March 2024

PFAS Water Quality and Fish Tissue Assessment Study - Year 2

Technical Report No. 2024-2

Managing, Protecting and Improving
the Water Resources of the
Delaware River Basin since 1961

Delaware River Basin Commission
DELAWARE • NEW JERSEY
PENNSYLVANIA • NEW YORK
UNITED STATES OF AMERICA

PFAS WATER QUALITY AND FISH TISSUE ASSESSMENT STUDY – YEAR 2

Written by Jeremy Landon Conkle, Ph.D., Senior Chemist/Toxicologist at the Delaware River Basin Commission (DRBC), based upon fieldwork completed by Ronald MacGillivray, Ph.D., retired Senior Environmental Toxicologist and other researchers at the DRBC.

ACKNOWLEDGEMENTS AND DISCLAIMERS

This report was funded in part by a grant from the U.S. Fish and Wildlife Service (FWS) through the National Fish and Wildlife Foundation (NFWF) Delaware Watershed Conservation Fund (DWCF), grant number 0403.21.072417.

The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the opinions or policies of the U.S. Government or the National Fish and Wildlife Foundation and its funding sources. Mention of trade names or commercial products does not constitute their endorsement by the U.S. Government, or the National Fish and Wildlife Foundation or its funding sources.

SUGGESTED CITATION

Conkle, Jeremy Landon. (2024). *PFAS Water Quality and Fish Tissue Assessment Study – Year 2.* (DRBC Report No. 2024-2). West Trenton, New Jersey. Delaware River Basin Commission.

EXECUTIVE SUMMARY

The Delaware River Basin Commission (DRBC) is conducting a three-year per- and polyfluoroalkyl substances (PFAS) Water Quality and Fish Tissue Assessment Study. This work is being performed as part of several grants from the U.S. Fish and Wildlife Service (FWS) through the National Fish and Wildlife Foundation (NFWF) Delaware Watershed Conservation Fund (DWCF). The Year 1 report of data collected in 2021 was published in July 2023 (NFWF grant number 0403.20.068693). In the Year 2 study reported here (NFWF grant number 0403.21.072417), the DRBC analyzed PFAS occurrence data along 215 miles of the mainstem Delaware River and one tributary in 2022. Surface water and sediment samples were collected in May and June 2022, focusing on 15 mainstem sites (4 non-tidal and 11 tidal) and one tidal tributary site on the Schuylkill River. Fish were sampled at three non-tidal and six tidal sites, while blue crabs were caught only at Pea Patch Island.

As with the Year 1 study, PFAS was detected in most sites and all sample matrixes. Sites higher in the basin tended to have lower concentrations and fewer detections. The number of target PFAS detected, and their concentrations in water, generally increased in samples as they got closer to Delaware Bay. The one exception was for water samples collected at the Burlington Bristol Bridge, where the sum PFAS (ΣPFAS) was 597 ng L^{-1}, which was 3x higher than the ΣPFAS of all the other sites combined. There were no observable trends with PFAS concentrations related to river mile for fish or sediment. The ΣPFAS concentrations were lowest in water and highest in fish and crab tissues. Within fish, the tidal fish generally had more detections per species at a site and higher concentrations. Additionally, fish livers had higher ΣPFAS concentrations than the fillet at every site examined. Perfluorooctanesulfonate (PFOS) was the dominant PFAS compound in fish liver and fillet. Unlike most PFAS compounds, PFOS has a chronic reference dose of 0.02 µg kg-1 day-1 for daily consumption. Based on a 70 kg adult, fish fillets at three sites exceeded this threshold. These results demonstrate that fish in the Delaware River Basin accumulate PFAS compounds, particularly PFOS, at levels exceeding existing toxicity thresholds. Furthermore, toxicity thresholds for PFAS are lacking for most compounds, and the existing ones have often been lowered when undergoing reviews of new data.

This report provides a snapshot of the concentrations of 40 PFAS compounds in multiple matrixes of the Delaware River Basin. The third year of data collection for 2023 (NFWF grant number 0403.22.075117) will replicate the efforts of Year 2. Then, the data from each of the three years will be synthesized to assess the presence of PFAS in the Delaware River Basin's water, sediment, fish, and crabs.

LIST OF ACRONYMS/ABBREVIATIONS

Σ	Sum
AFFF	Aqueous film-forming foams
C	Celsius
CECs	Contaminants of emerging concern
day-1	Per day
DI	Deionized water
DRBC	Delaware River Basin Commission
DWCF	Delaware Watershed Conservation Fund
FWS	United States Fish and Wildlife Service
g	GRams
HDPE	High-density polyethylene
kg	Kilograms
L-1	Per liter
µg	Micrograms
ml	Milliliters
mm	Millimeters
ng	Nanograms
NFDHA	Nonafluoro-3,6-dioxaheptanoic acid
NFWF	National Fish and Wildlife Foundation
NJ	New Jersey
NJDEP	New Jersey Department of Environmental Protection
NJDOH	New Jersey Department of Health
NYSDEC	New York State Department of Environmental Conservation
PA	Pennsylvania
PFBA	Perfluorobutanoate
PFHxA	perfluorohexanoate
PFBC	Pennsylvania Fish and Boat Commission

PPCPs	Pharmaceuticals and personal care products
PFAS	Per- and polyfluoroalkyl substances
PFDA	Perfluorodecanoate
PFDoA	Perfluorododecanoate
PFOS	Perfluorooctanesulfonate
PFOSA	Perfluorooctane sulfonamide
PFTeDA	Perfluorotetradecanoate
PFTrDA	Perfluorotridecanoate
PFUnA	Perfluoroundecanoate
RfD_C	Chronic Reference Dose
SPE	Solid phase extraction
USEPA	United States Environmental Protection Agency

TABLE OF CONTENTS

1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) constitute a diverse group of >10,000 human-made chemicals (USEPA 2023) with unique properties, including water and grease resistance and thermal stability. With a widespread presence in various consumer and industrial products, such as non-stick cookware, aqueous film-forming foams (AFFF), and water-resistant textiles, PFAS have become integral to modern life. However, their ubiquity and persistence, coupled with a growing body of toxicological data, have raised concerns about their adverse effects on human health and the environment. PFAS are characterized by strong carbon-fluorine bonds, rendering them resistant to degradation and allowing them to accumulate in the environment. As scientific research advances, the understanding of PFAS and their impact on environmental and human health continues to evolve, prompting increased scrutiny and efforts to mitigate their widespread use.

The Delaware River Basin Commission (DRBC) performs ongoing research and activities in various areas to support water resource management, including protecting water quality for drinking water and improving and restoring critical fish and wildlife habitats. Current and past research on contaminants of emerging concern (CECs) has included pharmaceuticals and personal care products (PPCPs), 1-4 dioxane, bromides, PFAS, microplastics, and chlorides/freshwater salinization.

The DRBC is conducting a three-year PFAS Water Quality and Fish Tissue Assessment Study. This work is being performed as part of several grants from the U.S. Fish and Wildlife Service (FWS) through the National Fish and Wildlife Foundation (NFWF) Delaware Watershed Conservation Fund (DWCF). The Year 1 report of data collected in 2021 was published in July 2023 (NFWF grant number 0403.20.068693). In Year 2 of the study reported here (NFWF grant number 0403.20.068693), the DRBC collected PFAS occurrence data along 215 miles of the mainstem Delaware River and one tributary in 2022. This work was completed as part of a grant from the U.S. Fish and Wildlife Service (FWS) through the National Fish and Wildlife Foundation (NFWF) Delaware Watershed Conservation Fund (DWCF), grant number 0403.20.072417. The project monitored fish, surface water, and sediment for 40 PFAS, including 11 perfluorinated carboxylates (C4-C14), 8 perfluorinated sulfonates (C4-C10, C12), 3 fluorotelomer sulfonates (2:4, 2:6, 2:8), 3 perfluorooctane sulfonamides, 2 perfluorooctane sulfonamide ethanols, 2 perfluococtane sulfonamideacetic acids, 4 additional analytes in the United States Environmental Protection Agency (EPA) Method 537 Rev 1, HFPO-DA, ADONA, 11CL-PF3OUdS, 9CL-PF3ONS, 4 analytes in EPA Method 533, PFEESA, PFMPA, PFMBA, NFDHA and three analytes associated with landfill leachate 3:3 FTCA, 5:3 FTCA, 7:3 FTCA.

Furthering the understanding, occurrence, and bioaccumulation of PFAS is vital to protecting water resources.

The third year of data collection for 2023 (NFWF grant number 0403.22.075117) will replicate the efforts of Year 2. Then, the data from each of the three years will be synthesized to assess the presence of PFAS in the Delaware River Basin's water, sediment, fish, and crabs.

2. SAMPLING AND ANALYSIS

2.1 SURFACE WATER SAMPLING

Surface water samples were collected for PFAS analysis (Table 1 and Figure 1) in May and June 2022. Sample collection followed the New York State Department of Environmental Conservation methods for PFAS sampling (NYSDEC 2022). Based on the lack of detections in Year 1 sampling at sites north of Trenton, New Jersey (NJ), sample volumes were doubled to increase the chances of measuring PFAS. Therefore, 1000 ml water samples in high-density polyethylene (HDPE) bottles were collected at Lackawaxen, Dingmans Ferry, Sandts Eddy, and Yardley, Pennsylvania (PA). All other water samples were collected in 500 ml HDPE bottles. Each water sample was collected in duplicate, with the second sample serving as a lab backup in the event of problems with the initial extraction and analysis. All samples were collected directly in the laboratory container by submerging them 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 before shipping to the laboratory for analyses. DRBC contracted laboratory, SGS AXYS, supplied PFAS-free water that was transferred to a second sample bottle on site as a field blank and left open during sampling at a single site. Field duplicates, a second sample at a given location, were also collected. In-field surface water parameters, including specific conductivity, water temperature, dissolved oxygen, and pH, were measured at sample sites.

2.2 SEDIMENT SAMPLING

Surface sediment sample collection (Table 1 and Figure 1) occurred in May and June 2022. Sampling followed the NYSDEC methods for PFAS sampling (NYSDEC 2022). Sediment samples were collected with a stainless-steel spoon, added to a large stainless-steel bowl, and homogenized with another spoon. Subsamples were then placed in 250 mL HDPE jars for PFAS. In the field, sediment samples were placed in a cooler maintained at 4 ± 2 ˚C using ice during transport to the lab. SGS AXYS PFAS-free water was used for the equipment blank. This involved decontaminating the sampling equipment with an Alconox cleaning solution followed by a

deionized water (DI) water rinse. The PFAS-free water was poured over the sampling equipment into a 250 mL HDPE jar.

