TOTAL ORGANIC FLUORINE CONCENTRATION ALONG THE LITTLE BIGHORN RIVER

by

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List of Abbreviations

4:2-FTS	1H, 1H, 2H, 2H-Perfluorohexanesulfonic acid
6:2-FTS	1H, 1H, 2H, 2H-Perfluorooctanesulfonic acid
8:2-FTS	1H, 1H, 2H, 2H-Perfluorodecanesulfonic acid
AFFF	Aqueous film forming foam
ALEC	Arizona Laboratory for Emerging Contaminants
CIC	Combustion ion chromatography
EPA	Environmental Protection Agency
FOSA	Perfluorooctanesulfonamide
GAC	Granular activated carbon
HDPE	High-density polyethylene
IC	Ion chromatography
KOH	Potassium hydroxide
LBHR	Little Bighorn River
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
$MeOH-NH_4OAc$	Methanolic ammonium acetate
MS	Matrix spike
MSD	Matrix spike duplicate
MT-WY	Montana-Wyoming
$NaNO_{3(aq)}$	Aqueous sodium nitrate
NEtFOSAA	N-ethyl perfluorooctanesulfonamidoacetic acid
NMeFOSA	N-methylperfluorooctanesulfonamide
NMeFOSAA	N-methyl perfluorooctanesulfonamidoacetic acid
NWIS	National Water Information System
OPR	On-going precision and recovery
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonic acid
PFC	Perfluorinated compounds
PFDA	Perfluorodecanoic acid

PFDoA	Perfluorododecanoic acid
PFDS	Perfluorodecanesulfonic acid
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptanesulfonic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFNA	Perfluorononanoic acid
PFNS	Perfluorononanesulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PFPeA	Perfluoropentanoic acid
PFPeS	Perfluoropentanesulfonic acid
PTFE	Polytetrafluoroethylene
PFTreA	Perfluorotetradecanoic acid
PFTriDA	Perfluorotridecanoic acid
PFUnA	Perfluoroundecanoic acid
RPD	Relative percent difference
RSE	Relative standard error
SPE	Solid phase extraction
TOF	Total organic fluorine
USGS	United States Geological Survey

Abstract

Per- and polyfluoroalkyl substances (PFAS), also known as forever chemicals, are increasingly problematic to humans and environmental health because of their toxicity and persistence in the environment due to the strong carbon-fluorine bond that is not easily broken. Although there are several thousand known individual PFAS compounds, many are not detected with typical targeted liquid chromatography tandem mass spectrometry (LC-MS/MS). Casting a wider net with non-targeted PFAS analysis via combustion ion chromatography to determine total organic fluorine (TOF) can better characterize the total PFAS at a given site, while also potentially including non-PFAS organic-fluorine-containing molecules. Threats of PFAS contamination in the Little Bighorn River, a 138-mile river that begins south of the Montana-Wyoming state line and flows northward through the Crow Indian Reservation, are being investigated because of the tribe's reliance on the river for diverse uses. Grab samples were collected weekly over a 15-month period at two United States Geological Survey (USGS) flow monitoring locations along the Little Bighorn River to assess the overall water quality in relation to the hydrologic discharge at both locations. The first USGS site is at the headwaters near the Montana-Wyoming state line and the second is at the Black Lodge Hall near Hardin, MT. TOF concentrations were found to increase with increasing discharge at both sites, with TOF concentrations ranging from 0.07-2.97 micrograms per liter (µg L-1). These TOF concentrations were compared with EPA Method 533, a standard analytical method targeting 25 PFAS compounds, to gain a better understanding of the total PFAS in the Little Bighorn River, and the fraction of PFAS that are untargeted by LC-MS/MS methods.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are highly fluorinated compounds that are an ever-increasing problem for humans and the environment. With a number that is continually increasing, more than 14,000 PFAS compounds have been found and identified (NIOSH, 2024). PFAS have been used in various industrial and commercial applications such as surface repellent coatings, surfactants, aqueous film forming foam (AFFF) used for fire-fighting, and pesticides (Yeung et al., 2017). These compounds are difficult to break down because of their strong carbon-fluorine bond, allowing them to accumulate in the environment. PFAS have been found in various surface water and groundwater systems across the world, further pushing the need for PFAS research.

The history of PFAS can be traced back to 1938 when DuPont first invented the perfluorinated compound polytetrafluoroethylene (PTFE), otherwise known as Teflon (Garg et al., 2020). Perfluorinated compounds (PFCs) have a unique chemical and physical makeup that make them particularly useful for industrial and commercial applications. These highly fluorinated compounds are oleophobic, hydrophobic, and can withstand high temperatures and pressures due to their strong carbon-fluorine bonds (Gaines, 2022). This makes it difficult for PFAS to break down naturally and leads to its accumulation in the environment. By the 1940s and 1950s, other companies, such as 3M and Gore-Tex, began to manufacture perfluorinated compounds into the varying types of PFAS and PFCs present today (Garg et al., 2020). Gaines (2022) discussed the different applications PFAS has been used for including adhesives, protective coatings, medical applications, and cosmetics. Other common applications include fire-fighting foam, cleaning products, mining materials, and construction materials (Gaines, 2022).

In 1968, PFAS had been detected in human blood samples and continued to be in widespread use until the early 2000s when companies began to phase out long-chain PFAS (Garg et al., 2020). PFAS chains are classified by how many carbons are present on the carbon-fluorine line. Longer-chained PFAS have, at a minimum, 6-8 carbons linked to varying amounts of fluorine. Short-chain PFAS and other PFAS precursors continue to have widespread use in everyday life and in the environment. Exposure to PFAS is linked to multiple long-term health impacts such as cardiovascular disorders, cancers, and hypothyroidism (Garg et al., 2020). These health impacts began to push scientists to assess the prevalence of PFAS in the environment and in drinking water. The United States Environmental Protection Agency (EPA) released an action plan to investigate and understand PFAS compounds and their effects on humans, including maximum contaminant levels for four individual PFAS compounds: PFOS, PFOA, PFHxS, and PFNA (EPA, 2024a).

Various methods have been used to analyze PFAS compounds. Solid phase extraction (SPE) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) are methods widely used to extract individual, targeted analytes and assess their concentrations in a sample. These methods can be altered for the analysis of any PFAS compound, including hydrophilic PFAS and hydrophobic PFSAs (Niu et al., 2022). These targeted analytical methods can detect only specific PFAS compounds under investigation, which is further complicated when accounting for the number of PFAS that have been identified. Total organic fluorine (TOF) analysis via combustion ion chromatography (CIC) can be used to complement information obtained from these targeted analyses to better understand the total PFAS burden of a sample (Aguilar et al., 2025). Organically bound fluorine from liquid samples is adsorbed onto granular activated carbon (GAC) cartridges that are placed in ceramic boats and introduced into a furnace where pyrohydrolysis occurs at 900 °C. This high-temperature and humid environment can break carbon-fluorine bonds, leading to the formation of gaseous hydrogen fluoride that is then ionized and measured using an ion chromatograph with a potassium hydroxide (KOH) gradient (Eurofins, 2018). A major limitation of TOF-CIC analyses is that this analysis may include non-PFAS organic fluorine containing molecules, such as fluorinated pesticides, as TOF analyses cannot identify individual PFAS compounds.

The Little Bighorn River (LBHR) is a 138-mile river that begins south of the Montana-Wyoming (MT-WY) State Line in the northwestern portion of the Bighorn National Forest in Wyoming and flows northward through the Crow Indian Reservation toward the Bighorn River near Hardin, Montana. The Crow Indian Reservation uses the LBHR throughout the year for ceremonial, municipal, agricultural, and recreational uses (LaFrance, 2023). Threats of PFAS contamination in the Little Bighorn River (LBHR) are being investigated because of the tribe's reliance on the river for diverse uses. Solid phase extraction (SPE)- and liquid chromatography-tandem mass spectrometry (LC-MS/MS) were used to understand individual, targeted PFAS chemical concentrations in grab river samples following EPA Method 533. A non-targeted PFAS analysis was conducted via combustion ion chromatography (CIC) to determine the total organic fluorine (TOF) concentrations of grab river samples to better characterize the total PFAS at each site.

2. Methods

2.1 Sample Collection

Grab river water samples were collected at both sites in 500 mL glass amber bottles and in 250 mL high-density polyethylene (HDPE) bottles weekly over a 15-month period from March 8th, 2022 to June 29th, 2023 near the headwaters at MT-WY state line (USGS Gage 0628900) and near the LBHR-Big Horn River confluence at the Black Lodge Hall near Hardin, MT (USGS Gage 06294000) as seen in Figure 1. Field blanks were created weekly with nanopure water. Samples were maintained cold and transported to the Arizona Laboratory for Emerging Contaminants (ALEC) at the University of Arizona in Tucson for processing and analysis.

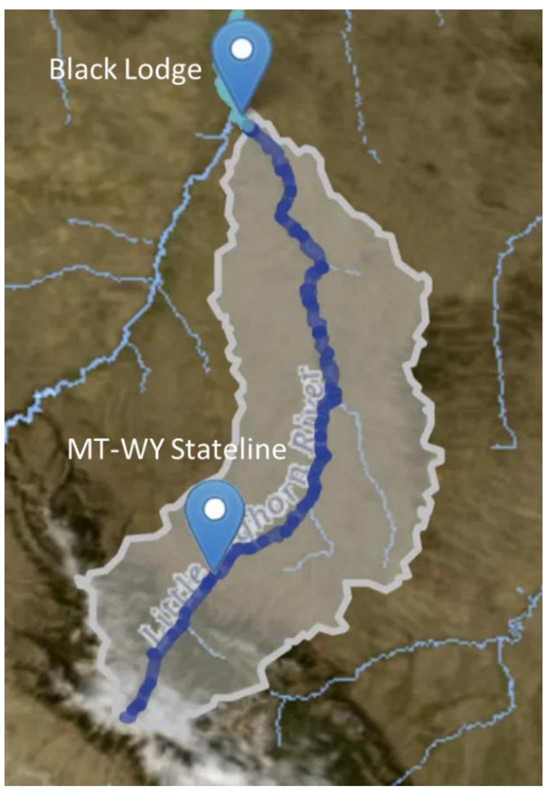

Figure 1. Map of the LBHR watershed and sampling sites near USGS Gages

2.2 Targeted Analysis via LC-MS/MS:

Samples (n = 82) collected in 250 mL high-density polyethylene (HDPE) bottles underwent solid phase extraction (SPE) and were analyzed using LC-MS/MS to determine the concentrations of 25 PFAS compounds according to EPA Method 533. The individual compounds separated by class can be found in Table 1.

