wells at the former Ford Motor Company in Saline.

A sample collected near the confluence with the River Raisin and adjacent to an old landfill had a PFOS concentration of 3.3 ng/L. The Saline River confluence is located approximately 1.2 km downstream of the Macon Creek confluence and approximately 1.3 km from sample location RR-0060 where a PFOS concentration of 230 ng/L was detected in August 2018. In October 2018, the Milan WWTP effluent had a PFOS and PFOA concentration of 7.3 and 7.2, respectively (Table 5);

however, the 3 surface water samples collected downstream of this WWTP were below the laboratory reporting limit for PFOS and PFOA. Additionally, the city of Milan found what may be infiltration of PFOS from contaminated sites (industries now closed) into the sanitary sewer at a concentration of 13.2 ng/L, and has 1 probable source that is expected to be sampled in early 2019. No samples collected from the Saline River during any sampling event exceeded the HNV for PFOA and all samples were below the PFOA laboratory reporting limit.

Ambient Water Sampling QA/QC

Neither PFOS nor PFOA were measured above their respective detection limit in the equipment, field, and trip blanks. All other analytes were below detection limits in these blanks with a few exceptions: PFHxS was measured at 0.24 ng/L and 0.27 ng/L in the equipment blanks for the June and August sampling events, respectively, which is above the detection limit but below the laboratory reporting limit. No equipment blank was collected during the October 2018 sampling event as all samples were collected by a gloved hand. The PFHxS analyte was also detected in both the field and trip blank samples collected during the June 2018 sampling event at 0.25 and 0.27 ng/L, respectively, at 0.31 and 0.25 ng/L in the August 2018 field and trip blanks, respectively, and at 0.34 and 0.29 ng/L in the October 2018 field and trip blanks, respectively. This compound was also detected at a similar level in the laboratory method blanks for each event, indicating the source was most likely within the analytical process. PFBA was measured at 0.40 ng/L in the June 2018 field blank, which is above the detection limit and below the laboratory reporting. This analyte was not detected in the laboratory method blanks for lab analysis of samples from either date.

Four replicate and 4 duplicate samples were collected over the June and August sampling events. Three of these samples exceeded the RPD threshold of 30% for PFOS concentrations (2 replicates and 1 duplicate; Table 2). Two of these samples were a replicate and duplicate collected at the same location (SR-0210) in the Saline River on separate sampling events (RPD = 185 and 118%, respectively; Table 2). The SR-0210 replicate and duplicate samples also exceeded the RPD for PFHxS (52.6% and 30.9%, respectively; Table 2). The TestAmerica laboratory report noted that the SR-0210 (June 2018 initial sample; 5.2 ng/L PFOS) and SR-0210R (June 2018 replicate sample; 130 ng/L PFOS) had excessive sedimentation present. No duplicate nor replicate sample exceeded the RPD for PFOA. Only 1 sample exceeded the RPD for the other PFAS analytes. The RPD for PFHpA in the SB-002R was 32.9% (Table 2). All other data quality control objectives and criteria were met (Table 2). While there were RPD exceedances for PFOS in the QA/QC samples, the field collected, and laboratory prepared blanks indicate that no PFOS contamination had occurred. Therefore, the differences between replicate and duplicate samples collected from the same sample location during the same sampling event suggest that variability in PFAS concentrations exists in the water column. We determined that failing to meet this data quality objective would not impact our decision to determine whether a source was present at these locations. In support of this statement, the detection of 130 ng/L PFOS concentration in the Saline River at the SR-0210 sampling location (RPD = 118 to 185%) resulted in a groundwater investigation finding contaminated groundwater at the Washtenaw Industrial Facility LLC (former Universal Die Cast) upstream of the SR-0210 sampling location.

CONCLUSIONS AND FUTURE WORK

The PFOS concentrations at locations sampled in both June and August 2018 were not consistent. Of the 6 locations sampled during both time periods, the following 4 sample locations had concentrations exceeding the HNV for PFOS in June, but not in August:

1. RR-0270: River Raisin d/s of Tecumseh WWTP.
2. SB-0010: South branch River Raisin u/s of confluence with main branch.
3. RR-0100: River Raisin at Witts End.
4. SR-0210: Saline River at Crestwood Circle.

In contrast, 1 of the 6 revisited sample locations (RR-0130: River Raisin at East Gorman Road) had PFOS concentrations below the HNV in June but exceeded the value in August. The sixth revisited sample location (RR-0210: River Raisin at North Wilmoth Highway) had PFOS concentrations below the laboratory reporting limit in both samples.

Overall these results indicate that sources are present in the upper River Raisin watershed in addition to the Saline River, but the sources may be intermittent due to facility operations, fluctuations in groundwater infiltration to the sanitary sewers and surface waters, rainfall timing and the quantity and duration of subsequent runoff, or a combination of those and other factors. The Saline WWTP is a known discharger of PFOS and the Washtenaw Industrial Facility LLC (former Universal Die Cast) site is a known source of PFAS to the Saline River. As a part of the MDEQ, WRD, IPP Initiative, the Saline WWTP will be working with identified sources within their system to control discharges of PFAS that may pass through their WWTP. The former Ford Saline Facility is a probable source of PFAS to the Saline River. Limited sampling near the former Tecumseh Products facility in Tecumseh, Wacker Chemical Company near Adrian, and the Silbond Corporation near Adrian has shown that these facilities are likely not significant sources of PFAS to the River Raisin watershed; therefore, the sources of the contamination near Tecumseh, Adrian, Deerfield, and Dundee are still unknown.

As our ambient surface water sampling results demonstrate, PFAS concentrations in a water body can be highly variable depending on the source of contamination. While single surface water grab samples can be useful in detecting sources of contamination, they may not be representative of average conditions in the water body over an extended period and, depending on factors such as weather conditions and facility operations, may not detect intermittent sources. Since fish are continuously exposed to contaminants in the water column and through their diet, fish tissue analysis can provide a more complete evaluation of water quality when the surface water concentrations of a bioaccumulative compound like PFOS are highly variable. Therefore, fish were collected from the River Raisin at Dundee upstream of the Dundee Dam and from Lake Adrian in Wolf Creek. These results are still pending. There are plans to collect fish from reaches of the river where HNV exceedances have been observed, specifically near Tecumseh, Deerfield, and Saline.

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