Figure 1. *Water, sediment and fish sampling locations in the Delaware River and its tributaries*

Table 1. *List of water, sediment, fish, and crab sampling sites from 2022.*

Name	ID	River Mile	Latitude	Longitude	River Zone	Sediment & Water	Fish & Crabs
Non-tidal main stem							
Lackawaxen, PA	LAC	277	41.4859	-74.9864	1B	Y	SMB, WS
Dingmans Ferry, PA	DIN	239	41.2195	-74.8600	1C	Y	SMB
Sandts Eddy, PA	SAN	189	40.7582	-75.1880	1D	Y	
Yardley, PA	YAR	139.5	40.2607	-74.8514	1E	Y	SMB
Tidal main stem							
Biles Channel	BC	132	40.1898	-74.7585	2	Y	WP
Crosswicks Creek	CC	128.5	40.1495	-74.7180	2		WP
Florence	FL	122.5	40.1309	-74.8134	2	Y	WP
Burlington Bristol Bridge	BU	117.5	40.0811	-74.8700	2	Y	
Torresdale	TD	110.5	40.0328	-74.9922	2	Y	WP, CC
Betsy Ross Bridge	BR	105	39.9882	-75.0675	3	Y	
Ben Franklin Bridge	BF	100	39.9497	-75.1390	3	Y	
Navy Yard	NV	92.5	39.8841	-75.1969	4	Y	
Philadelphia Airport	PB	90.5	39.8660	-75.2262	4	Y	
Eddystone	ES	85	39.8543	-75.3290	4	Y	CC
Chester	CH	82	39.8250	-75.3646	4	Y	CC
Pea Patch Island	PPI	62.5	39.6126	-75.5931	5	Y	BC
Tidal tributary							
Schuylkill River	SR		39.9131	-75.2059		Y	

SMB = smallmouth bass, WS = white sucker, WP = white perch, CC = channel catfish, BC = blue crab

2.3 Fish and Crab Sampling

Fish collection followed the protocols issued by the NYSDEC (NYSDEC 2022). Two tidal species, white perch, *Morone americana*, and channel catfish, *Ictalurus punctatus*, were collected by hook and line in May and June 2022 from a combined six sites as listed in Table 1. Two non-tidal species, smallmouth bass, *Micropterus dolomieu*, and white sucker, *Catostomus commersonii*, were collected by fisheries biologists from the Pennsylvania Fish and Boat Commission (PFBC) via nighttime boat electrofishing in July and September 2022 from a combined three sites as listed in Table 1. A minimum of three of each species was collected at each site. 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℃) before shipping and processing in the analytical laboratory. Fillets for white perch, white sucker, and smallmouth bass included the skin but without scales. Channel catfish fillets were not analyzed with their skin. The livers were

removed with care to avoid contamination from the gallbladder. A composite of fillets or livers for each species from fish of similar length and weight at each location was prepared at the laboratory.

Blue crabs, *Callinectes sapidus*, were collected as part of the Year 1 study, but the data were not available for its final report. Therefore, data from blue crabs collected in Year 1 (10/06/2021) and Year 2 (9/21/2022) are presented in this report. Blue crabs were collected only at Pea Patch Island (PPI) using a trotline (Figure 1) in both years. The trotline consists of evenly spaced bait (chicken necks) that run between two buoys and lays on the bottom of the river. After the bait has been in the water for ~10 minutes, one end of the line is placed over a hook extending from the side of the boat (Figure 2). The boat then motors down the line with the hook, pulling the bait to the surface. Crabs often hang onto the bait, reaching the water surface, before they let go and are captured by a net. Only crabs >6" (150 mm) were kept for analysis as dictated by local fishing regulations.

***Figure 2**. Fishing for crabs near Pea Patch Island using at trotline with chicken necks as bait.*

A minimum of three blue crabs were caught at the Pea Patch Island site. Each blue crab was wrapped in aluminum foil provided by SGS AXYS and placed into a single bag. Blue crab samples were stored frozen (-20℃) before shipping and processing in the analytical laboratory. In the lab, blue crab muscle sample was removed from the base of the legs and the cheliped, taking care not to contaminate the sample with internal organs or the hepatopancreas. The crabs were then composited and homogenized.

2.4 Sample Extraction and Analysis

Samples were processed and analyzed by a subcontracted laboratory, SGS AXYS, using Method MLA-110 (equivalent to Draft USEPA Method 1633) for 40 PFAS analytes (Table 2) out of the >10,000 chemicals in this class (USEPA 2023). All samples were spiked with isotopically labeled surrogate standards before extraction. Water samples (up to 1,000 mL) were extracted by solid phase extraction (SPE) using weak anion exchange sorbent. The extracts were then treated with ultra-pure carbon powder, spiked with recovery standards, and analyzed by liquid

chromatography with triple quadrupole mass spectrometry (LC-MS/MS). Sediment samples (up to 5 g dry weight) were extracted by shaking three times with methanolic ammonium hydroxide solution and combining the supernatants. Tissue samples (up to 2 g wet weight) were extracted with methanolic potassium hydroxide solution, followed by acetonitrile and methanolic potassium hydroxide solution. The supernatants were combined. Sediment and fish tissue extracts were treated with ultra-pure carbon powder, evaporated to remove the methanol, and diluted with water. The extract solution was then cleaned by SPE with weak anion exchange sorbent. The eluate was then spiked with recovery standards and analyzed with LC-MS/MS. Final sample concentrations were determined by isotope dilution/internal standard quantification.

2.5 Data Limitations and Interpretations

This experimental design, a single sampling of sediment and water at each site, provides a snapshot of concentrations at that time and may not represent long-term concentrations. That is particularly true for water, which can be highly variable in the short and long term. However, sediment is typically less temporally variable than water. While this experimental design limits DRBC's ability to interpret results broadly, it was implemented with the knowledge of data from previous years and the expectation that future funding would provide additional sampling resources. Therefore, below we present data from the Year 2 study and compare it with the data from the previous Year 1 study. The report for the Year 3 study will also include a synthesis of data from all three years to provide a more robust understanding of PFAS data in surface waters, sediment, and species of the Delaware River Basin.

Table 2. *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	Perfluorononanoate (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 WATER

Sixteen sites were sampled for PFAS in summer 2022. All but one (Schuylkill River) of the sites were in the mainstem Delaware River, with four non-tidal and 11 tidal sites (Figure 1). At least one target PFAS compound was detected at 14 of the 16 sites. The two most northern sites, Lackawaxen and Dingmans Ferry, had no PFAS above detection limits. Last year, these two sites, as well as Sandts Eddy and Yardley, were also non-detect. However, this year, the sample volume

collected at these four sites was doubled from 500 to 1,000 mL, which likely aided in the detection of PFAS at Sandts Eddy and Yardley, the two sites furthest downstream in the non-tidal section of the river sampled. When detections occurred, they ranged from 1-8 compounds (4.7 ± 2.1; Average ± Standard Deviation), with nine unique PFAS compounds identified across the sites in surface water samples.

Sum PFAS (ΣPFAS) water concentrations at sites with at least one detection ranged from 1.9 to 597 ng L^{-1} (Figure 3A). However, if you exclude the sample collected at the Burlington Bristol Bridge (BU; 597 ng L^{-1}), the ΣPFAS range drops to 1.9 to 46.5 ng L^{-1} (Figure 3B). The BU ΣPFAS is >3x higher than the ΣPFAS from all the other sites ***combined***. Additionally, four individual compounds (5:3 FTCA, PFBA, PFHxA, PFHpA) quantified at BU had higher concentrations than the ΣPFAS at the second-highest site, Pea Patch Island (46.5 ng L^{-1}). When excluding the BU site, there also appears to be a general increasing trend for ΣPFAS with decreasing river mile (moving from upstream to downstream; Figure 3B).

Due to differences in mainstem sampling sites between Year 1 and Year 2, there was only one site with samples collected each year that had detections, Pea Patch Island (PPI; Figure 4). The PFAS detections and their concentrations were of similar magnitude each year despite the potential dilution influence of tides (Robuck et al. 2023). PFAS concentrations during rising, high, or falling tides are likely diluted, resulting in lower measured concentrations, possibly resulting in non-detections. Samples collected at or near low tide are likely to have higher concentrations but also more detections, particularly for target analytes present near the limits of quantification. In Year 1, sampling occurred at a high but falling tide (~5.5 ft at the nearby Delaware City tidal gauge), while in Year 2, the tide was low but rising (~1.5 ft) at sampling. One additional compound was quantified in Year 2, perfluorobutanoate (PFBA). Tide at the sampling time could explain why PFBA was not detected in Year 1.