Table 1. Targeted 25 PFAS compounds separated by class

Carboxylates	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTriDA	PFTreA
Sulfonates	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	4:2-FTS	6:2-FTS	8:2-FTS	
Sulfonamides	FOSA	NMeFOSAA	NEtFOSAA	NMeFOSA							

2.3 Quality Control Samples

Method blanks and on-going precision and recovery (OPR) standards were prepared for every 20 field samples to ensure that the results provided by the method were accurate. Method blanks and OPR samples were prepared in 500mL glass amber bottles with nanopure water. OPR samples were spiked at the mid-level of the calibration curve with PFOS. PFOS was chosen for this project because it readily adsorbs onto surfaces and is a better indicator of the rinse method efficiency discussed in Section 2.4. The OPRs are expected to have a percent recovery of ± 30% of the theoretical value of fluoride (µg/L). The percent recovery of PFOS for each OPR was determined using Equation 1.

$$\%\ Recovery = \frac{C_{OPR}}{C_S} \times 100 \qquad \textit{Equation 1}$$

Where:

C_{OPR} = OPR measured concentration (µg/L)

C_s = Spiked concentration (µg/L)

Matrix spike (MS) and matrix spike duplicate (MSD) samples were prepared for every 20 field samples to assess any potential matrix interferences. MS and MSD samples were spiked at the mid-level of the calibration curve with PFOS and are expected to have ±50% recovery of the calculated fluoride concentrations. The percent recovery of PFOS was determined using Equation 2.

$$\%\ Recovery = \frac{C_{MS} - C_0}{C_s} \times 100 \qquad \textit{Equation 2}$$

Where:

C_{MS} = MS measured concentration (µg/L)

C_0 = Concentration of the unfortified sample (µg/L)

C_s = Spiked concentration (µg/L).

The relative percent difference (RPD) between the percent recovery of the MS and MSD is expected to be ≤30%. The RPD was determined using Equation 3.

$$RPD = \frac{|MSD_R - MSD_R|}{\frac{(MS_R + MSD_R)}{2}} \times 100 \qquad \textit{Equation 3}$$

Where:

MS_R = Percent recovery of the MS [-/-]

MSD_R = Percent recovery of the MSD [-/-]

2.4 Adsorption

Samples (n = 215) collected in 500 mL glass amber bottles were adsorbed using a TXA-04 Adsorption Unit. Prior to adsorption, all samples underwent a 1:10 sample dilution with nanopure water in 10 mL polypropylene tubes and were directly injected into a ThermoScientific

Dionex Integrion HPIC System[1]. This pre-analysis step confirmed that levels of inorganic fluoride were below 8 mg/L, preventing potential interference with the Mandel Scientific pre-packaged 0.08g granular activated carbon (GAC) cartridges. All samples were then spiked with 2.2 mLs of 2 M sodium nitrate ($NaNO_3$(aq)) to have a final concentration of 0.01 M $NaNO_3$(aq) to remove any inorganic fluoride (≤8 mg/L) that may be present in each sample prior to adsorption. Sample transfer lines were rinsed with 40 mL of nanopure water, 40 mL of ethanol, and again with 40 mL of nanopure water before being calibrated with 40 mL of the sample. The remaining 400 mL of each sample were then loaded onto the GAC cartridges at a flow rate of 3 mL/min until empty.

As noted in various studies (Zenobio et al., 2022; Mancini et al., 2023; Folorunsho et al., 2024) and EPA Method 1621, some PFAS readily adsorb to container surfaces. To ensure that the fluoride concentrations at the end of the analysis process were accurate, a rinse step was added to desorb any PFAS that may have adsorbed onto the surface walls of the sample containers. At the time of experimentation, there was no literature that recommended rinsing sample bottles for TOF-CIC analysis. Typically, organic solvents cannot be loaded directly onto the GAC cartridges as they may result in the loss of both the targeted analyte and GAC from the cartridges. Instead, the empty amber glass sample bottles were rinsed with 40 mL of 0.2 M methanolic ammonium acetate (MeOH-NH_4OAc). Methanol is commonly used as an extraction solvent for other PFAS analyses, including solid phase extraction. Initial tests with varying amounts of 100% methanol yielded poor recovery of PFOS (±25%) (Table 2). Merterns et al., 2023 discusses using various concentrations of methanolic ammonium acetate for PFAS extraction in mammalian tissues, while Nassazzi et al., 2022 uses methanolic ammonium acetate

[1] Brand names are included throughout this thesis only for informational purposes and do not constitute an endorsement by the author or the University of Arizona.

as the extraction solvent for plant tissue samples. Methanolic ammonium acetate is also used as a mobile phase for PFAS LC-MS analyses, including EPA Method 1633. Given its established use in PFAS extraction, LC-MS analysis and its superior recovery compared to pure methanol, MeOH-NH_4OAc was selected to rinse the empty amber glass bottles once after adsorption (Table 2). The total volume of MeOH-NH_4OAc used from Merterns et al., 2023 was scaled to better fit the sample size of the river water samples with the concentration of the MeOH-NH_4OAc being increased until PFOS recovery was within ±20%.

Table 2. Percent Recoveries of Rinse Methods

Sample	Theoretical F Conc. [ug/L]	Measured F Conc. [ug/L]	Percent Recovery
PFOS 1 (No Rinse)	1.98	2.47	119.1%
PFOS 2 (No Rinse)	2.05	1.34	65.39%
PFOS 3 (No Rinse)	1.99	1.32	66.44%
PFOS 1 (100% MeOH)	1.98	1.53	77.20%
PFOS 2 (100% MeOH)	1.98	1.53	77.24%
PFOS 2 (100% MeOH)	2.06	1.51	73.29%
PFOS 1 (0.2M MeOH-NH4OAc)	1.81	1.56	86.30%
PFOS 2 (0.2M MeOH-NH4OAc)	1.82	1.58	86.75%
PFOS 3 (0.2M MeOH-NH4OAc)	1.80	1.64	91.37%
PFOS 4 (0.2M MeOH-NH4OAc)	1.82	1.86	102.1%

The solvent that was used to rinse the empty glass amber bottles was then poured into a 50mL polypropylene tube and evaporated to dryness in a Biotage Turbovap at 55 ºC with an N2 flow of 1.2 L/min. The evaporation settings were determined from EPA Method 1633 to limit the loss of volatile PFAS compounds. The empty polypropylene tubes were reconstituted with 10 mL of nanopure water and adsorbed onto their respective GAC cartridges. Each GAC cartridge was immediately rinsed with 25 mL of 0.01 M $NaNO_{3(aq)}$ to fully remove any inorganic fluoride. Then, it was rinsed with 20 mL of nanopure water to remove any residual nitrate and dried with

10 mL of air to remove any excess liquid. The GAC cartridges were stored in aluminum foil in a desiccator at room temperature for no longer than 5 days, per EPA Method 1621.

2.5 Combustion Ion Chromatography (CIC)

The fluoride concentrations were determined using a ThermoScientific Dionex Integrion HPIC System coupled to a Mandel Scientific AQF-2100H combustion system. The IC parameters are shown in Table 3, and the combustion parameters are shown in Table 4.

Table 3. IC Conditions

Parameters	Value	
IC System	ThermoScientific Dionex Integrion HPIC	
Columns	ThermoScientific Dionex IonPac AS20 RFIC Analytical Column (2 x 250 mm), ThermoScientific Dionex IonPac AG20 RFIC Guard Column (2 x 50 mm)	
Eluent Source	ThermoScientific Dionex EGC 500 KOH Eluent Generator Cartridge	
KOH Gradient	Time (min)	KOH Conc. (mM)
	0.00 - 3.50	4.0
	3.50 - 9.00	4.0 - 75
	9 .00- 10.3	75
	10.3 - 18.0	75 - 4.0
Flow Rate	0.250 mL/min	
Injection Volume	200 µL	
Temperature	30.0°C	
Suppressed Conductivity Detection	ThermoScientific Dionex ADRS 600 2mm RFIC	

Table 4. Combustion Conditions

Parameter	Value		
Sample Introduction	Automated Boat Control		
Pyrolysis Tube	Outer quartz tube with ceramic insert and quartz wool		
Furnace Inlet Temperature	900°C		
Furnace Outlet Temperature	1000°C		
Argon Flow (carrier)	200 mL/min		
Oxygen Flow	400 mL/min		
Humidified Argon Flow	100 mL/min		
Sample Boat	Ceramic		
Absorption solution	Nanopure H_2O		
Final Absorption Volume	14.64 mL		
Boat Combustion Program	Position (mm)	Wait Time (sec)	Speed (mm/s)
	100	60	10
	End	600	10
	Cool	60	20
	Home	200	20

The injection sequence for each set of 20 field samples is shown in Table 5. The analytical sequence used follows the sequence recommended in EPA Method 1621.

Table 5. Analytical sequence followed

Step #	Analytical Sequence
1	IC Wash (Nanopure H_2O)
2	Calibration Curve
3	IC Wash (Nanopure H_2O)
4	Blank Oven (No Boat)
5	Blank Boat
6	Blank Boat
7	Low-Level Calibration Verification Standard (10 µg/L)
8	Method Blank
9	OPR
10	Samples (Set of 10)
11	MS
12	MSD
13	Mid-Level Calibration Verification Standard (50 µg/L)
14	Samples (Set of 10)
15	Mid-Level Calibration Verification Standard (50 µg/L)

A calibration curve with a calibration range of 0-100 µg/L was run every 20 samples. Each calibration point's measured value must be within ±20% of the theoretical fluoride concentration (µg/L). Additionally, the relative standard error (RSE) of the calibration curve must be ≤20%. This was calculated using Equation 4.

$$RSE = 100\ x \sqrt{\sum_{i=1}^{n} \frac{\left[\frac{x'_i - x_i}{x_i}\right]^2}{n-2}} \qquad \textit{Equation 4}$$

Where:

xi = The theoretical concentration of each calibration standard

x'_i = The measured concentration of each calibration standard

n = The number of standard levels in the curve

3. Results

3.1 Total Organic Fluorine (TOF) Analysis

The TOF concentrations (n = 64) at the MT-WY Stateline site had TOF concentrations ranging from 0.0674 to 1.7204 µg/L (Figure 2) with an average concentration of 0.4290 µg/L and standard deviation of 0.3722 µg/L. At this site, one sample was above the calibration range and excluded from the analysis. Because samples analyzed for TOF were used until empty, these samples could not be diluted further. Samples that were above the calibration range were unable to be quantified reliably and were excluded from the analysis.

