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PFAS IN SURFACE WATER, SEDIMENT AND FISH IN THE PENNSYLVANIA COASTAL ZONE FFY2020

Technical Report No. 2023-5

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Pennsylvania Coastal Resources Management Program

PFAS in Surface water, Sediment and Fish in the Pennsylvania Coastal Zone

Technical Report

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1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are in various industrial and household products, such as stain-repellant textiles, aqueous film-forming foams (AFFF), paper, toilet paper, and food wrappers. While these can be direct human exposure pathways, PFAS also enters the environment through industrial outfalls, municipal treatment plants, usage of AFFF for firefighting, stormwater runoff, and landfill leachate. Environmental releases expose wildlife and humans through direct (swimming, drinking water, etc.) and indirect (consumption of contaminated organisms, etc.) pathways. With PFAS' ubiquitous nature, there is increasing evidence of its adverse effects on human health and the environment. These adverse effects include liver damage, increased cholesterol, thyroid disease, decreased vaccine response, asthma, reduced fertility and birth weight, and pregnancy–induced hypertension.

This diverse group of >10,000 chemicals has varying degrees of persistence, toxicity, and bioaccumulation in the environment. While it is difficult to study such a broad class of chemicals, it is imperative that we quantify PFAS occurrence and bioaccumulation in urban areas to protect water resources that are vital to ecosystem and human health. The Delaware River has historical PFAS pollution as major chemical manufacturers in the catchment performed some of the earliest research and production of PFAS compounds. Therefore, various PFAS chemicals have been detected in Delaware River watershed surface waters raising environmental concerns related to recreation and use of this vital resource.

Previous work by the DRBC from 2004 to 2018 measured several PFAS congeners non-concurrently in fish fillet, surface water and sediment in the Delaware River. Concentrations of PFAS in resident fish varied by species, sample location and sample year. Fish tissue concentrations appear to be substantially decreasing for some long chain PFAS although PFOS concentrations continue to be of concern in the tidal river. Concentrations of PFAS decreased in varying amounts in tidal water with notable decreases in some longer chain PFAS and limited decreases in PFOS and shorter chain PFAS. Sediment samples collected by the DRBC in 2016 in the tidal Delaware River detected low concentrations of long chain PFAS.

2. METHODS

Understanding occurrence and bioaccumulation of PFAS in urban areas is important to protect water resources. Main stem sites were selected to be at or near Delaware Estuary Water Monitoring Program stations with historic data on water quality (https://www.nj.gov/drbc/programs/quality/boat-run.html) and at locations suitable for fish collection (Figure 1 and Table 1). Multiple matrix samples were collected at main stem and tributary sites in the Delaware Estuary within the Pennsylvania Coastal Zone between Morrisville, PA and Chester, PA. Surface water and surficial sediment samples were collected at seventeen sites and composite samples of two fish species were collected at six of the seventeen water and sediment sites. Tributaries were sampled near their confluence with the Delaware River. Sampling was conducted in the Spring of 2021 with the exception of two sites Neshaminy (NHC) and Pennypack (PPC) Creeks at head of tide sampled in the Fall of 2021. Main stem site samples

were collected from a boat. Tributary site samples were collected from stream bank or bridges. A separate smaller set of 4 samples was collected at 4 sites in November 2021 (Table 2) for non-targeted PFAS analysis.

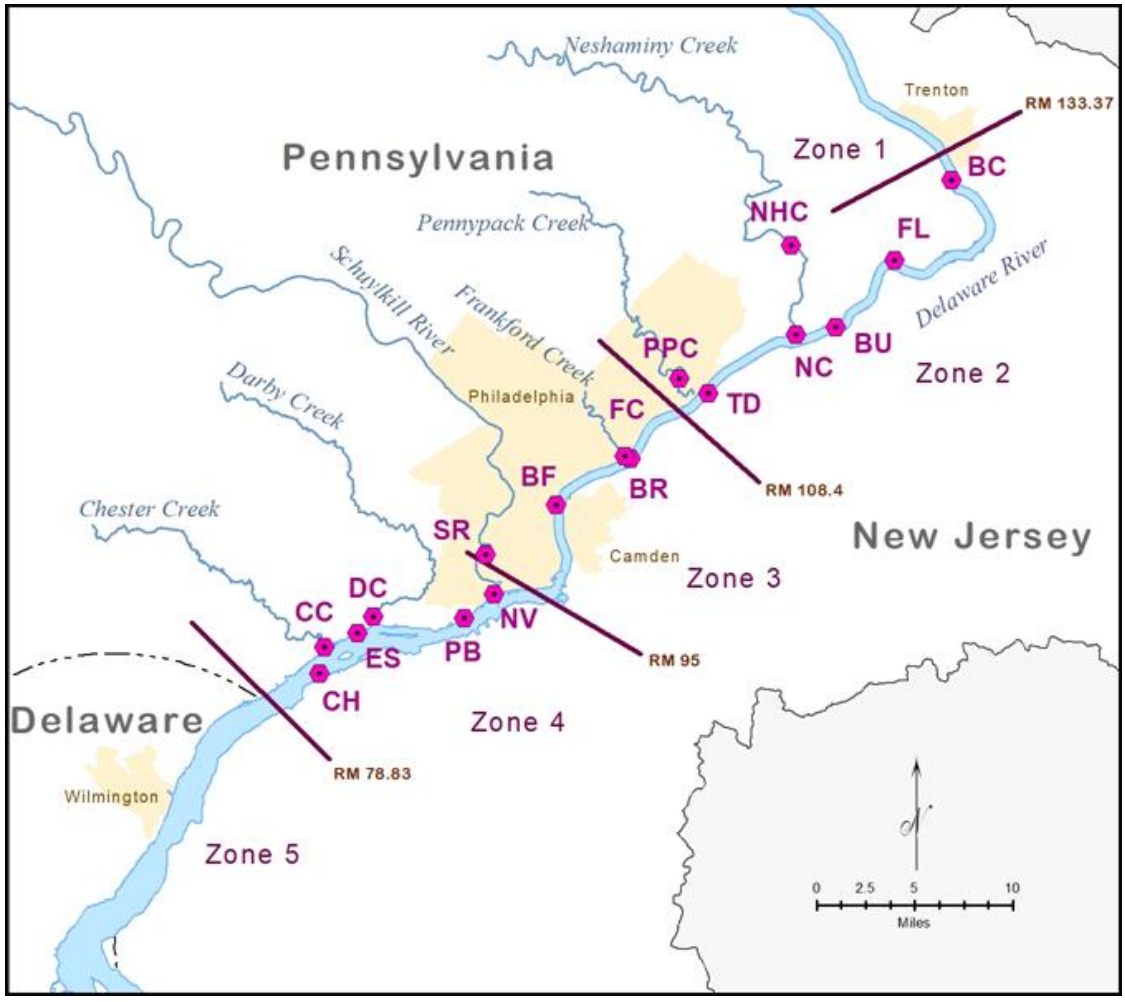

Figure 1. Delaware river and tributary sampling locations.

2.1 Surface Water Sampling

Surface water samples were collected for PFAS analysis. Sample collection followed the PFAS protocols for surface waters issued by the NY State Department of Environmental Conservation (NYSDEC 2020). Grab samples of surface water were collected in two, 500 ml HDPE bottles. Subsurface water samples were collected directly in the laboratory container by submerging with a gloved hand or bottle holder. The water samples were placed on ice in coolers to maintain a temperature of 4 ± 2 ˚C during transportation and then frozen prior to shipping to the laboratory for analyses. SGS AXYS laboratory supplied PFAS free water that was transferred to a second sample bottle on site for a field blank. A field duplicate consisting of an additional sample at a given location was collected. In-field measurements of surface water included specific

conductivity, water temperature, dissolved oxygen, turbidity, and pH were taken at each sample site.

For non-targeted analysis, 4 water samples and 1 field blank were analyzed at the Temple University Water Environment and Technology (WET) Center. These 1 L samples were collected and handled as described above, but then sent to Temple for processing and analysis. The processing, analytical methods and data are included in Attachment A.

Table 1. Targeted PFAS sampling site information.

Name	ID	River Mile	Water and Sediment		Fish	
			Latitude	Longitude	Latitude	Longitude
Main Stem Sites						
Biles Channel	BC	131.4	40.190	-74.758	40.184	-74.758
Florence	FL	122.4	40.131	-74.813	40.131	-74.813
Burlington Bristol Bridge*	BU	117.8	40.081	-74.870		
Torresdale	TD	110.2	40.033	-74.992	40.033	-74.992
Betsy Ross	BR	104.7	39.984	-75.068		
Ben Franklin Bridge*	BF	100.0	39.950	-75.139		
Navy Yard	NV	92.5	39.884	-75.197		
Philadelphia Airport	PB	90.5	39.866	-75.226		
Eddystone	ES	85.0	39.855	-75.328	39.855	-75.328
Chester*	CH	82.0	39.825	-75.365	39.825	-75.365
Tributary Sites						
Neshaminy Creek (head of tide Hulmeville Rd)	NHC		40.142	-74.913		
Pennypack Creek (head of tide Frankford Ave)	PPC		40.044	-75.020		
Neshaminy Creek	NC		40.076	-74.909		
Frankford Creek	FC		39.986	-75.073		
Darby Creek	DC		39.867	-75.313		
Chester Creek	CC		39.845	-75.360		
Schuylkill River	SR		39.913	-75.206	39.911	-75.214

*Sites where samples were also collected for non-targeted analysis at Temple University.

Table 2. Non-targeted PFAS sampling site information.

Site Name	ID	River Mile	Latitude	Longitude
Calhoun St. Bridge	BC	131.4	40.220	-74.778
Burlington Bristol Bridge	BU	117.8	40.094	-74.856
Ben Franklin Bridge	BF	100	39.950	-75.138
Chester	CH	82	39.823	-75.377

2.2 SEDIMENT SAMPLING

Surficial sediment sample collection followed the PFAS protocols for sediment issued by the NYSDEC (NYSDEC 2020). Sediment samples were collected by a decontaminated Ponar

stainless-steel grab or stainless-steel spoon. The sediment was discharged into a large decontaminated stainless-steel bowl and a pre-washed stainless-steel spoon was used to mix the sample and to collect a sample for analysis. Sample containers were 250 ml HDPE jars for PFAS, 500 ml amber glass jars for grain size and 120 ml amber glass jars for total organic carbon (TOC). Sediment samples were placed in a cooler maintained at 4 ± 2˚ C using ice. A field duplicate consisting of an additional sample at a given location was collected. SGS AXYS PFAS free water was used as an equipment rinsate blank. Total organic carbon was measured in sediment. Sediment size was determined.

2.3 Fish Collection

Fish collection followed the protocols issued by the NYSDEC (NYSDEC 2020). Two tidal species white perch, *Morone americana,* and channel catfish, *Ictalurus punctatus,* were collected by hook and line. Each fish was wrapped in aluminum foil provided by SGS AXYS. All fish of one species at each site were placed into a single bag. Fish samples were stored frozen (-20 ˚C) prior to shipping and processing in the analytical laboratory. Fillets included the skin for white perch. Fillets did not include the skin for channel catfish. A composite of 3 fillets for each species from fish of similar length and weight at each location was prepared at the laboratory.

2.4 PFAS Analysis

Surface water, surficial sediment and fish fillets were analyzed by SGS AXYS Method MLA-110 (equivalent to Draft EPA Method 1633) for 40 PFAS analytes (Table 3). After spiking with isotopically labeled surrogate standards and cleanup on SPE-WAX cartridges, samples were analyzed by LC-MS/MS. Final sample concentrations were determined by isotope dilution/internal standard quantification against extracted calibration standards in water.

This project originally included investigating the applicability of two alternative effects-based tests Yeast Endocrine Screen (YES) and Yeast Androgen Screen (YAS) to evaluate the impact of complex chemical mixtures on water quality. However, with PACZM approval the task was changed to analysis of selected surface water samples by Temple University WET Center for non-targeted analysis of 260 PFAS analytes using Time of Flight (TOF) mass spectrometry. This analysis enabled the tentative identification (detection) of 220 PFAS analytes beyond the 40 included in the Draft EPA Method 1633. Thus, providing a broader picture of the PFAS contamination in the Delaware River and allowing for more accurate targeting of compounds unique to the river in future sampling efforts.

Table 3. Targeted PFAS analytes.