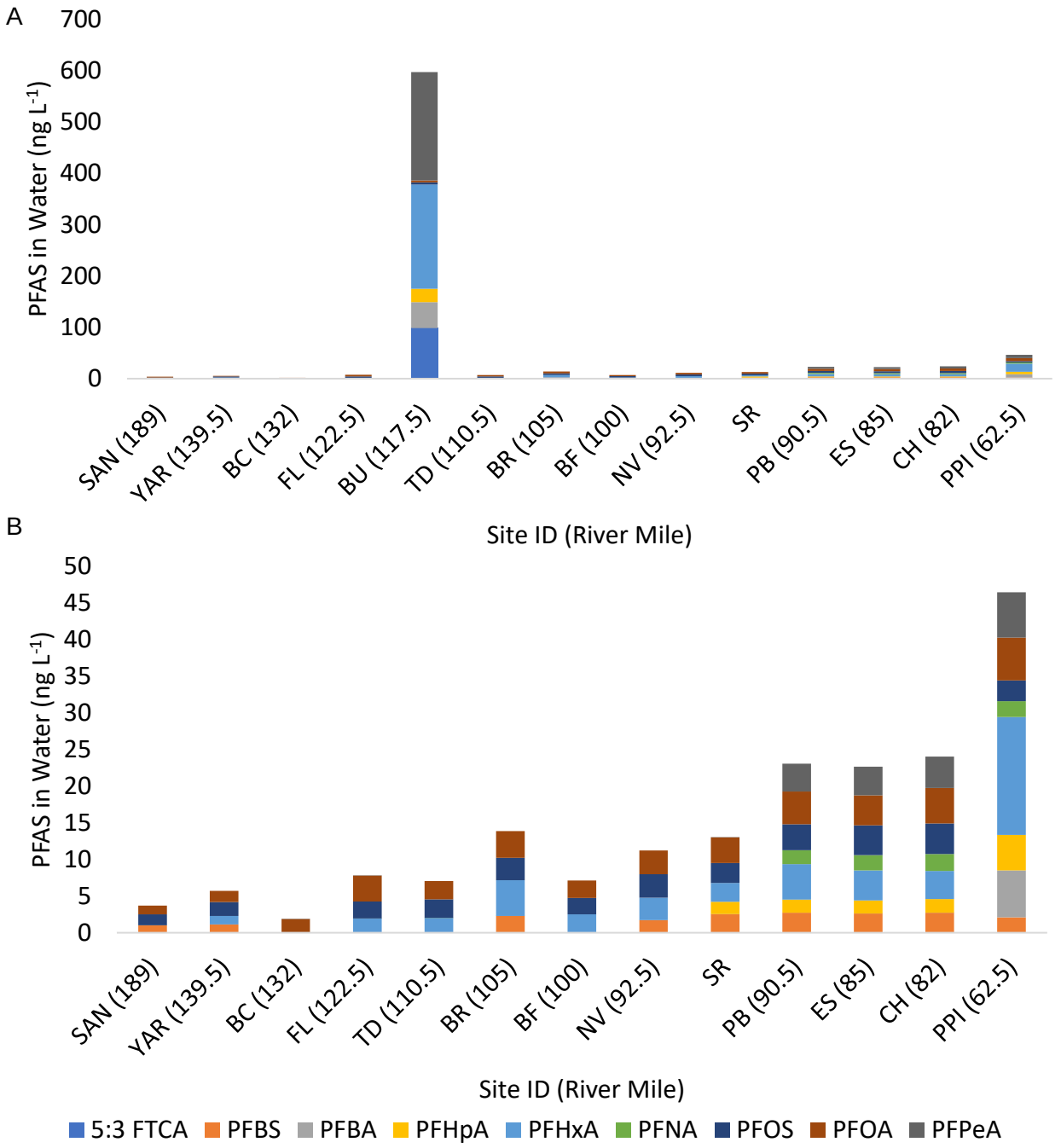

***Figure 3**. Concentrations of PFAS compounds organized by river mile. A) All sites with detections are shown, including concentrations at the Burlington Bristol Bridge (BU), which dwarfs all other sites. B) The Burlington Bristol Bridge (BU) site is removed to better show data from the other sites with detections.*

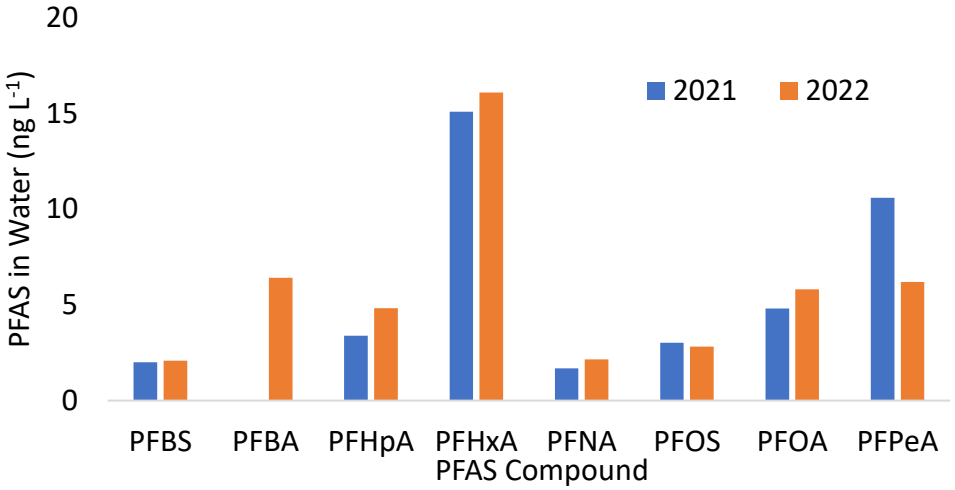

***Figure 4**. Surface water detections of PFAS compounds at the Pea Patch Island site in years 1 and 2 of NFWF funding. This site was the only site that was sampled in both year 1 and 2.*

The EPA study of tidal influence on PFAS detections was not completed before sample collection in this study (Robuck et al. 2023). However, tides have been accounted for with Year 3 sampling and will be compared with the two previous years of data when the synthesis report is submitted in 2024. All samples for that study were collected at or near low tide.

3.2 SEDIMENT

At least one target PFAS compound was detected in sediment at 12 of the 16 sites. No detections occurred at the three most northern non-tidal sites, Lackawaxen (LAC; river mile 277), Dingmans Ferry (DIN; 239), and Sandts Eddy (SAN; 189), as well as the tidal site at the Betsy Ross Bridge (BR; 105). When detections occurred, they ranged from 1-6 compounds (4.0 ± 1.5; Average ± Standard Deviation), with seven unique PFAS compounds identified across the sites in surface sediment samples.

Total PFAS (ΣPFAS) sediment concentrations at sites with at least one detection ranged from 203 to 3,104 ng kg^{-1} (Figure 5). Yardley (YAR; 139.5) was the site of the lowest ΣPFAS (203 ng kg^{-1}) and least detections (1) among the sites with a detection. The Year 1 (2021) sampling also found that PFOS was the only target PFAS compound at the Yardley site, and while it was higher last year (386 ng kg^{-1}), it was of similar magnitude. The highest sediment ΣPFAS occurred at the Eddystone site (ES; 85), ~ 5 miles downstream of the Philadelphia Airport. No general trend for sediment data regarding increasing or decreasing river mile was observed. Additionally, while the BU site had exceptionally high concentrations of multiple PFAS compounds in water, they were not observed in sediment at the site.

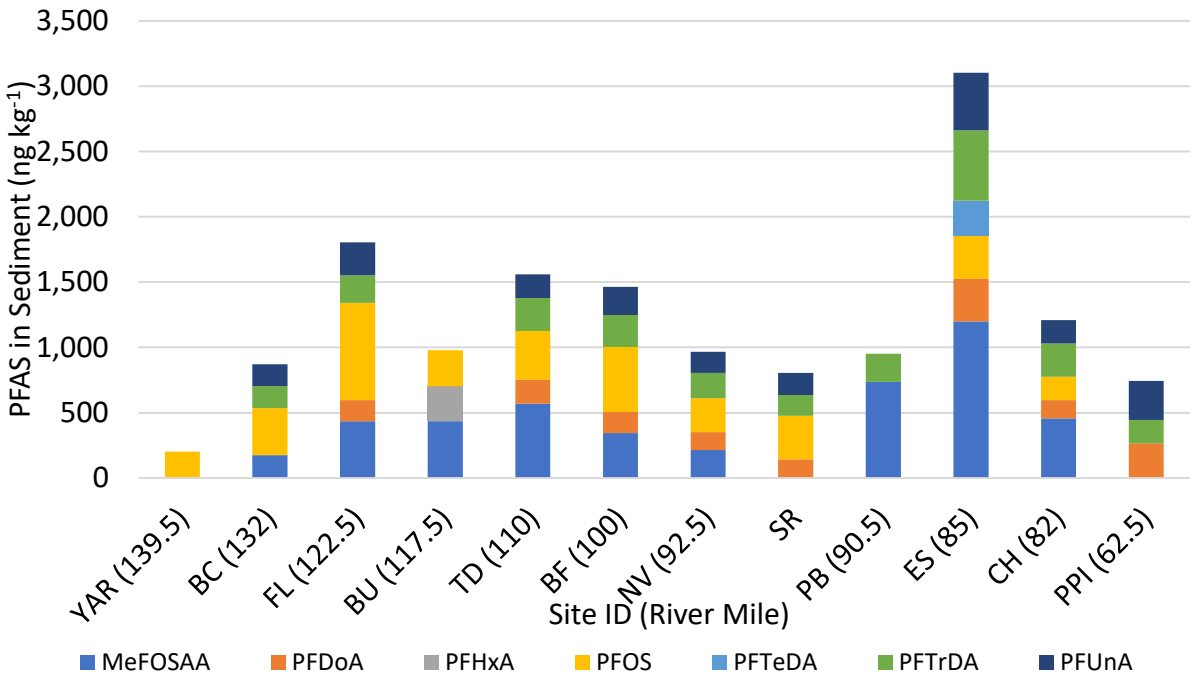

***Figure 5**. Sediment concentrations of PFAS. Sites without detections are not shown, this includes non-tidal sites Lackawaxen (river mile 277), Dingmans Ferry (239) and Sandts Eddy (189) as well as the tidal site near the Betsy Ross Bridge (105).*

Seven of the 40 target analytes were found in sediment and 9 in water. Only two of those compounds, perfluorohexanoate (PFHxA) and perfluorooctanesulfonate (PFOS), were found in both matrixes. The presence and concentrations of PFAS in sediment represent a longer-term and less variable pool of contamination than water concentrations, which can vary across short time scales. Therefore, direct and concrete comparisons cannot be made, but general discussions can help understand PFAS occurrence at sites. PFHxA was found at 12 water sites and only one sediment site, Burlington Bristol Bridge (BU). The BU concentrations of PFHxA in sediment (268 ng kg-1) and water (203 ng L-1) were similar. PFOS was found at 13 water and 10 sediment sites, with overlapping detections at nine sites (Figure 6). Generally, PFOS concentrations in sediment were two orders of magnitude higher, ranging from 42 to 321 times higher than water.