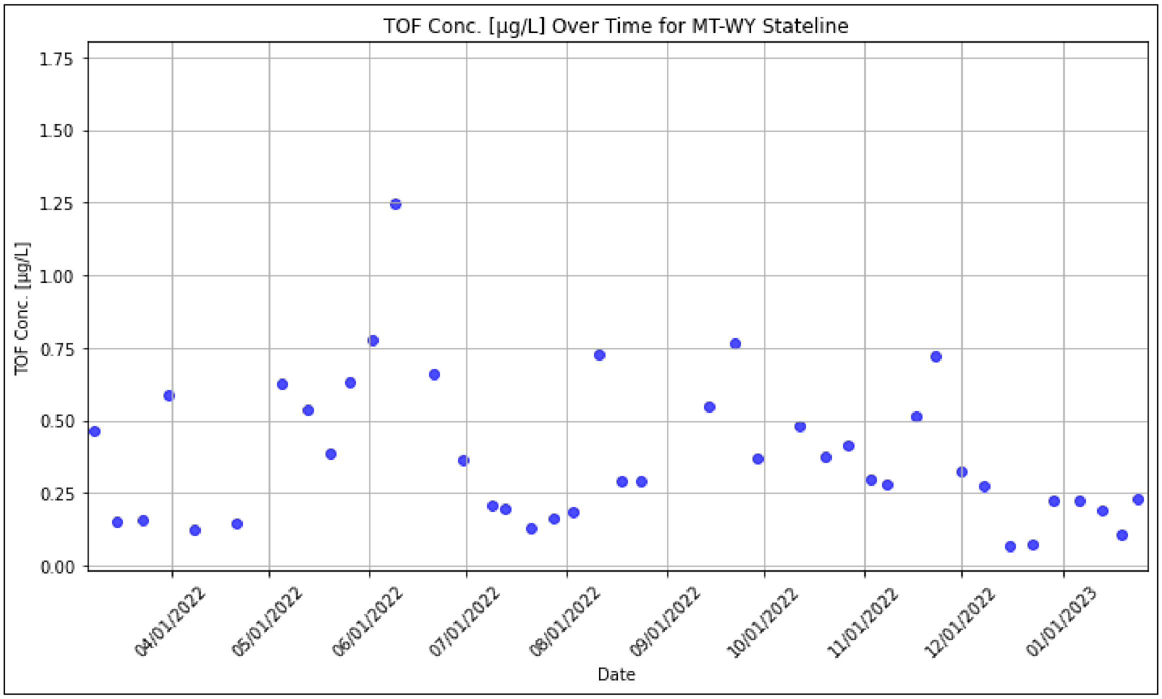

Figure 2. Time series of TOF concentrations for MT-WY Stateline

At the Black Lodge site, TOF concentrations (n = 49) ranged from 0.2405 to 2.9681 µg/L (Figure 3) with an average concentration of 1.2124 µg/L and standard deviation of 0.7890 µg/L. The Black Lodge site had 13 samples above the calibration range and were subsequently excluded from the analysis. Most of the quality control samples were within the recommended percent recoveries and values recommended in EPA Method 1621 (Table 6).

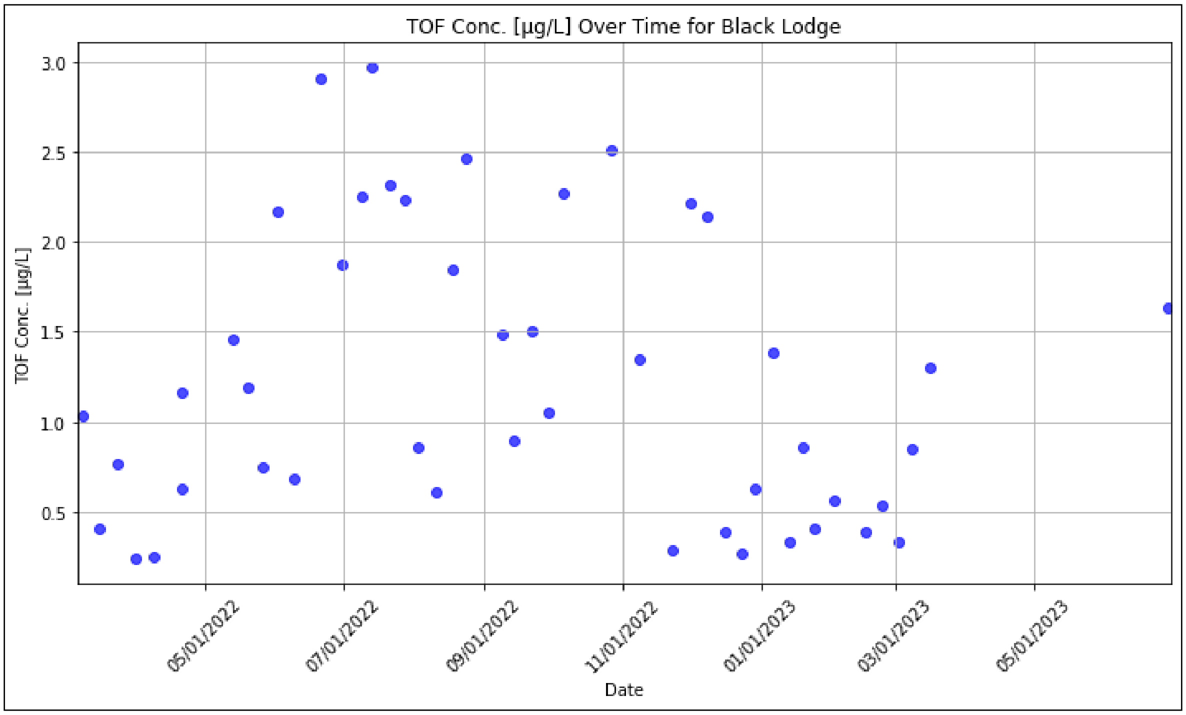

Figure 3. Time series of TOF concentrations for Black Lodge

One set of MS and MSD samples were an exception to this, where the fortified sample that corresponded to the final set was outside of the calibration range (Table 7). Because the previous quality control samples had passed for that set of field samples, the analysis proceeded.

Table 6. OPR TOF Concentrations and Percent Recoveries

Sample ID	Measured TOF Conc. [µg/L]	Theoretical TOF Conc. [µg/L]	% Recovery
OPR (1)	1.8962	1.7907	105.89%
OPR (2)	1.9449	1.7840	109.02%
OPR (3)	1.2490	1.7924	69.68%
OPR (4)	1.1063	1.5757	70.21%
OPR (5)	1.2532	1.8100	69.24%
OPR (6)	1.8802	1.7302	108.67%
OPR (7)	1.9358	1.7260	112.16%
OPR (8)	1.5410	1.8316	84.13%
OPR (9)	2.0727	1.7853	116.10%
OPR (10)	1.4072	1.7911	78.57%

Table 7. MS and MSD TOF Concentrations and Percent Recoveries

Sample ID	Measured TOF Conc. [µg/L]	Theoretical TOF Conc. [µg/L]	% Recovery
LBHR 1 MS	2.9590	3.5513	83.32%
LBHR 1 MSD	2.6889	3.5513	75.72%
LBHR 13 MS	2.8303	3.5600	79.50%
LBHR 13 MSD	3.5368	3.5600	99.35%
LBHR 21 MS	2.4301	3.5734	68.01%
LBHR 21 MSD	2.5562	3.5734	71.53%
LBHR 25 MS	4.1650	3.5884	116.07%
LBHR 25 MSD	4.4928	3.5884	125.20%
LBHR 31 MS	3.9447	3.5829	110.10%
LBHR 31 MSD	3.7504	3.5829	104.67%
LBHR 36 MS	3.8941	3.5581	109.44%
LBHR 36 MSD	3.9666	3.5581	111.48%
LBHR 40 MS	4.0837	3.5855	113.89%
LBHR 40 MSD	2.7823	3.5855	77.60%
LBHR 42 MS	4.6536	3.5820	129.92%
LBHR 42 MSD	4.5608	3.5820	127.33%
LBHR 45 MS	3.1444	3.5711	88.05%
LBHR 45 MSD	3.1343	3.5711	87.77%
LBHR 52 MS	5.9013	3.5490	166.28%
LBHR 52 MSD	4.4001	3.5490	123.98%

3.2 TOF and Targeted PFAS Analysis

The targeted 25-PFC data accounted for only a small percentage of the TOF detected in the samples with no significant changes over the entire sampling period at both sites. Time series plots were created to compare the TOF concentration sums (nmol/L) of each PFAS class from the targeted analysis to the TOF concentration (nmol/L) (Figures 4 and 5).

