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PFAS Water Quality and Fish Tissue Assessment Study - Year 3

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PFAS Water Quality and Fish Tissue Assessment Study – Year 3

This project was conceived by Ron Macgillivray, Senior Toxicologist at the Delaware River Basin Commission (DRBC), prior to his retirement. It was overseen, carried out, and written by Jeremy Landon Conkle, Ph.D., Senior Chemist/Toxicologist at DRBC, with the assistance of Senior Water Resource Scientist Elaine Panuccio, Senior Aquatic Biologist Jake Bransky, and interns Bailey Adams and Kyle McAllister.

Acknowledgements and Disclaimers

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EXECUTIVE SUMMARY

The Delaware River Basin Commission (DRBC) conducted a three-year assessment of per- and polyfluoroalkyl substances (PFAS) in surface water, sediment, and aquatic biota of the Delaware River mainstem and selected tributaries. The work was funded in part by grants from the U.S. Fish and Wildlife Service through the National Fish and Wildlife Foundation's Delaware Watershed Conservation Fund. This Year 3 report (2023 sampling) complements findings from Year 1 (2021) and Year 2 (2022), providing critical data on PFAS occurrence and distribution in surface water, sediment, fish tissues, and blue crabs across the Delaware River mainstem and selected tributaries.

Study Design: In summer 2023, DRBC sampled 16 sites along the Delaware River (four non-tidal and 11 tidal mainstem sites, plus the Schuylkill River tributary). Samples included surface water, sediment, four fish species (white sucker, smallmouth bass, white perch, and channel catfish), and blue crabs. Additionally, passive samplers (POCIS) were deployed at seven sites to capture time-weighted average PFAS concentrations over 28 days. All samples were analyzed for 40 PFAS compounds using the United States Environmental Protection Agency (EPA) Method 1633, though this represents only a small fraction of the more than 14,000 known PFAS chemicals.

Surface Water and Passive Sampling: PFAS were detected in surface water grab samples at 15 of 16 sites, with 1 to 8 compounds detected per site (5.1 average). Summed PFAS (Σ_{PFAS}) in surface water increased downstream, from 0.94 ng L^{-1} at Lackawaxen to 48.61 ng L^{-1} at Pea Patch Island. Despite a 13-fold increase in river volume between Biles Channel and Pea Patch Island, PFAS mass per one-mile river parcels of water rose from <0.05 kg to 1.55 kg, indicating ongoing inputs along this tidal reach. In particular, the large increase of PFHxA and PFPeA between Chester, PA and Pea Patch Island, DE suggests PFAS sources south of Chester. Furthermore, Pea Patch Island was the only site sampled in each of the three years, and it had similar PFAS concentrations, including PFHxA and PFPeA, indicating that the levels seen in these samples from 2023 were persistent in recent years.

POCIS passive samplers detected 14 compounds (vs. 8 in grab samples) and, on average, more compounds per site (8.1 vs. 5.1), demonstrating better sensitivity, especially for low-level and less frequently observed compounds. POCIS identified PFHpS, which was not previously detected in mainstem Delaware Estuary samples, demonstrating the value of this complementary monitoring approach. Estimated PFAS concentrations from POCIS were generally of the same order of magnitude as grab samples but tended to be higher.

Sediment: In 2023, PFAS were detected in surface sediments at 7 of 16 sites, fewer than in Year 2 (12 of 16). The highest Σ_{PFAS} concentration (15.4 µg kg^{-1}) was recorded at the Philadelphia Airport site, driven primarily by EtFOSAA at 11.6 µg kg^{-1}. This represents the highest sediment PFAS concentration ever recorded in the Delaware River mainstem. However, a sample collected at the same site just 28 days later had a much lower concentration (0.82 µg kg^{-1}), highlighting the challenge of obtaining representative sediment samples and the heterogeneous nature of PFAS in subtidal surface sediments. Lastly, cursory evidence suggests that samples collected from embayments or side channels may accumulate more PFAS than those from the main channel.

Fish and Blue Crabs: PFAS were detected in all fish samples across all four species and 10 sites. A consistent suite of seven compounds (PFDA, PFDoA, PFOS, PFOSA, PFTeDA, PFTrDA, and PFUnA) was detected in white perch at all six tidal sites, matching patterns observed in previous DRBC studies. PFOS dominated fish tissue concentrations, accounting for 36–78% of total quantifiable PFAS. White perch and smallmouth bass had higher average PFOS concentrations (8.11 and 8.00 ng g^{-1}, respectively) compared to channel catfish (1.21 ng g^{-1}) and white sucker (2.75 ng g^{-1}).

Blue crabs were collected at Pea Patch Island in 2021, 2022, and 2023. Across all three years, a consistent suite of seven PFAS compounds was observed, with Σ_{PFAS} of 11.8, 23.0, and 15.2 ng g^{-1} (mean 16.7 ± 5.8 ng g^{-1}). Concentrations of individual compounds ranged from 0.6 to 5.8 ng g^{-1}. PFOS was present but not dominant while PFTrDA and PFTeDA were the most abundant compounds.

Fish Consumption and Human Exposure: Based on the EPA's Chronic Reference Dose (RfD_C) for PFOS of 0.02 µg kg^{-1} day^{-1} and an 8 oz serving size, several fish samples exceeded the threshold for a 70 kg adult (1.4 µg day^{-1}). Smallmouth bass from both Sandts Eddy and Yardley exceeded the threshold, as did white perch from four of six sites (Biles Channel, Florence, Torresdale, and Schuylkill River). However, the RfD_C is based on daily consumption over a lifetime, and most people do not consume locally caught fish daily. New Jersey currently has fish consumption advisories in place that recommend limiting consumption of these species, although the advisories vary by location and do not specifically address PFOS pollution at any particular location.

Cross-Matrix PFAS Presence: An integrated review of PFAS presence across water, sediment, fish, and crabs shows compound-specific behavior consistent with known physicochemical properties. For example, compounds with higher organic carbon partitioning coefficients (Log K_{OC}) and lower solubility were mostly found in sediment or biota. Whereas lower Log K_{OC} and higher solubility were found predominantly in water. This underscores the importance of multi-matrix sampling to ensure that studies capture the broadest suite of PFAS present at each site.

Key Findings and Implications: This three-year study conclusively demonstrates that PFAS contamination is widespread and persistent in the Delaware River Basin, particularly in tidal waters. Specifically:

1. PFAS concentrations and mass loads increase substantially as water flows downstream, with evidence of significant inputs from currently unidentified sources south of Chester, PA.
2. Sediments and biota act as PFAS sinks but are highly variable. Spatial and temporal heterogeneity—especially in subtidal surface sediments—complicates efforts to define representative concentrations and highlights the need for carefully designed sampling strategies.
3. PFOS is ubiquitous in fish and crabs and often dominant in fish. Some fillet PFOS concentrations, when evaluated against the current RfD_C, suggest that regular consumption at standard serving sizes could pose long-term exposure concerns. However, view state advisories for consumption guidance.
4. Passive samplers can enhance compound detection. POCIS improved the detection of low-level and otherwise undetected PFAS compared to grab samples and provided time-weighted concentration estimates, making them a potentially valuable complement to traditional monitoring.
5. Analytical and toxicological limitations constrain full risk assessment. Current analytical methods detect only 40 of more than 14,000 known PFAS compounds, meaning the full extent of contamination remains unknown. Additionally, health-based thresholds exist for only a few compounds. These constraints limit DRBC's ability to fully quantify risk and guide management.

All PFAS data, past and present, generated by DRBC on PFAS is publicly available in the Water Quality Portal, with links for this project's dataset provided at the end of this report. DRBC will continue to assess PFAS through monitoring, trend analysis, and source identification to reduce their presence and impacts in the Delaware River Basin.

LIST OF ACRONYMS/ABBREVIATIONS

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
EPA	United States Environmental Protection Agency
FWS	United States Fish and Wildlife Service
g	Grams
HDPE	High-density polyethylene
HLB	Hydrophobic lipophilic balance
kg	Kilograms
L^{-1}	Per liter
LC-MS/MS	Triple Quadrupole Liquid Chromatography
Log K_{OC}	Organic carbon soil partitioning coefficient
µg	Micrograms
mL	Milliliters
mm	Millimeters
ng	Nanograms
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
oz	ounce
PA	Pennsylvania
PACZM	Pennsylvania Coastal Zone Management
PFAS	Per and polyfluoroalkyl substances
PFBC	Pennsylvania Fish and Boat Commission
POCIS	Polar organic compound integrative sampler
PPCPs	Pharmaceuticals and personal care products
PFAS	Per- and polyfluoroalkyl substances
RfD_C	Chronic Reference Dose
SPE	Solid phase extraction
Σ_{PFAS}	Summed PFAS

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1. INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) constitute a diverse group of >14,000 human-made chemicals with unique properties, including water- and grease-resistance and thermal stability.[1] Widespread in consumer and industrial products such as non-stick cookware, aqueous film-forming foams (AFFF), and water-resistant textiles, PFAS are silently present in our day-to-day lives. However, their ubiquity and persistence, coupled with a growing body of toxicological data, threaten human health and the environment. PFAS are characterized by strong carbon-fluorine bonds, rendering them resistant to degradation and resulting in indefinite environmental persistence. As research progresses, understanding of PFAS and their impact on ecosystems and human health continues to evolve, rightly leading to more scrutiny and efforts to mitigate their use and release into the environment.

The Delaware River Basin Commission (DRBC) conducts ongoing research and activities across various areas to support water resource management, including protecting drinking water quality 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. This work builds on those efforts.

With this report, DRBC concludes a three-year survey of PFAS in water, sediment, and fish tissues of the Delaware River. This work was supported in part by three grants from the U.S. Fish and Wildlife Service (FWS) through the National Fish and Wildlife Foundation (NFWF) Delaware Watershed Conservation Fund (DWCF). For the Year 1 report, data collected in 2021 were published in July 2023 (NFWF grant number 0403.20.068693).[2] In Year 2 (NFWF grant number 0403.21.072417), DRBC collected PFAS occurrence data in sediment and water along 215 miles of the mainstem Delaware River and one tributary in 2022. Additionally, fish were collected at three non-tidal and six tidal sites, while blue crabs were sampled near Pea Patch Island, Delaware. The Year 2 report was published in March 2024.[3] The Year 2 sampling design was replicated for this third-year study, and samples were collected in the summer of 2023. This Year 3 report was supported by the NFWF grant number 0403.22.075117.

2. SAMPLING AND ANALYSIS

2.1 SURFACE WATER SAMPLING

Surface water samples for PFAS analysis (Table 1 and Figure 1) were collected in August and September 2023, and estuary samples were collected at or near low tide. Sample collection followed the New York State Department of Environmental Conservation (NYSDEC) methods for PFAS sampling.[4] 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 likelihood of detecting PFAS. Therefore, 1 L water samples were collected in high-density polyethylene (HDPE) bottles at Lackawaxen, Dingmans Ferry, Sandts Eddy, and Yardley, Pennsylvania (PA). All other water samples were collected in 0.5 L HDPE bottles. Each water sample was collected in duplicate, with the second serving as a lab backup in the event of problems with the initial extraction and analysis. All samples were collected directly into the laboratory container by submerging it 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 analysis. DRBC contracted analysis with SGS AXYS, which 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 samples were collected in August and September 2023 (Table 1 and Figure 1) and followed NYSDEC methods for PFAS sampling.[4] Sediment samples were collected with a stainless-steel spoon, transferred to a large stainless-steel bowl, and homogenized with another spoon. Subsamples were then placed in 250 mL HDPE jars for PFAS analysis. 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. The sampling equipment was decontaminated with an Alconox cleaning solution, followed by a deionized water (DI) rinse. To generate equipment blanks, PFAS-free water was poured over the sampling equipment into a 250 mL HDPE jar.