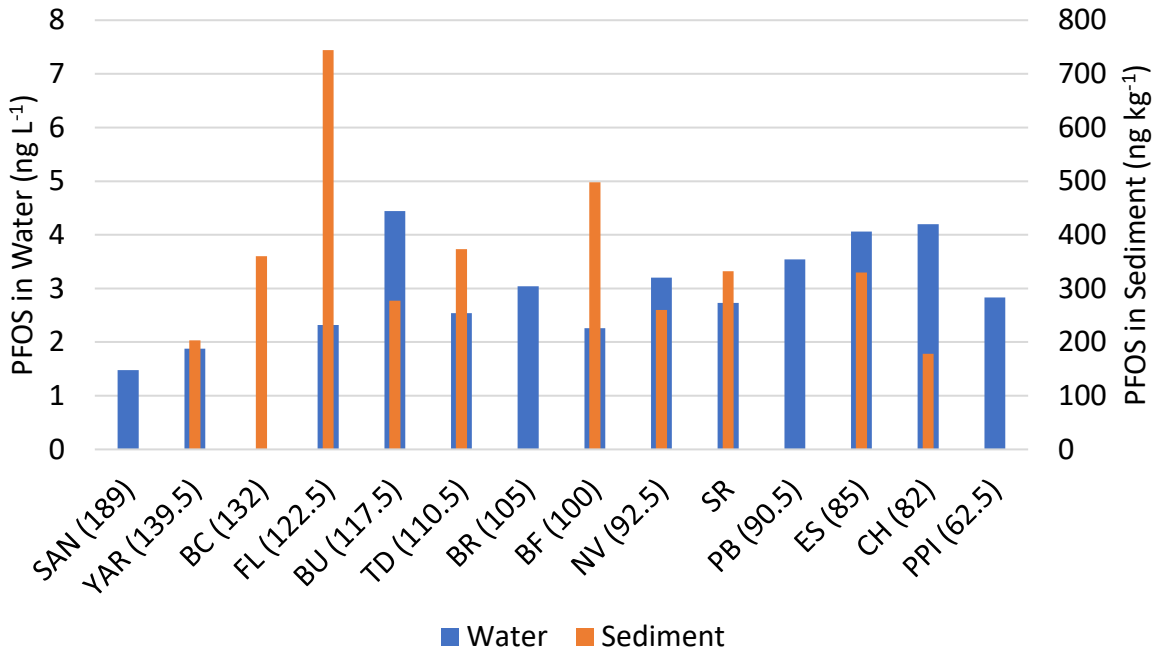

***Figure 6**. Comparison of perfluorooctanesulfonate (PFOS) concentration in water and sediment.*

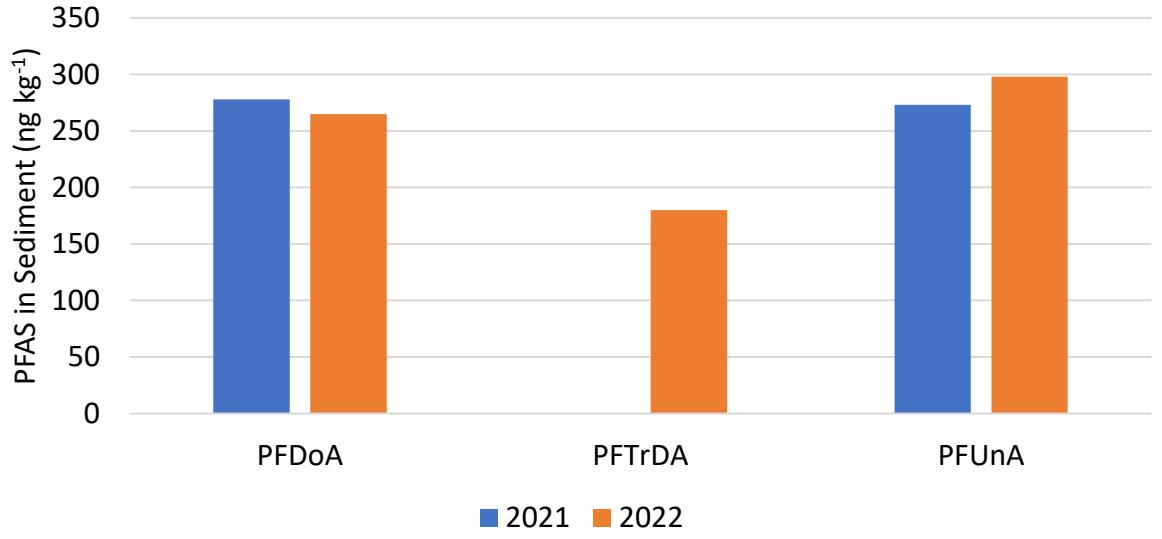

***Figure 7**. PFAS compounds quantified in sediment at Pea Patch Island in 2021 and 2022.*

There were two sites where PFAS was detected in sediment during Year 1 (2021) and Year 2 (2022). At Yardley (YAR), PFOS was quantified at 386 and 203 ng kg^{-1}, respectively. At Pea Patch Island (PPI), perfluorododecanoate (PFDoA) and perfluoroundecanoate (PFUnA) were found each year, with concentrations varying less than 10% (Figure 7). It is difficult to draw conclusions about the consistency of the data since these are single-grab samples that multiple variables could influence. Still, in general, these compounds were found each year at these sites. Data from Year 3 will also be compared to assess the trends over the three years.

3.3 Fish & Crabs

3.3.1 Non-Tidal Fish

The Pennsylvania Fish and Boat Commission collected smallmouth bass at three non-tidal sites and white sucker at one (Table 1). The fish composite samples had quantifiable concentrations of at least two of the 40 target PFAS compounds. All fish concentrations are reported as wet weight. The white sucker composite sample from Lackawaxen had two compounds quantified in the fillet, the carboxylic acid NFDHA (nonafluoro-3,6-dioxaheptanoic acid) and PFOS (perfluorooctane sulfonate) at 1.57 and 0.782 ng g^{-1}. NFDHA was not detected in the liver, but PFOS was detected at 4.07 ng g^{-1}. In smallmouth bass, up to 6 compounds were detected in the fillet (Figure 8) and 5 in the liver (Figure 9). Smallmouth bass fillet tissue at the Lackawaxen site had the highest ΣPFAS at 21.0 ng g^{-1}, while fillet tissue from Dingmans Ferry and Yardley were 5.85 and 4.08 ng g^{-1} respectively. Liver ΣPFAS from the same fish spescies was 3.8x to 21.4x higher than the fillet, with values of 93.30 ng g^{-1} at Lackawaxen, 83.87 ng g^{-1} at Yardley, and 28.29 ng g^{-1} at Dingmans Ferry (Figure 10). While there were limited data generated on the white sucker, PFOS was the dominant target analyte found in smallmouth bass, accounting for 75-80% in fillet and 64-86% in liver tissues of the ΣPFAS.

In the Year 1 study, no target PFAS analytes were found above quantification limits in water or sediment at Lackawaxen, Dingmans Ferry, or Sandts Eddy. The Yardley site had no quantifiable PFAS concentration in water but 386 ng kg^{-1} PFOS in sediment. The Year 2 study found PFAS in water at Sandts Eddy and Yardley and only PFOS in sediment at Yardley. No quantifiable PFAS were found in the Sandts Eddy sediment and the water and sediment at Lackawaxen. However, up to 6 target PFAS compounds were found in fish collected at these sites. This indicates that fish, even though they may migrate within a range from where they are caught, may be a more sensitive method to establish the presence of PFAS compounds in a water body due to their ability to bioaccumulate these compounds at concentrations higher than their surrounding environment. Last, the presence of these PFAS in fish indicates that even though these non-tidal sites are less contaminated than the downstream tidal sites, to the point where concentrations in water and

sediment are below detection limits, PFAS is present and potentially affecting ecosystem and organismal health.

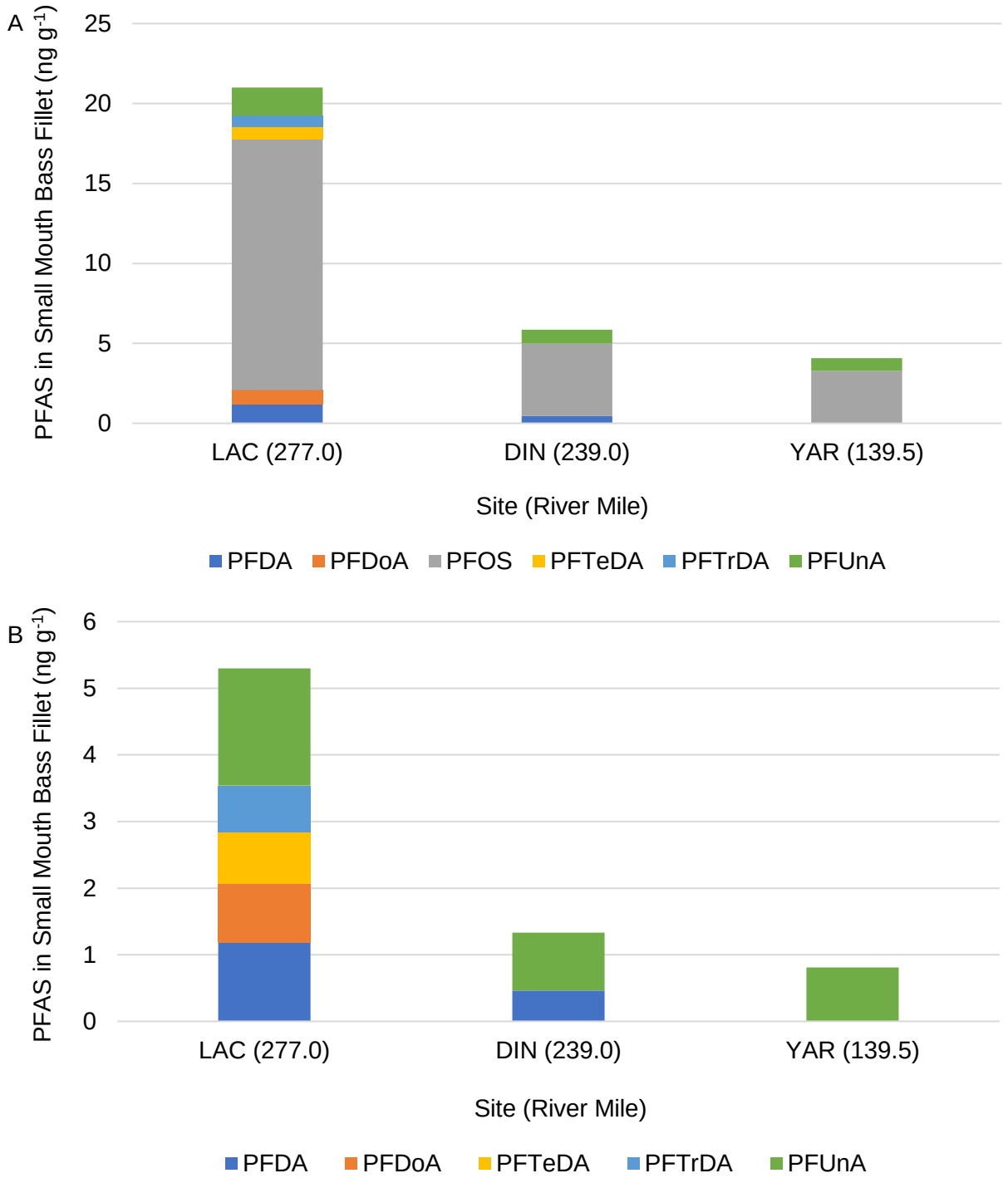

***Figure 8**. A) PFAS compounds quantified in smallmouth bass fillet tissue at three non-tidal Delaware River sties. B) PFOS data was removed to better show the relative concentrations of the other quantified compounds in smallmouth bass fillet tissue samples.*