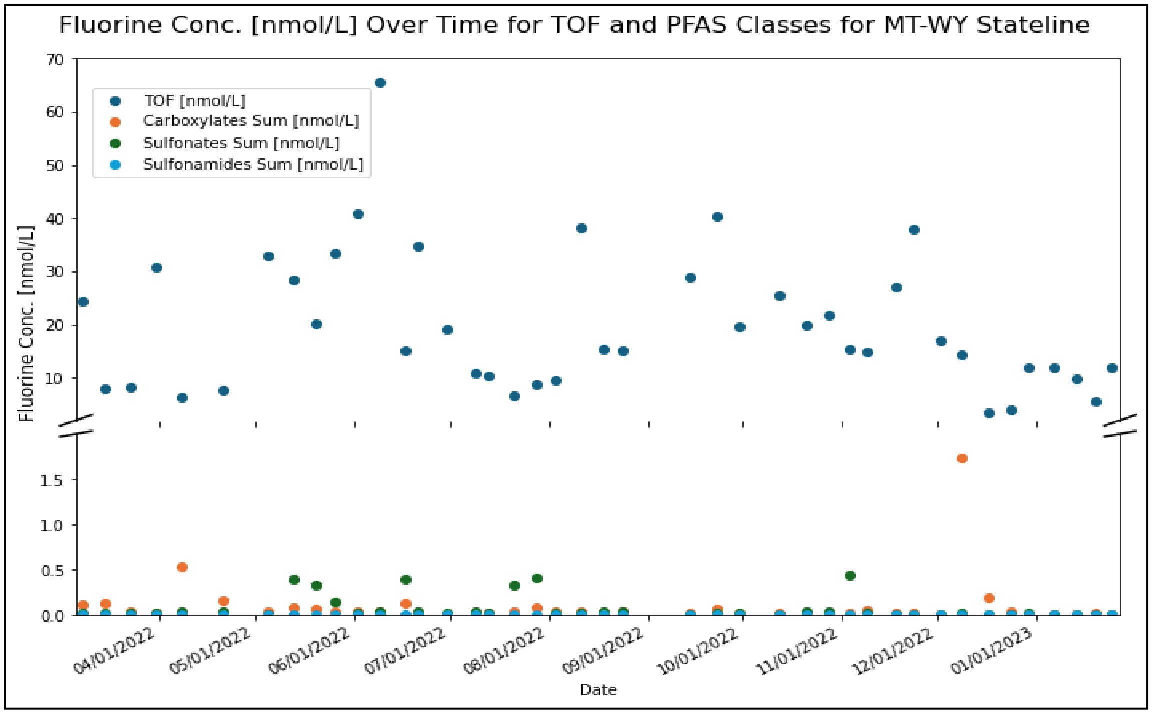

Figure 4. Time series of TOF and PFAS class results for MT-WY Stateline

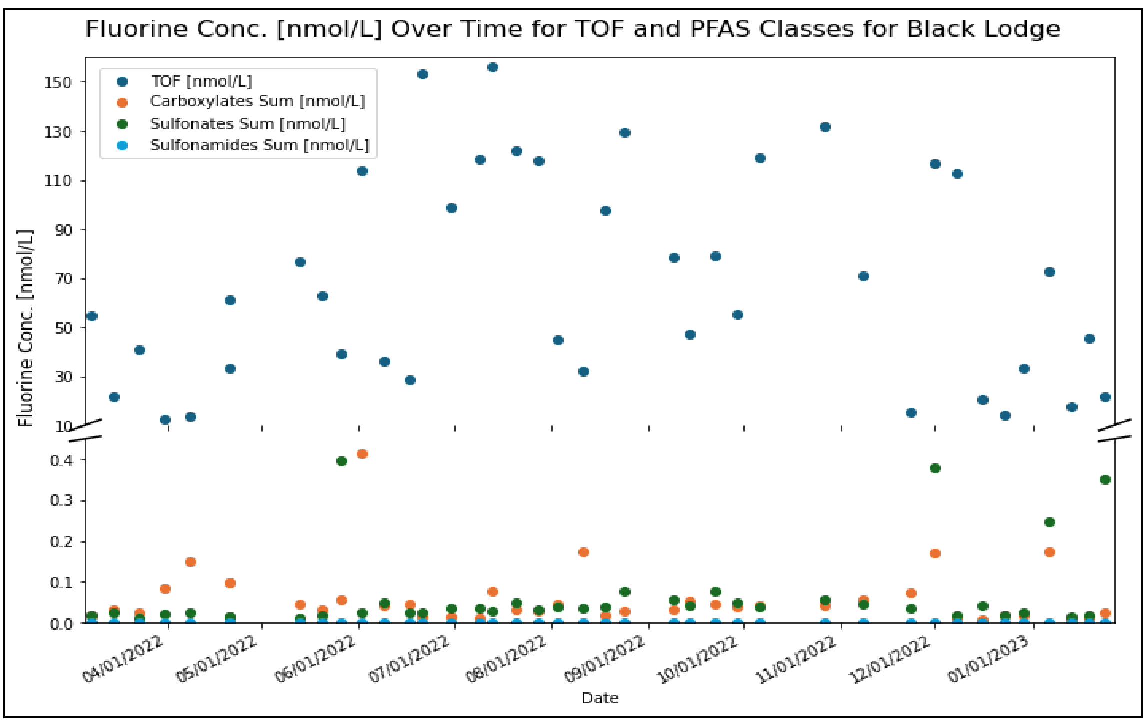

Figure 5. Time series of TOF and PFAS class results for Black Lodge site, MT

At the MT-WY Stateline site, the sum of TOF concentrations over the entire sampling period was 832.83 nmol/ with targeted compounds being 7.12 nmol/L or 0.85% of the total organic fluorine. Of that 0.85%, carboxylate PFAS compounds contributed 3.99 nmol/L or 0.48%, sulfonates were 3.13 nmol/L or 0.37%, and the sulfonamides contribution was negligible at 0.003 nmol/L (Figure 6).

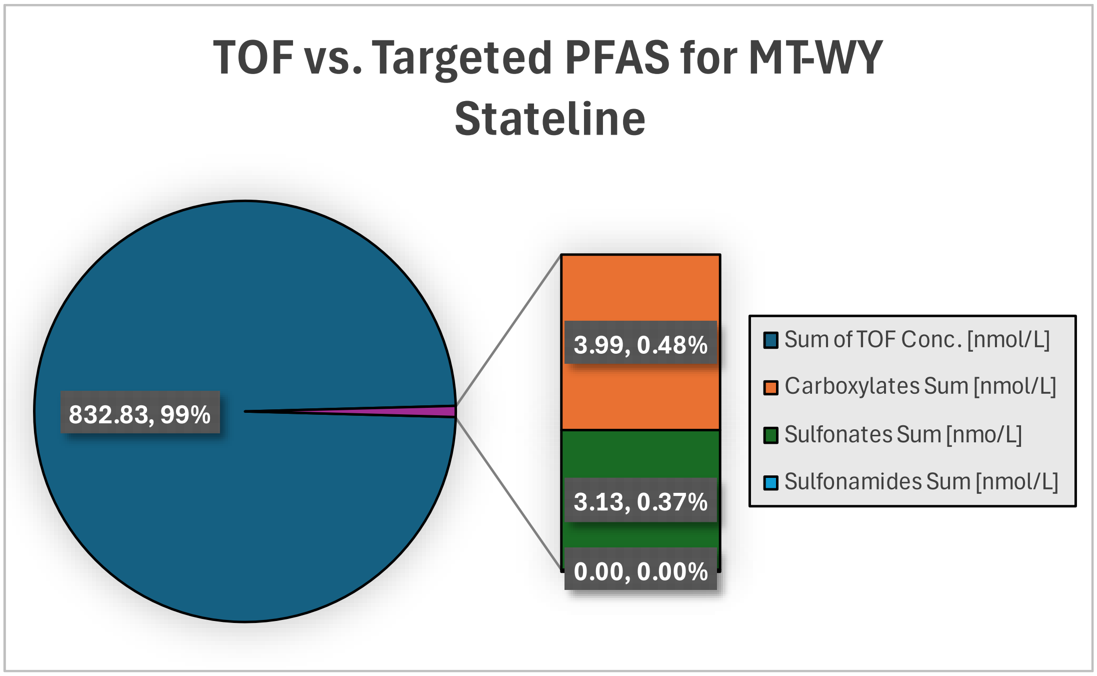

Figure 6. TOF vs. Targeted PFAS results for MT-WY Stateline

The Black Lodge site had a significantly higher sum of TOF at 2692.92 nmol/L. At this site, the targeted PFAS compounds only contributed 5.00 nmol/L of the total 2692.93 nmol/L detected from the TOF analysis, equivalent to 0.19% of the total percentage of TOF detected. Of that 0.19%, 0.09% were carboxylates with sulfonates contributing 0.10% (Figure 7). Again, the contribution of sulfonamides can be considered negligible with a total concentration of 0.0021 nmol/L.

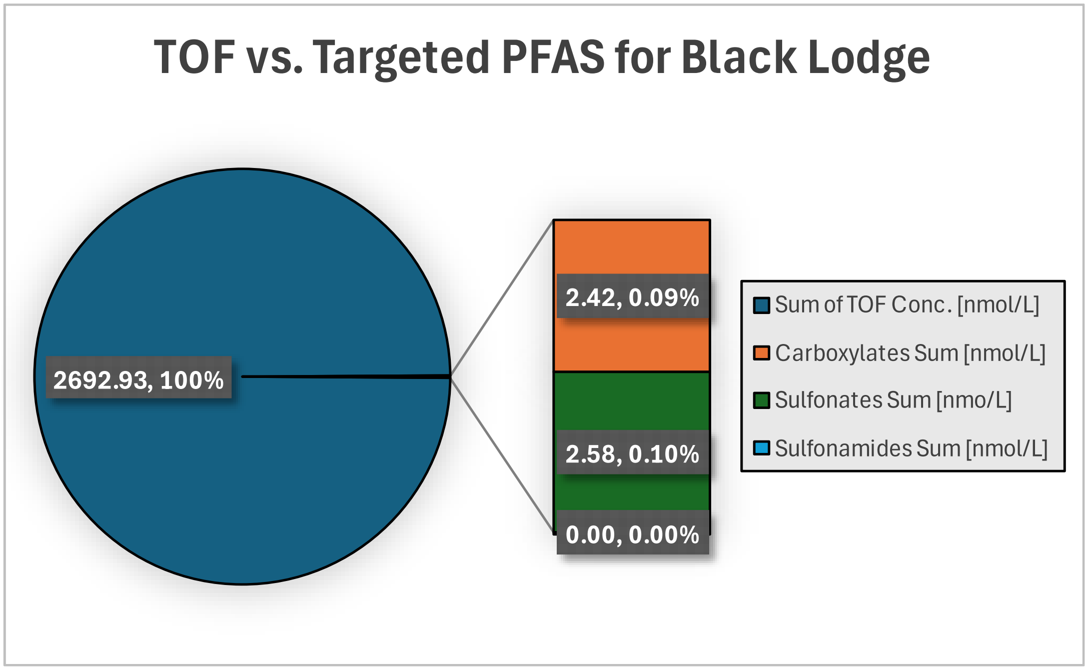

Figure 7. TOF vs. Targeted PFAS results for Black Lodge

3.3 Concentration-Discharge Analyses

Discharge data for each site was downloaded from the USGS National Water Information System (NWIS) and compared to the measured TOF concentrations. The TOF concentrations were found to increase slightly with increasing discharge at both sites, with a stronger flushing response being noticeable at the MT-WY Stateline. The R^2 value at the MT-WY Stateline site was 0.2139 (Figure 8) while the R^2 value at the Black Lodge Site was 0.0725 (Figure 9). The total carboxylates and total sulfonates at the MT-WY Stateline were found to have near zero correlation with discharge (Figure 10). The Black Lodge site found the total carboxylate to increase with increasing discharge with an R^2 of 0.2379 while the total sulfonates decreased with increasing discharge and an R^2 of 0.0015 (Figure 11). Because the sulfonamides concentrations were negligible at both sites, there is no correlation between the total sulfonamides and the discharge.