Group	Analyte	CAS #
carboxylates	Perfluorobutanoate (PFBA)	45048-62-2
carboxylates	Perfluoropentanoate (PFPeA)	45167-47-3
carboxylates	Perfluorohexanoate (PFHxA)	92612-52-7
carboxylates	Perfluoroheptanoate (PFHpA)	120885-29-2
carboxylates	Perfluorooctanoate (PFOA)	45285-51-6
carboxylates	Perfluorononaoate (PFNA)	72007-68-2
carboxylates	Perfluorodecanoate (PFDA)	73829-36-4
carboxylates	Perfluoroundecanoate (PFUnA)	196859-54-8
carboxylates	Perfluorododecanoate (PFDoA)	171978-95-3
carboxylates	Perfluorotridecanoate (PFTrDA)	862374-87-6
carboxylates	Perfluorotetradecanoate (PFTeDA)	365971-87-5
sulfonates	Perfluorobutanesulfonate (PFBS)	45187-15-3
sulfonates	Perfluoropentanesulfonate (PFPeS)	175905-36-9
sulfonates	Perfluorohexanesulfonate (PFHxS)	108427-53-8
sulfonates	Perfluoroheptanesulfonate (PFHpS)	146689-46-5
sulfonates	Perfluorooctanesulfonate (PFOS)	45298-90-6
sulfonates	Perfluorononanesulfonate (PFNS)	474511-07-4
sulfonates	Perfluorodecanesulfonate (PFDS)	126105-34-8
sulfonates	Perfluorododecanesulfonate (PFDoS)	343629-43-6
precursors/fluorotelomer sulfonic acids	4:2 fluorotelomersulfonic acid (4:2 FTS)	414911-30-1
precursors/fluorotelomer sulfonic acids	6:2 fluorotelomersulfonic acid (6:2 FTS)	425670-75-3
precursors/fluorotelomer sulfonic acids	8:2 fluorotelomersulfonic acid (8:2 FTS)	481071-78-7
precursors	Perfluorooctane sulfonamide (PFOSA)	754-91-6
precursors	N-Methylperfluorooctanesulfonamide (N-MeFOSA)	31506-32-8
precursors	N-Ethylperfluorooctanesulfonamide (N-EtFOSA)	4151-50-2
precursors	N-methyl perfluorooctane sulfonamido acetic acid (MeFOSAA)	2355-31-9
precursors	N-ethyl perfluorooctane sulfonamido acetic acid (EtFOSAA)	2991-50-6
precursors	N-Methylperfluorooctanesulfonamidoethanol (N-MeFOSE)	24448-09-7
precursors	N-Ethylperfluorooctanesulfonamidoethanol (N-EtFOSE)	1691-99-2
replacements/carboxylates	Perfluoro-2-proxypropanoate (HFPO-DA), aka GenX	13252-13-6
replacements/carboxylic acids	Dodecafluoro-3H-4,8-dioxanonanoic acid (ADONA)	2127366-90-7
replacements/ether sulfonic acids	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9Cl-PF3ONS)	1621485-21-9
replacements/ether sulfonates	11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS)	2196242-82-5
precursors/fluorotelomer carboxylates	4,4,5,5,6,6,6-Heptafluorohexanoate (3:3 FTCA)	1169706-83-5
precursors/fluorotelomer carboxylates	2H,2H,3H,3H-Perfluorooctanoate (5:3 FTCA)	1799325-94-2
precursors/fluorotelomer carboxylic acids	4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluorodec-2-enoic acid (7:3 FTCA)	755-03-3
ether sulfonates	Perfluoro(2-ethoxyethane)sulfonate (PFEESA)	113507-82-7
carboxylic acids	Perfluoro-3-methoxypropanoic acid (PFMPA)	377-73-1
carboxylates	Perfluoro-4-methoxybutanoate (PFMBA)	863090-89-5
carboxylic acids	Nonafluoro-3,6-dioxaheptanoic acid (NFDHA)	151772-58-6

3. Results and Discussion

3.1 Surface Water – Delaware River Main Stem

Nine PFAS out of forty method analytes were reported at concentrations above quantification levels in surface water from the main stem river (Figure 2). Sample specific detection limits were between 0.4 and 4 ng/L for most analytes with the exception of detection limits at ~10 ng/L for

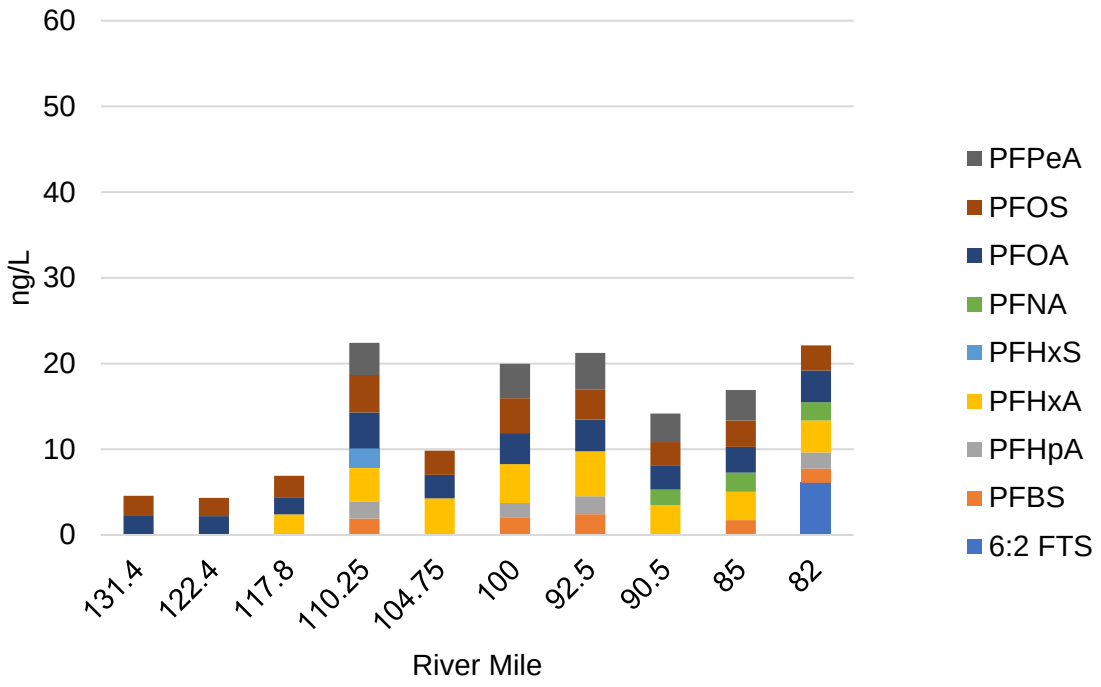

Figure 2. PFAS quantified in Delaware River main stem surface water samples.

two fluorotelemer carboxylates: 7:3 FTCA and 5:3 FTCA. Surface water concentrations of PFAS in main stem areas designated as drinking water sources (≥ river mile 95) were below adopted and proposed MCLs for PFAS by basin states. The maximum measured concentrations of PFOS was 4.37 ng/L and PFOA was 4.21 ng/L, both at river mile 110.25. PFOS and PFOA were measured between 2 to 4 ng/L throughout the sampling area (river miles 82 to 131.4). PFNA was found at concentrations of 1.83 to 2.24 between river mile 82 to 90.5. PFHxA maximum concentration was 5.25ng/L at river mile 92.5 and was found at 2.4 to 5.25 ng/L between river miles 82 to 117.8. PFPA was found at concentrations of 3.32 to 4.3 ng/L between river miles 85 to 110.25. PFBS and PFHpA were measured near 2 ng/L between river miles 82 and 110.25. FtS 6:2 ion was measured at 6.09 ng/L only from one site at river mile 82 while PFHxS was also measured at only one site, river mile 110.25, with a concentration of 2.29 ng/L.

3.2 Surface Water – Delaware River Main Stem: Non-targeted Analysis

EPA Draft method 1633 targets more compounds than previous methods, but still only includes 40 PFAS compounds. This is significantly less than the >10,000 known PFAS compounds. While still relatively low, the non-targeted method used by the Temple WET Center can identify 6.5 times (260 PFAS molecules) the compounds of EPA Draft Method 1633. However, the WET Center method is qualitative, rather than quantitative. Therefore, it can tentatively identify compounds, but not tell us what concentration was present without additional analysis. However, this is powerful in that it allows for the identification of compounds that are known to be in a system, those that might be in a system but have not yet been identified and those that were not even know to be a possibility in the system being studied. Furthermore, these newly identified

compounds could then be added to future target analyte lists to better capture the diversity of PFAs in sample from the Delaware River Basin.

Non-targeted analysis identified 5 PFAS compounds in the 4 samples analyzed. Three of these compounds (PFOA, PFBS and 6:2 FTS) were also identified during the targeted analysis. The 2 new compounds that were found in the non-targeted analysis are PFEtS (perfluoroethane sulfonate) and PFPrS (perfluoropropanesulfonic acid), which are not included in EPA Draft Method 1633. While this analysis does not allow for quantification of these two PFAS compounds, it demonstrates that they are potentially present in the Delaware River. Future analysis could now include these compounds to better understand their presence and concentrations.

3.3 Surface Water – Delaware River Tributaries

PFAS concentration in surface water sampled from tributaries varied by tributary and location in the tributary (Figure 3). The highest total PFAS concentrations were found at the two head of tide sample sites. Neshaminy Creek (NHC) had seven PFAS totaling 55.26 ng/L with PFOS at 14.7 ng/L, PFOA at 8.22 ng/L, PFHxA at 7.75 ng/L, PFHxS at 7.72 ng/L, PFPeA at 7.29 at ng/L, PFBS at 6.35 ng/L and PFHpA at 3.23 ng/L. In contrast, the Neshaminy Creek site (NC) near the confluence with the Delaware River had only three detections (PFOS, PFOA and PFHxA) totaling 8.72 ng/L. Pennypack Creek at head of tide (PPC) had a total of eight PFAS at 50.06 ng/L with PFOA at 8.77 ng/L, PFPeA at 7.86 ng/L, PFOS at 7.55 ng/L, PFHxA at 7.37 ng/L, PFBS at 7.06

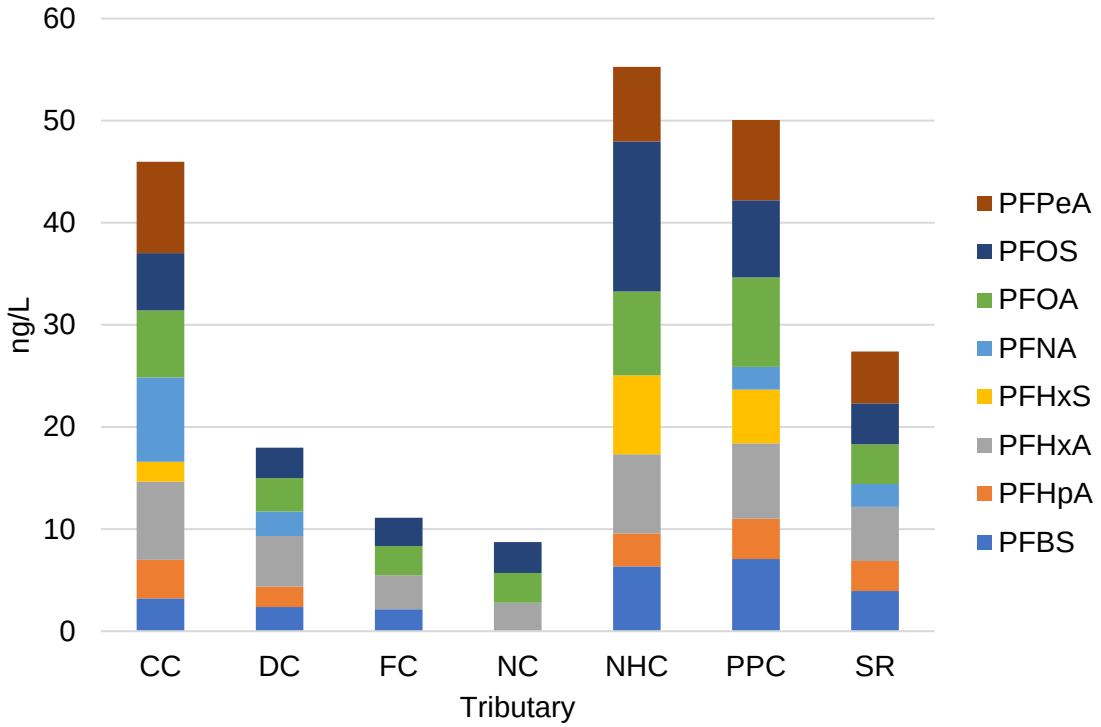

Figure 3. PFAS quantified in Delaware River tributary surface water samples. CC = Chester Creek, DC = Darby Creek, FC = Frankford Creek, NC= Neshaminy Creek, NHC = Neshaminy at head of tide, PPC = Pennypack Creek at head of tide, SR = Schuylkill River

ng/L, PFHxS at 5.27ng/L, PFHpA at 3.96 ng/L and PFNA at 2.22 ng/L. Of the tributary sample sites near to the confluence with the Delaware River, Chester Creek had the highest concentration with eight PFAS totaling 45.98 ng/L ranging from 1.95 ng/L PFHxS to 8.95 ng/L PFPeA. The second highest was the Schuylkill River site with seven PFAS totaling 27.39 ng/L ranging from 2.23 ng/L PFNA to 5.3 ng/L PFHxA. The Darby Creek site had a total of six PFAS at 17.97 ng/L and the Frankford Creek site had a total of four PFAS at 11.11 ng/L

3.4 Sediment – Main Stem and Tributaries

Sediment from the tidal main stem Delaware River and sampled tributaries have long-chain PFAS detected at low concentrations. The highest total PFAS concentrations in the main stem were 2.47 µg/kg at river mile 122.4 and 1.86 µg/kg at river mile 82 (Figure 4). In tributaries, the highest total PFAS concentrations were 2.12 µg/kg at the Darby Creek site and 1.48 µg/kg at the Schuylkill River site. PFAS was below the detection limits near the mouth of the Frankford Creek. Inconsistent with higher concentrations observed in surface water samples at head of tide in these two creeks, PFAS was below the detection limits in head of tide sediment samples from both Pennypack and Neshaminy Creeks (Figure 5). Sample specific detection limits were between 0.04 and 0.16 µg/kg for most analytes except for detection limits at 1 µg/kg for two fluorotelemer carboxylates, 7:3 FTCA and 5:3 FTCA. Elevated concentrations of TOC commonly suggest greater potential of contaminants to accumulate and impact the aquatic food web (Partnership for the Delaware Estuary. 2017). At relevant environmental pH values, PFCAs and PFSAs are present as anions that generally tend to associate with the organic carbon fraction that may be present in sediment (Higgins and Luthy 2006). However, a correlation between TOC and total