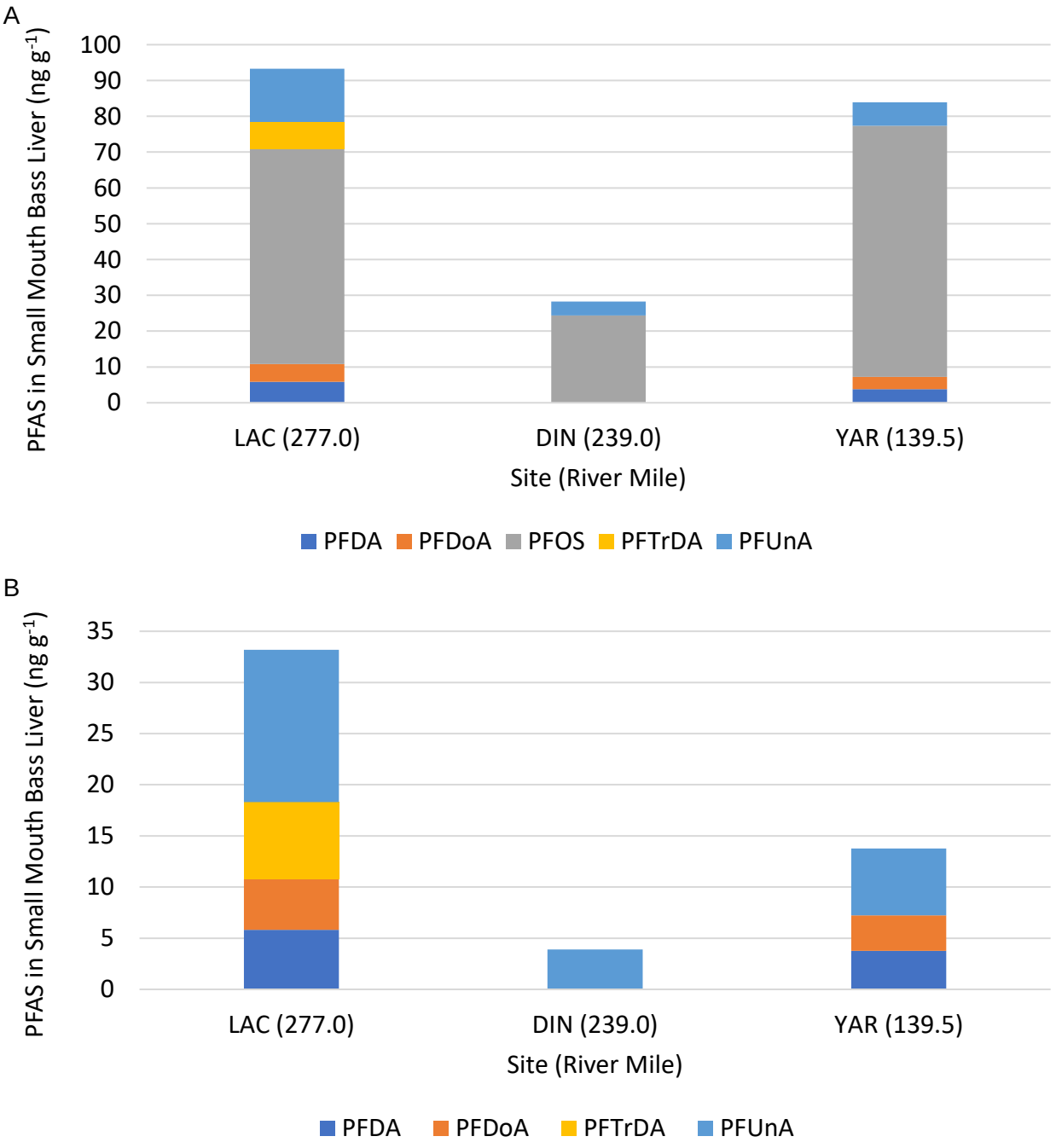

***Figure 9**. A) PFAS compounds quantified in smallmouth bass liver tissue at three non-tidal Delaware River sties. B) PFOS data was removed to better show the relative concentrations of the other quantified compounds in smallmouth bass liver tissue samples.*

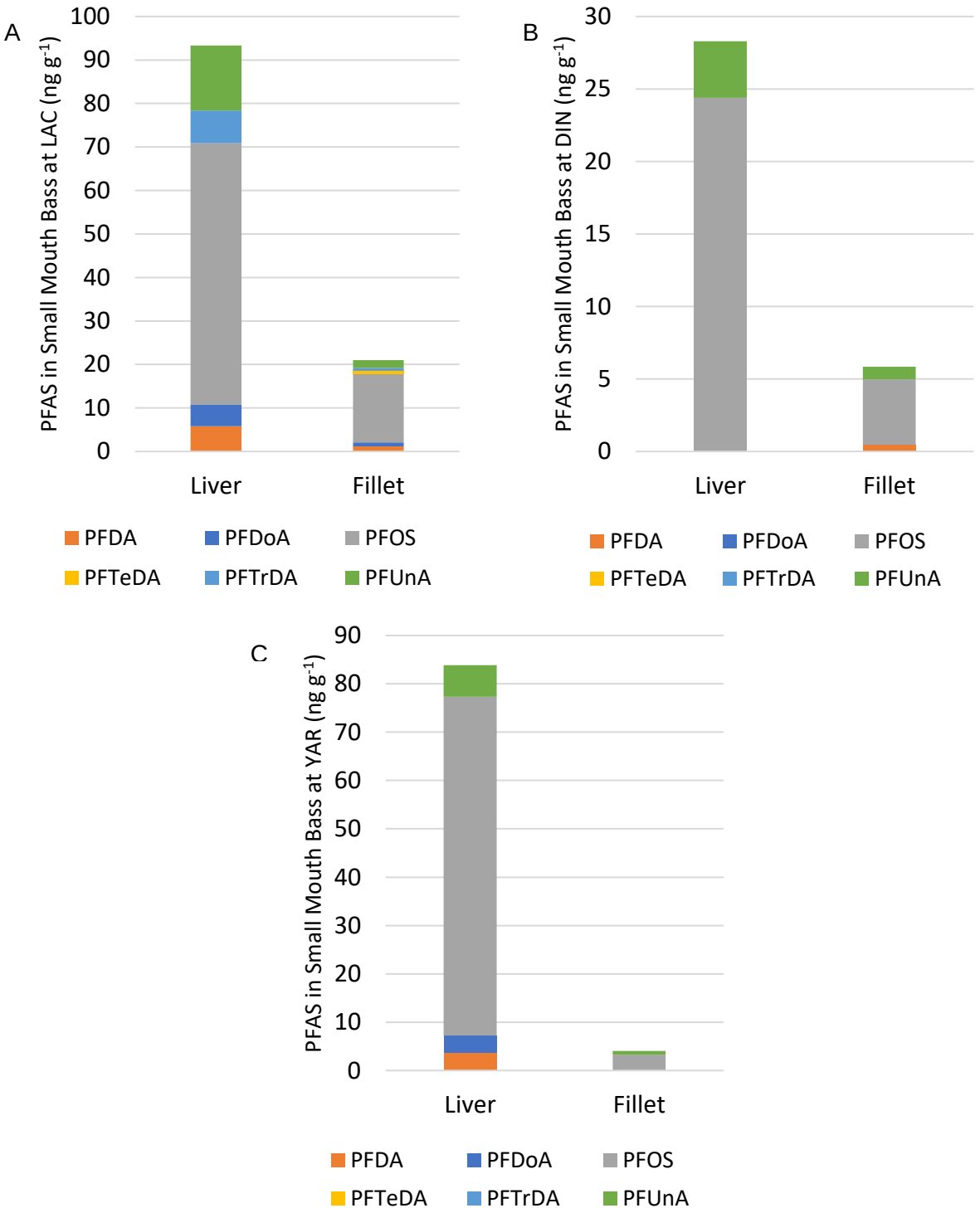

***Figure 10**. Comparisons of quantified PFAS in smallmouth bass liver and fillet tissues at A) LAC, B) DIN and C) YAR.*

3.3.2 Tidal Fish

3.3.2.1 White Perch

White perch were caught at four of the six tidal sites (Table 1). They had 6-8 target PFAS quantified in their fillet composite samples and 10-11 in their liver. The ΣPFAS ranged from 6.5 to 39.2 ng g^{-1} in the fillet to 67.1 to 259.1 ng g^{-1} in the liver (Figures 11 and 12). As with the non-tidal fish samples, PFOS was the dominant compound at 49-56% of ΣPFAS in white perch fillet and 38-58% in the liver. The ΣPFAS in Liver tissues were 6.3x to 14.2x higher than fillet concentrations (Figure 13), with individual PFAS compound differences ranging from 4.7x to 15.4x higher in the liver.

3.3.2.2 Channel Catfish

Channel catfish were caught at three of the six tidal sites (Table 1). They had 4-7 target PFAS quantified in their fillet composite samples and 8-10 in their liver. The ΣPFAS ranged from 1.7 to 83.0 ng g^{-1} in the fillet and 56.4 to 184.1 ng g^{-1} in the liver (Figures 14 and 15). In the liver, PFOS represented 57 to 79% of ΣPFAS quantified. PFOS in channel catfish liver was less dominant than in the other fish species samples, with its highest contribution at 29% for samples collected at Chester. Instead, ΣPFAS in channel catfish fillets were dominated by the precursor PFAS compounds 5:3 FTCA and 7:3 FTCA, accounting for 62% at Torresdale and 96% at Eddystone, respectively. ΣPFAS concentrations were 8.0x and 33.2x higher in the liver than fillets at Torresdale and Chester (Figure 16). The Eddystone ΣPFAS difference between the liver and fillet was the lowest across all samples. It was only 1.2x higher in the liver due to the disproportionate presence of 5:3 FTCA and 7:3 FTCA in the fillet (Figure 16). Additionally, 7:3 FTCA is the only target analyte detected in both the liver and fillet of a composite sample across all species and sites where the fillet concentration (41.10 ng g^{-1}) was higher than the liver (12.40 ng g^{-1}).