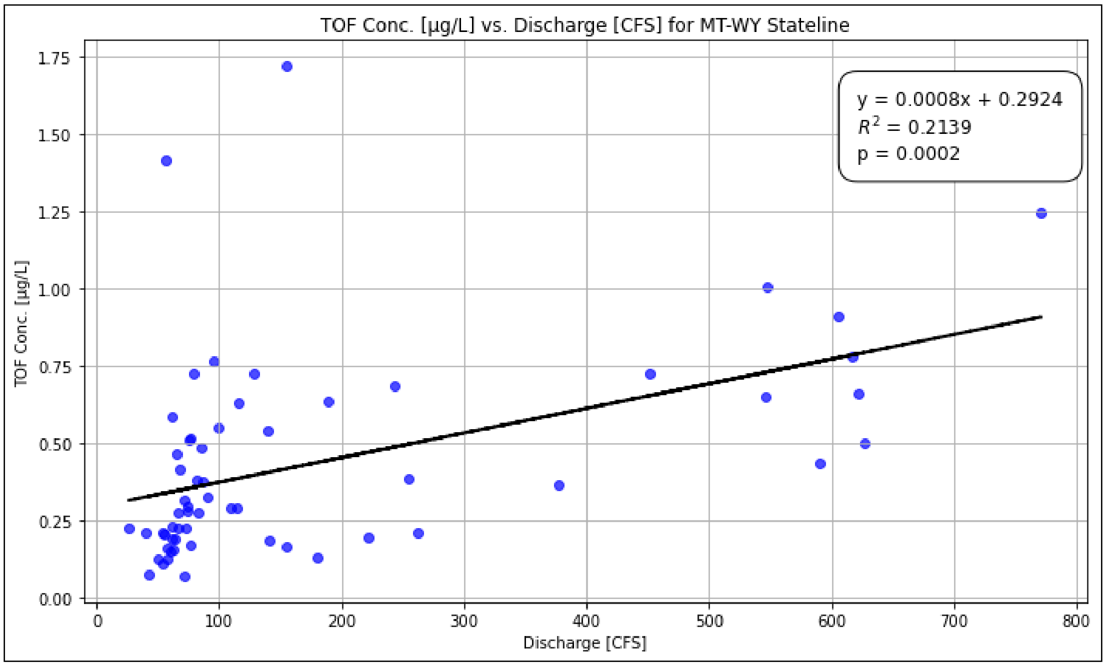

Figure 8. TOF Concentration vs. Discharge Results for MT-WY Stateline

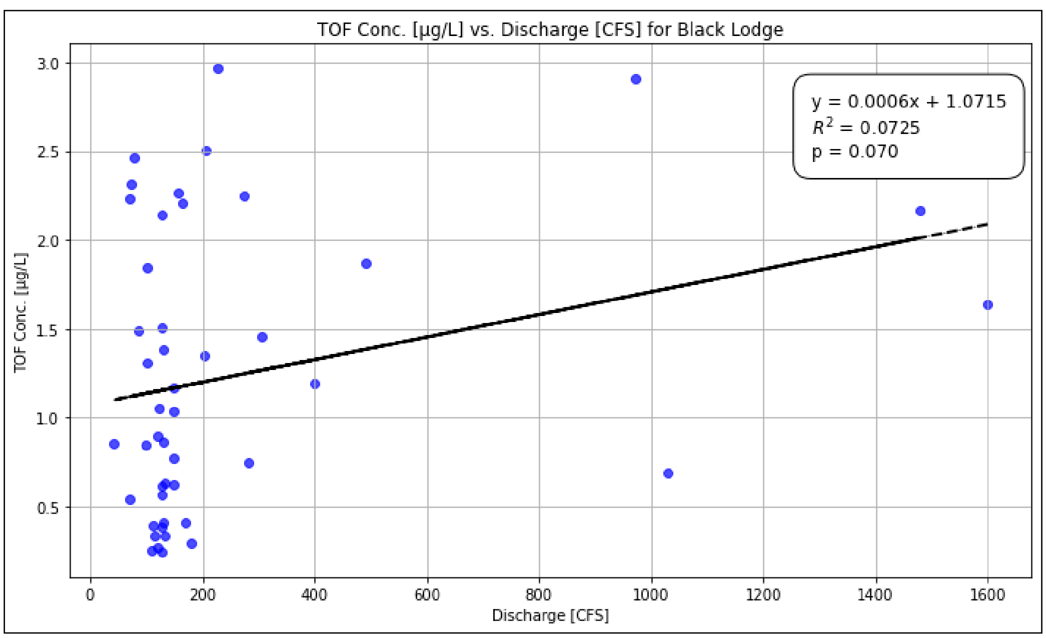

Figure 9. TOF Concentration vs. Discharge Results for Black Lodge

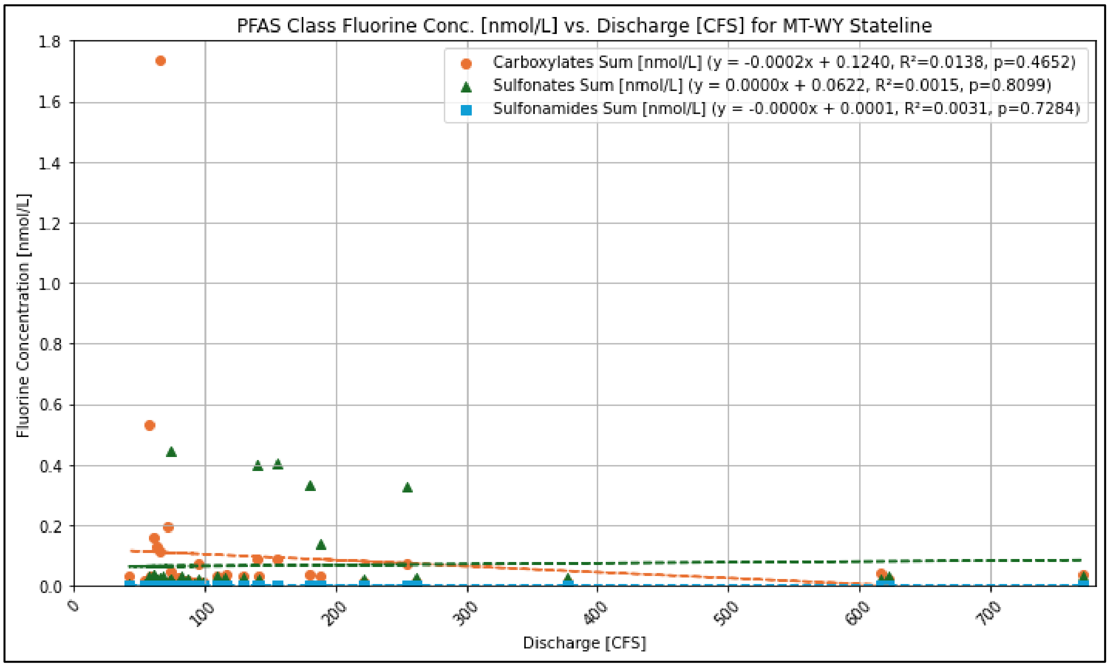

Figure 10. PFAS Class Fluorine Concentrations vs. Discharge for MT-WY Stateline

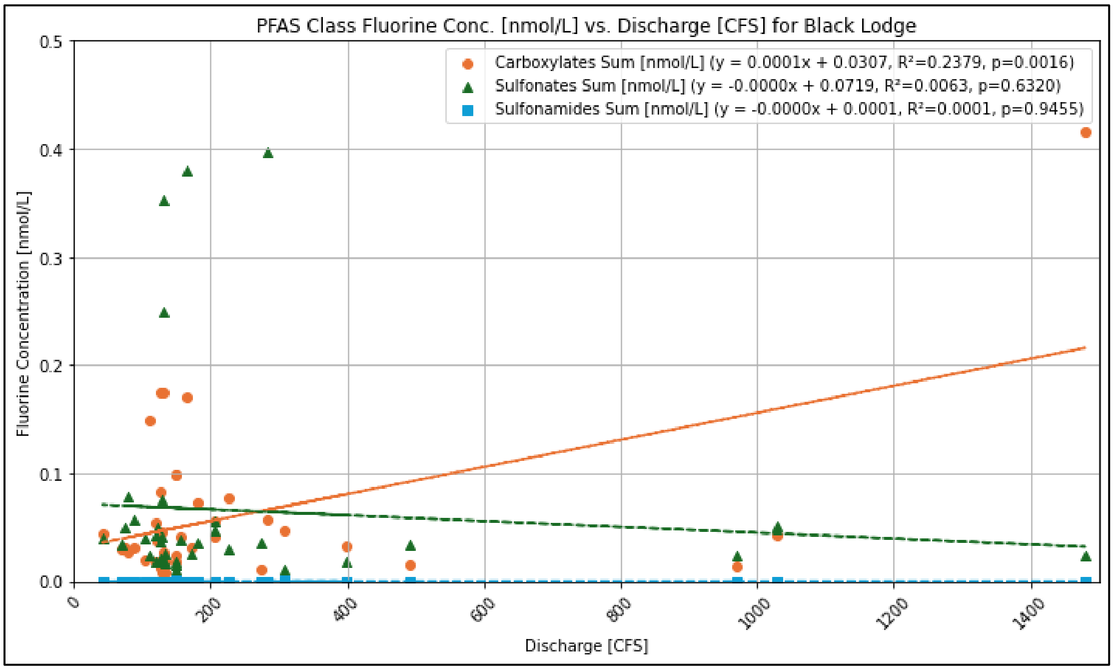

Figure 11. PFAS Class Fluorine Concentrations vs. Discharge for Black Lodge site, MT

Figures 12 and 13 show the time series of the TOF concentration measured with the USGS' discharge values while Figures 14 and 15 show the same relationship using the total PFAS class data and the USGS' discharge values. These graphs were crafted for each site to better visualize the relationship between the two variables, further showing the correlations discussed previously.