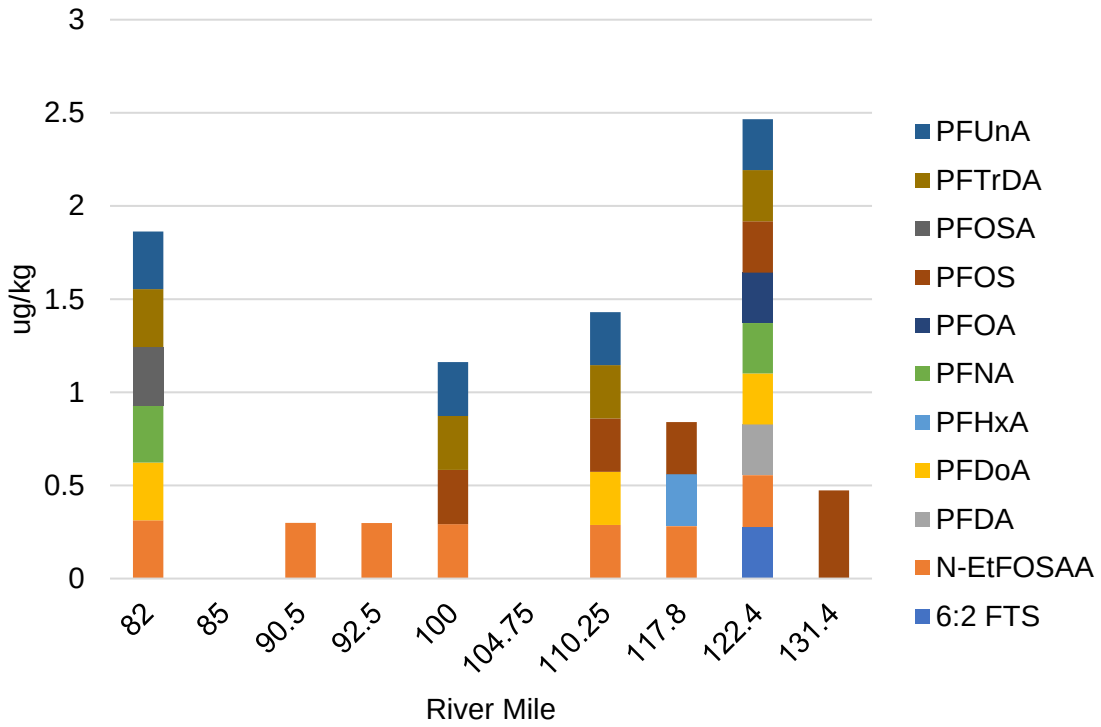

Figure 4. Quantifiable PFAS in Delaware River main stem sediment 2021

PFAS was not observed in the sediments collected for this Pennsylvania Coastal Zone study. Heterogeneity of sediment types and patchy distribution have been observed at many locations within the Delaware Estuary (Haaf et al. 2017). Although some contaminants are associated with fine clay and silt (< 0.063 mm diameter), no correlation was observed between total PFAS and percent clay and silt in the sediments collected for this Pennsylvania Coastal Zone study. Continued collection of sediment samples for analysis is recommended in a Phase 2 study.

3.5 Fish – Main Stem and Schuylkill River

PFAS was found in every composite fish sample analyzed. The number of the 40 target PFAS compounds detected in Channel Catfish ranged from 2-9, with fish from 5 of the 6 sites having at least 4 compounds. The number of compounds detected in Channel Catfish generally increased for sites as you got closer to the bay. For White Perch, the number of compounds detected in the composited fish samples ranged from 7-9. Carboxylates were the most common type of PFAS found in each species, with the same five (PFDA, PFDoA, PFTeDA, PFTrDA, PFUnA) being found in each White Perch.

Total PFAS concentration for Channel Catfish ranged from 1.5 to 177.7 ng/g (Figure 6a). However, two fluorotelomer sulfonic acid precursors (5:3 FTCA and 7:3 FTCA) accounted for 84 to 93% of the total PFAS concentrations observed at every site except Biles Channel. The other PFAS compounds account for 1.5 to 13.6 ng/g in Channel Catfish (Figure 6b). Total PFAS

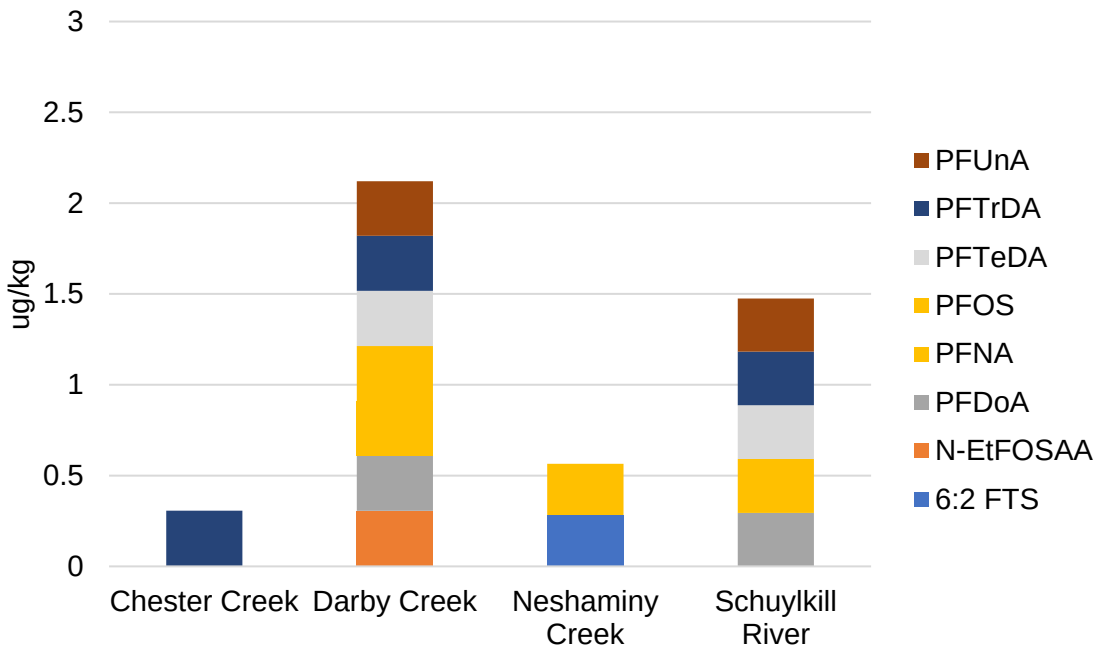

Figure 5. Quantifiable PFAS in Delaware River tributary sediment.

concentration generally increased with decreasing river mile. The two precursors were not detected in White Perch, where concentrations ranged from 14.4 to 27.2 ng/g. In White Perch, PFOS had the highest concentration in each sample, averaging 8.7 ± 4.7 ng/g.

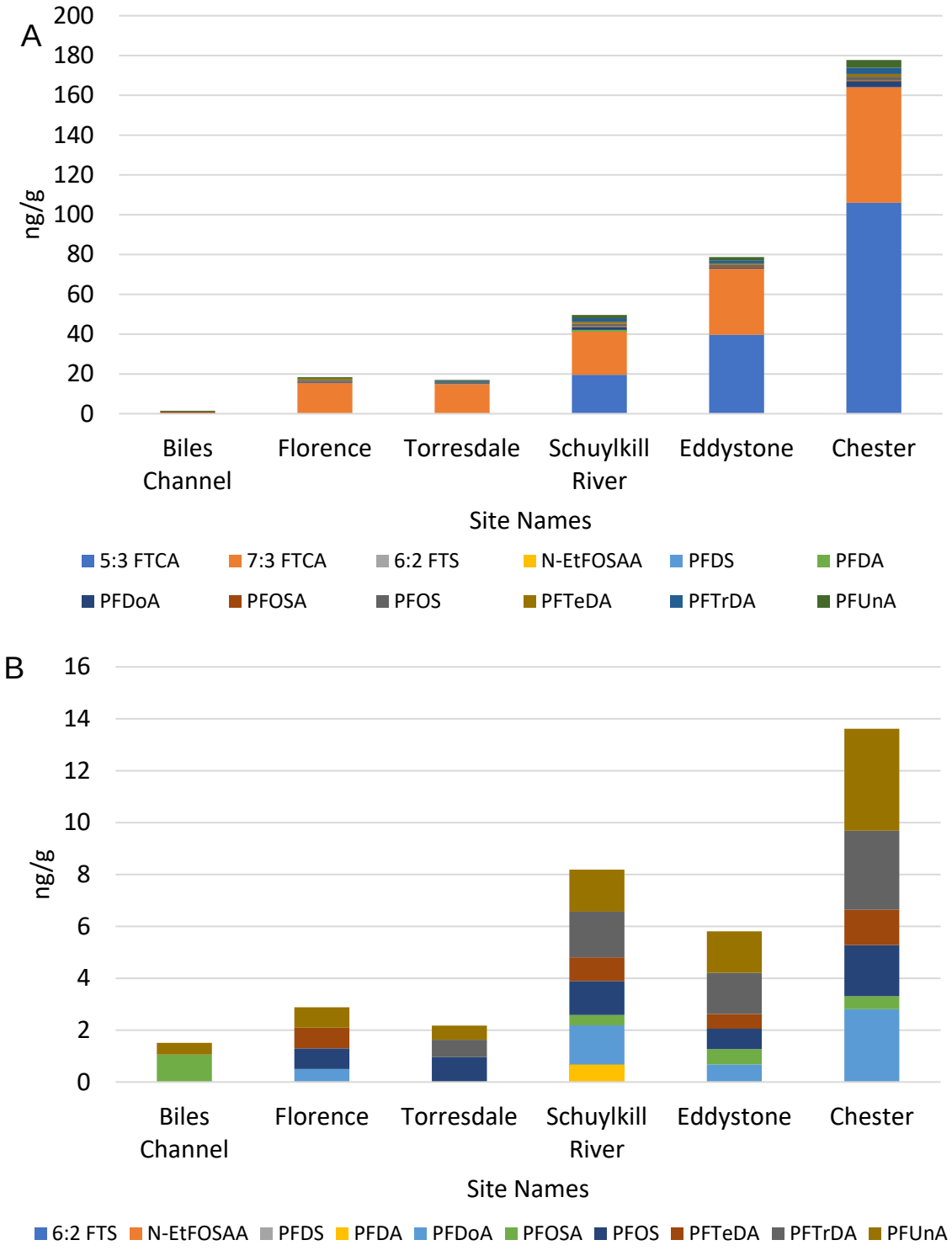

Figure 6. Quantifiable PFAS in Channel Catfish composite samples. A) Concentration of all PFAS target analytes. B) Concentrations of PFAS with the two precursor compounds, 5:3 FTCA and 7:3 FTCA, removed to highlight the other analytes detected.

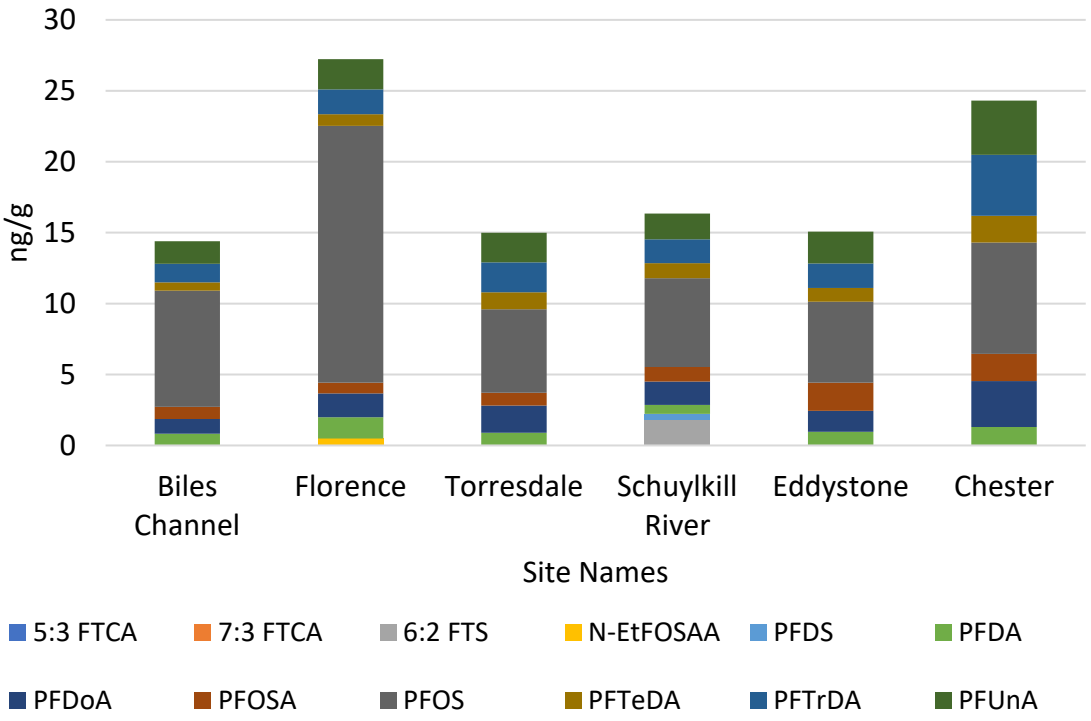

Figure 7. Quantifiable PFAS in White Perch composite samples.