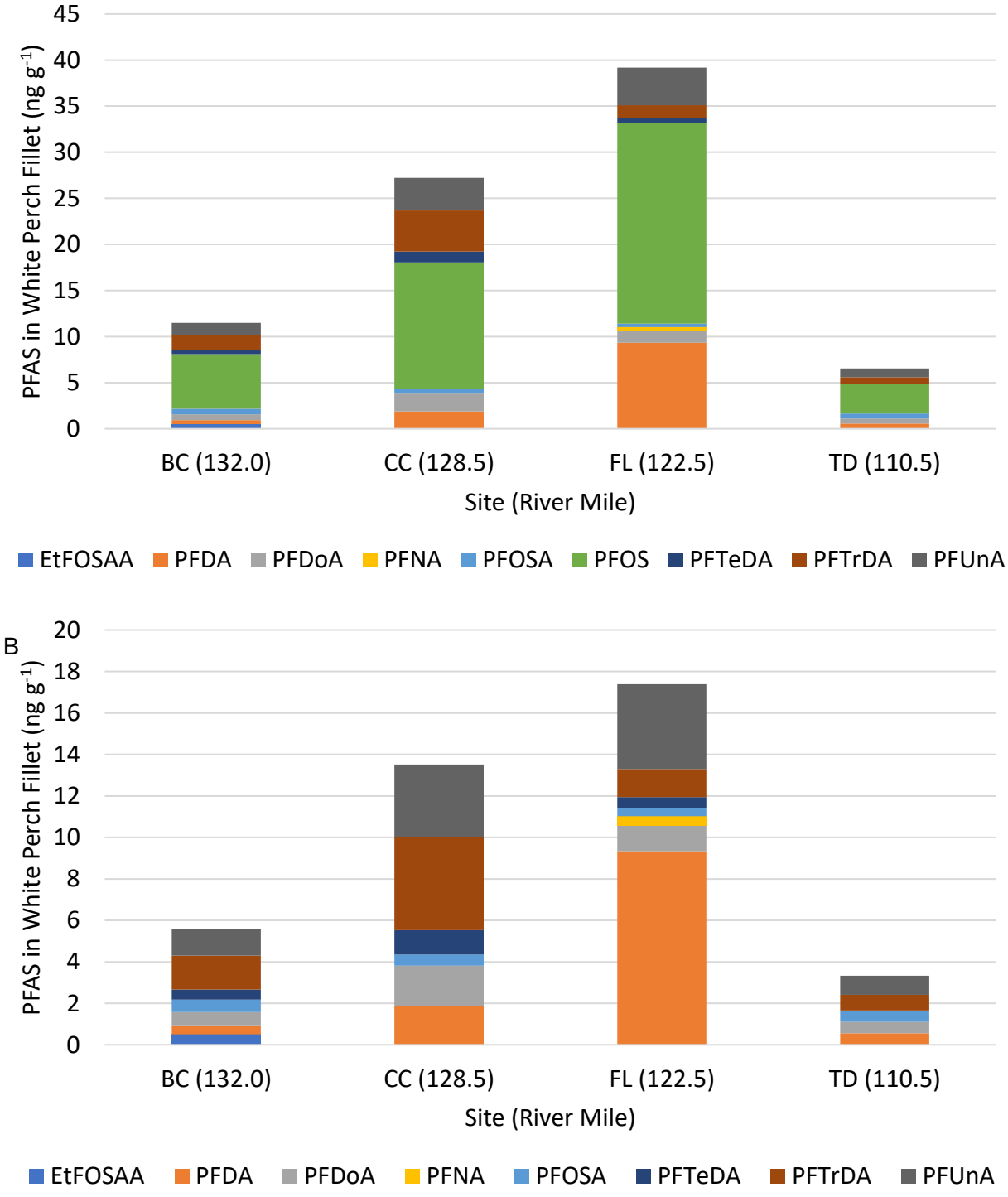

***Figure 11**. A) PFAS compounds quantified in white perch fillet tissue at three tidal Delaware River sties. B) PFOS data was removed to better show the relative concentrations of the other quantified compounds in white perch fillet tissue samples.*

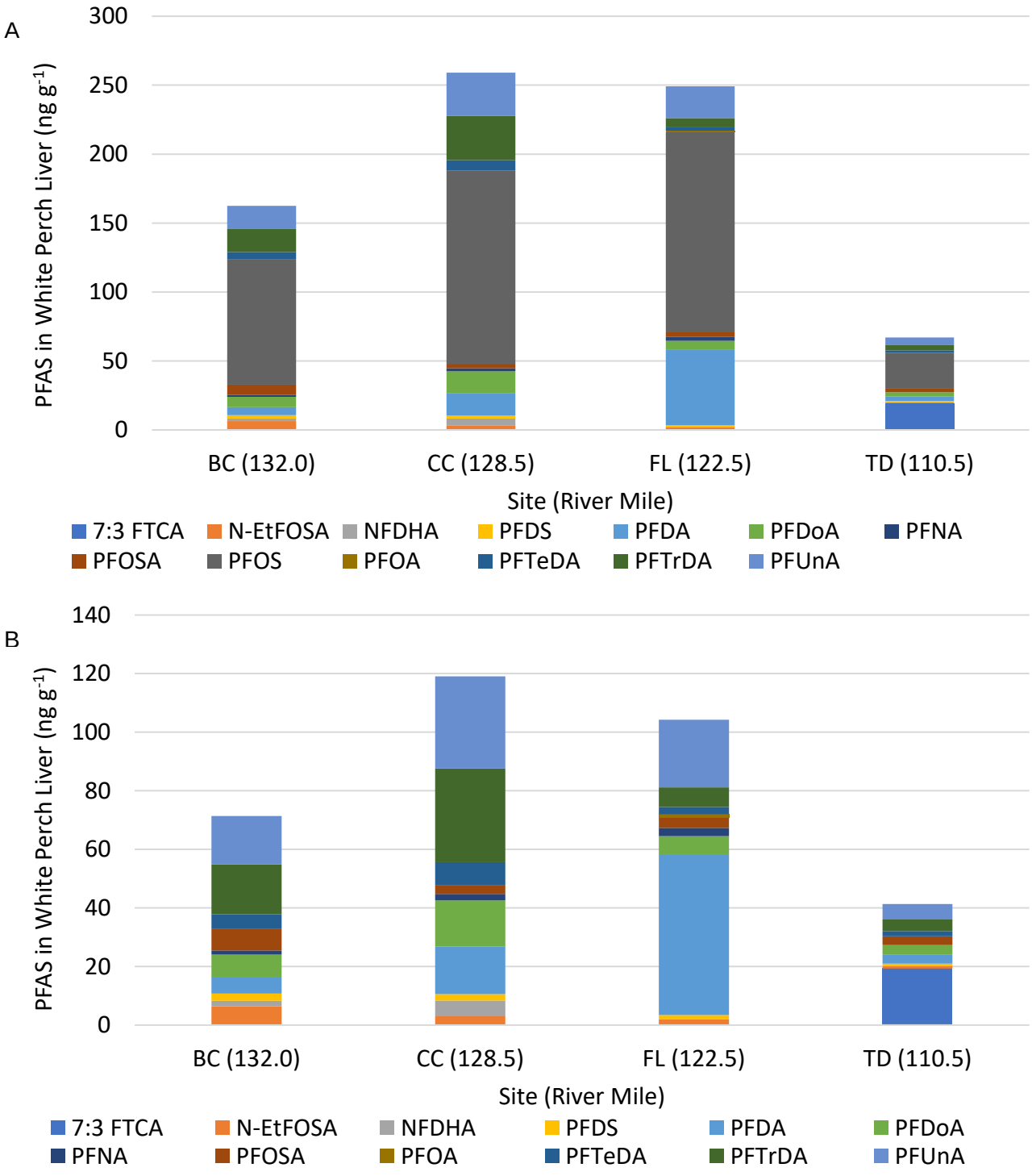

***Figure 12**. A) PFAS compounds quantified in white perch liver tissue at three tidal Delaware River sties. B) PFOS data was removed to better show the relative concentrations of the other quantified compounds in white perch liver tissue samples.*

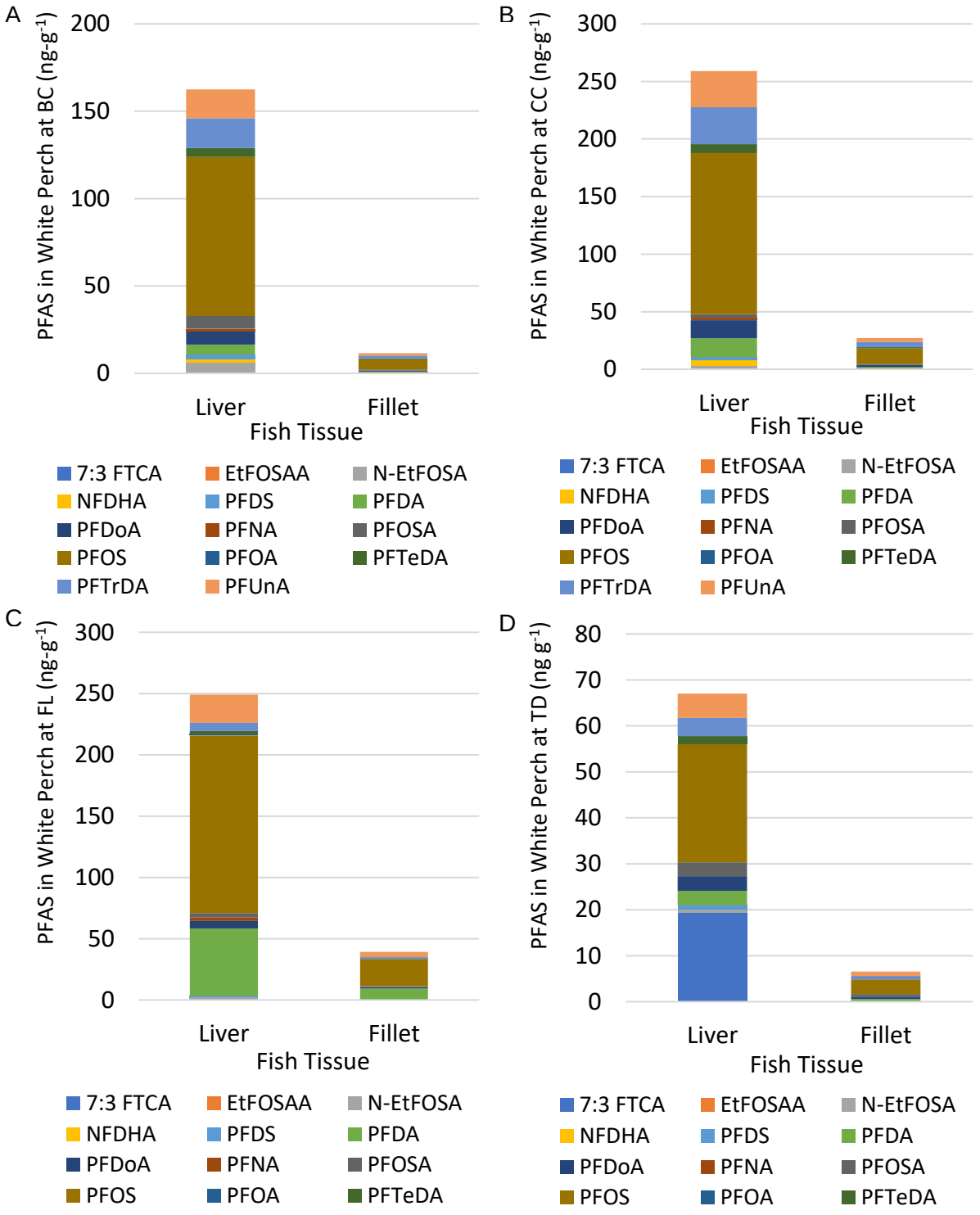

***Figure 13**. Comparisons of quantified PFAS in white perch liver and fillet tissues at A) BC, B) CC, C) FL and D) TD.*