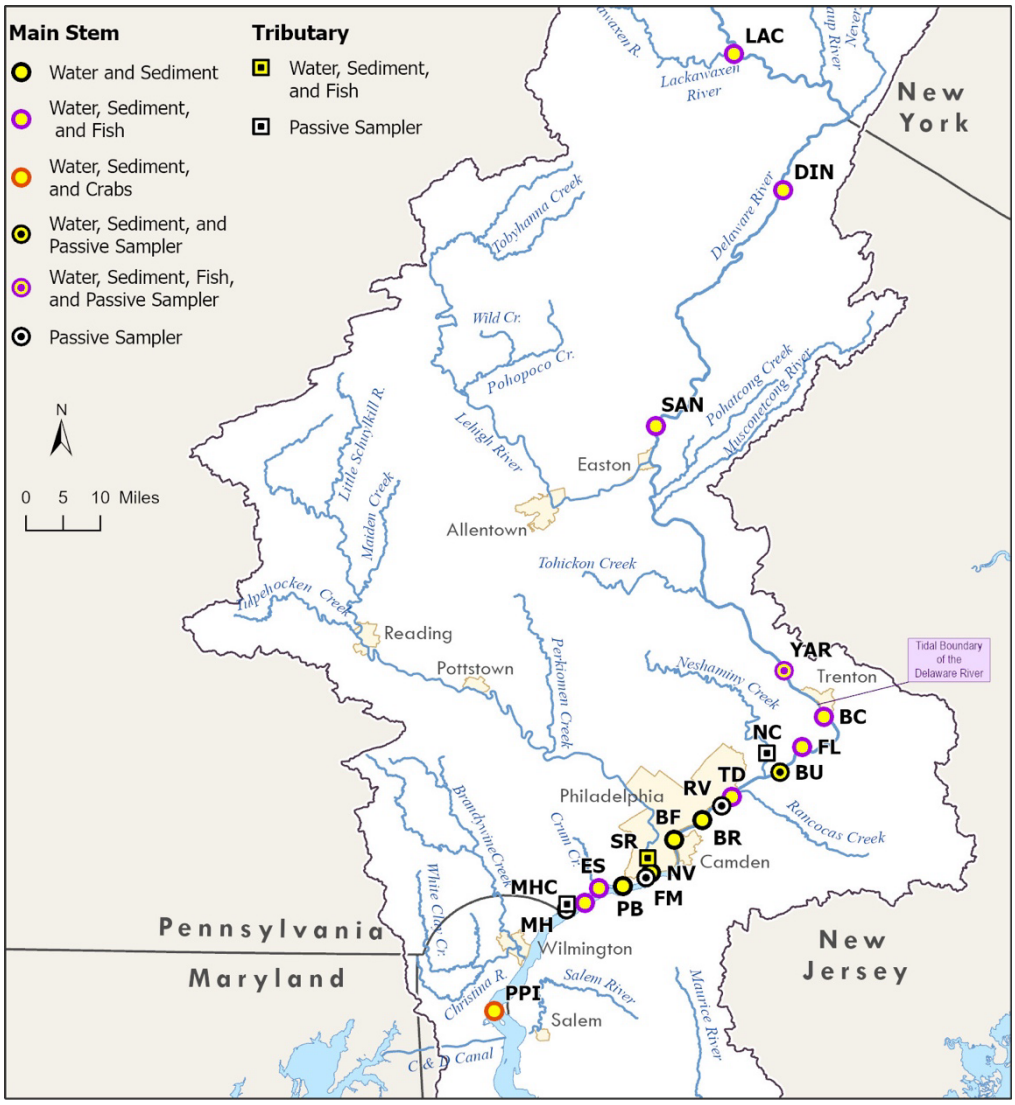

Figure 1. *Water, sediment, and fish sampling locations in the Delaware River and its tributaries.*

Table 1. *List of water, sediment, fish, and crab sampling sites from 2023.*

Name	ID	River Mile	Latitude	Longitude	River Zone	Sediment & Water	Fish & Crabs	Passive Sampler
Non-tidal mainstem								
Lackawaxen, PA	LAC	277	41.4859	-74.9864	1B	Y	SMB, WS	
Dingmans Ferry, PA	DIN	239	41.2195	-74.8600	1C	Y	SMB, WS	
Sandts Eddy, PA	SAN	189	40.7582	-75.1880	1D	Y	SMB, WS	
Yardley, PA	YAR	139.5	40.2795	-74.8593	1E	Y	SMB, WS	Y
Tidal mainstem								
Biles Channel	BC	132	40.1898	-74.7585	2	Y	CC, WP	
Florence	FL	122.5	40.1309	-74.8134	2	Y	CC, WP	
Burlington Bristol Bridge	BU	117.5	40.0811	-74.8700	2	Y		Y
Torresdale	TD	110.5	40.0328	-74.9922	2	Y	CC, WP	
Riverton Yacht Club	RV	108.5	40.0153	-75.0183	2			Y
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		
Fort Mifflin	FM	91.5	39.8748	-75.2103	4			Y
Philadelphia Airport	PB	90.5	39.8584	-75.2687	4	Y		
Eddystone	ES	85	39.8543	-75.3290	4	Y	CC, WP	
Chester	CH	82	39.8250	-75.3646	4	Y	CC, WP	
Marcus Hook	MH	79	39.8116	-75.4115	4			Y
Pea Patch Island	PPI	62.5	39.6126	-75.5931	5	Y	BC	
Tidal tributary								
Neshaminy Creek	NC		40.1186	-74.9034				Y
Schuylkill River	SR		39.9131	-75.2059		Y	CC, WP	
Marcus Hook Creek	MHC		39.8227	-75.4101				Y

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

2.3 Fish and Crab Sampling

Fish collections followed protocols issued by the NYSDEC.[4] Two tidal species, white perch (*Morone americana*) and channel catfish (*Ictalurus punctatus*), were collected by hook and line in May 2023 from the six sites 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 from July to October 2023 at the four sites 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 in a single bag. Fish samples were stored frozen (-20 ˚C) before shipping and processing in the analytical laboratory. Fillets for white perch, white sucker, and smallmouth bass included the skin but no scales. Channel catfish fillets were not analyzed with their skin. A composite of fillets for each species from fish of similar length and weight at each location was prepared in the laboratory.

Figure 2*. Collecting crabs near Pea Patch Island using a trotline with chicken necks as bait.*

Blue crabs (*Callinectes sapidus*) were collected only at Pea Patch Island using a trotline (Figure 2) in September 2023. The trotline consists of evenly spaced bait (chicken necks) that runs between two buoys and lies on the river bottom. 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 cling to the bait and reach the water surface before letting go and being captured by a net. Only crabs >5” (127 mm) carapace width were kept for analysis, as required by local fishing regulations.

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 in a single bag. Blue crab samples were stored frozen (-20 ˚C) before shipping and processing in the analytical laboratory. In the lab, blue crab muscle samples were removed from the base of the legs and the cheliped, taking care not to contaminate the samples with internal organs or the hepatopancreas. The crabs were then composited and homogenized.

2.4 PFAS Passive Sampling

One-time water grab samples provide a snapshot of aqueous PFAS concentrations. This snapshot may or may not represent typical PFAS concentrations at that site. POCIS (Polar organic chemical integrative samplers) are passive samplers that enable the determination of time-weighted average PFAS concentrations over their deployment period. Each sampler consists of a solid-phase sorbent (Oasis HLB) trapped between two polyethersulfone membranes

***Figure 3**. A) POCIS membrane triplicate resting inside of a stainless-steel canister prior to deployment. B) Closed sampler canister prior to deployment.*

that allow water to flow freely in and out. The samplers are mounted in triplicate on stainless-steel rings and housed within a stainless-steel container for protection when deployed (Figure 3). POCIS samplers were deployed at seven sites (Figure 1, Table 1), although the sampler at the Marcus Hook site in the mainstem was lost, resulting in no data for that site. Of the six surviving samplers, four (Yardley, Burlington, Riverton, and Fort Mifflin) were in the mainstem Delaware River, while the Neshaminy Creek and Marcus Hook Creek sites were in tidally influenced tributaries. The samplers were deployed on July 26, 2023, and retrieved on August 23, 2023, after 28 days. SGS AXYS extracted and analyzed the solid-phase material from the POCIS samplers using Method MLA-110 (equivalent to Draft USEPA Method 1633) for 40 PFAS analytes. Results were reported to DRBC as the mass of the target analyte per gram of sorbent (ng g^{-1}). The reported concentrations of PFAS can be compared across sites to assess relative PFAS concentrations over the 28-day deployment. However, Equation 1 can be used to calculate PFAS concentrations in water ($\boldsymbol{C_w}$, ng L^{-1}) by dividing the reported concentration ($\boldsymbol{N_{POCIS}}$, ng) by the sampling rate ($\boldsymbol{R_s}$, L d^{-1}) and deployment length ($\boldsymbol{t}$, days).[5] The sampling rate is an empirically derived value and has not been determined for four of the 14 PFAS compounds quantified with the POCIS samplers. These are EtFOSAA, PFBA, PFOSA, and PFUnA. Therefore, the

discussion of POCIS results will include both the measured amounts of the target analyte on the samplers and, where possible, the estimated concentrations in water.

Equation 1. $$C_w = \frac{N_{POCIS}}{R_s t}$$

Numerous sampling rates have been reported in the peer-reviewed literature for compounds detected by POCIS samplers. However, it is important to select values from studies that used the same sorbent material (Oasis HLB) and had a similar deployment time (28 days) and water flow conditions. Based on comparisons of published studies' sampling rates, the closest matches to this study were Gobelius et al. (2019) and Barber et al. (2023), which were used to convert POCIS sampler data to PFAS water concentrations where appropriate.[6,7]

2.5 Sample Extraction and Analysis

Samples were processed and analyzed by the subcontracted laboratory SGS AXYS using Method MLA-110 (equivalent to Draft EPA Method 1633) for 40 PFAS analytes (Table 2) out of the >14,000 chemicals in this class.[1] 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) with a 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 and combining the supernatants. Tissue samples (up to 2 g wet weight) were extracted with methanolic potassium hydroxide, followed by acetonitrile and methanolic potassium hydroxide, with the supernatants combined. Sediment and fish tissue extracts were treated with ultra-pure carbon powder, evaporated to remove methanol, and diluted with water. The extract was then cleaned by SPE with a weak anion-exchange sorbent. The eluate was spiked with recovery standards and analyzed by LC-MS/MS. Final sample concentrations were determined by isotope dilution/internal standard quantification.

The results for sediment and water contained no field, equipment or lab blank contamination. There was lab blank contamination for N-EtFOSE in fish tissues. This compound was detected in only one catfish sample, as discussed in detail below.

2.6 Data Limitations and Interpretations

This experimental design, which involves a single sampling of sediment and water at each site, provides a snapshot of concentrations at that moment and may not accurately reflect long-term concentrations. This is particularly true for water samples, which can be highly variable over both

short and long periods. While this design limits DRBC's ability to interpret results broadly, it was implemented with the knowledge that data from the previous two years of this study would provide additional context. Therefore, below we present data from Year 3 and, where possible, compare them with the results from the previous 2 years.

To provide context for PFAS water concentrations, the mass of PFAS compounds in a 1-mile parcel of river water at the river mile of each sampling site from Biles Channel to Pea Patch Island was estimated. The Schuylkill River site was excluded because it is located in a tributary. Water volume estimates were previously determined by DRBC using simulated, tidally averaged, along-river water-surface elevation data coupled with bathymetry data.[8] Then, the concentrations of PFAS measured at each site were used with the volume data for a 1-mile parcel of river water to estimate the mass of each compound within that parcel.

When viewing and interpreting the PFAS mass values, important factors and limitations must be considered. First, these estimates are based on the estimated, tidally averaged water volumes in the mainstem Delaware River at only the 11 tidal sites from Biles Channel to Pea Patch Island. Therefore, the calculated mass values are at best rough estimates. However, the relative magnitudes of PFAS mass at each site provide a snapshot of the estimated mass in the river for a 1-mile parcel of water at each site. Additionally, the conversion from concentration (ng L^{-1}) to mass (kg) assumes that concentrations are homogeneous throughout the 1-mile parcel of water. While homogeneity is highly unlikely, the rough estimate provides valuable information on the PFAS mass load in the Delaware River.

Lastly, the state-of-the-art analytical method for PFAS analysis is EPA Method 1633. This method is an improvement over previous methods, but it is currently limited to 40 compounds out of >14,000 identified by the EPA.[1] Therefore, it is possible and likely that there are more PFAS compounds in the samples collected that were not identified due to analytical limitations.