While PFAS compounds are receiving significant attention, there are limited toxicity thresholds. PFOS is one exception, where the USEPA in 2016 published a Chronic Reference Dose (RfD) of 0.02 µg/kg-day (USEPA 2016). This is an estimate (with uncertainty of an order of magnitude) of the amount of a chemical a person can ingest daily based on their body weight over a lifetime without considerable risk of negative effects. Therefore, a 70 kg (154 lb) adult could potentially consume 1.4 µg/day of PFOS over the course of their life.

$$0.02\ \frac{\mu g}{kg\ \cdot\ day} \times\ 70kg = 1.4 \frac{\mu g}{day}$$

The NJ Departments of Environmental Protection and Health's 2021 Fish Smart, Eat Smart guide, uses 8 ounces or 226.8 g as a single serving of fish (NJDOH, NJDEP 2021). The serving size can then be used to estimate the potential exposure based on concentrations observed in the fish collected during this study for comparisons with USEPA RfD values. For Channel Catfish, the exposure based on an 8 oz serving would be 0.22 ± 0.15 µg. Therefore, all were below the EPA RfD of 1.4 µg/day for a 70 kg adult. However, with White Perch the average across all sites was 1.96 ± 1.07 µg, with a maximum of 4.1 µg and a minimum of 1.3 µg. White Perch exceeded the EPA RfD at 4 of the 6 sites sampled. To reiterate, the EPA RfD value is based on chronic effects occurring with daily consumption over a lifetime. Individual consumption of these fish likely does not occur daily. The state of Pennsylvania does not have a fish consumption advisory for PFOS in the section of the river sampled for this study. However, New Jersey does have a fish consumption advisory for the section of the Delaware river where this fish were collected and while it includes PFOS, the advisory does not distinguish between species based on specific

pollutants. The advisory does recommend limiting consumption of White Perch in these area to 4 meals per year (with some site specific variations) (NJDOH, NJDEP 2021). To expand our dataset and improve our assessment of PFAS accumulation, continued collection of fish for analysis is recommended in a Phase 2 study.

3.6 Outreach

Furthering the understanding, occurrence, and bioaccumulation of PFAS in coastal waters is important to protect water resources. In this project, the Delaware River Basin Commission (DRBC) conducted a deliberate scientifically based research study to focus on PFAS in the Delaware Estuary. This consisted of collecting surface water, sediment and fish from main stem and tributary sites for analysis of PFAS including replacement compounds currently being used as alternatives to legacy long chain PFAS, persistent short chain PFAS being used in increasing amounts, and precursors that can be transformed to PFOS and other persistent PFAS. The work reported here increases information on the occurrence of PFAS in the Delaware Estuary using EPA Draft Method 1633 with an extended list of targeted PFAS analytes. The results from this work inform management actions in cooperation with the EPA and basin states including adoption of fish consumption advisories, development of stream quality objectives, and other environmental management to minimize impacts to human health and aquatic life.

Outreach and intergovernmental coordination were accomplished by sharing information gained with the scientific community and stakeholders by presentations at the following meetings:

- Joint Chesapeake-Potomac Regional Chapter and Hudson-Delaware Chapter Society of Environmental Toxicology and Chemistry Meeting on April 11, 2022
- Joint meeting of the DRBC Toxics Advisory Committee and Southeast Pennsylvania Regional PFAS Discussion Group on January 19, 2022, and
- Schuylkill Action Network on May 11, 2022.

3.7 Environmental Data Sets

Data generated with this funding was uploaded to the USEPA's Water Quality Exchange (WQX; https://www.epa.gov/waterdata/water-quality-data-upload-wqx). This data is then accessible through the U.S. Governments National Water Quality Portal (WQP; https://www.waterqualitydata.us). All data was received from the lab between Fall 2021 and Winter 2023 and uploaded within 2 months of receiving. The following links provide direct access to the numerous data sets generated and uploaded to the WQP.

Fish Tissue Data:
https://www.waterqualitydata.us/data/Result/search?organization=31DRBCSP&organization=31DRBCSP_WQX&organization=DRBC&project=PFAS%20Fish&startDateLo=04-20-2021&startDateHi=06-01-2021&mimeType=csv&zip=yes&dataProfile=narrowResult&providers=NWIS&providers=STEWARDS&providers=STORET

Surface Water Data:
https://www.waterqualitydata.us/data/Result/search?organization=DRBC&organization=31DRBCSP&organization=31DRBCSP_WQX&project=PFAS%20Surface%20Water&startDateLo=05-20-2021&startDateHi=10-06-2021&mimeType=csv&zip=yes&dataProfile=narrowResult&providers=NWIS&providers=STEWARDS&providers=STORET

Sediment Data:
https://www.waterqualitydata.us/data/Result/search?organization=DRBC&organization=31DRBCSP&organization=31DRBCSP_WQX&project=PFAS%20Sediment&startDateLo=04-20-2021&startDateHi=11-08-2021&mimeType=csv&zip=yes&dataProfile=narrowResult&providers=NWIS&providers=STEWARDS&providers=STORET

3.8 Recommendations for Phase 2

DRBC is collecting and analyzing water, sediment and fish samples for PFAS chemicals across multiple studies within the mainstem and tributaries of the Delaware River. Upon completion, the data from these studies will be synthesized to provide DRBC with a broad picture of PFAS presence and concentrations in various environmental matrixes as well as hotspots in the mainstem and tributaries. The goals of this work are to provide the public with freely available data and transparency regarding PFAS in the Delaware River Basin, but to also regulate these discharges to ensure water quality and public health. Phase 2 funding will generally contribute to these goals by providing a second year of water, sediment and fish data points to help understand the variability of data at the sampling sites. Year 2 will support additional non-targeted analysis at new sites to look for the presence of unknown PFAS compounds. The inclusion of the Total Oxidizable Precursor (TOP) assay in year 2 will also allow for the potential identification of additional PFAS not detected with the Phase 1 analysis. Outreach for Phase 2 will consist of presentations of results at conferences to the scientific community and public meetings such as the DRBC Toxics Advisory Committee. The final report will also be posted to the DRBC website.

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APPENDIX A

REPORT

NON-TARGET ANALYSIS OF SURFACE WATER SAMPLES

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Executive Summary: The objective of this project was to perform a non-target analysis of PFAS in the Delaware river watershed using a time of flight (TOF). Samples was performed using direct injections as well as solid-phase extraction. Solid phase extraction was performed following the guidelines of US EPA draft Method 1633. Samples were suspect screened for PFAS (30 – 2500 Da) using QToF and chloro-perfluoropolyether carboxylates (ClPFPECA) congeners using Sciex-X500R QToF as well as Water Xevo-TQs (LC/MS/MS). Data obtained from the TOF was compared to a library of 260 PFAS chemicals.

Sample Collection: One time sample collection was performed by DRBC – 5 Samples were collected in 1L HDPE bottles and sent to Temple University. Samples were stored in the freezer until analysis was performed.

Equipment: All the equipment cleaned with the water, methanol, and methanolic ammonium hydroxide as specified in the EPA draft Method 1633. Following equipment were used for sample preparation.

- Polyethylene gloves;
- Laboratory fume hood;
- Disposable spoons, polypropylene;
- HDPE bottles, with liner less HDPE caps;
- Disposable polypropylene collection tubes (13 x 100 mm, 8 mL);
- Silanized glass wool (Sigma-Aldrich, Cat # 20411) – stored in a clean glass jar and rinsed with methanol (2 times) prior to use;
- Disposable syringe filter, 25-mm, 0.2-µm Nylon membrane, PALL;
- Variable volume pipettes with disposable HDPE and polypropylene tips;
- Solid-phase extraction (SPE) cartridges (Waters Oasis WAX 150 mg, Cat # 186002493) - the SPE sorbent had a pKa above 8 so that it remains positively charged during the extraction;
- Vacuum manifold for SPE Cartridges;
- Manual solvent evaporation system; and
- Polypropylene LC/MS vials with polypropylene caps

Reagents and Standards: Reagents prepared by the laboratory were stored in either glass or HDPE containers. Following reagents were prepared/purchased and used:

- Acetic acid - ACS grade or equivalent, stored at room temperature
- Acetic acid (0.1%) - dissolve acetic acid (1 mL) in reagent water (1 L), stored at room temperature, replaced after 3 months. This reagent is used only for sample extract dilution.
- Acetonitrile – UPLC grade or equivalent, verified before use, stored at room temperature
- Ammonium acetate - (Ultra LC/MS grade), stored at 2-8° C,
- Ammonium hydroxide - certified ACS+ grade or equivalent, 30% in water, stored at room temperature
- Aqueous ammonium hydroxide (3%) - add ammonium hydroxide (10 mL, 30%) to reagent water (90 mL), stored at room temperature,
- Methanolic ammonium hydroxide

  - Methanolic ammonium hydroxide (0.3%) - add ammonium hydroxide (1 mL, 30%) to methanol (99 mL), store at room temperature, replaced after 1 month
  - Methanolic ammonium hydroxide (1%) - add ammonium hydroxide (3.3 mL, 30%) to methanol (97 mL), store at room temperature, replaced after 1 month
  - Methanolic ammonium hydroxide (2%) - add ammonium hydroxide (6.6 mL, 30%) to methanol (93.4 mL), store at room temperature, replaced after 1 month
  - Methanolic potassium hydroxide (0.05 M) – add 3.3 g of potassium hydroxide to 1 L of methanol, store at room temperature, replaced after 3 months
  - Methanol with 4% water, 1% ammonium hydroxide and 0.625% acetic acid - add ammonium hydroxide (3.3 mL, 30%), reagent water (1.7 mL) and acetic acid (0.625 mL) to methanol (92 mL), store at room temperature, replace after 1 month
- Formic Acid
  - Formic acid (aqueous, 0.1 M) - dissolve formic acid (4.6 g) in reagent water (1 L), stored at room temperature,
  - Formic acid (aqueous, 0.3 M) - dissolve formic acid (13.8 g) in reagent water (1 L), store at room temperature,
  - Formic acid (aqueous, 5% v/v) - mix 5 mL formic acid with 95 mL reagent water, store at room temperature,
  - Formic acid (aqueous, 50% v/v) - mix 50 mL formic acid with 50 mL reagent water, store at room temperature,
  - Formic acid (methanolic 1:1, 0.1 M formic acid/methanol) - mix equal volumes of methanol and 0.1 M formic acid, stored at room temperature
- Potassium hydroxide – certified ACS grade, stored at room temperature,
- Reagent water – Laboratory reagent water, test by lot/batch number for residual PFAS content
- Carbon – EnviCarb® 1-M-USP or equivalent, verified by lot number before use, store at room temperature. Loose carbon allows for better adsorption of interferent organics.
- Extraction internal standards and non-Extracted internal standards were purchased from Wellington Laboratories

Solid Phase Extraction: Sample extraction was performed following the guidelines of draft EPA Method 1633. Samples were homogenized and spiked with labeled internal standards. Sample pH was adjusted to 6.5 ± 0.5 using 50% formic acid and/or 3% aqueous ammonium hydroxide. SPE wax cartridges were packed with silanized glass wool and placed on the vacuum manifold. The cartridges were pre-conditioned by washing them with 15ml of 1% methanolic ammonium hydroxide followed by 5mL of 0.3% formic acid (care was taken to avoid WAX SPE to go dry). The wash solvents were discarded. Samples were passed through the activated cartridges at a rate of 5 ml/min. Multiple cartridges were needed for all the samples due to clogging of the samples – all the cartridges were pre-conditioned prior to use. Process was continued until all the sample aliquot was passed. The sample containers were rinsed twice with 5mL reagent water followed by 5 mL of 1:1 0.1M formic acid/methanol. The rinses were passed through the SPE cartridges under vacuum. The cartridges were then dried by pulling air through them for 15-20 seconds followed by elution and extract concentration. Clean collection tubes (13x100 mm polypropylene tubes) were placed inside the vacuum manifold ensuring the extract needles do not touch the walls of the test tubes. The sample container was rinsed with 5mL of 1% methanolic

ammonium hydroxide. This solution was carefully transferred to the SPE reservoir, washing the walls of the reservoir. Vacuum was used to pull this eluent through the cartridge into the collection tubes. A 25 µL of concentrated acetic acid was added to each sample eluted in the collection tubes and vortexed to mix. 10 mg of carbon was added to each sample extract, using a 10-mg scoop. Hand-shaken occasionally for no more than 5 minutes. This step was important to minimize the time the sample extract is in contact with the carbon. Samples were immediately vortexed (30 seconds) and centrifuged at 2800 rpm for 10 minutes. NIS solution was added to a clean collection tube. A syringe filter (25-mm filter, 0.2-µm nylon membrane) was placed on a 5-mL polypropylene syringe and the sample supernatant was carefully into the syringe barrel. The plunger was replaced and the entire extract was filtered into the new collection tube containing the NIS, vortexed to mix and transferred a portion of the extract into a 1-mL polypropylene vial for QToF analysis. The collection tube containing the remaining extract was capped and stored at 0°C.

