April 2025

Enhanced Monitoring for Toxics and Emerging Contaminants in Delaware Estuary Tributaries

Technical Report No. 2025-2

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

AUTHORSHIP

This project was overseen and undertaken by Jeremy Landon Conkle, Ph.D., Senior Chemist/Toxicologist at the Delaware River Basin Commission (DRBC), with the assistance of Elaine Panuccio, Senior Water Resource Scientist, and Jacob Bransky, Senior Aquatic Biologist. Water Resource Scientist, Matthew Amato, Ph.D., significantly contributed to data processing and report writing.

ACKNOWLEDGEMENTS AND DISCLAIMERS

This project was made possible, in part, by funding from the Partnership for the Delaware Estuary through the Bipartisan Infrastructure Law under CDFA grant number 66.456. 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 and its funding sources. Mention of trade names or commercial products does not constitute their endorsement by the U.S. Government or its funding sources.

Partnership for the Delaware Estuary, Inc. received financial support from the EPA under an Assistance Agreement funded by the 2021 Bipartisan Infrastructure Law to support this work.

SUGGESTED CITATION

Conkle, J. L.; Amato, M.T; Panuccio, E.; Bransky, J. (2025). *Enhanced Monitoring for Toxics and Emerging Contaminants in Delaware Estuary Tributaries*. (DRBC Report No. 2025-2). West Trenton, New Jersey. Delaware River Basin Commission.

EXECUTIVE SUMMARY

The Delaware River Basin is the source of drinking water for >14 million people while also having a large industrial footprint and the world's largest freshwater port complex. This diverse watershed faces ongoing pollution-related challenges stemming from urban, agricultural and industrial activities. Recognizing the need for more monitoring of toxic chemicals and emerging contaminants, the Delaware River Basin Commission (DRBC) sampled surface water in 12 tributaries of the Delaware Estuary in the fall of 2023 for various hazardous substances, including per- and polyfluoroalkyl substances (PFAS), polychlorinated biphenyls (PCBs), dioxins and furans (DxF), organochlorine insecticides (OC), neonicotinoids, pyrazoles and polycyclic aromatic hydrocarbons (PAHs).

Compounds from all pollutant groups analyzed were present in each tributary, albeit at varying concentrations. Exceedances of USEPA and/or DRBC Human Health Surface Water criteria were found for four different PAH compounds, eight OC compounds and for the total concentration of PCBs. Concentrations below these criteria protect against adverse effects to human health. Additionally, USEPA has released draft Human Health Surface Water Criteria for three PFAS compounds: PFOA, PFOS and PFBS. These criteria are still draft and subject to change. While there were no exceedances for PFBS, PFOS and PFOA exceeded the draft criteria for each site. Some tributaries stood out due to one or more pollutant groups. Pennsylvania's Frankford Creek had the highest concentrations of both legacy and current-use insecticides. Delaware's Christina River had the highest levels of PFAS, as well as the second-highest levels of PCBs, PAHs and DxF. Marcus Hook Creek (Pa.), Mantua Creek (N.J.) and the Cooper River (N.J.) also stood out for their pollutant concentrations. The unique pollutant profiles of each are a testament to the broad human influence over each system while demonstrating the challenge to remediate and prevent future releases.

The Partnership for the Delaware Estuary funded this project through the Bipartisan Infrastructure Law. The project addresses an ongoing and critical need for improved data collection and monitoring specific to toxics and emerging contaminants, facilitating better tracking of their impacts on water quality over time. The findings will provide essential insights to inform regulatory efforts, remediation strategies and public health initiatives aimed at mitigating the risks associated with these hazardous substances. This report encapsulates pivotal results and discussions regarding the identified pollutants, ultimately contributing to the DRBC's overarching goal of safeguarding water quality for present and future generations.

LIST OF ACRONYMS/ABBREVIATIONS

AFFF	Aqueous film-forming foams
DRB	Delaware River Basin
DRBC	Delaware River Basin Commission
DxF	Dioxins and furans
HpCDD	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin
OC	Organochlorine insecticides
OCDD	1,2,3,4,6,7,8,9-Ocachlorodibenzo-p-dioxin
OCDF	1,2,3,4,6,7,8,9-Ocachlorodibenzofuran
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PCB_{TOTAL}	Sum of all quantifiable PCB features in a sample
PFAS	Per and polyfluoroalkyl substances
S_{NN}	Sum of all neonicotinoids quantified in a sample
S_{OC}	Sum of all organochlorine insecticides quantified in a sample
S_{PAH}	Sum of all PAHs quantified in a sample
S_{PFAS}	Sum of all quantifiable PFAS compounds in a sample
TMDL	Total maximum daily load
USEPA	United States Environmental Protection Agency

TABLE OF CONTENTS

1. INTRODUCTION

The Delaware River Basin is diverse in its environments and land use. It is home to 8.63 million residents and supplies water to an additional 5.56 million people outside the Basin. The Delaware River Port Complex is the largest freshwater port in the world and the third largest petrochemical port, hosting five of the largest East Coast refineries. Urban, suburban, agricultural, industrial and petrochemical activities have significantly influenced the Delaware River Basin, as evidenced by legacy and ongoing pollution in the system.