Table 2. *Targeted PFAS analytes.*

Analyte		Group		CAS #
Full Name	**Abbreviation**	**Full Name**	**Abbreviation**	
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (*replacement*)	11Cl-PF3OUdS	Ether Sulfonic Acids	ESA	2196242-82-5
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (*replacement*)	9Cl-PF3ONS	Ether Sulfonic Acids	ESA	1621485-21-9
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	Ether Sulfonic Acids	ESA	113507-82-7
2H,2H,3H,3H-Perfluorooctanoate (*precursor*)	5:3 FTCA	Fluorotelomer Carboxylic Acids	FTCA	1799325-94-2
4,4,5,5,6,6,6-Heptafluorohexanoate (*precursor*)	3:3 FTCA	Fluorotelomer Carboxylic Acids	FTCA	1169706-83-5
4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluorodec-2-enoic acid (*precursor*)	7:3 FTCA	Fluorotelomer Carboxylic Acids	FTCA	755-03-3
4:2 fluorotelomersulfonic acid (*precursor*)	4:2 FTS	Fluorotelomer Sulfonic Acids	FTSA	414911-30-1
6:2 fluorotelomersulfonic acid (*precursor*)	6:2 FTS	Fluorotelomer Sulfonic Acids	FTSA	425670-75-3
8:2 fluorotelomersulfonic acid (*precursor*)	8:2 FTS	Fluorotelomer Sulfonic Acids	FTSA	481071-78-7
4,8-dioxa-3H-perfluorononanoate (*replacement*)	ADONA	Per- and Polyfluoroether Carboxylic Acids	PFECA	2127366-90-7
Hexafluoropropylene oxide dimer acid (*replacement*)	HFPO-DA	Per- and Polyfluoroether Carboxylic Acids	PFECA	13252-13-6
Perfluoro(4-methoxybutanoic) acid	PFMBA	Per- and Polyfluoroether Carboxylic Acids	PFECA	863090-89-5
Perfluoro-3-methoxypropanoic acid	PFMPA	Perfluoroalkyl Carboxylic Acids	PFCA	377-73-1
Perfluoro-3,6-dioxaheptanoic acid	NFDHA	Perfluoroalkyl Carboxylic Acids	PFCA	151772-58-6
Perfluorobutanoate	PFBA	Perfluoroalkyl Carboxylic Acids	PFCA	45048-62-2
Perfluorodecanoate	PFDA	Perfluoroalkyl Carboxylic Acids	PFCA	73829-36-4
Perfluorododecanoate	PFDoA	Perfluoroalkyl Carboxylic Acids	PFCA	171978-95-3
Perfluoroheptanoate	PFHpA	Perfluoroalkyl Carboxylic Acids	PFCA	120885-29-2
Perfluorohexanoate	PFHxA	Perfluoroalkyl Carboxylic Acids	PFCA	92612-52-7
Perfluorononanoate	PFNA	Perfluoroalkyl Carboxylic Acids	PFCA	72007-68-2
Perfluorooctanoic acid	PFOA	Perfluoroalkyl Carboxylic Acids	PFCA	45285-51-6
Perfluoropentanoate	PFPeA	Perfluoroalkyl Carboxylic Acids	PFCA	45167-47-3
Perfluorotetradecanoate	PFTeDA	Perfluoroalkyl Carboxylic Acids	PFCA	365971-87-5

Perfluorotridecanoate	PFTrDA	Perfluoroalkyl Carboxylic Acids	PFCA	862374-87-6
Perfluoroundecanoate	PFUnA	Perfluoroalkyl Carboxylic Acids	PFCA	196859-54-8
Perfluorobutanesulfonate	PFBS	Perfluoroalkyl Sulfonic Acids	PFSA	45187-15-3
Perfluorodecanesulfonate	PFDS	Perfluoroalkyl Sulfonic Acids	PFSA	126105-34-8
Perfluorododecanesulfonate	PFDoS	Perfluoroalkyl Sulfonic Acids	PFSA	343629-43-6
Perfluoroheptanesulfonate	PFHpS	Perfluoroalkyl Sulfonic Acids	PFSA	146689-46-5
Perfluorohexanesulfonic acid	PFHxS	Perfluoroalkyl Sulfonic Acids	PFSA	108427-53-8
Perfluorononanesulfonate	PFNS	Perfluoroalkyl Sulfonic Acids	PFSA	68259-12-1
Perfluorooctanesulfonate	PFOS	Perfluoroalkyl Sulfonic Acids	PFSA	45298-90-6
Perfluoropentanesulfonate	PFPeS	Perfluoroalkyl Sulfonic Acids	PFSA	175905-36-9
N-Ethyl perfluorooctane sulfonamido ethanol (*precursor*)	N-EtFOSE	Perfluorooctane Sulfonamide Ethanols	FOSE	1691-99-2
N-Methylperfluorooctane sulfonamido ethanol (*precursor*)	N-MeFOSE	Perfluorooctane Sulfonamide Ethanols	FOSE	24448-09-7
N-Ethylperfluorooctane-1-sulfonamide (*precursor*)	N-EtFOSA	Perfluorooctane Sulfonamides	FOSA	4151-50-2
N-Methyl perfluorooctane sulfonamide (*precursor*)	N-MeFOSA	Perfluorooctane Sulfonamides	FOSA	31506-32-8
Perfluorooctanesulfonamide (*precursor*)	PFOSA	Perfluorooctane Sulfonamides	FOSA	754-91-6
N-ethyl perfluorooctanesulfonamidoacetic acid (*precursor*)	EtFOSAA	Perfluorooctane Sulfonamidoacetic Acids	FOSAA	2991-50-6
N-methyl perfluorooctanesulfonamidoacetic acid (*precursor*)	MeFOSAA	Perfluorooctane Sulfonamidoacetic Acids	FOSAA	2355-31-9

3. RESULTS AND DISCUSSION

3.1 WATER

3.1.1 Grab Samples

Sixteen sites were sampled for PFAS in summer 2023. All but one (Schuylkill River) 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 15 of the 16 sites. Dingmans Ferry was the only site where none of the 40 EPA Method 1633 PFAS compounds were detected. When detections occurred, they ranged from 1 to 8 compounds, with an average of 5.1 ± 2.3 compounds per sample. The Navy Yard led all sites with 8 detections, but five other sites had 7 compounds quantified above detection limits. These sites with ≥7 compounds were sequential, starting at the Navy Yard and flowing downstream to Pea Patch Island. This group also includes the Schuylkill River, which discharges into the Delaware River at the Navy Yard site.

Summed PFAS (Σ_{PFAS}) is the sum of all quantifiable EPA Method 1633 PFAS compounds in a single sample. Σ_{PFAS} is used rather than total PFAS because Method 1633 includes only 40 out of >14,000 PFAS compounds identified by the EPA.[1] The Σ_{PFAS} at sites with at least one detection ranged from 0.94 ng L^{-1} at the site furthest upstream, Lackawaxen, to 48.61 ng L^{-1} at the furthest downstream site, Pea Patch Island (Figure 4A). With the exception of a spike at the Navy Yard site, there is a general increase in PFAS concentrations as river miles decrease (e.g., water moves downstream). The spike at the Navy Yard site is likely influenced by the Schuylkill River, given that this water sample was collected at the surface near the mouth of the Schuylkill River, one hour before low tide. That collection context, coupled with the Schuylkill River sample result, which is similar to the Navy Yard sample, supports that conclusion.

To examine PFAS levels from an alternate angle, the tidally averaged water volume per river mile was used to estimate mass loads of each compound at the sampling sites. The Delaware River mainstem water volume is 13 times greater at Pea Patch Island (31,898,639 m^3) than upstream at Biles Channel (2,364,121 m^3).[8] Because concentrations increase as water flows downstream despite the large increase in volume along that stretch of the river, the total mass of PFAS compounds increases at a higher rate than the water volume. This implies PFAS compounds are being released into this section of the river faster than they are being diluted, likely due to point and nonpoint PFAS sources. The estimated PFAS mass per river mile increases exponentially (Figure 4B), from <0.05kg at Biles Channel (river mile 132) to 1.55 kg at Pea Patch Island (river mile 62). The greatest increase in PFAS mass occurs in the 20-mile stretch from Chester to Pea Patch Island, where river volume doubles and the estimated PFAS mass roughly triples.

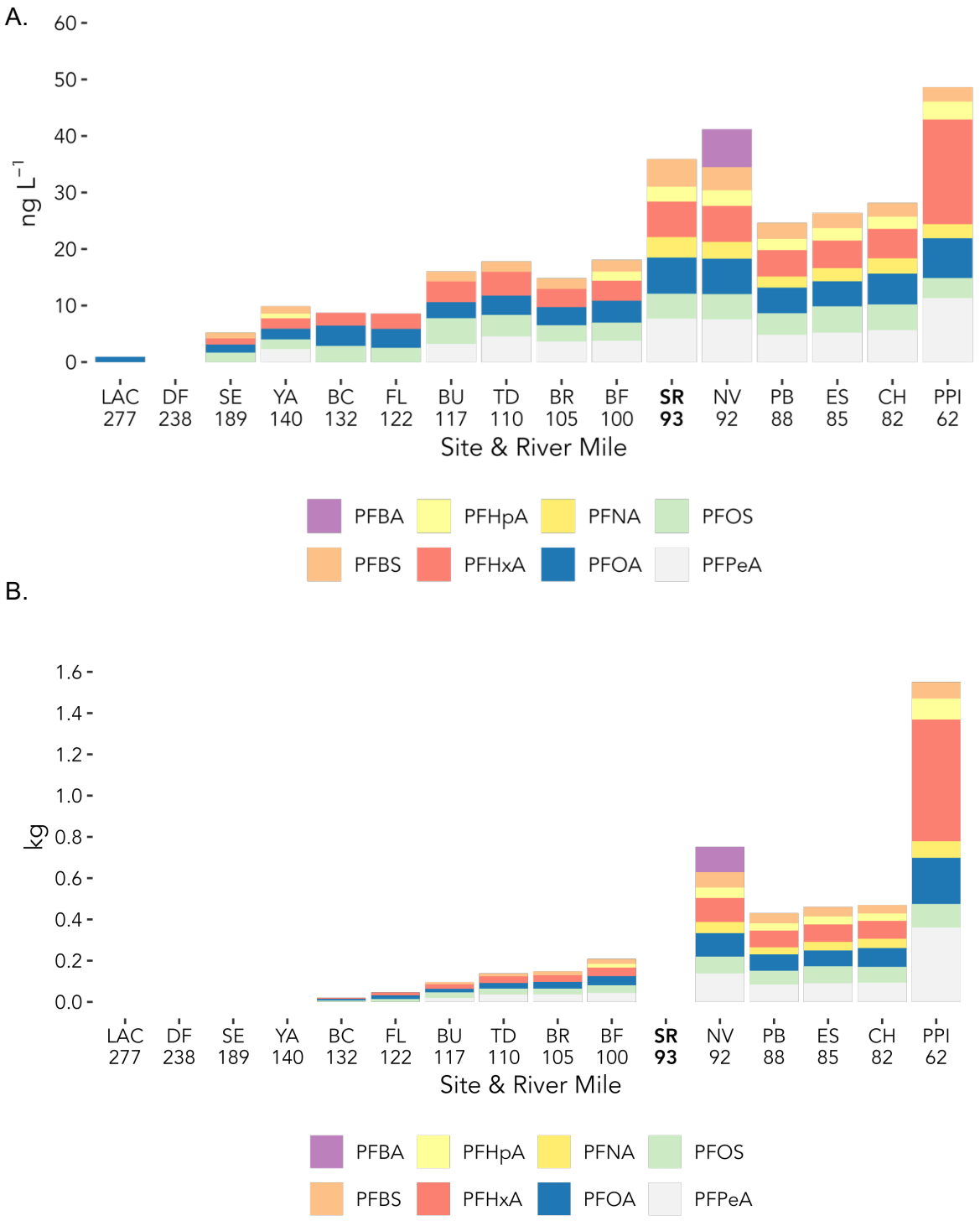

Figure 4. *A) Concentrations of PFAS detected in the Delaware River, organized from upstream (LAC) to downstream (PPI). B) Estimates of PFAS compound mass per 1-mile parcel of water surrounding the sampling site. Bold x-axis labels indicate tributary sites.*

While PFOS only increased by 50%, the mass along this stretch of the river was driven by PFHpA, PFPeA, and PFHxA, which increased by 180%, 285%, and 575%, respectively. Although the sources of these chemicals are currently unknown, the data suggest that one or more sources are located near or south of Chester, PA.