Non-Target Analysis: Non-target analysis of samples was performed using SCIEX X500R-QToF system with electrospray ionization in negative mode (ESI-). Samples were analyzed using SWATH acquisition programming, a data -independent acquisition technique that collects MS/MS spectra for all compounds. TOFMS scans were performed from 30 – 2500 Da with DP= -40V, CE = 0.35V and CES = 30V. The SCIEX ExionLC system was modified to replace the tubing with PEEK and included a delay column to separate PFAS contamination from the LC system. Analytes were separated using a Phenomenex Gemini C-18 column (50 mm × 3 mm, 3 µm; Phenomenex, USA). A delay column (Luna C18(2) phase, 30 mm × 3 mm, 5 µm; Phenomenex, USA) and a guard column (Gemini C18 phase, 4 mm × 2 mm; Phenomenex, USA) were also employed during the analysis to minimize contamination. The injection volume was 10 µL and the column temperature was maintained at 40°C. The analytes were eluted using 10 mM ammonium acetate in LC/MS grade water and 10 mM ammonium acetate in LC/MS grade methanol as mobile phases at a flow rate of 0.5 mL/min. Table 1 shows the LC solvent gradient profile.

Table 1: LC method solvent gradient profile.

Time (min)	Flow rate (mL/min)	% Solvent A (10mM ammonium acetate in Water)	% Solvent B (10 mM ammonium acetate in Methanol)
0.00	0.5	99	1
0.25	0.5	99	1
0.50	0.5	50	50
4.50	0.5	1	99
8.50	0.5	1	99
10.0	0.5	99	1
13.0	0.5	99	1

RESULTS: All the samples were analyzed initially using direct injection, however, there were no matches to the library. Samples were analyzed using SPE. Table 2 shows the instrument QA/QC. DI water was spiked with known concentration of analytes (PFOA, PFOS, PFNA, PFBS, and PFHxA) and analyzed using the SWATH mode. The presence of spiked internal standards was confirmed for all the samples (direct as well as extracted samples) on the instrument. All the analytes were present in the spiked sample and were confirmed using data analysis.

Table 2: QA/QC spiked DI Water - Sample spiked with PFBS, PFHxA, PFOA, PFOS, and PFNA

#	Analyte	Precursor Mass	Accuracy Acceptance	Concentration Acceptance	Found At Mass	Library Hit	Library Score
1	PFOA neg	412.966	Pass	Pass	412.9646	PFOA neg [Smart Confirmation]	100.0
2	PFOA with IS neg	412.966	Pass	Pass	412.9646	PFOA neg [Smart Confirmation]	100.0
3	PFOS neg	498.930	Pass	Pass	498.9281	PFOS neg [Smart Confirmation]	100.0
4	PFNA neg	462.963	Pass	Pass	462.9608	PFNA neg [Smart Confirmation]	100.0
5	PFHxA neg	268.983	Pass	Pass	268.9818	PFHxA in-source fragment (perfluoro-n-hexanoic acid) neg [Smart Confirmation]	100.0
6	PFBS neg	298.943	Pass	Pass	298.9417	PFBS neg [Smart Confirmation]	100.0

Figures 1 and 2 show the TIC and suspect m/z's for field blank sample. Table 3 shows the analytes present in the field blank sample. Sample shows the presence of 6:2 FTS and probable hydrocarbon sulfate at a 100% library match confirmation and PFEtS at 82% library match. The other compounds showed very low confidence (<50% match) on the MS/MS spectra.

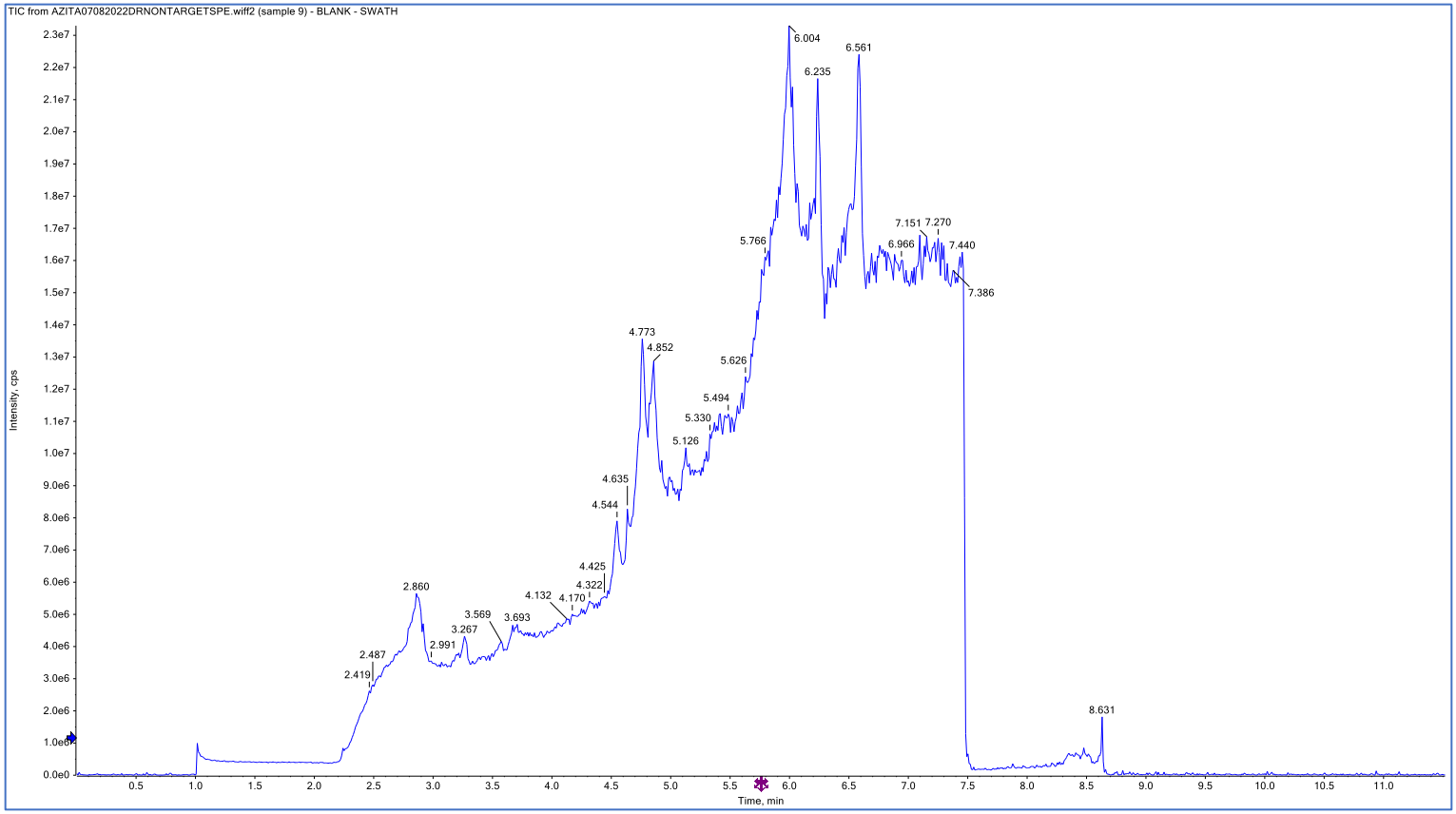

Figure 1: TIC - Field Blank

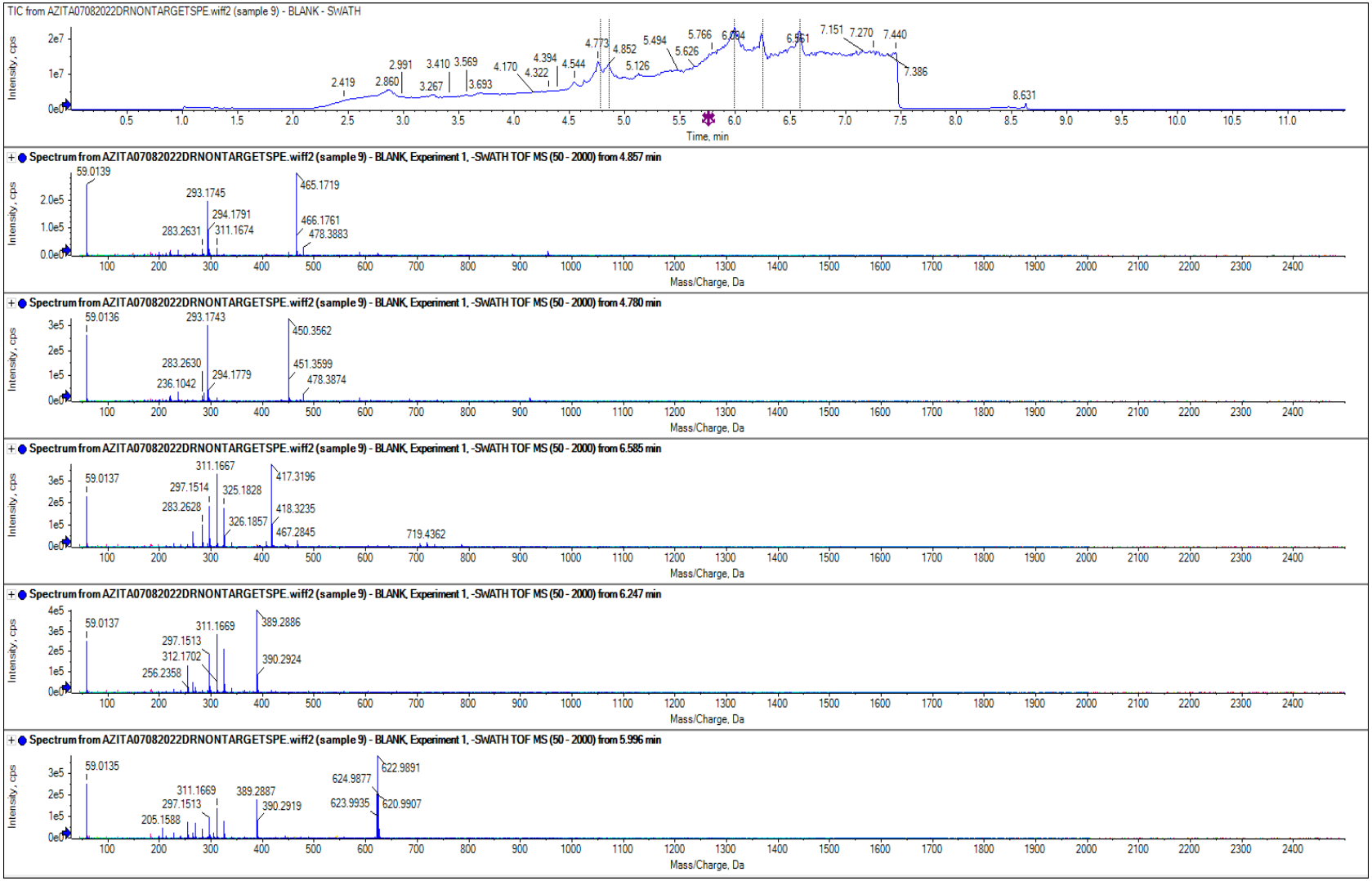

Figure 2: Field Blank - Suspect ions

Table 3: Field Blank

#	Analyte Peak Name	Precursor Mass	Accuracy Acceptance	Concentration Acceptance	Found At Mass	Library Hit	Library Score
1	213.1848 / 6.78	213.185	Pass	Pass	213.1849	PFBA [neg] [Smart Confirmation]	20.6
2	265.1475 / 7.17	265.147	Pass	Pass	265.1466	Probable hydrocarbon sulfate [Smart Confirmation]	100.0
3	249.1846 / 6.48	249.185	Pass	Pass	249.1839	PFPrS [neg] [Smart Confirmation]	22.4
4	199.1697 / 5.94	199.170	Pass	Pass	199.1697	PFEtS [neg] [Smart Confirmation]	82.5
5	233.1532 / 5.40	233.153	Pass	Pass	233.1534	PFPrSi [neg] [Smart Confirmation]	43.9
6	426.9664 / 5.44	426.966	Pass	Pass	426.9662	6:2 FTS [neg] [Smart Confirmation]	100.0
7	263.1647 / 4.97	263.165	Pass	Pass	263.1644	PFPeA [neg] [Smart Confirmation]	33.0

Note: data in red represents low confidence in the XIC-MS/MS fragmentation when compared to the library

Figures 3 and 4 show the TIC and suspect m/z's for Burlington Bristol Bridge sample. Table 4 shows the analytes present in the sample. Data analysis showed the presence of PFBS, 6:2 FTS and probable hydrocarbon sulfates at > 89.6% library match and low confidence with <50% match on PFPeA, PFOA, PFPrSi, PFEtS, PFPrS, and PFBA.