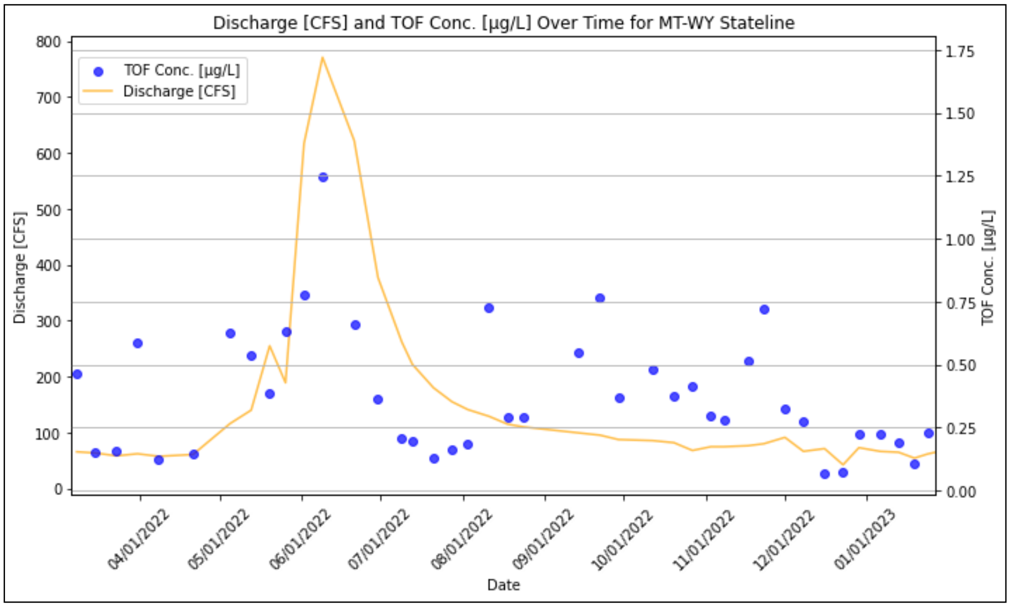

Figure 12. Discharge and TOF Concentration Results for MT-WY Stateline

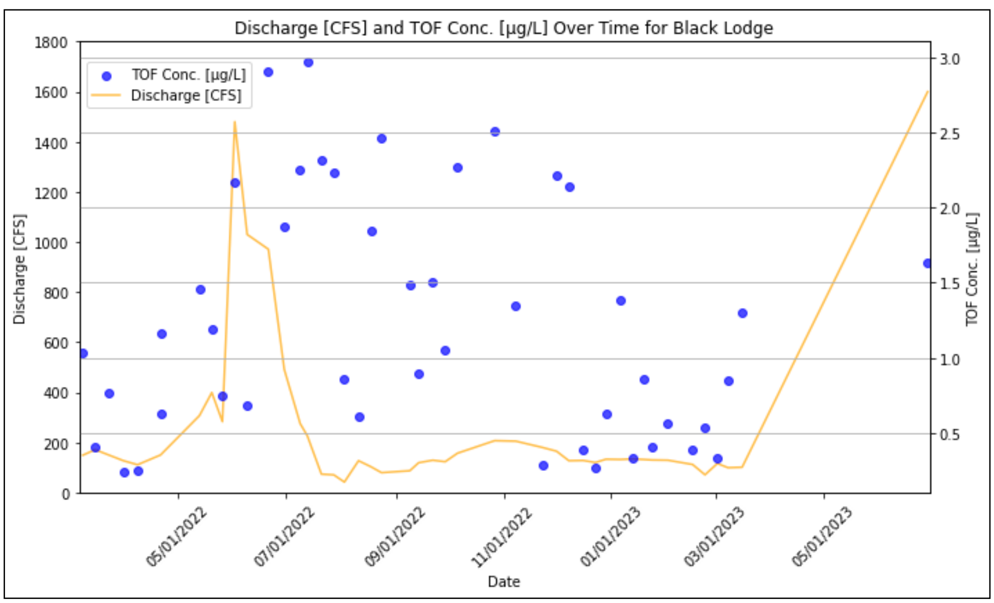

Figure 13. Discharge and TOF Concentration Results for Black Lodge site, MT

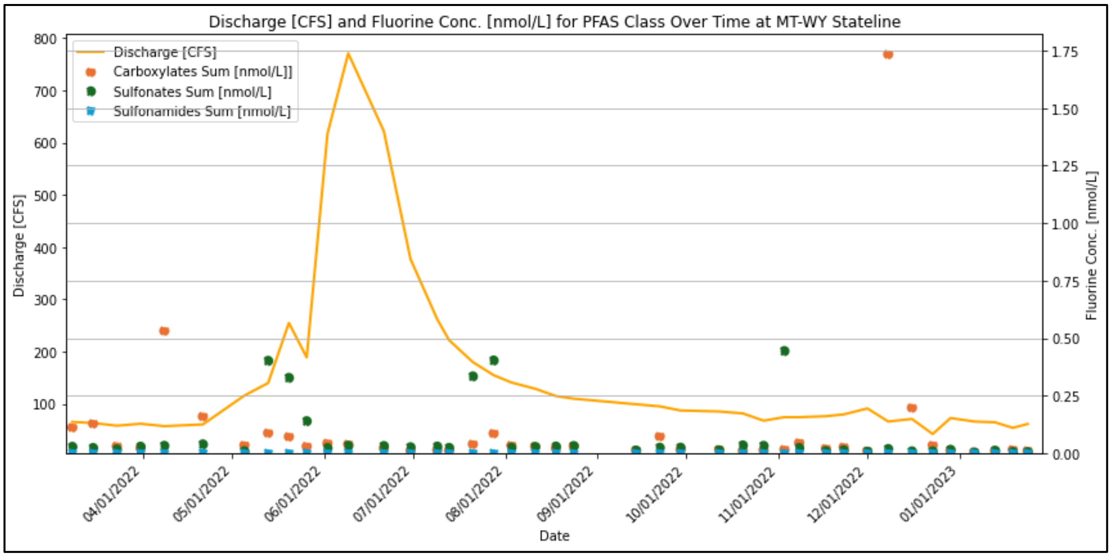

Figure 14. Discharge and PFAS Class Concentration Results for MT-WY Stateline

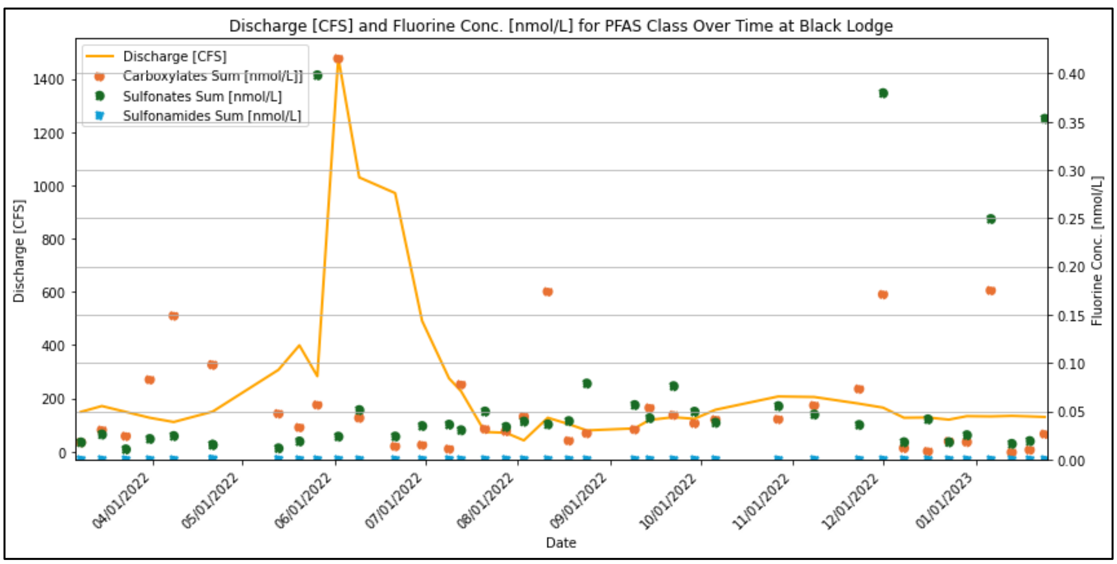

Figure 15. Discharge and PFAS Class Concentration Results for Black Lodge site, MT

4. Discussion

4.1 Total Organic Fluorine (TOF) Analysis

Low concentrations of TOF were found at both sites, with the Black Lodge site having higher concentrations of TOF. This difference can likely be attributed to the Black Lodge site's proximity to infrastructure and downstream positioning compared to the MT-WY Stateline site. Various land-uses upstream, including agricultural and recreational uses, can increase the amount of TOF found downstream. The TOF analysis may include non-PFAS organic fluorine containing molecules, such as organofluorine pesticides which may be contributed from agricultural practices in the watershed. Ogawa et al., 2020 found that nearly 67% of agrochemicals used in agricultural practices contain organofluorine compounds. Additionally, the Black Lodge site is located near the city of Hardin, Montana where additional urban infrastructure can be found, including the outflow of a water treatment plant, which may be another source of fluoride.