Pea Patch Island was also the only mainstem site sampled during each of the three study years. While the Year 1 (2021) sample was collected early in a falling tide, both Year 2 (2022) and Year 3 (2023) samples were collected on a rising tide. Therefore, tidal dilution complicates direct comparisons of observations across years.[9] However, as shown in Figure 5, the PFAS compounds and concentrations observed across the three years were similar, and—with the exception of PFBA in Year 2—the same suite of compounds was detected each year. The compounds that dominated Pea Patch Island each year were PFHxA (37%, 34%, and 38%, respectively) and PFPeA (26%, 13%, and 23%, respectively). In Year 2 and 3 sampling, both compounds increased as water moved downstream, but they reached their highest concentrations at Pea Patch Island, also indicating a source somewhere south of the Chester

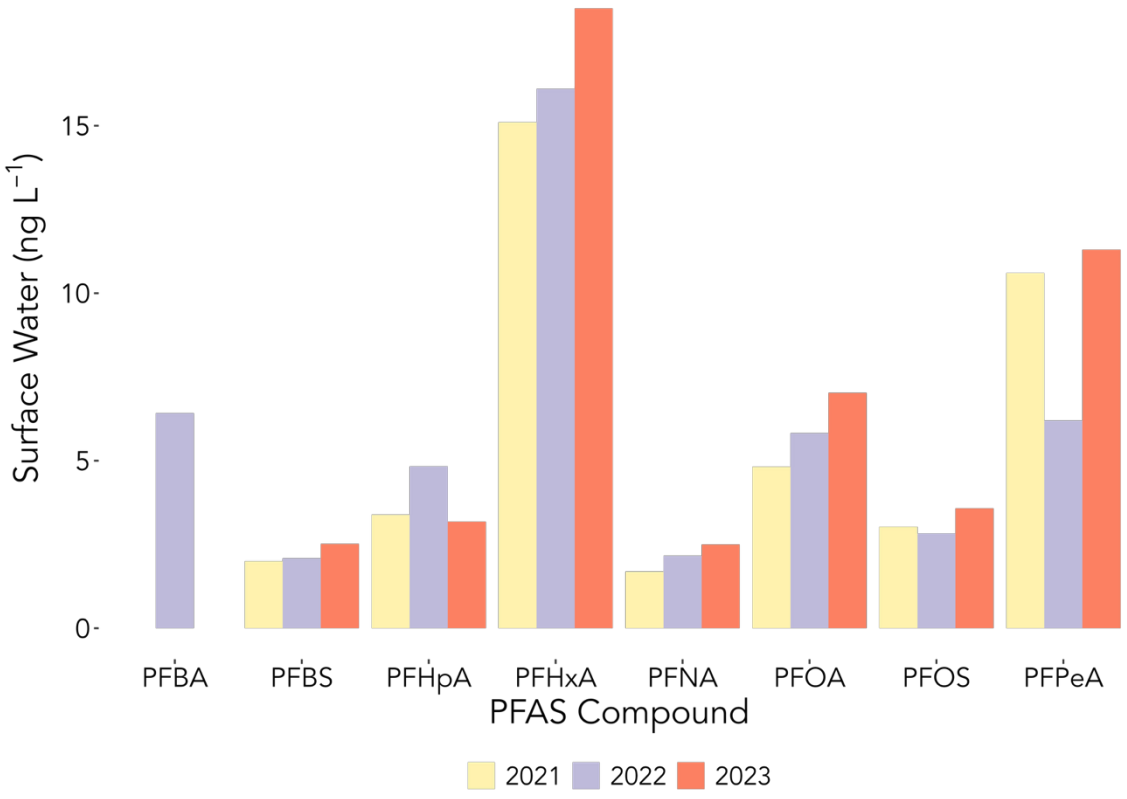

Figure 5. *Surface water PFAS concentrations at Pea Patch Island (PPI) for each of the three sampling years.*

site. Within this stretch of the Delaware River are numerous industrial sites, wastewater treatment facilities, the City of Wilmington, and the Christina River—a known hotspot for PFAS pollution.

There was consistency in the specific PFAS compounds detected in surface water between the Year 2 and Year 3 projects. While Year 2 detected 9 compounds in surface water, 8 of those were also observed in this Year 3 study. The one exception was 5:3 FTCA, a fluorotelomer carboxylic acid precursor. Across all of DRBC's previous PFAS water sampling in the Delaware River Basin, 5:3 FTCA has been observed only once, in the Year 2 study at the Burlington Bristol Bridge. That sample is an outlier among all water samples collected by DRBC in the Delaware River Basin, with a PFAS concentration of 597 ng L^{-1}, three times higher than the combined total from all other sites sampled that year. The reason for the elevated concentration in that sample is currently unknown.[3]

3.1.2 POCIS Passive Samplers

While POCIS samplers were deployed at seven sites, the sampler at Marcus Hook in the mainstem Delaware River was lost. Additionally, one of the POCIS membranes in the Marcus Hook Creek sampler was damaged, resulting in quantifiable results from only two of the three membranes deployed there. The number of unique compounds quantifiable across all sites was 14, with the number of compounds per site ranging from 7 to 10 (Figure 6). Six compounds (PFHpA, PFHxS, PFHxA, PFNA, PFOS, and PFOA) were quantified at every site, and PFBS was detected at five sites (not found at Yardley).

The average number of detections with POCIS was 8.1 ± 1.3, whereas for surface water grab samples it was 5.1 ± 2.3. When comparing only mainstem sites, POCIS detected 7.5 ± 1.1 with grab samples at 4.9 ± 2.3 compounds. Furthermore, the 14 unique compounds detected in water with POCIS are more than the 8 found in grab samples. This indicates that POCIS can be more effective for identifying compounds in water than grab samples.

POCIS samplers captured 7 of the 8 compounds found with grab samples, with PFPeA being the exception. It is unclear why the POCIS samplers failed to capture PFPeA, as it was found in 70% of surface water samples in this study. The seven compounds unique to POCIS are PFOSA, EtFOSAA, PFUnA, PFDA, PFPeS, PFHpS, and PFHxS. However, five of these compounds were found in fish and/or sediment samples, indicating that physicochemical properties like solubility may influence uptake by the POCIS samplers. Only PFPeS and PFHpS were not detected in any other samples during the study. In fact, among all publicly available data from the Delaware River Basin on PFPeS (n = 359), it was detected in ~44% of those surface water samples, with none occurring in the mainstem Delaware River. Most previous PFPeS detections were in Neshaminy Creek, which is where it was detected by POCIS. It has also been detected in groundwater at low concentrations and in fish tissues from tributaries. PFHpS is similar (n = 200), with detection in

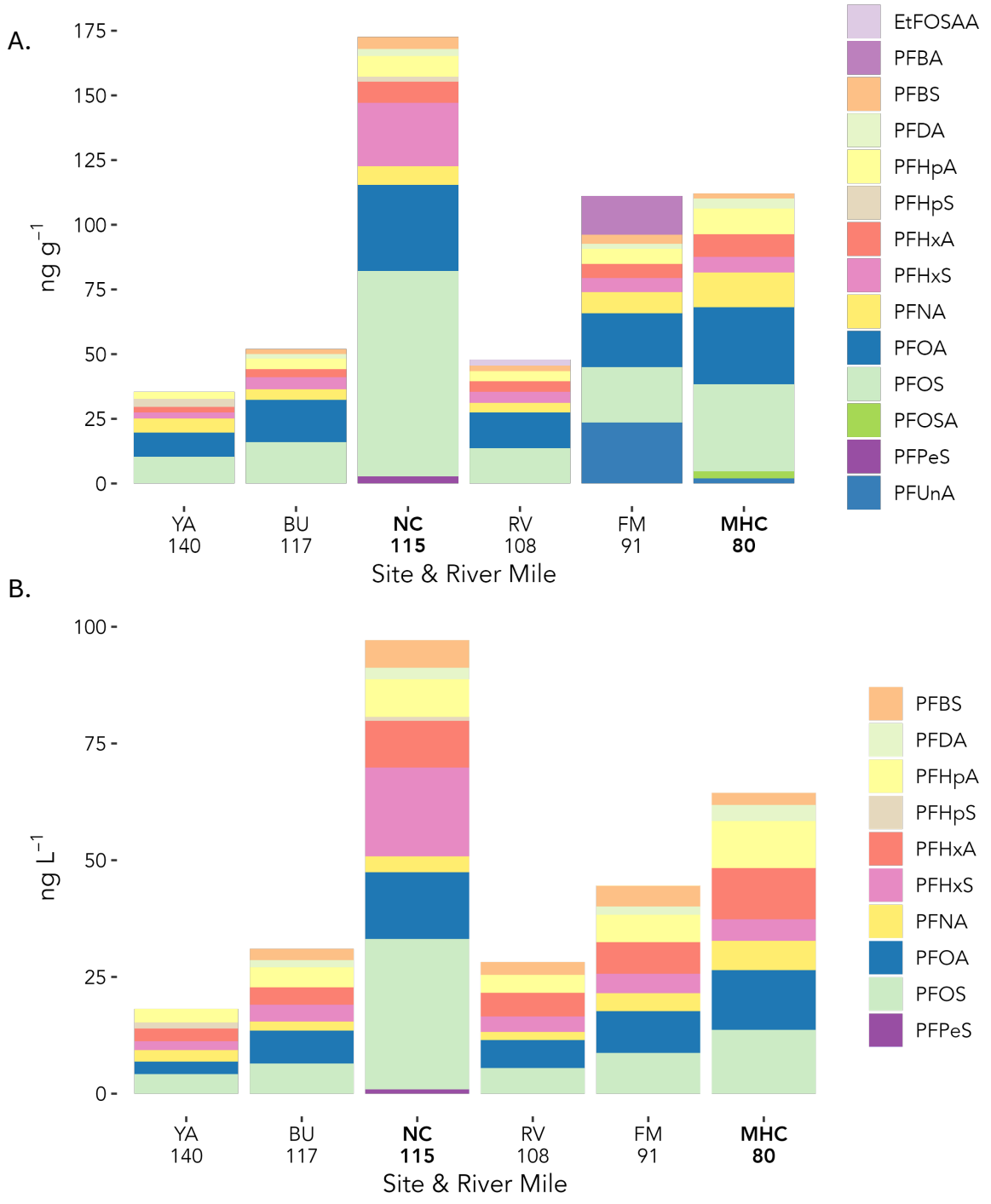

***Figure 6**. A) Reported concentrations (ng g^{-1}) of PFAS compounds detected using POCIS passive samplers. B) Estimated PFAS water concentrations (ng L^{-1}) based on the reported concentrations of compounds sorbed to the POCIS samplers. Four compounds (PFUnA, PFOSA, PFBA, and EtFOSAA) shown on panel A do not appear on panel B because they could not be converted to water concentrations. Bold x-axis labels indicate tributary sites.*

~25.5% of water samples and no previous detections in the mainstem Delaware Estuary. Previous detections were mostly found in Neshaminy Creek, which is where it was detected via POCIS in this study along with the Yardley site. It has also been detected in only 2.6% of tissue samples and in no sediment samples. This implies that while some PFAS detected in tributaries may not be quantifiable in the Delaware River mainstem, they are likely present, but at levels below the detection limits for grab samples. This demonstrates one advantage of using POCIS to identify PFAS in surface water samples compared to traditional grab samples.

The reported concentrations (ng g^{-1}) on the POCIS samplers allow comparisons of PFAS compounds and concentrations across sites (Figure 6A).[5] While the loss of the mainstem sampler at the Marcus Hook site limits the ability to assess PFAS trends in water moving downstream in the Delaware River, PFAS levels do increase along that gradient. However, the highest Σ_{PFAS} was located in the two tributaries that were sampled in this study: Neshaminy and Marcus Hook Creeks. Neshaminy Creek is well known for its PFAS pollution, particularly PFOS, which was the dominant compound at that site. Marcus Hook Creek has only been sampled once previously, in 2023, where the Σ_{PFAS} was 82.84 ng L^{-1}. The results of this passive sampler analysis (64.42 ng L^{-1}) further confirm the persistence of PFAS in this small tributary.