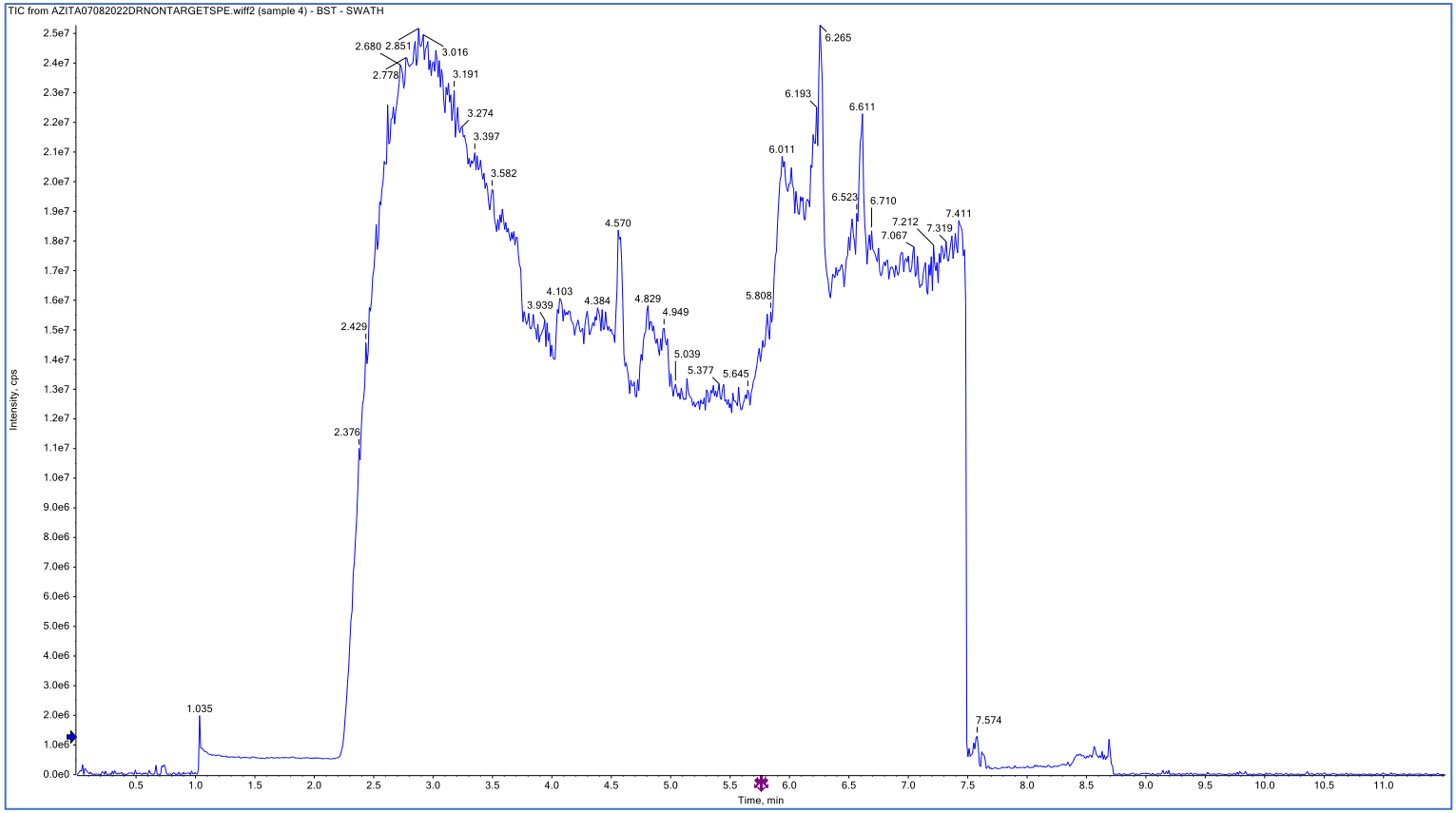

Figure 3: Burlington Bristol Bridge Sample - TIC

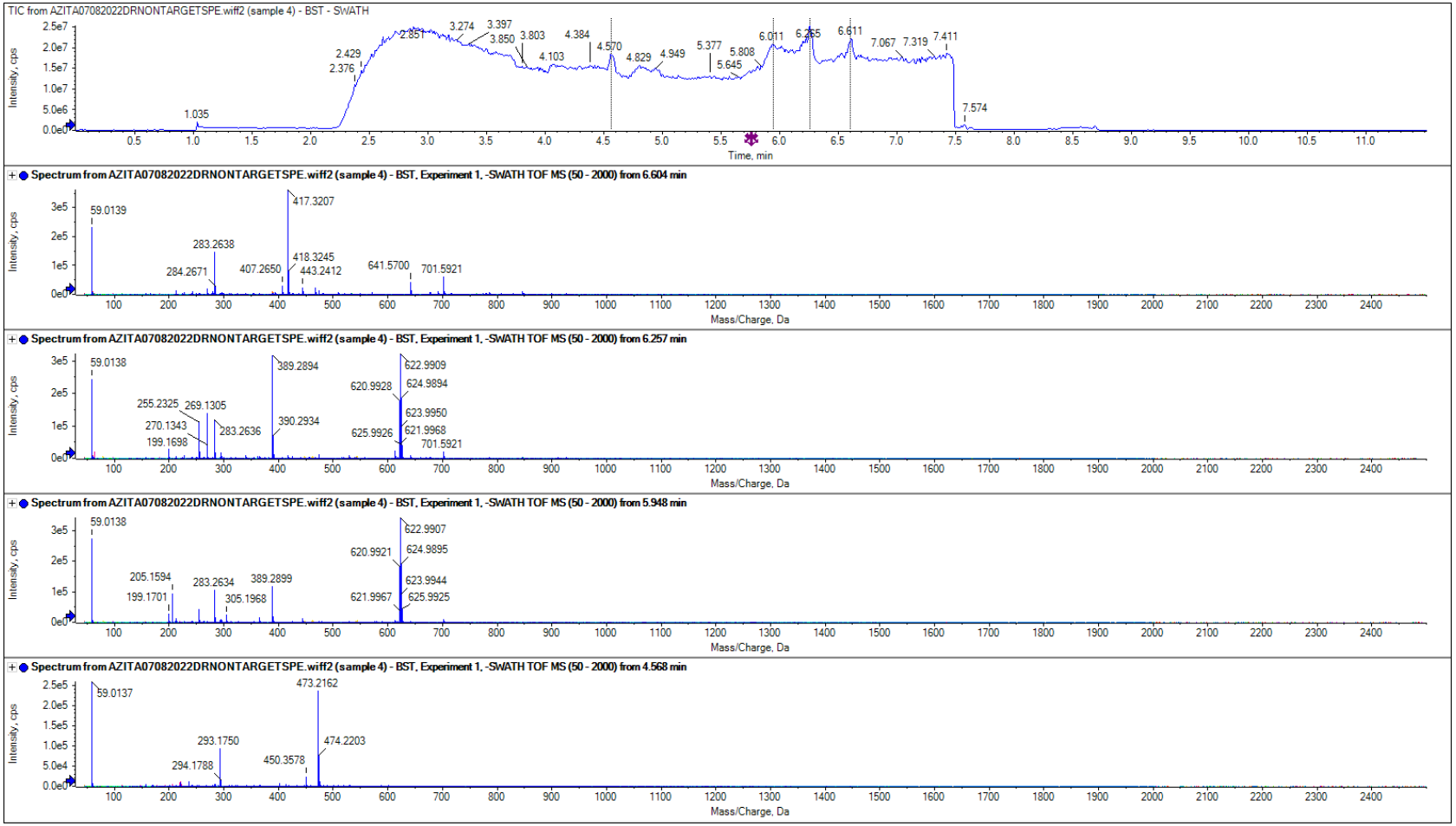

Figure 4: Burlington Bristol Bridge Sample - suspect M/Zs

Table 4: Burlington Bristol Bridge

#	Analyte Peak Name	Precursor Mass	Accuracy Acceptance	Concentration Acceptance	Found At Mass	Library Hit	Library Score
1	299.0950 / 3.07	299.095	Pass	Pass	299.0949	PFBS [neg] [Smart Confirmation]	89.6
2	263.1647 / 4.97	263.165	Pass	Pass	263.1649	PFPeA [neg] [Smart Confirmation]	31.8
3	412.9663 / 5.35	412.966	Pass	Pass	412.9662	PFOA with IS [neg] [Smart Confirmation]	11.4
4	233.1532 / 5.40	233.153	Pass	Pass	233.1540	PFPrSi [neg] [Smart Confirmation]	40.5
5	426.9664 / 5.44	426.966	Pass	Pass	426.9667	6:2 FTS [neg] [Smart Confirmation]	95.7
6	199.1697 / 5.94	199.170	Pass	Pass	199.1699	PFEtS [neg] [Smart Confirmation]	48.1
7	249.1846 / 6.48	249.185	Pass	Pass	249.1849	PFPrS [neg] [Smart Confirmation]	22.4
8	265.1475 / 7.17	265.147	Pass	Pass	265.1472	Probable hydrocarbon sulfate [Smart Confirmation]	96.4
9	213.1854 / 7.33	213.185	Pass	Pass	213.1855	PFBA [neg] [Smart Confirmation]	21.7
10	265.1476 / 8.56	265.148	Pass	Pass	265.1474	Probable hydrocarbon sulfate [Smart Confirmation]	98.7

Figures 5 and 6 show the TIC and suspect m/z's for Chester sample. Table 5 shows the analytes present in the sample. Data analysis showed the presence of PFEtS, PFPrS, and probable hydrocarbon sulfates at > 91.3 % library match and low confidence with <50% match on PFOA and PFPrSi.

Figure 5: Chester Sample - TIC

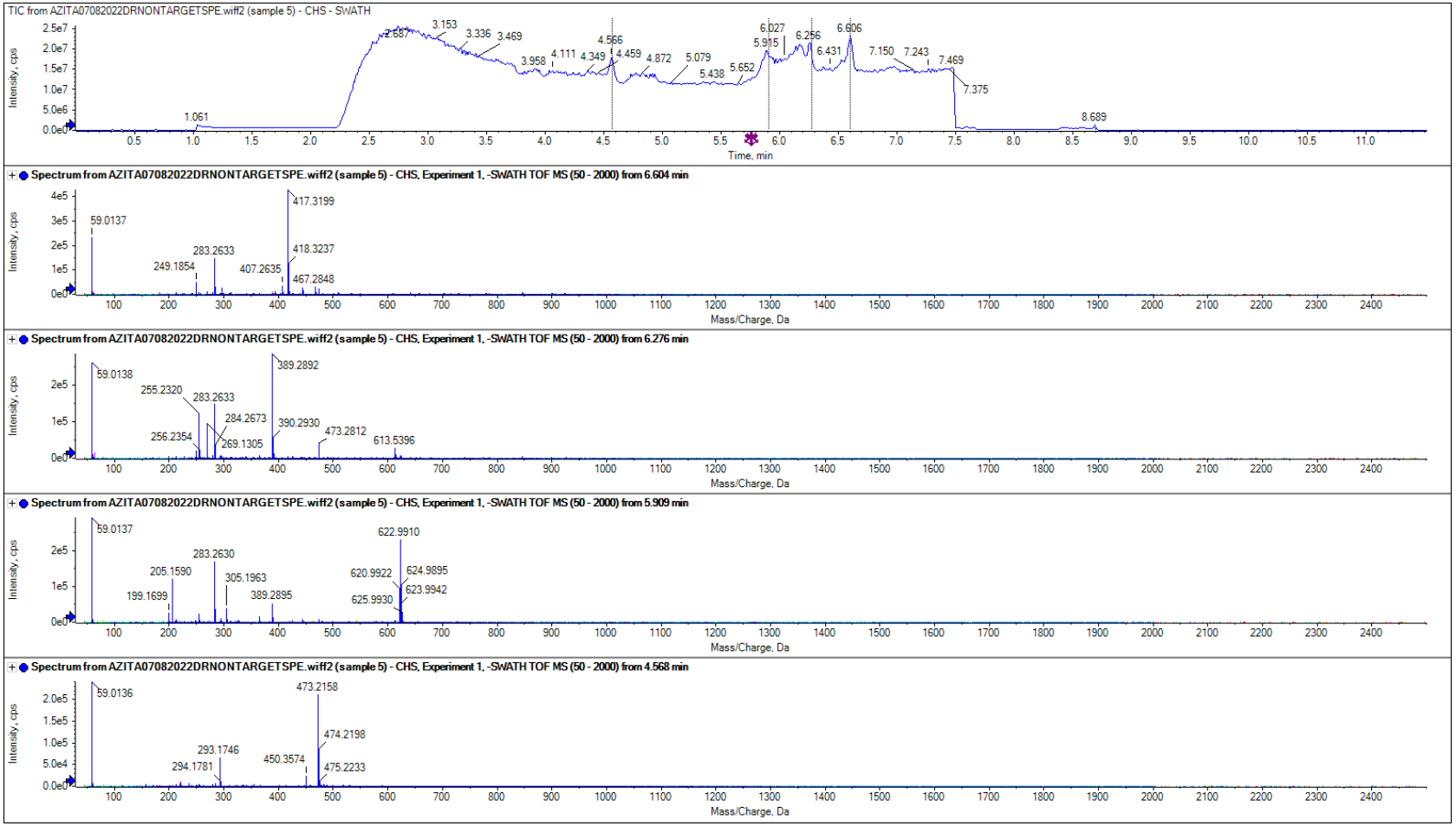

Figure 6: Chester sample – suspect M/Zs

Table 5: Chester

#	Analyte Peak Name	Precursor Mass	Accuracy Acceptance	Concentration Acceptance	Found At Mass	Library Hit	Library Score
1	199.0430 / 3.07	199.043	Pass	Pass	199.0431	PFEtS [neg] [Smart Confirmation]	91.3
2	412.9663 / 5.35	412.966	Pass	Pass	412.9664	PFOA with IS [neg] [Smart Confirmation]	22.6
3	233.1532 / 5.40	233.153	Pass	Pass	233.1539	PFPrSi [neg] [Smart Confirmation]	42.0
4	249.1846 / 6.48	249.185	Pass	Pass	249.1850	PFPrS [neg] [Smart Confirmation]	91.9
5	265.1464 / 6.60	265.146	Pass	Pass	265.1469	Probable hydrocarbon sulfate [Smart Confirmation]	98.1
6	265.1475 / 7.17	265.147	Pass	Pass	265.1473	Probable hydrocarbon sulfate [Smart Confirmation]	98.1
7	265.1476 / 8.56	265.148	Pass	Pass	265.1474	Probable hydrocarbon sulfate [Smart Confirmation]	17.7

Figures 7 and 8 show the TIC and suspect m/z's for the Benjamin Franklin Bridge sample. Table 6 shows the analytes present in the sample. Data analysis showed the presence of 6:2 FTS and probable hydrocarbon sulfates at > 75 % library match and low confidence (<50%) match on PFPrSi.