4.2 TOF and Targeted PFAS Analysis

The 25 targeted PFAS compounds only accounted for a small percentage of the TOF detected in each sample. These results are in agreement with similar TOF-CIC studies done by Han et al., 2021 and Forester et al., 2023. Both papers found that their targeted PFAS compounds only contributed a small percentage to the TOF concentrations measured. Although the contribution of the targeted PFAS to the TOF found at each LBHR site is <1%, the MT-WY Stateline site had a slightly higher contribution of targeted PFAS compared to the Black Lodge site for each PFAS class. For both sites, the carboxylate and sulfonate PFAS were the majority contribution of the targeted PFAS in the analysis while the contribution of the sulfonamide PFAS can be considered negligible. While the overall concentrations detected for each targeted PFAS compound were low (<1.728 ng/L) or not detected, the four sulfonamide PFAS analyzed had the most non-detections (91.5 % of sulfonamide PFAS) out of any of the other PFAS classes. Potential sources of PFAS contamination at both sites may originate from long-range transportation of PFAS via processes like atmospheric deposition and bioaccumulation of PFAS in plants and animals. Due to the Black Lodge site's proximity to infrastructure at both the sampling site and upstream of the site, additional sources of PFAS may originate from anthropogenic sources from industrial and commercial uses, wastewater, and biosolids. Despite these potential sources, there are several thousand individual PFAS compounds that may be missed in a targeted PFAS analysis and instead captured in a TOF analysis. However, since the TOF analysis cannot identify individual PFAS compounds, it may also include non-PFAS organic fluorine containing molecules. These factors can influence why there is such a start difference between the concentration of fluoride measured in the targeted PFAS and the TOF.

4.3 Concentration-Discharge Analyses

The MT-WY Stateline site was found to have increasing TOF concentrations with increasing discharge, indicating that a flushing response was occurring. This flushing response may be attributed to snowmelt in the surrounding mountains at the Bighorn National Forest. Snow will accumulate in the surrounding mountains from October to April before rapidly melting in the spring. The snowmelt's contribution to discharge can be seen in the discharge peak from May to August in Figures 12-15. While there are rainfall events from March to November in the Crow Reservation, snowmelt is the major contributor for streamflow during the warmer months. The runoff from these precipitation events has the potential to carry fluorinated compounds and deposit them into neighboring water sources. Because some PFAS can adsorb to soil surfaces, studies are currently underway to investigate the role of sediments as a source or sink for PFAS (Balgooyen & Remucal, 2022). There is a possibility that increased discharge from the snowmelt and precipitation events could have caused a more turbulent flow that produced a soil washing effect with fluorinated compounds. While the downstream site did have slight increasing concentrations with increasing discharge, the relationship was not as prominent as it was at the MT-WY Stateline. This may be due to the increased potential sources of PFAS contamination downstream versus upstream.

5. Conclusion

The targeted 25-PFC accounted for a small percentage of the TOF concentrations with carboxylate and sulfonamide PFAS compounds accounting for less than 1% of the TOF found at both sites on the LBHR. The elevated TOF concentrations suggest significant contributions from other PFAS or organofluorine containing compounds. These results highlight the potential of using TOF-CIC as a screening method to address the limitations of targeted PFAS analyses and guide future targeted PFAS analyses to better understand the PFAS burden in both the Crow Indian Reservation and the general environment. EPA Method 1633 targeted 40-PFAS compounds and can be paired with a TOF-CIC analysis using EPA Method 1621 to continue analyzing different fluoride fractions and balances in general PFAS analyses. With the growing amount of PFAS in the environment, it is important to continue expanding the accuracy and capacity of these analytical methods to further quantify PFAS and address any health impacts from these compounds.

6. Appendix A – Supplementary Data

Table A1. TOF Sample Information and TOF Data

Sample ID	Location	Discharge [CFS]	TOF [µg/L]
LBHR 1	MT-WY Stateline	65.5	0.4639
LBHR 5	Black Lodge	149	1.034
LBHR 5 Duplicate	Black Lodge	149	14.64
LBHR 13	MT-WY Stateline	63.4	0.1530
LBHR 18	Black Lodge	171	0.4083
LBHR 21	MT-WY Stateline	58.3	0.1572
LBHR 25	Black Lodge	149	0.7691
LBHR 31	MT-WY Stateline	62	0.5850
LBHR 36	Black Lodge	127	0.2405
LBHR 40	MT-WY Stateline	57.4	0.1228
LBHR 42	Black Lodge	111	0.2524
LBHR 45	MT-WY Stateline	60.7	0.1484
LBHR 47	Black Lodge	150	0.6261
LBHR 47 Duplicate	Black Lodge	150	1.1636
LBHR 52	Black Lodge	595	7.312
LBHR 54	MT-WY Stateline	116	0.6269
LBHR 56	Black Lodge	335	12.04
LBHR 60	MT-WY Stateline	140	0.5389
LBHR 62	Black Lodge	307	1.458
LBHR 66	MT-WY Stateline	255	0.3839
LBHR 68	Black Lodge	399	1.190
LBHR 72	MT-WY Stateline	189	0.6349
LBHR 74	Black Lodge	283	0.7438
LBHR 79	MT-WY Stateline	617	0.7770
LBHR 81	Black Lodge	1480	2.165
LBHR 86	MT-WY Stateline	771	1.245
LBHR 88	Black Lodge	1030	0.6858
LBHR 100	MT-WY Stateline	622	0.6604

Sample ID	Location	Discharge [CFS]	TOF [µg/L]
LBHR 102	Black Lodge	971	2.907
LBHR 107	MT-WY Stateline	377	0.3633
LBHR 109	Black Lodge	491	1.872
LBHR 114	MT-WY Stateline	262	0.2066
LBHR 116	Black Lodge	275	2.253
LBHR 121	MT-WY Stateline	222	0.1964
LBHR 123	Black Lodge	227	2.968
LBHR 128	MT-WY Stateline	180	0.1276
LBHR 130	Black Lodge	73.5	2.313
LBHR 135	MT-WY Stateline	155	0.1646
LBHR 137	Black Lodge	70.6	2.234
LBHR 142	MT-WY Stateline	141	0.1840
LBHR 144	Black Lodge	41.9	0.8559
LBHR 149	MT-WY Stateline	129	0.7245
LBHR 151	Black Lodge	127	0.6117
LBHR 156	MT-WY Stateline	115	0.2905
LBHR 158	Black Lodge	103	1.848
LBHR 163	MT-WY Stateline	110	0.2896
LBHR 165	Black Lodge	79.4	2.463
LBHR 170	MT-WY Stateline	130	5.739
LBHR 172	Black Lodge	87	1.486
LBHR 177	MT-WY Stateline	99.3	0.5479
LBHR 179	Black Lodge	119	0.8977
LBHR 184	MT-WY Stateline	95.3	0.7641
LBHR 186	Black Lodge	129	1.505
LBHR 191	MT-WY Stateline	87.4	0.3723
LBHR 193	Black Lodge	123	1.054
LBHR 200	Black Lodge	157	2.266

Table A1. TOF Sample Information and TOF Data, Continued

Sample ID	Location	Discharge [CFS]	TOF [µg/L]	Sample ID	Location	Discharge [CFS]	TOF [µg/L]
LBHR 205	MT-WY Stateline	85.5	0.4841	LBHR 319	Black Lodge	129	0.5656
LBHR 207	Black Lodge	141	5.224	LBHR 331	MT-WY Stateline	40	0.2070
LBHR 212	MT-WY Stateline	81.8	0.3770	LBHR 333	Black Lodge	112	0.3931
LBHR 214	Black Lodge	186	5.444	LBHR 338	MT-WY Stateline	26.5	0.2239
LBHR 219	MT-WY Stateline	67.9	0.4156	LBHR 340	Black Lodge	70.9	0.5409
LBHR 221	Black Lodge	207	2.507	LBHR 345	MT-WY Stateline	61.4	0.1879
LBHR 226	MT-WY Stateline	74.6	0.2945	LBHR 347	Black Lodge	116	0.3372
LBHR 233	MT-WY Stateline	74.6	0.2801	LBHR 352	MT-WY Stateline	51	0.1214
LBHR 235	Black Lodge	205	1.347	LBHR 354	Black Lodge	99.2	0.8493
LBHR 240	MT-WY Stateline	76.4	0.5164	LBHR 359	MT-WY Stateline	56.3	1.414
LBHR 242	Black Lodge	162	4.426	LBHR 361	Black Lodge	101	1.305
LBHR 247	MT-WY Stateline	79.9	0.7230	LBHR 373	MT-WY Stateline	55.6	0.2048
LBHR 249	Black Lodge	180	0.2911	LBHR 375	Black Lodge	103	4.412
LBHR 254	MT-WY Stateline	91.3	0.3248	LBHR 380	MT-WY Stateline	53.9	0.2094
LBHR 256	Black Lodge	165	2.211	LBHR 382	Black Lodge	106	3.582
LBHR 261	MT-WY Stateline	66.3	0.2739	LBHR 387	MT-WY Stateline	82.6	0.2728
LBHR 263	Black Lodge	127	2.143	LBHR 394	MT-WY Stateline	75.8	0.5103
LBHR 268	MT-WY Stateline	71.2	0.0674	LBHR 401	MT-WY Stateline	76.6	0.1695
LBHR 270	Black Lodge	128	0.3857	LBHR 403	Black Lodge	364	8.814
LBHR 275	MT-WY Stateline	42.3	0.0760	LBHR 408	MT-WY Stateline	155	1.720
LBHR 277	Black Lodge	120	0.2672	LBHR 410	Black Lodge	310	6.521
LBHR 282	MT-WY Stateline	72.9	0.2246	LBHR 415	MT-WY Stateline	244	0.6822
LBHR 284	Black Lodge	133	0.6299	LBHR 417	Black Lodge	393	6.225
LBHR 289	MT-WY Stateline	66.3	0.2263	LBHR 429	MT-WY Stateline	606	0.9119
LBHR 291	Black Lodge	132	1.381	LBHR 436	MT-WY Stateline	452	0.7267
LBHR 296	MT-WY Stateline	64.7	0.1884	LBHR 443	MT-WY Stateline	548	1.004
LBHR 298	Black Lodge	134	0.3298	LBHR 450	MT-WY Stateline	591	0.4323
LBHR 303	MT-WY Stateline	54.2	0.1082	LBHR 452	Black Lodge	1200	5.355
LBHR 305	Black Lodge	132	0.8589	LBHR 457	MT-WY Stateline	546	0.6473
LBHR 310	MT-WY Stateline	61.6	0.2273	LBHR 459	Black Lodge	1200	10.63
LBHR 312	Black Lodge	130	0.4086	LBHR 464	MT-WY Stateline	627	0.4999
LBHR 317	MT-WY Stateline	71.2	0.3134	LBHR 466	Black Lodge	1600	1.637