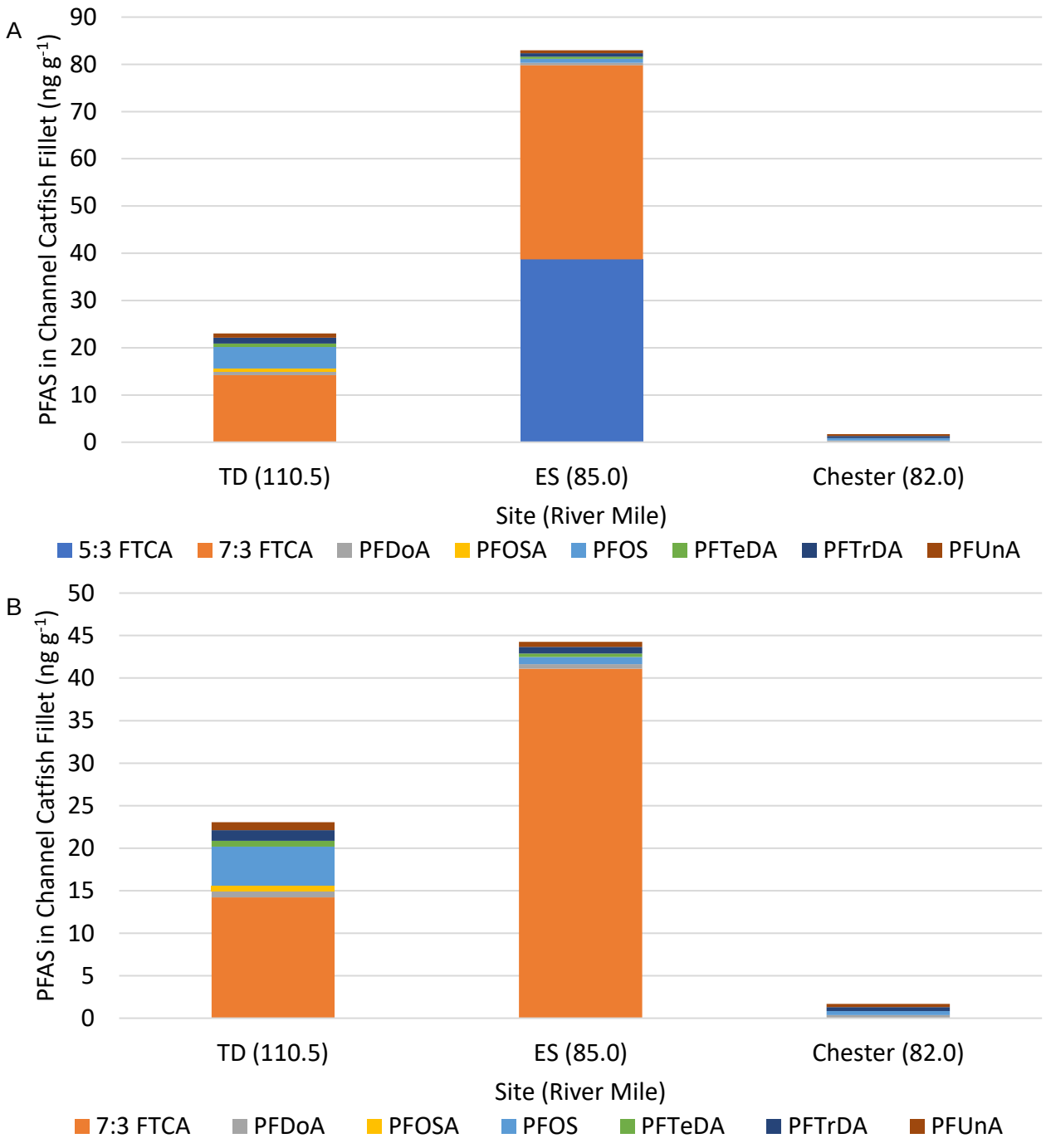

***Figure 14**. A) PFAS compounds quantified in channel catfish fillet tissue at three tidal Delaware River sties. B) PFOS data was removed to better show the relative concentrations of the other quantified compounds in channel catfish fillet tissue samples.*

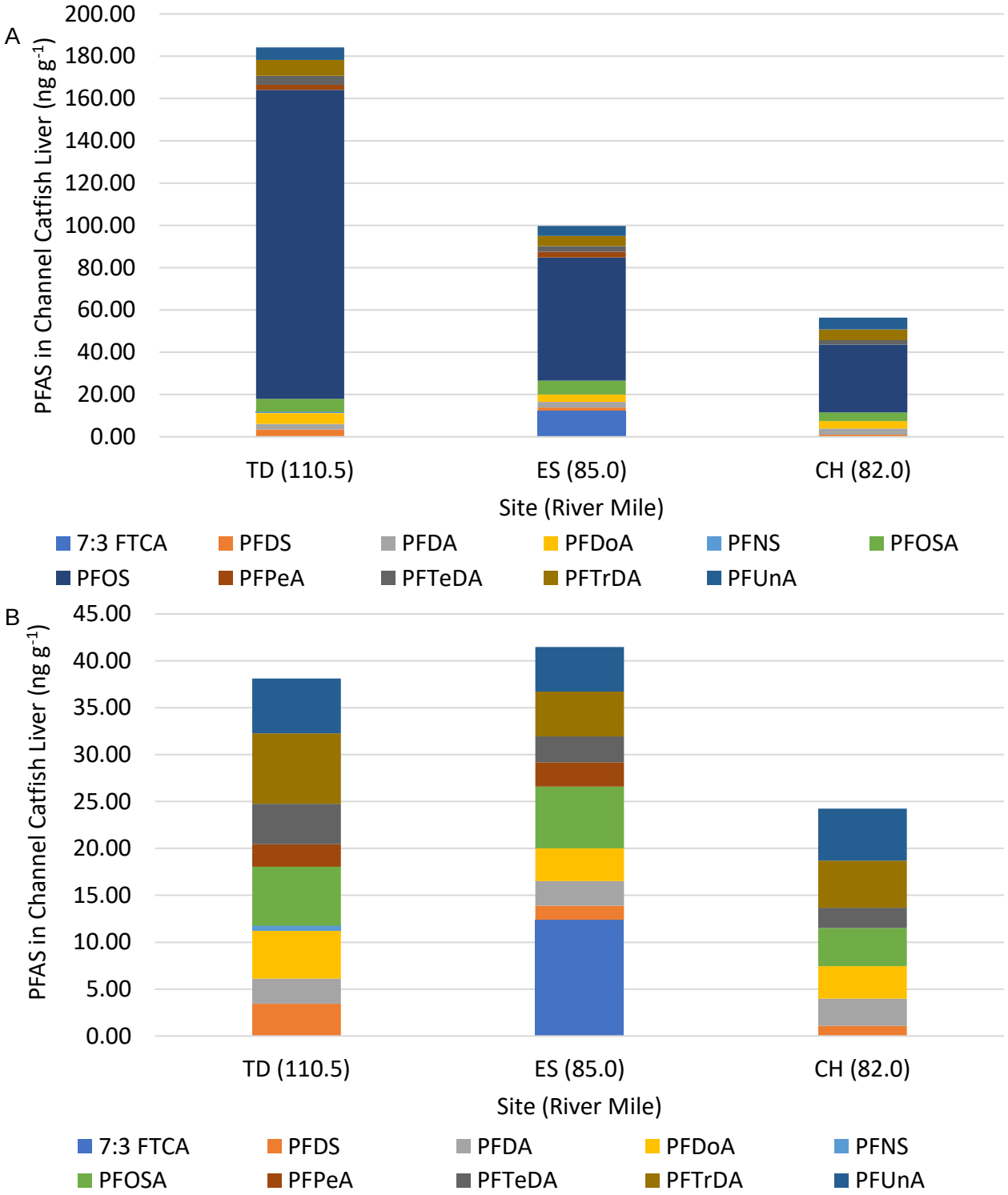

***Figure 15**. A) PFAS compounds quantified in channel catfish liver tissue at three tidal Delaware River sties. B) PFOS data was removed to better show the relative concentrations of the other quantified compounds in channel catfish liver tissue samples.*