Figure 7: Benjamin Franklin Bridge Sample – TIC

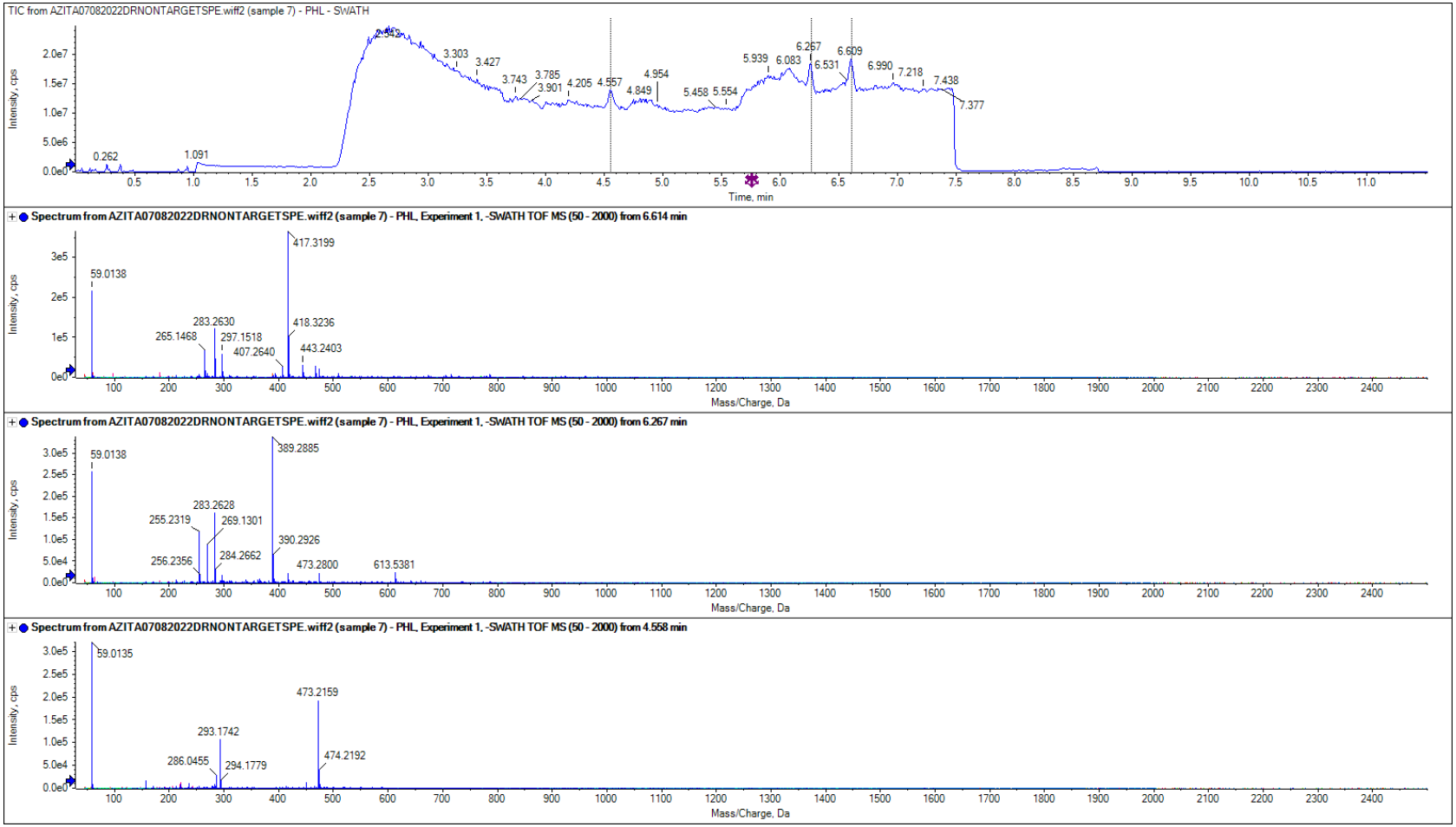

Figure 8: Benjamin Franklin Bridge sample suspect M/Zs

Table 6: Benjamin Franklin Bridge

#	Analyte Peak Name	Precursor Mass	Accuracy Acceptance	Concentration Acceptance	Found At Mass	Library Hit	Library Score
1	233.1532 / 5.40	233.153	Pass	Pass	233.1533	PFPrSi [neg] [Smart Confirmation]	43.1
2	426.9664 / 5.44	426.966	Pass	Pass	426.9660	6:2 FTS [neg] [Smart Confirmation]	75.0
3	265.1464 / 6.60	265.146	Pass	Pass	265.1466	Probable hydrocarbon sulfate [Smart Confirmation]	75.7

Figures 9 and 10 show the TIC and suspect m/z's for the Trenton sample at the Calhoun St. Bridge sample. Table 7 shows the analytes present in the sample. Data analysis showed the presence of PFOA with a 99.9% library match and low confidence (34 %) match on PFPrSi.

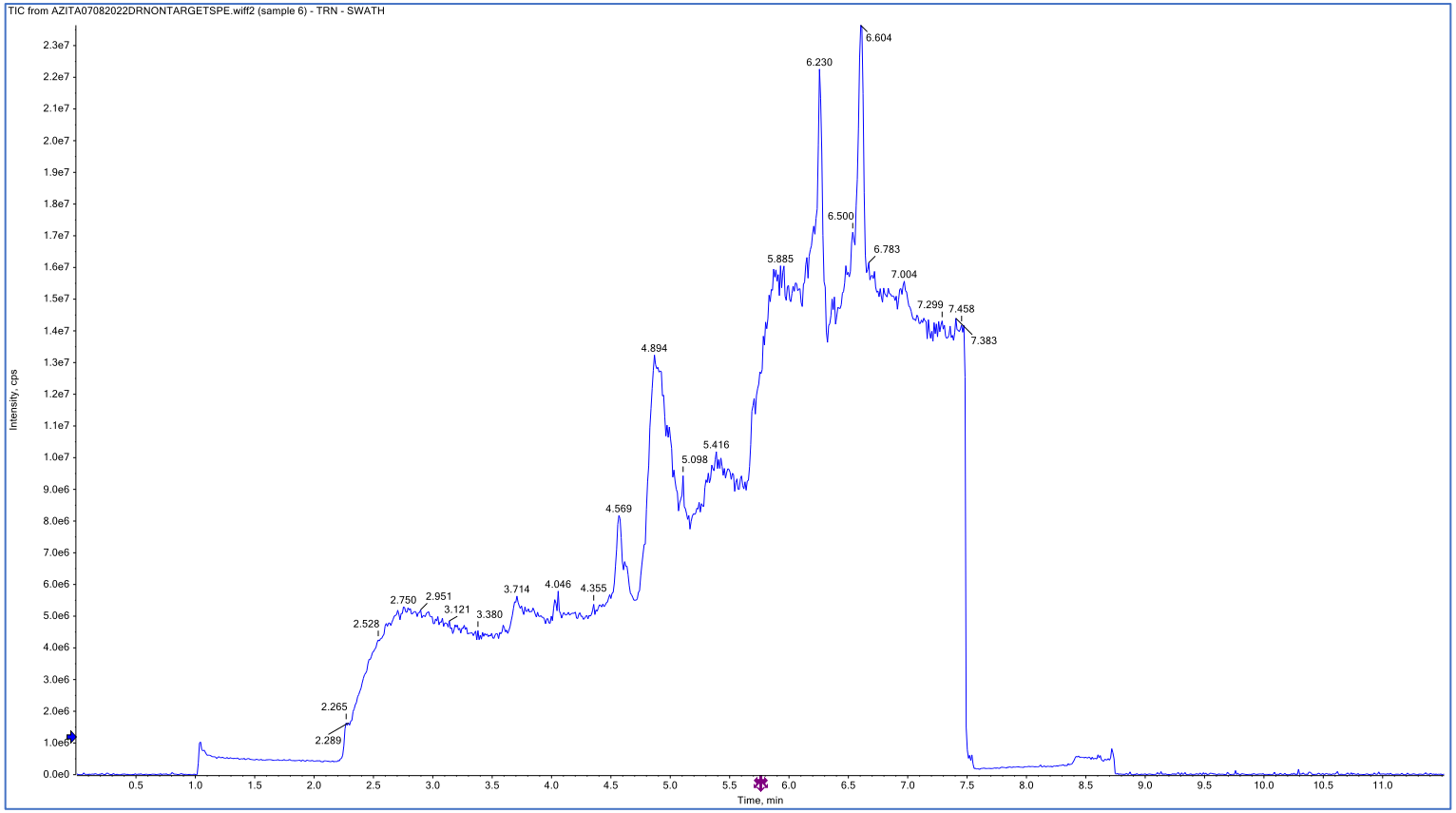

Figure 9: Trenton at Calhoun St. Bridge Sample - TIC

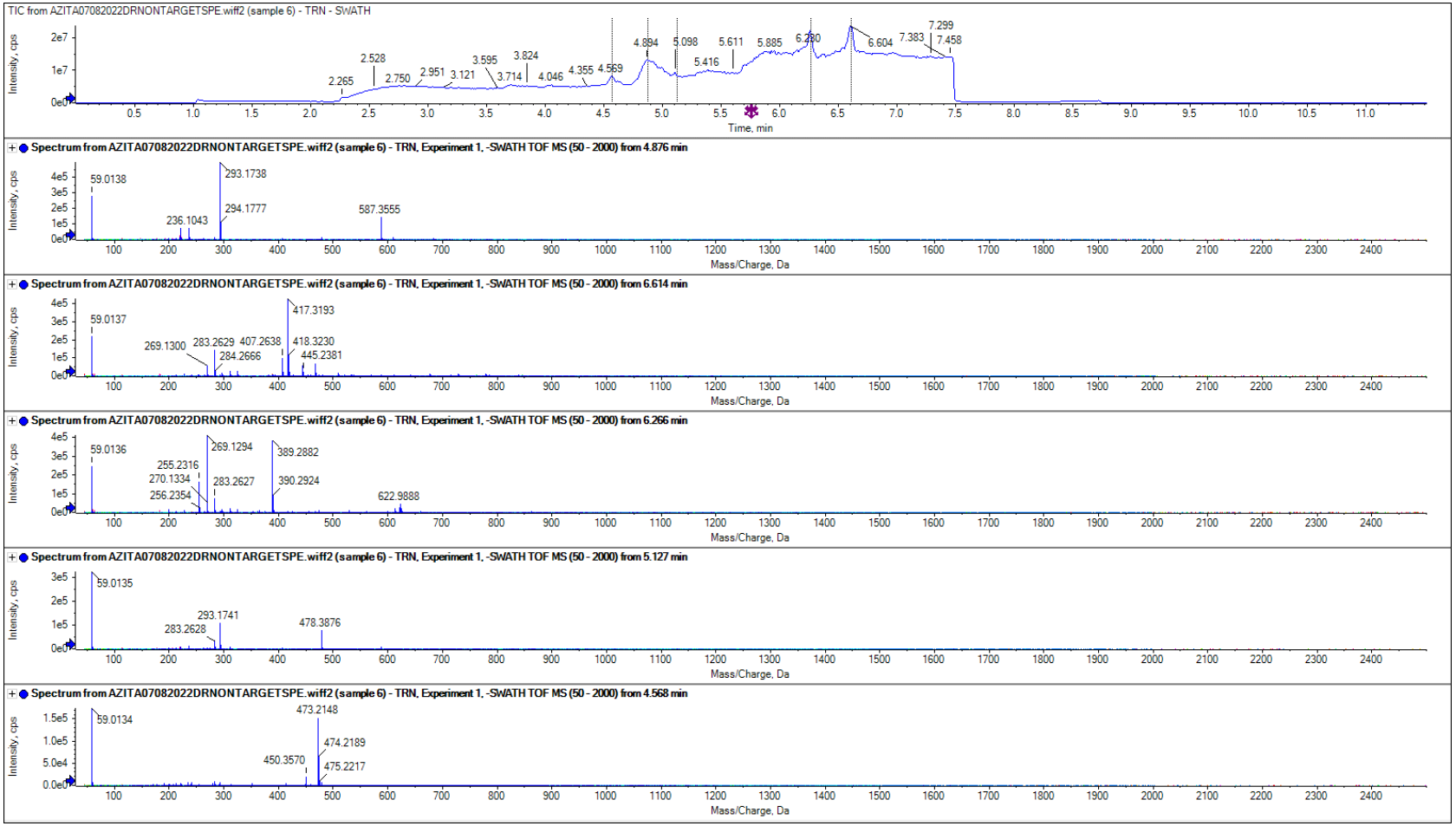

Figure 10: Trenton at Calhoun St. Bridge Sample Suspect M/Zs

Table 7: Sample Trenton at Calhoun St. Bridge

#	Analyte Peak Name	Precursor Mass	Accuracy Acceptance	Concentration Acceptance	Found At Mass	Library Hit	Library Score
1	412.9663 / 5.35	412.966	Pass	Pass	412.9644	PFOA [neg] [Smart Confirmation]	99.7
2	368.9763 / 5.36	368.976	Pass	Pass	368.9745	PFOA in-source fragment (perfluoro-n-octanoic acid) [neg] [Smart Confirmation]	99.9
3	233.1532 / 5.40	233.153	Pass	Pass	233.1535	PFPrSi [neg] [Smart Confirmation]	34.1

All the samples were also suspect screened for chloro-perfluoro-polyether carboxylates (ClPFPECA) congeners (Table 9). Sample analysis was performed on QToF as well Waters Xevo-TQs. However, none of the congeners were detected in any of the samples.