Using predetermined uptake rates from the published literature,[6,7] most reported compound concentrations can be converted to estimated time-weighted average water concentrations (ng L^{-1}). However, four detected compounds lack uptake rates and therefore do not appear in Figure 6B. Caution should be taken when directly comparing actual water sample concentrations with POCIS estimates due to various factors (e.g., differences in sampling dates/durations, single-time-point vs time-weighted average, etc.). That being said, the grab samples from mainstem sites nearest to the POCIS sites are of the same order of magnitude, although the estimated POCIS concentrations for individual compounds are higher when each compound was detected with both methods (Figure 7). Therefore, the Σ_{PFAS} time-weighted average PFAS water concentration POCIS estimates tend to be higher, sometimes nearly double the values from the nearest grab sample site.

While interpreting POCIS data for PFAS has limitations, it offers benefits over traditional grab samples. POCIS can detect compounds at lower concentrations than grab samples, revealing the presence of more PFAS in the water column. For compounds with known uptake rates, it also provides estimates of water concentrations, although these estimates are higher than those observed with grab sampling. Therefore, POCIS provides value as a tool that complements traditional grab sampling of PFAS, and, where appropriate, it should be considered for use in future studies.

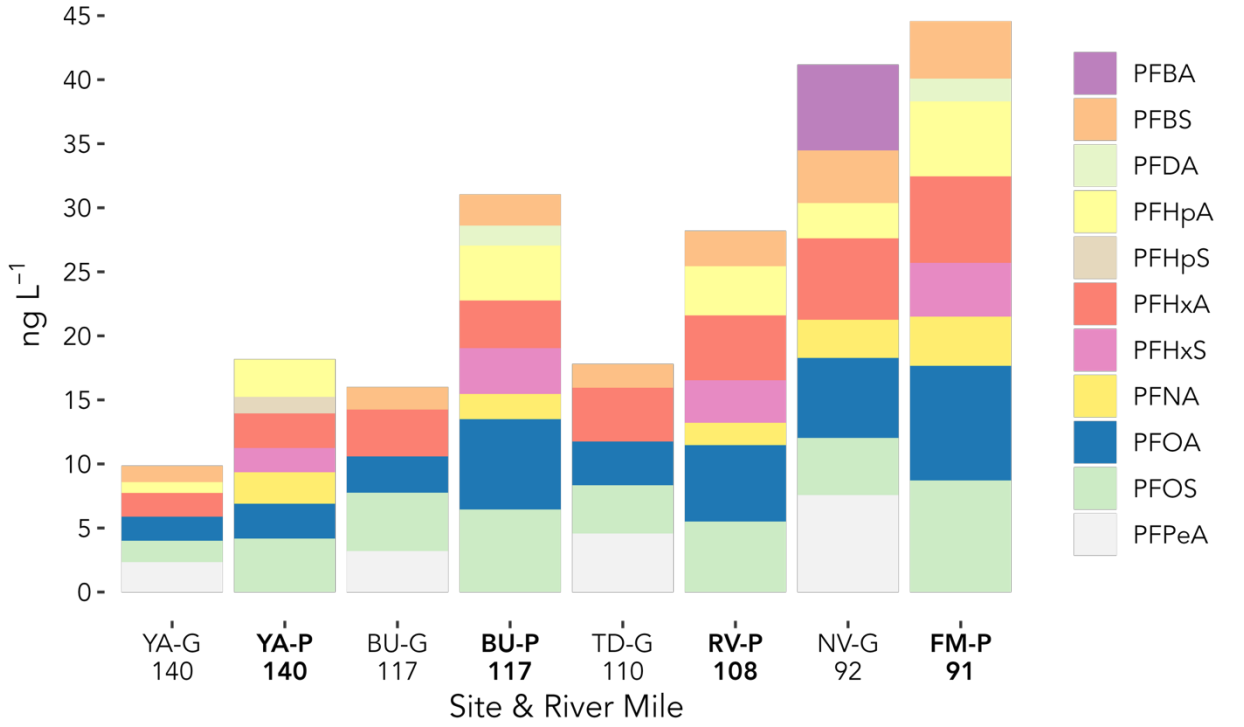

***Figure 7**. Comparisons of mainstem POCIS samples with their nearest surface water grab sample. POCIS site names are in bold and their labels end with "**-P**", while grab sample names end with "-G".*

3.2 SEDIMENT

At least one target PFAS compound was detected in sediment at only 7 of the 16 sites (Figure 8). No detections occurred at the four non-tidal mainstem sites and at five of the tidal mainstem sites. This contrasts with Year 2 sampling, in which 12 of the 16 sites had quantifiable PFAS levels. In Year 3, 8 compounds were identified, as compared to 7 in Year 2. Of the sites with PFAS detections, only Eddystone and Philadelphia Airport had more than two detections, with 4 and 7, respectively. Since 2021, DRBC has sampled 11 of these 16 sites for sediment across 4 studies (PA Coastal Zone Management Program (PACZM) grant-funded sampling in 2021 and 2023 and NFWF grant-funded sampling in 2022 and 2023). When viewed together, the data show high variability within and across sites, yielding no discernible overall trends across the four studies over 3 years. However, there is cursory evidence that the location of sediment, whether the sample is collected directly on the mainstem or slightly offset from the mainstem in an embayment or side channel, may play a role in PFAS accumulation. For example, samples collected at Biles Channel, Betsy Ross Bridge, and Navy Yard were taken directly on the riverbank from subtidal surface sediment. Those samples had PFAS detections in only one or two of the four studies. Samples collected from small embayments at the Florence Bend, Torresdale, Ben Franklin Bridge, and Schuylkill River sites had detections in each of the four studies. The Burlington Bristol

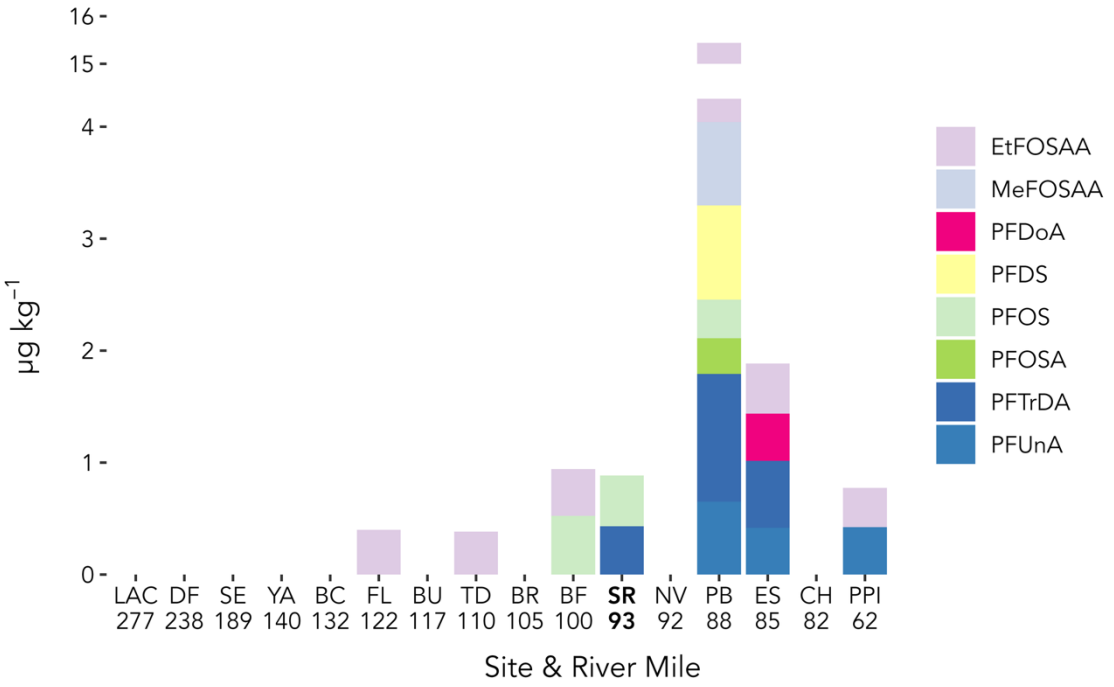

Figure 8. *Mainstem Delaware River sediment PFAS concentrations ordered by river mile. Note the y-axis break from 4.25 to 15 due to the presence of EtFOSAA at concentrations much higher than the other compounds. Bold x-axis labels indicate tributary sites.*

Bridge, Eddystone, and Chester sites also had detections in three of the four studies, although at those sites, it is unclear whether all samples were collected directly from the embayments or from nearby locations due to the tide levels at the time of sampling. Based on this cursory evidence, future DRBC sediment sample planning at sites where multiple collections will occur will attempt to limit this methodological artifact by selecting sites slightly off the main river channel, where surface sediment is less mobile, and by determining a radius around the initial sampling site within which future samples should be collected.

In samples collected for this study, Σ_{PFAS} sediment concentrations at sites with at least one detection ranged from 0.4 to 15.4 µg kg^{-1} (Figure 8). The highest Σ_{PFAS} was observed at the Philadelphia Airport (PB) site. Among the sediment samples collected across the four studies mentioned above, as well as a database of all publicly available PFAS sediment data for the Delaware Basin, this sample has the highest recorded Σ_{PFAS} value in the river's mainstem. Most samples from that database have Σ_{PFAS} values ranging from below detection to 1 µg kg^{-1}, and only seven have been collected from the mainstem Delaware River that exceed 5 µg kg^{-1}. The PFAS compound driving the high concentration at this site is EtFOSAA at 11.6 µg kg^{-1}, accounting for ~74% of the detected PFAS in this sample. This is by far the highest detection of this compound among all samples on the mainstem, with the next closest just over 1 µg kg^{-1}. It is unknown why

this compound is elevated at this site in this particular sample. A second sample collected at the same site 28 days later during the 2023 PACZM sampling had a Σ_{PFAS} of 0.82 µg kg^{-1}, of which only 0.16 µg kg^{-1} was EtFOSAA. In addition to EtFOSAA, these two samples also have three other compounds in common (PFOS, PFTrDA, and PFUnA), which were present at concentrations 2 to 5.5 times higher than in the sample collected less than a month later. The sample from this study also had MeFOSAA, PFDS, and PFOSA, while the 2023 PACZM sample only had PFDA. The reason for such pronounced differences in concentrations and compounds between these two sampling events at the same site, separated by only 28 days, is unknown. However, this likely reflects the heterogeneity and mobility of subtidal surface sediment, as well as the overall difficulty of determining the representative concentration of PFAS compounds in the environment from a single grab sample.

In the PACZM Year 1 (2021) and NFWF Year 2 studies, Philadelphia Airport samples were collected ~2.5 river miles upstream of where this Year 3 sample was collected. This new site was selected because it is adjacent to the Philadelphia International Airport and located at a stormwater outfall that drains the Aircraft Rescue and Fire Fighting Training Facilities (Figure 9). It was anticipated that sampling at this new location could capture the presence of PFAS-based aqueous film-forming foams (AFFF) used to extinguish fires. While some compounds used in AFFF over the past 60 years are known, specifically PFOS and PFOA, many aspects of product formulations and their subsequent environmental presence remain unknown.[10] At the PB site, 7 PFAS compounds were detected; however, it is unclear to what extent AFFF may have influenced the results. If AFFF was the dominant source of pollution at this site, PFOS would be a large contributor to the Σ_{PFAS} at this site, rather than just 2%. Further complicating the interpretation is that several of the detected compounds, including EtFOSAA, PFOSA, and MeFOSAA, are precursors that can form PFOS but are also used in other applications. These compounds, as well as PFTrDA and PFUnA, have also been found at AFFF-contaminated sites. Therefore, it is possible that some of the PFAS pollution at this site is from AFFF, but the results in the present study are inconclusive.