Table A2. Targeted PFC Sample Information and PFAS Class Data

Sample ID	Location	Discharge [CFS]	Total F Carboxylates [nmol/L]	Total F Sulfonates [nmol/L]	Total F Sulfonamides [nmol/L]
LBHR 3	MT-WY Stateline	65.5	0.1116	0.0269	0.0004
LBHR 7	Black Lodge	149	0.0179	0.0176	0.0000
LBHR 11	MT-WY Stateline	63.4	0.1283	0.0219	0.0001
LBHR 15	Black Lodge	171	0.0306	0.0258	0.0001
LBHR 23	MT-WY Stateline	58.3	0.0305	0.0157	0.0000
LBHR 27	Black Lodge	149	0.0243	0.0104	0.0000
LBHR 33	MT-WY Stateline	62	0.0227	0.0275	0.0000
LBHR 37	Black Lodge	127	0.0828	0.0212	0.0000
LBHR 41	MT-WY Stateline	57.4	0.5315	0.0313	0.0000
LBHR 43	Black Lodge	111	0.1490	0.0242	0.0000
LBHR 46	MT-WY Stateline	60.7	0.1594	0.0376	0.0010
LBHR 48	Black Lodge	150	0.0983	0.0151	0.0005
LBHR 55	MT-WY Stateline	116	0.0343	0.0077	0.0001
LBHR 61	MT-WY Stateline	140	0.0875	0.4009	0.0000
LBHR 63	Black Lodge	307	0.0476	0.0115	0.0003
LBHR 67	MT-WY Stateline	255	0.0716	0.3269	0.0000
LBHR 69	Black Lodge	399	0.0333	0.0186	0.0000
LBHR 73	MT-WY Stateline	189	0.0295	0.1385	0.0005
LBHR 75	Black Lodge	283	0.0567	0.3979	0.0000
LBHR 80	MT-WY Stateline	617	0.043	0.0215	0.0000
LBHR 82	Black Lodge	1480	0.4154	0.0236	0.0001
LBHR 87	MT-WY Stateline	771	0.0387	0.0312	0.0001
LBHR 89	Black Lodge	1030	0.0431	0.0511	0.0000
LBHR 94	MT-WY Stateline	622	0.0220	0.0304	0.0000
LBHR103	Black Lodge	971	0.0137	0.0237	0.0000
LBHR101	MT-WY Stateline	377	0.0108	0.0251	0.0000

Table A2. Targeted PFC Sample Information and PFAS Class Data, Continued

Sample ID	Location	Discharge [CFS]	Total F Carboxylates [nmol/L]	Total F Sulfonates [nmol/L]	Total F Sulfonamides [nmol/L]
LBHR110	Black Lodge	491	0.0151	0.0346	0.0000
LBHR108	MT-WY Stateline	262	0.0136	0.0280	0.0000
LBHR117	Black Lodge	275	0.0110	0.0360	0.0001
LBHR115	MT-WY Stateline	222	0.0120	0.0224	0.0001
LBHR124	Black Lodge	227	0.0778	0.0302	0.0000
LBHR122	MT-WY Stateline	180	0.0389	0.3331	0.0000
LBHR 131	Black Lodge	73.5	0.0317	0.0496	0.0001
LBHR 129	MT-WY Stateline	155	0.0857	0.4023	0.0000
LBHR 138	Black Lodge	70.6	0.0293	0.0337	0.0002
LBHR 136	MT-WY Stateline	141	0.0336	0.0228	0.0000
LBHR 145	Black Lodge	41.9	0.0445	0.0392	0.0000
LBHR 143	MT-WY Stateline	129	0.0292	0.0266	0.0002
LBHR 152	Black Lodge	127	0.1740	0.0363	0.0001
LBHR 150	MT-WY Stateline	115	0.0227	0.0282	0.0000
LBHR 159	Black Lodge	103	0.0196	0.0397	0.0000
LBHR 157	MT-WY Stateline	110	0.0300	0.0303	0.0000
LBHR 166	Black Lodge	79.4	0.0272	0.0786	0.0000
LBHR 173	Black Lodge	87	0.0312	0.0563	0.0000
LBHR 164	MT-WY Stateline	99.3	0.0120	0.0108	0.0000
LBHR 180	Black Lodge	119	0.0536	0.0427	0.0000
LBHR 178	MT-WY Stateline	95.3	0.0728	0.0231	0.0000
LBHR 187	Black Lodge	129	0.0462	0.0759	0.0000
LBHR 185	MT-WY Stateline	87.4	0.0154	0.0232	0.0000
LBHR 194	Black Lodge	123	0.0375	0.0494	0.0000
LBHR 201	Black Lodge	157	0.0414	0.0380	0.0000
LBHR 192	MT-WY Stateline	85.5	0.0154	0.0117	0.0000
LBHR 206	MT-WY Stateline	81.8	0.0097	0.0332	0.0000

Table A2. Targeted PFC Sample Information and PFAS Class Data, Continued.

Sample ID	Location	Discharge [CFS]	Total F Carboxylates [nmol/L]	Total F Sulfonates [nmol/L]	Total F Sulfonamides [nmol/L]
LBHR 213	MT-WY Stateline	67.9	0.0126	0.0312	0.0000
LBHR 222	Black Lodge	207	0.0418	0.0552	0.0000
LBHR 220	MT-WY Stateline	74.6	0.0158	0.4434	0.0000
LBHR 227	MT-WY Stateline	74.6	0.0451	0.0221	0.0000
LBHR 236	Black Lodge	205	0.0561	0.0465	0.0001
LBHR 234	MT-WY Stateline	76.4	0.0203	0.0082	0.0002
LBHR 241	MT-WY Stateline	79.9	0.0266	0.0119	0.0000
LBHR 250	Black Lodge	180	0.0732	0.0357	0.0000
LBHR 248	MT-WY Stateline	91.3	0.0096	0.0058	0.0000
LBHR 257	Black Lodge	165	0.1711	0.3794	0.0000
LBHR 255	MT-WY Stateline	66.3	1.734	0.0174	0.0000
LBHR 264	Black Lodge	127	0.0118	0.0178	0.0000
LBHR 262	MT-WY Stateline	71.2	0.1972	0.0072	0.0000
LBHR 271	Black Lodge	128	0.0086	0.0415	0.0000
LBHR 269	MT-WY Stateline	42.3	0.0341	0.0070	0.0000
LBHR 278	Black Lodge	120	0.0189	0.0178	0.0000
LBHR 276	MT-WY Stateline	72.9	0.0119	0.0140	0.0000
LBHR 285	Black Lodge	133	0.0181	0.0251	0.0000
LBHR 283	MT-WY Stateline	66.3	0.0047	0.0024	0.0000
LBHR 292	Black Lodge	132	0.1752	0.2490	0.0000
LBHR 290	MT-WY Stateline	64.7	0.0092	0.0102	0.0000
LBHR 299	Black Lodge	134	0.0075	0.0161	0.0000
LBHR 297	MT-WY Stateline	54.2	0.0152	0.0045	0.0000
LBHR 306	Black Lodge	132	0.0100	0.0190	0.0000
LBHR 304	MT-WY Stateline	61.6	0.0104	0.0040	0.0000
LBHR 313	Black Lodge	130	0.0265	0.3528	0.0000

Table A3. Field Blank and Method Blank Data

Sample ID	TOF [µg/L]
LBHR 9 FB	0.3312
LBHR 9 FB Duplicate	0.4879
LBHR 19 FB	0.3348
LBHR 19 FB Duplicate	0.2420
LBHR 29 FB	0.3362
LBHR 29 FB Duplicate	0.3126
LBHR 39 FB	0.4814
LBHR 39 FB Duplicate	0.3553
LBHR 44 FB	0.4127
LBHR 44 FB Duplicate	0.4547
LBHR 58 FB	0.5547
LBHR 64 FB	0.2782
LBHR 70 FB	0.5349
LBHR 76 FB	0.3725
LBHR 83 FB	0.4143
LBHR 90 FB	0.2227
LBHR 97 FB	0.2699
LBHR 104 FB	0.4699
LBHR 111 FB	0.2426
LBHR 118 FB	0.4766
LBHR 125 FB	0.2358
LBHR 132 FB	0.1693
LBHR 139 FB	0.0916
LBHR 146 FB	1.032
LBHR 153 FB	0.3425
LBHR 160 FB	0.5594
LBHR 167 FB	0.4809

Sample ID	TOF [µg/L]
LBHR 174 FB	0.5577
LBHR 181 FB	0.2368
LBHR 188 FB	0.2471
LBHR 195 FB	0.2718
LBHR 202 FB	0.3953
LBHR 209 FB	0.2149
LBHR 223 FB	0.4027
LBHR 230 FB	0.3335
LBHR 237 FB	0.3234
LBHR 244 FB	2.2131
LBHR 251 FB	0.2891
LBHR 258 FB	0.2880
LBHR 265 FB	0.2203
LBHR 272 FB	0.1086
LBHR 279 FB	0.1327
LBHR 286 FB	0.1304
LBHR 293 FB	0.0834
LBHR 300 FB	0.1815
LBHR 307 FB	0.0781
LBHR 314 FB	4.4072
LBHR 321 FB	0.1371
LBHR 328 FB	0.2331
LBHR 335 FB	0.1348
LBHR 342 FB	0.0704
LBHR 349 FB	0.0620
LBHR 356 FB	0.3244
LBHR 363 FB	0.1895

Sample ID	TOF [µg/L]
LBHR 370 FB	0.1504
LBHR 377 FB	0.1024
LBHR 384 FB	0.1345
LBHR 391 FB	0.1324
LBHR 398 FB	0.1022
LBHR 405 FB	0.1735
LBHR 412 FB	0.1872
LBHR 419 FB	0.1875
LBHR 433 FB	0.2096
LBHR 440 FB	0.1424
LBHR 447 FB	0.1191
LBHR 454 FB	0.2066
LBHR 461 FB	0.1835
LBHR 468 FB	0.1331
Method Blank 1	0.4222
Method Blank 2	0.4242
Method Blank 3	0.1720
Method Blank 4	0.2599
Method Blank 5	0.1924
Method Blank 6	0.1754
Method Blank 7	0.0543
Method Blank 8	0.0751
Method Blank 9	0.0866
Method Blank 10	0.1400

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