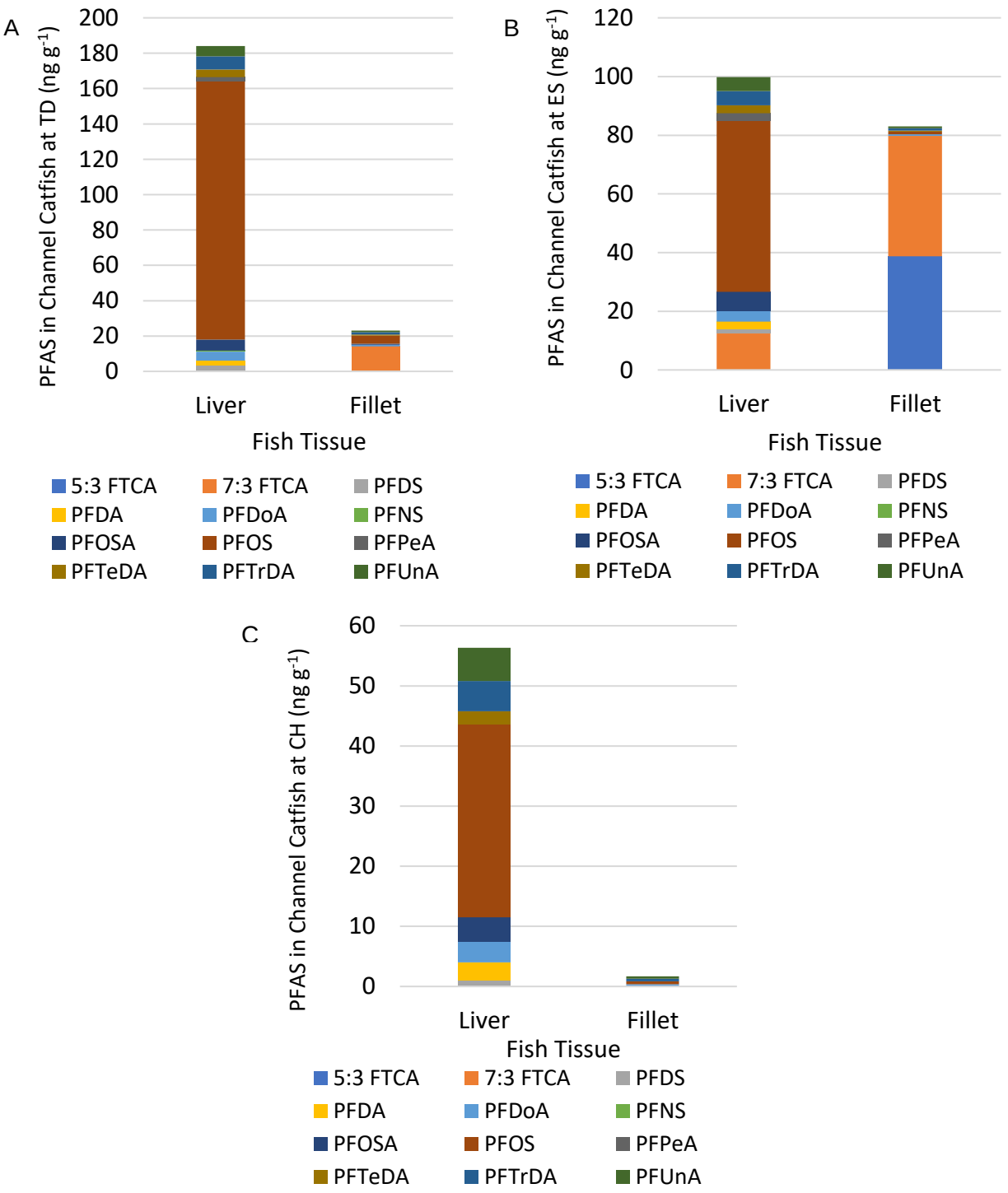

***Figure 16**. Comparisons of quantified PFAS in channel catfish liver and fillet tissues at A) TD, B) ES and C) CH.*

3.3.3 Fish Data Synthesis

Seven target PFAS analytes were found in >50% of all samples analyzed. PFOS was found in every sample (n=24) with an average concentration of 36.44 ± 48.28 ng g^{-1} and in three liver samples between 140.0 and 146.0 ng g^{-1}. However, the fillet average across all species and sites was 5.98 ± 6.76 ng g^{-1} and better reflects potential human exposure due to fish consumption. There was no difference between PFOS fillet concentrations at the non-tidal (6.07 ± 6.61) and tidal (5.93 ± 7.23) sites, although these sample sizes are relatively small. While there are no established toxicity thresholds for nearly all PFAS, PFOS does have a Chronic Reference Dose (RfD_C) of 0.02 µg kg^{-1} day^{-1} (USEPA 2016). This is the amount of a chemical a person can ingest daily, based on body weight, over a lifetime without considerable risk of adverse effects. Therefore, a 70 kg (154 lb) adult could consume 1.4 µg day^{-1} of PFOS throughout 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). Based on these parameters, the smallmouth bass fillet composite at Lackawaxen (3.56 µg per 8 oz fillet) and white perch at Crosswicks Creek (3.11 µg per 8 oz fillet) and Florence (4.94 µg per 8 oz fillet) exceeded the 1.4 µg day^{-1} RfD_c. The white perch at Biles Channel was also near the limit at 1.34 µg per 8 oz fillet. To reiterate, the EPA RfD_C is based on chronic effects with daily consumption over a lifetime.

PFUnA (perfluoroundecanoate) was the second most common target analyte found at 92% (22 of 24) of all samples. The two samples that did not include PFUnA were the fillet and liver of the white sucker from the Lackawaxen site. However, the smallmouth bass sampled at Lackawaxen did have PFUnA in both the liver and fillet. While prevalent in fish, its average concentration across all sites, species, and tissues was 6.27 ± 8.10 ng g^{-1}, with a max of 31.50 ng g^{-1}. PFDoA (perfluorododecanoate) was found in 79% (19 or 24) of all samples but 100% (16/16) of tidal samples. Four additional compounds were also quantified in >50% of samples, PFTrDA (perfluorotridecanoate; 75%), PFDA (perfluorodecanoate; 71%), PFTeDA (perfluorotetradecanoate; 63%) and PFOSA (perfluorooctane sulfonamide; 58%). All remaining target PFAS compounds quantified were found in ≤29% of samples.

Lastly, it is vital to acknowledge the relative scales of PFAS concentrations found in water, sediment, and fish. PFAS water concentrations are reported above as ng L^{-1} and sediment as ng kg^{-1}. However, fish and blue crab values are reported as ng g^{-1}. Therefore, water and sediment concentrations are reported in units with three orders of magnitude relative difference from that of fish and crabs. When converting the range of fish ΣPFAS concentrations across all sites,

species, and tissues from ng g^{-1} (1.7 to 259.1) to ng kg^{-1} (1,695 to 259,070), a similar magnitude as sediment and water, fish concentrations often greatly exceed most sediment (203 – 3,104 ng kg^{-1}) and all water (2 – 597 ng L^{-1}) samples in PFAS contamination. These higher concentrations are due to the bioaccumulative properties of PFAS.

3.3.4 Blue Crabs

Blue crabs were collected at one site, Pea Patch Island, in the fall of 2021 (Year 1) and 2022 (Year 2), with the detection of the same seven compounds each year (Figure 17). All blue crab concentrations are reported as wet weight. The ΣPFAS in 2021 (23 ng g^{-1}) was double the 2022 (11.8 ng g^{-1}) amount. Concentrations of the detected PFAS compounds ranged from 0.6 to 5.8 ng g^{-1}. Blue crab ΣPFAS concentrations (11,800 - 23,000 ng kg^{-1}) are higher than sediment concentrations (203 – 3,104 ng kg^{-1}).

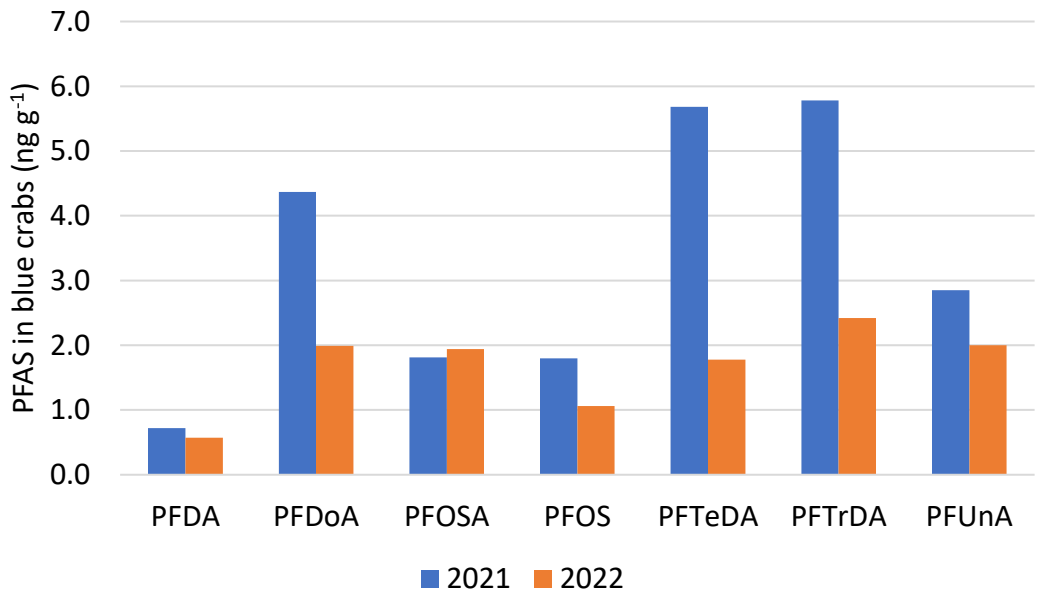

***Figure 17**. PFAS quantified in blue crabs (Callinectes sapidus) during sampling in Fall 2021 and 2022 just north of Pea Patch Island (river mile 62.5).*

4. CONCLUSIONS

PFAS is pervasive in the Delaware River mainstem and many of its tributaries, particularly in the tidal portion of the system. These pollutants were found in all sample matrixes – fish, crabs, and sediment – and in water examined by the Delaware River Basin Commission. Based on the results of the Year 1 and 2 studies, and a recently finished Pennsylvania Coastal Zone Management

program grant, DRBC has observed that PFAS water detections and concentrations generally increase with decreasing river mile. This means that as water flows from the non-tidal portion of the river above Trenton, through Philadelphia, and into Delaware, the number of targeted PFAS compounds detected and their concentrations increase. Trends were not as clear for PFAS detected in sediment and fish or crab tissues, although PFAS was prevalent in these matrixes. In this study, at least one of the targeted PFAS compounds was detected in 12 of 16 sediment samples (4.0 ± 1.5) and in every fish or crab sample (6.5 ± 3.1). Furthermore, PFOS was found in every fish or crab sample, with concentrations in fish exceeding the USEPA RfD_C at three sites. This implies that concentrations are currently near or above existing toxicity thresholds in some instances, although thresholds have not been established for the overwhelming majority of compounds classified as PFAS. In the future, DRBC will continue its monitoring of PFAS in the Delaware River Basin but will also make efforts to consolidate and synthesize all publicly available data from the system to better inform those efforts.

5. Environmental Data Sets

All data from this Year 2 study can be downloaded from the National Water Quality Monitoring Council's Water Quality Portal. The links below provide freely available access to this data. While all data from this study can be downloaded at the links below, there may also be additional PFAS data provided in these links from other studies conducted by DRBC.

Data Query:

https://www.waterqualitydata.us/#organization=DRBC&characteristicType=Organics%2C%20PFAS&characteristicType=PFAS%2CPerfluorinated%20Alkyl%20Substance&startDateLo=10-01-2021&startDateHi=10-01-2022&mimeType=csv&dataProfile=resultPhysChem&providers=NWIS&prov

Data Download:

https://www.waterqualitydata.us/data/Result/search?organization=DRBC&characteristicType=Organics%2C%20PFAS&characteristicType=PFAS%2CPerfluorinated%20Alkyl%20Substance&startDateLo=10-01-2021&startDateHi=10-01-2022&mimeType=csv&zip=yes&dataProfile=resultPh

REFERENCES

NJDOH, NJDEP. 2021. 2021 Fish Smart, Eat Smart: A guide to Health Advisories for Eating Fish and Crabs Caught in New Jersey Waters.

NYSDEC. 2022. Sampling, analysis, and assessment of per and polyfluoroalkyl substances (PFAS).

Robuck, A., S. Valsecchi, J. McCord, and others. 2023. Environmental distribution and bioaccumulation of understudied PFAS surrounding two fluoropolymer manufacturing sites in Italy and the United States. Proceedings of the SETAC Europe.

USEPA. 2016. Health Effects Support Document for Perfluorooctane Sulfonate (PFOS). EPA 822R16002. EPA 822R16002.

USEPA. 2023. CompTox Chemicals Dashboard.