3.3 Fish & Crabs

3.3.1 Non-Tidal Fish

3.3.1.1 White Sucker

The Pennsylvania Fish and Boat Commission collected white sucker at four non-tidal sites (Table 1). This species has a home range of ~1.6 miles (2.6 km) throughout most of the year.[11] However, only a portion of the population spawns annually, and some may begin their pre-spawn migration as early as February, traveling up to 25 miles (40 km), although fish typically travel

Figure 9. *A) The stormwater outfall where the Philadelphia Airport sample was collected. B) View of the stormwater outfall from a Google Earth image that shows the proximity to the firefighting training facility.*

~10 miles (16 km).[11] Spawning occurs when water temperatures range from 53 to 73 ˚F (11.6 to 22.7 ˚C) between April and June,[12] although spawning migration in the Delaware River Basin would likely occur in the early months of that timeframe. White sucker sampling occurred after the spawning migration, but it is unknown whether any of the fish caught migrated for spawning. Therefore, the PFAS observed in white sucker may be representative of exposure in their home range.

There appears to be an increasing trend in the Σ_{PFAS} accumulation in white sucker with decreasing river mile (Figure 10). The Σ_{PFAS} concentrations in white sucker were of similar magnitude to smallmouth bass, but slightly lower, while the compound suite observed was identical (Figure 10), except for the one PFNA detection in white sucker at Sandts Eddy. PFOS was also dominant, ranging from 50 to 63% of the quantifiable PFAS across white sucker at the sites. Unfortunately, there was only one white sucker sampling in the previous Year 2 study. That sample from the Lackawaxen site had 2.34 ng L^{-1} $\Sigma_{PFAS,}$ with 1.57 ng L^{-1} of PFOS. That is higher than was observed with this study.

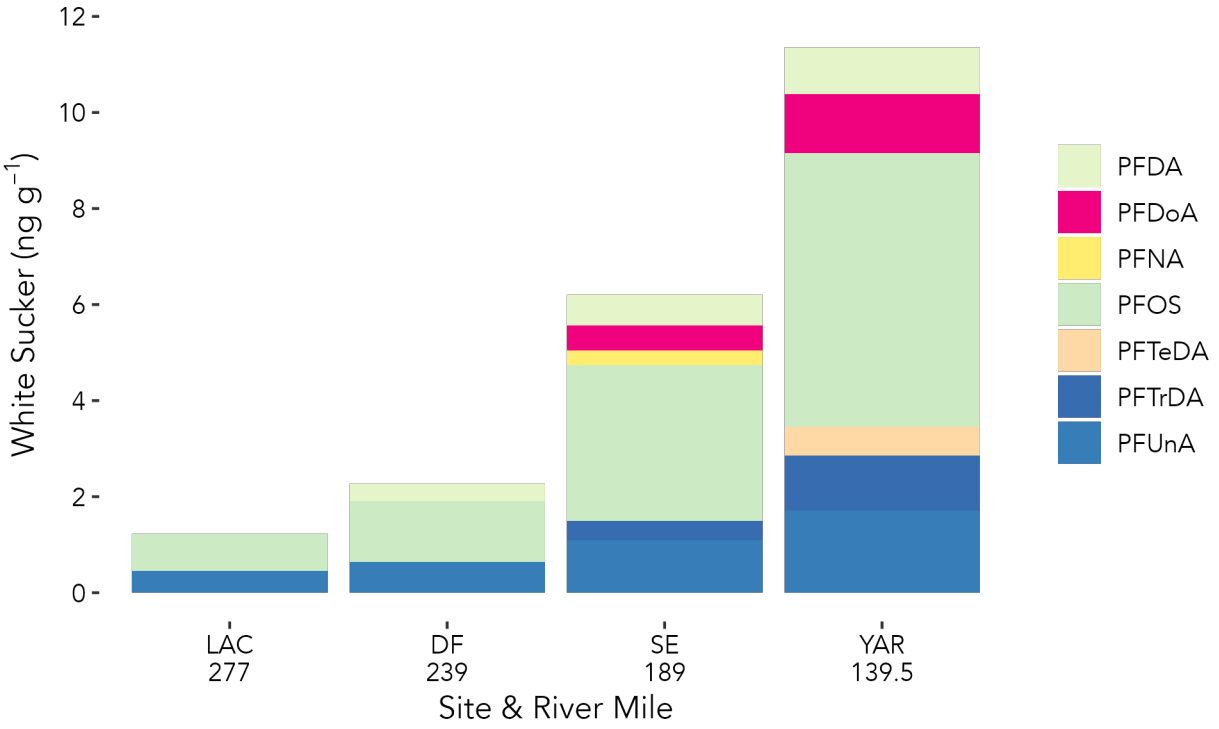

***Figure 10**. PFAS compounds quantified in white sucker fillet tissue at four non-tidal Delaware River sites.*

3.3.1.2 Smallmouth Bass

The Pennsylvania Fish and Boat Commission collected smallmouth bass at four non-tidal sites (Table 1). The home range of this fish can vary widely based on the properties of its watershed.

In a section of the Susquehanna River, the average home range was 15.2 ± 16.1 miles (24.5 ± 25.9 km), but across all the fish sampled, the home range varied from 0.01 to 73.3 miles (.016 to 118 km).[13] Much of their migration is associated with spawning-season travel, but they may also migrate to deeper waters during winter.[13] Therefore, if smallmouth bass have similar ranges in the Delaware River Basin, the PFAS values observed in smallmouth bass would be difficult to attribute to sources nearby where the fish was caught.

There appears to be an increasing trend in the Σ_{PFAS} accumulation in smallmouth bass with decreasing river mile (Figure 11). However, in the Year 2 study, which sampled Lackawaxen, Dingmans Ferry, and Yardley, the opposite trend was observed.[3] The compound suite was identical across these two studies. PFOS was the dominant compound, accounting for 39-78% of quantifiable PFAS in smallmouth bass tissue.

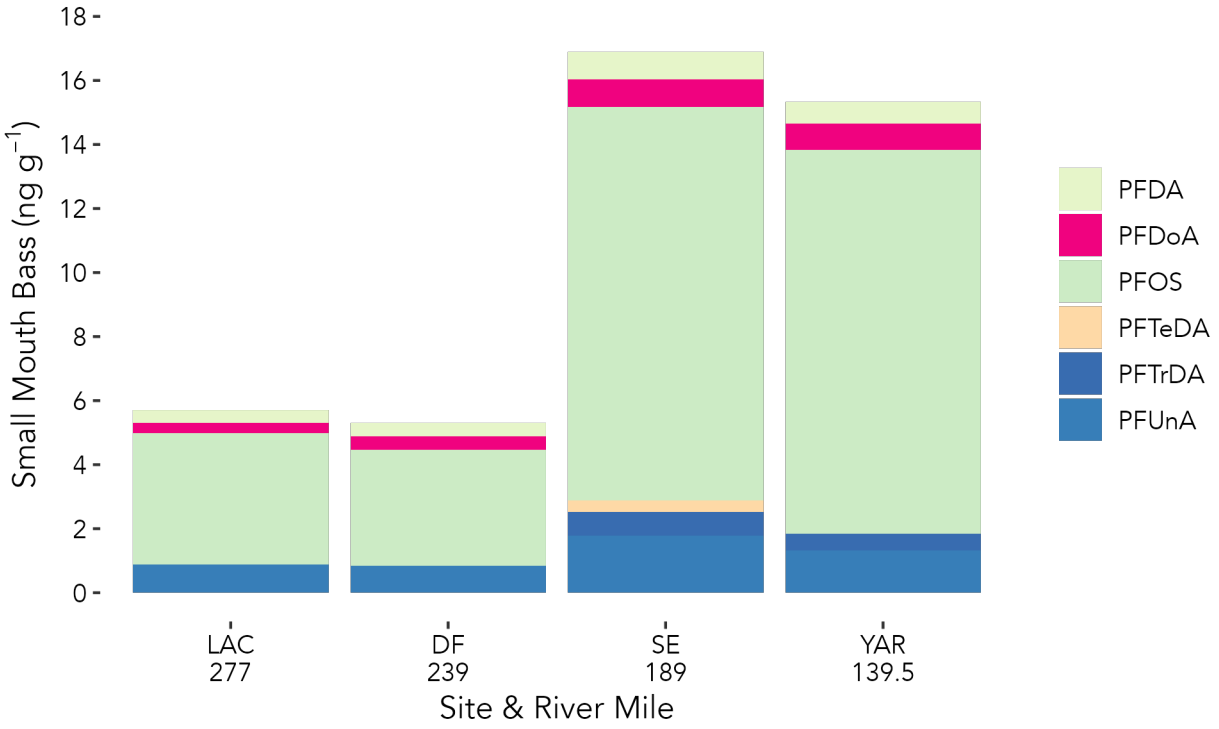

***Figure 11**. PFAS compounds quantified in smallmouth bass fillet tissue at four non-tidal Delaware River sites.*

3.3.2 Tidal Fish

3.3.2.1 White Perch

White perch were caught at all six tidal sites (Table 1) from May 18th to 30th, 2023. They are semi-anadromous fish that overwinter in the lower Delaware Estuary. Spawning adults migrate upstream between March and June when water temperatures reach 50 to 70 ˚F (10 to 20 ˚C).[14] After spawning, they return to their home range, which is relatively small (0.7 mi or 0.11 km^2).[15]

White perch are opportunistic foragers that consume macroinvertebrates, crustaceans, and other small fish, but they may also serve as prey for larger fish, such as catfish.[16] White perch are abundant and provide an opportunity to examine PFAS accumulation at a trophic level similar to channel catfish, but with a smaller home range outside the spring spawning season. However, the samples for this study were collected toward the end of their annual spawning season, and therefore, the PFAS concentrations observed may reflect exposure from either or both their spawning or home ranges.

Each composite white perch sample contained the same seven PFAS compounds (PFDA, PFDoA, PFOS, PFOSA, PFTeDA, PFTrDA, and PFUnA), with the Schuylkill River site having two additional compounds (PFDS and 5:3 FTCA) (Figure 12). DRBC also sampled white perch in the fall of 2023 and spring of 2024, for the PACZM Year 2 project,[17] and in May and June of 2022 for the NFWF Year 2 project.[3] The same suite of seven PFAS compounds was detected in all white perch sampled in these three recent studies, demonstrating that this suite accumulates in white perch from the head of tide at Trenton, NJ, to Chester, PA. A few other compounds also appeared infrequently in white perch across the recent DRBC studies, including PFNA, EtFOSAA, PFDS, and 5:3 FTCA. No consistent pattern in their presence was observed among these infrequent compounds, which could indicate a local and inconsistent source.