Table 8: Samples were also scanned for Chloro-perfluoropolyether-carboxylate (ClPFPECA) congeners which were of interest to DRBC – Non detect for all samples – Sample analysis was performed using direct injection as well as solid phase extraction

	Chloro-perfluoropolyether carboxylate congeners by group number of ethyl, propyl Solvay replacement compounds									
	1,0	0,1	2,0	1,1	0,2	3,0	2,1	1,2	4,0	0,3
Anion Formula	$C_7ClF_{12}O_4$	$C_8ClF_{14}O_4$	$C_9ClF_{16}O_5$	$C_{10}ClF_{18}O5$	$C_{11}ClF_{20}O_5$	$C_{11}ClF_{20}O_6$	$C12ClF_{22}O_6$	$C_{13}ClF_{24}O_6$	$C_{13}ClF_{24}O_7$	$C_{14}ClF_{26}O_6$
Molecular Mass	411.9372	461.9340	527.9257	577.9225	627.9193	643.9142	693.9110	743.9078	759.9028	793.9046
Precursor Mass	316.9427	366.9395	432.9312	482.9280	532.9249	548.9198	598.9166	648.9134	664.9083	698.9102
Fragment Mass	200.9542	200.9542	200.9542	200.9542	200.9542	200.9542	200.9542	200.9542	366.9395	532.9249

Table 9: Library compounds

#	Analyte Peak Name
1	10:2 fluorotelomer phosphate diester ethanol neg
2	10:2 FTCA neg
3	10:2 FTS neg
4	10:2 FTSO-PrAd-DiMePrS neg,pos
5	10:2 FTTh-PrAd-DiMeEtS neg,pos
6	12:2 FTS neg
7	14:2 FTS neg
8	16:2 FTS neg
9	18:2 FTS neg
10	1-HO-4:2 FTS neg
11	1-HO-6:2 FTS neg
12	1-HO-8:2 FTS neg
13	1-HO-8:2 FTS neg (TTU)
14	2:2 FTS neg
15	3:3 FTCA neg
16	4:2 FTS neg
17	4:2 FTSO-PrAd-DiMePrS neg,pos
18	4:2 FTTh-PrAd-DiMeEtS neg,pos
19	5:1 PFHxS neg
20	5:3 FTCA neg
21	6:2 fluorotelomer phosphate diester ethanol neg
22	6:2 FTCA neg
23	6:2 FTS neg
24	6:2 FTS neg (TTU)
25	6:2 FTSA-PrB neg (TTU)
26	6:2 FTSO-PrAd-DiMePrS neg,pos
27	6:2 FTTh-PrAd-DiMeEtS neg,pos
28	6:2 PAP (6:2 fluorotelomer phosphate ester) neg
29	6:2 PFPi (6:6 fluorotelomer phosphinate) neg
30	6:2, 6:2 fluorotelomer phosphate diester neg
31	6:2, 8:2 fluorotelomer phosphate diester neg
32	7:1 PFOS neg
33	7:3 FTCA neg
34	8:2 fluorotelomer phosphate diester ethanol neg
35	8:2 FTCA neg
36	8:2 FTS neg
37	8:2 FTS neg (TTU)
38	8:2 FTSO-PrAd-DiMePrS neg,pos
39	8:2 FTTh-PrAd-DiMeEtS neg,pos
40	8:2, 10:2 fluorotelomer phosphate diester neg
41	8:2, 8:2 fluorotelomer phosphate diester neg
42	AmPr-FBSA neg,pos
43	AmPr-FBSA neg,pos (TTU)
44	AmPr-FBSA-PrA neg,pos
45	AmPr-FHpSA neg,pos
46	AmPr-FHpSA-PrA neg,pos
47	AmPr-FHxSA neg,pos
48	AmPr-FHxSA-PrA neg,pos
49	AmPr-FOSA-PrA neg,pos
50	AmPr-FPeSA neg,pos
51	AmPr-FPeSA-PrA neg,pos
52	AmPr-FPrSA neg,pos
53	AmPr-FPrSA neg,pos 60
54	AmPr-FPrSA-PrA neg,pos

55	Chloroperfluorohexyl phosphonic acid neg
56	Cl-PFHxS neg
57	Cl-PFOS neg
58	DiMeA-MeOHPr-FHxSAPrS neg
59	DiMeA-MeOHPr-FPeSAPrS neg
60	diOHBAmPr-FBSA neg
61	diOHBAmPr-FHxSA neg
62	diOHBAmPr-FPeSA neg
63	diOHPrAm-MeOHPr-FBSA neg
64	diOHPrAm-MeOHPr-FBSAPrS neg
65	diOHPrAm-MeOHPr-FEtSAPrS neg
66	diOHPrAm-MeOHPr-FHxSA neg
67	diOHPrAm-MeOHPr-FHxSAPrS neg
68	diOHPrAm-MeOHPr-FPeSA neg
69	diOHPrAm-MeOHPr-FPeSAPrS neg
70	diOHPrAm-MeOHPr-FPrSA neg
71	diOHPrAm-MeOHPr-FPrSAPrS neg
72	EtFBSA neg
73	EtFBSAA neg
74	EtFDoSAA neg
75	EtFDSAA neg
76	EtFEtSA neg
77	EtFEtSAA neg
78	EtFHpSA neg
79	EtFHpSAA neg
80	EtFHxSA neg
81	EtFHxSAA neg
82	EtFNSA neg
83	EtFNSAA neg
84	EtFOSA neg
85	EtFOSAA neg
86	EtFPeSA neg
87	EtFPeSAA neg
88	EtFPrSA neg
89	EtFPrSAA neg
90	EtFUdSAA neg
91	F5S-PFBS neg
92	F5S-PFDS neg
93	F5S-PFHpS neg
94	F5S-PFHxS neg
95	F5S-PFNS neg
96	F5S-PFOS neg
97	F5S-PFPeS neg
98	FBSA neg
99	FEtSA neg
100	FHpSA neg
101	FHpSA neg (TTU)
102	FHxSA neg
103	FHxSAA neg
104	FHxSAA neg (TTU)
105	FOSA neg
106	FOSA neg (TTU)
107	FPeSA neg
108	FPrSA neg
109	H-PFBS neg
110	H-PFEtS neg
111	H-PFHpS neg

112	H-PFHxS neg
113	H-PFNS neg
114	H-PFOA neg
115	H-PFOS neg
116	H-PFPeS neg
117	H-PFPrS neg
118	H-UPFHpS neg
119	H-UPFHxS neg
120	H-UPFNS neg
121	H-UPFOS neg
122	H-UPFPeS neg
123	K-PFDS neg
124	K-PFHpS neg
125	K-PFHxS neg
126	K-PFNS neg
127	K-PFOS neg
128	K-PFPeS neg
129	K-PFUdS neg
130	MeFBSAA neg
131	MeFHpSAA neg
132	MeFHxSAA neg
133	MeFNSAA neg
134	MeFOSA neg
135	MeFOSAA neg
136	MeFPeSAA neg
137	O-PFDS neg
138	O-PFHpS neg
139	O-U-PFNA neg
140	PFBA neg
141	PFBA in-source dimer (perfluorobutane carboxylic acid) neg
142	PFBA in-source fragment (perfluorobutane carboxylic acid) neg
143	PFBS neg
144	PFBSi neg
145	PFDA neg
146	PFDA in-source dimer (perfluoro-n-decanoic acid) neg
147	PFDA in-source fragment (perfluoro-n-decanoic acid) neg
148	PFDoA neg
149	PFDoA in-source dimer (perfluoro-n-dodecanoic acid) neg
150	PFDoA in-source fragment (perfluoro-n-dodecanoic acid) neg
151	PFDoS neg
152	PFDS neg
153	PFEtA neg
154	PFEtCHxS neg
155	PFEtS neg
156	PFEtSi neg
157	PFHpA neg
158	PFHpA in-source dimer (perfluoro-n-heptanoic acid) neg
159	PFHpA in-source fragment (perfluoro-n-heptanoic acid) neg
160	PFHpA+1 in-source fragment neg
161	PFHpDA neg
162	PFHpS neg
163	PFHpSi neg
164	PFHxA neg
165	PFHxA in-source dimer (perfluoro-n-hexanoic acid) neg
166	PFHxA in-source fragment (perfluoro-n-hexanoic acid) neg
167	PFHxA+1 in-source fragment neg
168	PFHxDA neg

169	PFHxS neg
170	PFHxSi neg
171	PFNA neg
172	PFNA in-source dimer (perfluoro-n-nonanoic acid) neg
173	PFNA in-source fragment (perfluoro-n-nonanoic acid) neg
174	PFNDA neg
175	PFNS neg
176	PFNSi neg
177	PFOA neg
178	PFOA in-source dimer (perfluoro-n-octanoic acid) neg
179	PFOA in-source fragment (perfluoro-n-octanoic acid) neg
180	PFOA with IS neg
181	PFODA neg
182	PFOS neg
183	PFOSi neg
184	PFPeA neg
185	PFPeA in-source dimer (perfluoro-n-pentanoic acid) neg
186	PFPeA in-source fragment (perfluoro-n-pentanoic acid) neg
187	PFPeDA neg
188	PFPeS neg
189	PFPeSi neg
190	PFPrA neg
191	PFPrS neg
192	PFPrSi neg
193	PFTeDA neg
194	PFTeDS neg
195	PFTrDA neg
196	PFTrDA in-source fragment (perfluoro-n-tetradecanoic acid) neg
197	PFTrDS neg
198	PFUdA neg
199	PFUdS neg
200	PFUnA in-source dimer (perfluoro-n-undecanoic acid) neg
201	PFUnA in-source fragment (perfluoro-n-undecanoic acid) neg
202	S-OHPrAmPr-FBSA neg,pos
203	S-OHPrAmPr-FBSA-OHPrS neg,pos
204	S-OHPrAmPr-FHxSA neg,pos
205	S-OHPrAmPr-FHxSA-OHPrS neg,pos
206	S-OHPrAmPr-FPeSA neg,pos
207	S-OHPrAmPr-FPeSA-OHPrS neg,pos
208	S-OHPrAmPr-FPrSA neg,pos
209	S-OHPrAmPr-FPrSA-OHPrS neg
210	SPrAmPr-FBSA neg,pos
211	SPrAmPr-FBSAA neg,pos
212	SPrAmPr-FBSAPrS neg,pos
213	SPrAmPr-FHpSA neg,pos
214	SPrAmPr-FHpSAPrS neg,pos
215	SPrAmPr-FHxSA neg,pos
216	SPrAmPr-FHxSAA neg,pos
217	SPrAmPr-FHxSAPrS neg,pos
218	SPrAmPr-FOSA neg,pos
219	SPrAmPr-FOSAPrS neg,pos
220	SPrAmPr-FPeSA neg,pos
221	SPrAmPr-FPeSAA neg,pos
222	SPrAmPr-FPeSAPrS neg,pos
223	SPrAmPr-FPrSA neg,pos
224	SPrAmPr-FPrSAA neg,pos
225	SPrAmPr-FPrSAPrS neg,pos

226	SPr-FBSA neg
227	SPr-FHxSA neg
228	SPr-FOSA neg
229	SPr-FPeSA neg
230	SPr-FPrSA neg
231	Tentative TTU K-PFUdS neg (6.490)
232	UPFDS neg
233	UPFHpS neg
234	UPFHxS neg
235	UPFNS neg
236	UPFOS neg
237	UPFUdS neg
238	6:2 FTS neg (MEERG)
239	8:2 FTS neg (MEERG)
240	PFBA neg (MEEERG)
241	PFBA_13C4 (MEERG)
242	PFBS neg (MEERG)
243	PFDA neg (MEERG)
244	PFDoA neg (MEERG)
245	PFDoS neg (MEERG)
246	PFDS neg (MEERG)
247	PFHpA neg (MEERG)
248	PFHxA neg (MEERG)
249	PFHxDA neg (MEERG)
250	PFHxS neg (MEERG)
251	PFNA neg (MEERG)
252	PFNA_13C9 neg (MEERG)
253	PFNA_13C9 neg (MEERG; SWATH)
254	PFOA neg (MEERG)
255	PFODA neg (MEERG)
256	PFOS neg (MEERG)
257	PFPeA neg (MEERG)
258	PFTeDA neg (MEERG)
259	PFTrDA neg (MEERG)
260	PFUdA neg (MEERG)