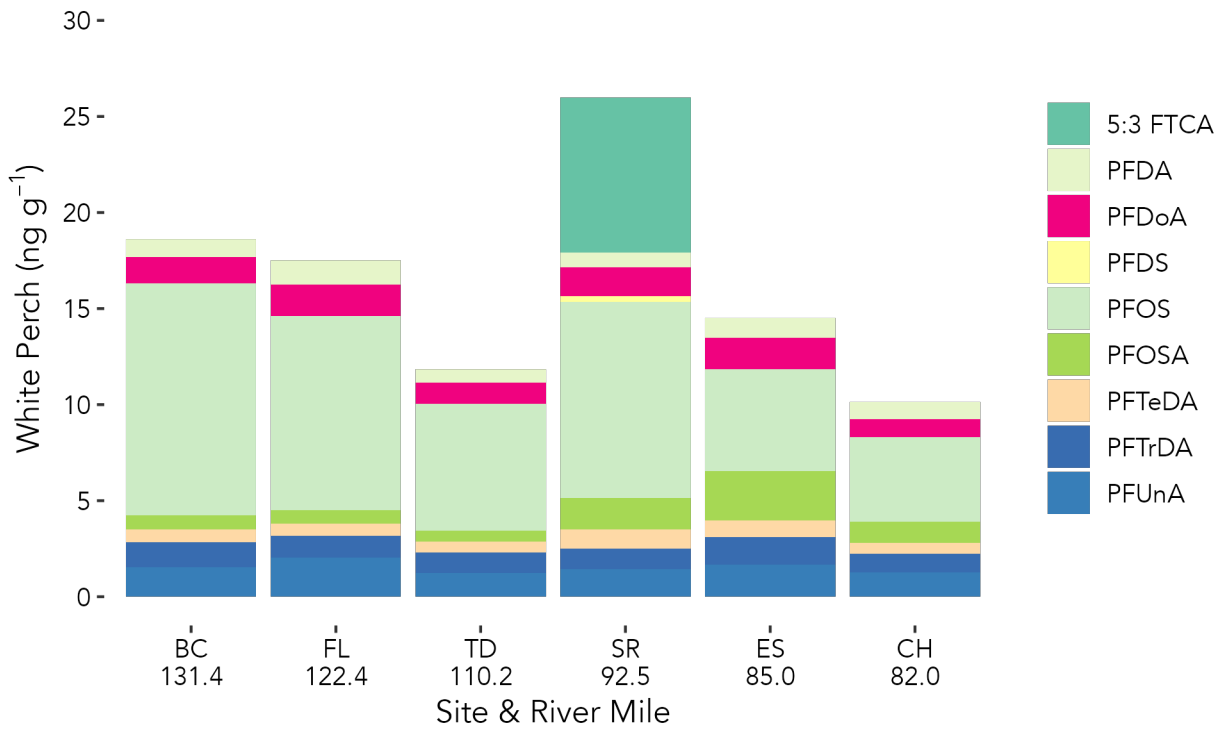

***Figure 12**. Quantifiable PFAS found in white perch fillet tissues at tidal Delaware River sites from Biles Channel to Chester.*

In this study, the Σ_{PFAS} ranged from 10.1 to 26.0 ng g^{-1}, with an average of 16.4 ± 5.7 ng g^{-1}, which was similar to the NFWF Year 2 and PACZM Year 2 studies. As observed in the previous NFWF Year 2 and PACZM Year 2 studies, PFOS was the dominant compound, accounting for 36-65% of the quantifiable PFAS in white perch at each site.

3.3.2.2 Channel Catfish

Channel catfish were caught at all six tidal sites (Table 1) from May 18th to 30th, 2023, at the start of their spawning season, when water temperatures reach their optimal range of 68 to 77 ˚F (20 to 25 ˚C).[18] However, unlike white perch, channel catfish do not travel long distances to spawn and typically remain within their home range, covering 1.2 to 3 miles per day (1.9 to 4.8 km).[19,20] Therefore, channel catfish PFAS levels would reflect exposure occurring within a few miles of the capture site.

There were 10 PFAS compounds detected in the channel catfish fillet composite samples (Figure 13). One compound, N-EtFOSE, was observed at 3.37 ng g^{-1} in the analytical lab blank, which is above the concentration at the only site where it was detected, the Schuylkill River (2.66 ng g^{-1}).

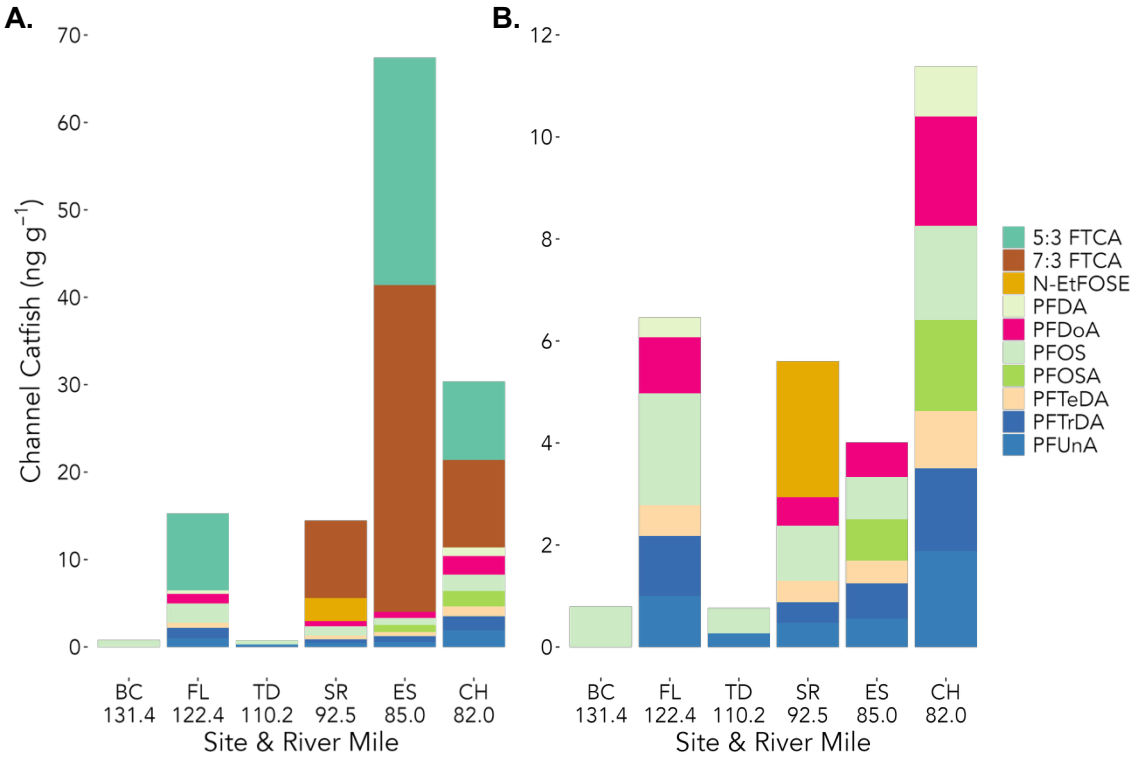

***Figure 13**. A) PFAS compounds quantified in channel catfish fillet tissue at tidal Delaware River sites. B) The two dominant PFAS precursor compounds, 5:3 FTCA and 7:3 FTCA, have been removed to better depict the presence of the less dominant compounds found in these channel catfish samples.*

This detection is considered "estimated" and may be an artifact of contamination. In the PACZM Year 2 study, samples collected in late summer 2023 and spring 2024, N-EtFOSE was also detected at the Schuylkill River site, as well as at Chester and Eddystone. However, no other samples from this set of fish tissue samples contained N-EtFOSE above the quantification limits. Based on this information, we have decided to include N-EtFOSE in Figure 12, but caution the interpretation of its presence in the channel catfish sample from the Schuylkill River.

Similar to the PACZM Year 2 study, two precursor compounds dominated the channel catfish detections: 5:3 FTCA and 7:3 FTCA. They were detected in samples from four of the six sites, where they more than doubled the Σ_{PFAS}, and at the Eddystone site, increasing it 16-fold (Figure 13A). A recent study found that 7:3 FTCA could be a false positive due to a biological interferent.[21] Therefore, its presence in samples from this study and others should be interpreted cautiously.

The compound profile across the sites was somewhat variable, with only PFOS detected at each location. Across the 4 studies conducted by DRBC since 2020 in which channel catfish have been sampled, 5:3 FTCA, 7:3 FTCA, PFDoA, PFOS, PFTeDA, PFTrDA, and PFUnA were detected each year and in most samples.

3.3.3 Fish Consumption Exposure

Human exposure thresholds for PFAS compounds from fish consumption are limited to PFOS, which was quantifiable in all samples. Concentrations ranged from 0.78 to 12.3 ng g^{-1}, with white perch (8.11 ± 3.11 ng g^{-1}) and smallmouth bass (8.00 ± 4.79 ng g^{-1}) having higher average concentrations than channel catfish (1.21 ± 0.66 ng g^{-1}) and white sucker (2.75 ± 2.24 ng g^{-1}). The Chronic Reference Dose (RfD_C) for PFOS is 0.02 µg kg^{-1} day^{-1}.[22] 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 without considerable health risk.

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

The 2025 "Fish Smart, Eat Smart" guide from the NJ Departments of Environmental Protection and Health defines a single serving of fish as 8 oz (226.8 g).[23] With this standard serving size, potential PFOS exposure from fish consumption can be estimated.

In the non-tidal river, no white sucker samples exceeded the 1.4 µg threshold, although the Yardley sample (1.30 µg) was close. For smallmouth bass, both Sandts Eddy (2.79 µg) and Yardley (2.72 µg) exceeded the threshold. Among tidal species, there were no exceedances for channel catfish, while four of the six white perch sites exceeded the threshold. These include

Biles Channel (2.74 µg), Florence (2.29 µg), Torresdale (1.49 µg), and the Schuylkill River (2.31 µg). The same species that exceeded the threshold in the NFWF Year 2 (smallmouth bass and white perch) and the PACZM Year 2 (white perch) matched this study.

Last, it should be emphasized that the EPA RfD_C is based on chronic effects from daily consumption over a lifetime. Most people do not consume locally caught fish daily, and PFOS concentrations can vary widely among individual fish. The state of Pennsylvania does not issue a fish consumption advisory for PFOS at any sites where fish samples for this study were collected. New Jersey does have an advisory in place, although it does not specifically target PFOS. For example, New Jersey recommends that statewide, smallmouth bass should be limited to one meal per week for the general population or one meal per month for high-risk populations.[23] For white perch in the Delaware River Estuary, New Jersey recommends limiting consumption to four meals per year and advises against eating if you are high-risk (infants, children, pregnant women, nursing mothers and women of childbearing age). Channel catfish is only recommended for one meal per year, and none if you are high-risk.[23] There are also site-specific recommendations for these species that should be considered before consuming them.

3.3.4 Blue Crabs

Blue crabs were collected at one site, Pea Patch Island, in the fall of 2021, 2022, and 2023. The same seven compounds, except PFDA in 2023, were detected in blue crabs each year (Figure 14). All blue crab concentrations are reported as wet weight. The Σ_{PFAS} varied across the three years of the study, with 11.8, 23.0, and 15.2 ng g^{-1} in 2021, 2022, and 2023, respectively, and averaged 16.7 ± 5.8 ng g^{-1} over the three years. Concentrations of quantifiable PFAS compounds ranged from 0.6 (PFDA) to 5.8 (PFTrDA) ng g^{-1}. PFOS was detected in each crab sample, although, unlike other environmental media sampled, it was not one of the dominant compounds. PFTrDA had the highest average concentration (4.3 ± 1.7 ng g^{-1}) across the three years, followed by PFTeDA (3.4 ± 2.1 ng g^{-1}). Although some variability is expected, the quantifiable compounds and their concentrations were generally consistent for blue crabs at Pea Patch Island over the three years.

3.4 Cross-Matrix PFAS Presence

The overlap in compounds detected across the environmental matrices in this study was examined to identify trends. Table 3 was created to compare the presence of compounds across environmental matrices with their compound properties, including organic carbon soil partitioning (Log K_{OC}) values and solubility ranges (mg L^{-1}). Compound properties were obtained from Table 4-1 of the Interstate Technology & Regulatory Council's PFAS Regulatory Guidance Document.[24] As expected, PFAS compounds with the highest Log K_{OC} and lower solubility ranges

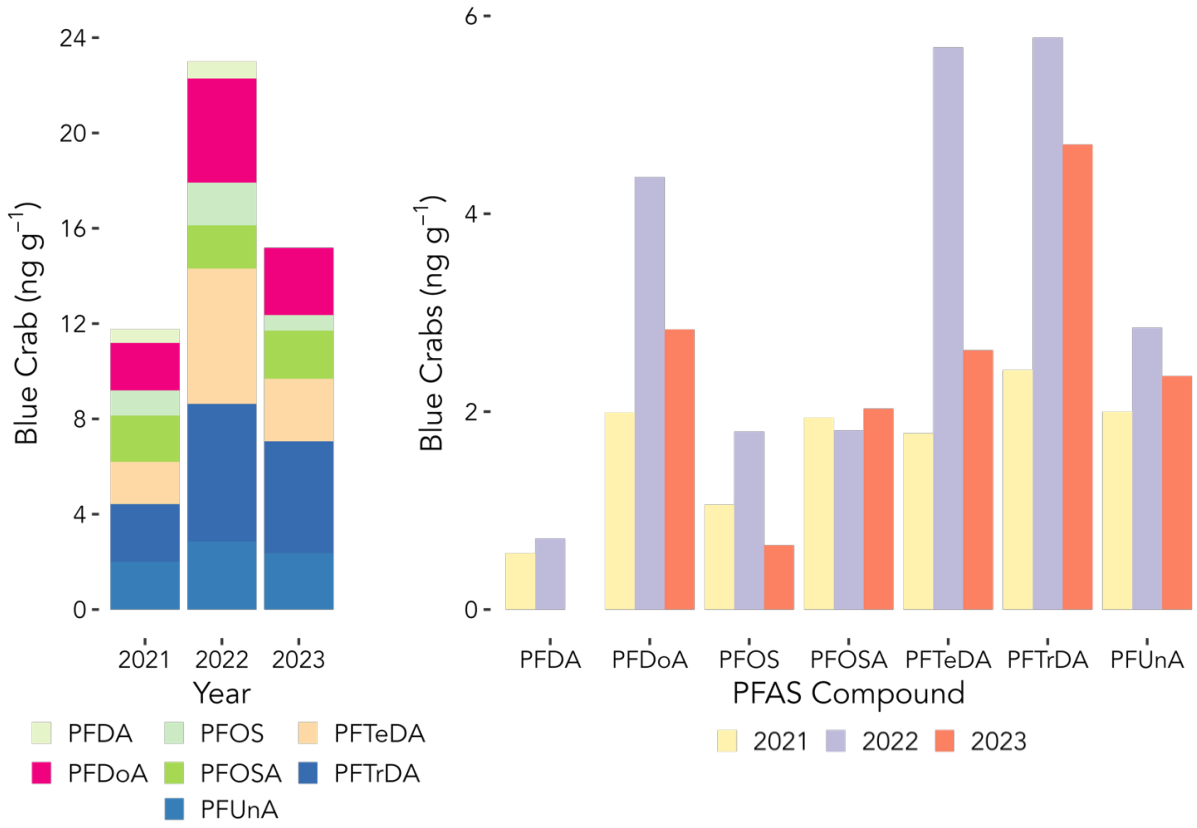

***Figure 14**. A) PFAS quantified in blue crabs (Callinectes sapidus) by year at Pea Patch Island (river mile 62.5). B) PFAS compound comparison in blue crabs across the three years of sampling.*

were largely found in sediment and biota (Table 3, Category 1), with only a few compounds overlapping with water (grab sample and POCIS; Category 2). Therefore, multi-matrix sampling is required to uncover a more complete picture of PFAS contamination in any aquatic system. For example, across the four matrices sampled, 22 compounds were identified. However, only 8, 8, 11, and 14 unique compounds were detected in water, sediment, tissue, and POCIS, respectively. If only one matrix is sampled, many compounds would be missed. Even sampling both water and sediment, only 15 compounds, or roughly 70%, would have been identified (PFOS was detected in both water and sediment samples). Sampling water and tissue would have identified 19 compounds (86%), while sampling water, sediment, and tissue found 20 (91%) of the compounds. When planning future studies, the project's end goals should factor into which matrix is sampled. To generally explore contamination of a system, the maximum number of PFAS should be captured by sampling water, sediment, and tissue. However, if the goal is to assess human health, water and tissue samples might be sufficient. If generally exploring contamination, but funds are limited, water and sediment samples may capture ~70% of the compounds detectable by EPA Method 1633. The key message is that multi-matrix sampling should be prioritized when assessing PFAS presence in aquatic systems.

Table 3. *Listing of PFAS compounds detected across each of the sampling matrices in this study, along with their Log K_{OC} values and solubilities from the ITRC PFAS Guidance Document.[24] N/A – Not available.*

Category	Group	Compound	Surface Water	Sediment	White Perch	Channel Catfish	White Sucker	Smallmouth Bass	Blue Crab	POCIS	Log Koc	Solubility (mg/L)
1	FOSE	N-EtFOSE				X					3.95	.0000069-150000000
1	PFCA	PFTrDA		X	X	X	X	X	X		3.71-5.2	.0000025-28
1	PFCA	PFTeDA			X	X	X	X	X		3.68-5.2	.0000000033-23
1	PFCA	PFDoA		X	X	X	X	X	X		3.57-5.6	.00000068-83
1	PFSA	PFDS		X	X						3.53-4.03	0.000016-1.94
1	FOSA	PFOSA		X	X	X			X	X	3.3-5.3	0.00012-30
1	FOSAA	EtFOSAA		X						X	3.23-4.8	0.000073-2.2
1	FOSAA	MeFOSAA		X							3.11-4.6	0.03-2.2
2	PFCA	PFUnA		X	X	X	X	X	X	X	3.19-5.6	.0000096-93
2	PFCA	PFNA	X				X			X	2.39-5.4	0.0019-1,309
2	PFSA	PFOS	X	X	X	X	X	X	X	X	2.27-5.6	0.0031-2,701
2	PFCA	PFDA			X	X	X	X	X	X	1.5-5.1	0.00013-5,141
3	PFSA	PFHxS								X	1.15-4.5	.060-56,014
3	PFCA	PFPeA	X								.7-4.2	61-110,000
3	PFCA	PFOA	X							X	0.041-5	.0095-13,748
3	PFCA	PFHxA	X							X	0.2-4.7	4.7-21,730
3	PFCA	PFHpA	X							X	-0.2-2.9	0.35-440,000
3	PFCA	PFBA	X							X	-0.8-2.76	327-560,000
3	PFSA	PFBS	X							X	-0.7-2.09	107-1,000,000
4	FTCA	5:3 FTCA			X	X					N/A	113-179
4	FTCA	7:3 FTCA				X					N/A	N/A
4	PFSA	PFPeS								X	N/A	N/A
4	PFSA	PFHpS								X	N/A	N/A

4. CONCLUSIONS

The third and final year of the PFAS Water Quality and Fish Tissue Assessment Study further confirms that PFAS contamination is widespread and persistent in the Delaware River mainstem and selected tributaries, particularly in the tidal portion of the system. Across three years of sampling and complementary DRBC studies, PFAS were consistently detected in surface water, sediment, fish, and blue crab tissues, underscoring the complexity and scope of PFAS pollution in the basin.

Surface water, which was sampled at identical sites in 2022 and 2023, had similar results, with PFAS detected at nearly every site and concentrations increasing as water moved downstream. Using the 2023 data, PFAS mass per river mile was estimated, showing that the sum of quantifiable EPA Method 1633 compounds more than tripled between the Chester and Pea Patch Island sites. This suggests one or more PFAS sources, particularly for PFHxA and PFPeA, south of Chester, PA. Pea Patch Island is also the only location where water samples were collected across all three years of the study, with concentrations generally similar throughout the period, indicating consistent levels of PFAS flowing through that site.

Sediment results were variable across both sites and years. While only 7 of 16 sites had quantifiable PFAS in 2023 (compared to 12 of 16 in Year 2), comparisons of data across four recent DRBC studies with overlapping sampling sites appear to show that there are more frequent and consistent detections at sites located just off the mainstem of the river in side channels or embayments where sediment is more likely to accumulate. This study also collected the sediment sample with the highest Σ_{PFAS} observed in the Delaware River mainstem at 15.84 µg kg^{-1} near the Philadelphia Airport. Another sample was also taken near this site for a different study, less than a month later, but it was substantially lower at 0.82 µg kg^{-1}. This further highlights the difficulty in collecting representative sediment samples, which will require forethought when planning future projects.

PFAS bioaccumulation in fish and crabs is a pathway for human exposure. PFAS were detected in every sample, and while concentrations varied by species and site, a consistent suite of compounds was present in every 2023 sample and in nearly all 2022 samples: PFDA, PFDoA, PFOS, PFTeDA, PFTrDA, and PFUnA. Of these, PFOS dominated the other compounds, accounting for 36-78% of the Σ_{PFAS} in samples. This compound also has a RfD_C, where a 70 kg adult should not exceed 1.4 µg day^{-1} to limit potential health effects. Based on a single serving, defined as 8 oz by New Jersey, smallmouth bass at two sites and white perch at four sites would exceed that threshold. However, as seen across multiple studies by DRBC, fish concentrations

at the same sites varied. The presence of PFAS in the species that were studied, and their potential as a human exposure pathway, warrants continued monitoring as well as regular assessment of potential impacts as researchers continue to refine the levels of PFAS that are considered safe.

Collectively, the three-year PFAS assessment and associated DRBC studies demonstrate that:

1. PFAS are pervasive and persistent in waters of the Delaware River mainstem and tributaries, with higher occurrence and concentrations in the tidal river.
2. Downstream increases in Σ_{PFAS} concentration and mass indicate ongoing inputs from unknown sources, which could include point and non-point sources.
3. Sediments and biota are sinks for some PFAS compounds, but have high spatial and temporal variability, complicating efforts to define representative concentrations and locate sources.
4. PFOS is ubiquitous in fish and crabs and is often the dominant PFAS in fish tissues, with some fillet concentrations high enough to raise potential exposure concerns when considered against current RfD_C thresholds.
5. Passive samplers (POCIS) are a valuable complement to grab sampling, improving detection of low-level and less frequently observed PFAS.
6. Current analytical methods capture only a small fraction of known PFAS compounds, and toxicological thresholds are still being determined, which limits DRBC's ability to fully assess and respond to the threat of PFAS in the Delaware River Basin.

Together, the results of this three-year study provide a robust foundation for understanding PFAS occurrence and distribution in the Delaware River Basin. Continued monitoring, especially in portions of the tidal river and tributaries highly impacted by urbanization and industrialization, will be necessary to track trends and determine sources. Moving forward, DRBC will build on this work by consolidating, synthesizing, and publicly sharing all open-access PFAS data for the Delaware River Basin to enhance public understanding, boost regional coordination, and support science-based management actions that reduce PFAS inputs, protect aquatic life and wildlife, and safeguard human health.

5. ENVIRONMENTAL DATASETS

All data from this Year 3 study can be downloaded from the National Water Quality Monitoring Council's Water Quality Portal. The links below provide free access to this data. If the links do not

work, visit the USEPA Water Quality Portal data search webpage. Under the Advanced search option, find the Project ID field and enter “NFWF Yr3 PFAS”. While this Project ID retrieves the entire dataset, search the Sample Media field for "water," "sediment," or “tissue” to select media-specific datasets. Finally, in the Data Profiles section, click the “Sample Results (physical/chemical metadata)” button, scroll to the bottom of the page, and click download. Data can also be downloaded in various formats; choose the one that best fits your needs. The Water Quality Portal may change over time, but consider these general instructions to help retrieve all data from this study.

Complete Project Dataset

Query

https://www.waterqualitydata.us/#organization=DRBC&project=NFWF%20Yr3%20PFAS&mimeType=csv&dataProfile=resultPhysChem&providers=NWIS&providers=STORET

Data Download

https://www.waterqualitydata.us/data/Result/search?organization=DRBC&project=NFWF%20Yr3%20PFAS&mimeType=csv&zip=yes&dataProfile=resultPhysChem&providers=NWIS&providers=STORET

Water Dataset (Including POCIS)

Query

https://www.waterqualitydata.us/#sampleMedia=Water&project=NFWF%20Yr3%20PFAS&mimeType=csv&dataProfile=resultPhysChem&providers=NWIS&providers=STORET

Data Download

https://www.waterqualitydata.us/data/Result/search?sampleMedia=Water&project=NFWF%20Yr3%20PFAS&mimeType=csv&zip=yes&dataProfile=resultPhysChem&providers=NWIS&providers=STORET

Sediment Dataset

Query

https://www.waterqualitydata.us/#sampleMedia=Sediment&project=NFWF%20Yr3%20PFAS&mimeType=csv&dataProfile=resultPhysChem&providers=NWIS&providers=STORET

Data Download

https://www.waterqualitydata.us/data/Result/search?sampleMedia=Sediment&project=NFWF%20Yr3%20PFAS&mimeType=csv&zip=yes&dataProfile=resultPhysChem&providers=NWIS&providers=STORET

Tissue Dataset

Query

https://www.waterqualitydata.us/#sampleMedia=Tissue&project=NFWF%20Yr3%20PFAS&mimeType=csv&dataProfile=resultPhysChem&providers=NWIS&providers=STORET

Data Download

https://www.waterqualitydata.us/data/Result/search?sampleMedia=Tissue&project=NFWF%20Yr3%20PFAS&mimeType=csv&zip=yes&dataProfile=resultPhysChem&providers=NWIS&providers=STORET

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