The Delaware River Basin Commission has been monitoring trace organic pollutants and their presence in sediment and organisms for several decades. Recent technical reports and assessments of the Delaware River have called for improved monitoring and assessment of toxic chemicals and emerging contaminants to reduce their levels in the river. This requires additional sampling to track concentrations upstream and identify their sources. With this funding, DRBC performed tributary-focused sampling for toxics and emerging contaminants, including per- and polyfluoroalkyl substances (PFAS), polychlorinated biphenyls (PCBs), dioxins/furans (DxF), organochlorine insecticides (OC), neonicotinoid and pyrazole insecticides and polycyclic aromatic hydrocarbon (PAHs) for selected tributaries in the Delaware River Estuary (Del., N.J. and Pa.). The project will deliver expanded data collection on toxics and emerging contaminants, with the long-term goal of enhancing the ability to track their impacts on water quality over time. Monitoring will focus primarily on the urban areas of the Estuary, where legacy contaminants and other pollutants are found in higher concentrations than in other parts of the Basin. This targeted monitoring provides crucial information that informs future actions addressing this ongoing concern.

PCBs are a class of human-manufactured compounds used extensively in electrical equipment, such as transformers and capacitors, paints, printing inks, pesticides, hydraulic fluids and lubricants. Although their manufacture and use were generally banned by federal regulations in the late 1970s, existing uses in electrical equipment and certain exceptions to the ban were allowed. Due to their hydrophobic nature, PCBs preferentially sorb to organic particles, such as in soils and sediments, and concentrate in the tissues of aquatic biota either by direct contact or through the food chain. PCBs are classified as a probable human carcinogen by the U.S. Environmental Protection Agency and have also been shown to have reproductive effects, suppress the immune system and are a possible endocrine disruptor. Starting in the late 1980s, the States of Delaware, New Jersey and Pennsylvania began issuing fish consumption advisories for portions of the Delaware River Estuary for PCBs due to their elevated levels in the tissues of resident and anadromous fish species. In December 2003, PCB TMDLs were established for the tidal Estuarine waters in Zones 2-5.[1]

PFAS are found in various industrial and household products, including stain-repellant textiles, aqueous film-forming foams (AFFF) and paper coatings. These substances vary in their persistence, toxicity and bioaccumulation in the environment. Human and wildlife exposure to several types of PFAS is widespread due to the ubiquity of environmental discharges from industrial outfalls, municipal treatment plants, usage of AFFF for firefighting, stormwater runoff and landfill leachate. Increasing evidence highlights the adverse effects of certain PFAS on human health and the environment. Health risks linked to PFAS exposure include liver damage, increased cholesterol, thyroid disease, reduced vaccine effectiveness, asthma, decreased fertility and birth weight and

pregnancy-induced hypertension. As these health risks became known, DRBC took action to monitor PFAS in the Delaware River Basin starting in 2004. Our data set now stretches 20 years, covering fish, sediment and surface waters. This project adds to that dataset as DRBC seeks to understand PFAS presence, sources and impacts on organisms, ecosystems, recreation, drinking water and fishing.

In addition to PCBs and PFAS, other toxics of concern in this report are insecticides (legacy and current use), DxF and PAHs. Many of these other toxics have a long history of being studied in the DRB and have been identified as pollutants of concern in previously published technical reports on the Delaware River Basin.[2–4] The Technical Report for the Delaware Estuary and Basin highlights among its "actions and needs" the importance of continuing and expanding cooperative efforts to reduce bioaccumulative contaminants in the Delaware River, focusing on addressing persistent toxic pollutants.[5] Additionally, the most recent Delaware River and Bay Water Quality Assessment Report recommends monitoring and assessment of toxics.[6]

2. Project Overview

This project aims to characterize concentrations of various toxic pollutants in tributaries feeding into the Delaware River Estuary. The scope of this project involves the collection of water samples from 12 Estuary tributaries for the analysis of toxics and emerging contaminants, including PFAS, PCBs, DxF, PAHS, as well as OC, neonicotinoid and pyrazole insecticides. This monitoring aims to protect the Delaware Estuary's water resources by tracking toxic pollutants in ambient water, with data collected for water quality assessment and source tracking.

3. Sampling and Analysis

Water samples were collected from 12 tributary locations within Zones 2-5 of the Delaware River Basin on Oct 17, 18 and 23 of 2023 (Figure 1, Table 1). Since all 12 tributary sampling locations are tidally influenced, sampling was conducted at or near low tide to reduce the influence of tidal dilution on concentrations. Flows for the Delaware River at Trenton provide more than 65 percent of freshwater inflows into the Delaware Estuary with an average daily discharge of 12,690 cfs. During the sampling period, flows at Trenton were 10,200, 10,100 and 7,500 cfs, respectively, indicating slightly below-average flow conditions. The last rain event of >0.5 inches in the region prior to sampling was recorded on September 25, 2023.

Water grab samples were collected by hand using standard sampling equipment (e.g., Niskin bottles, bailers or peristaltic pump) appropriate to the site conditions and sample volume needed for PCB, DxF, insecticides and PAH analysis. Amber glass jars (2.5 L) were used for the PCB, DxF, insecticides and PAH samples. For PFAS analysis, water was collected directly into 0.5 L HDPE bottles. Sample collection follows the PFAS protocols described by the New York State Department of Environmental Conservation.[7] All certified clean sample bottles were supplied by the contract analytical lab, SGS Axys. Field blanks, equipment blanks and duplicates were collected at a frequency of once per sampling day.

All samples were preserved at < 6 °C onsite (with ice), during transport, storage and shipment to the lab for PCB, DxF, insecticides and PAH analyses. For PFAS, samples were preserved on ice at < 6 °C onsite and during transport. PFAS samples were frozen for storage at the DRBC and shipment to the lab. A temperature blank was also included with samples shipped to labs for analysis.

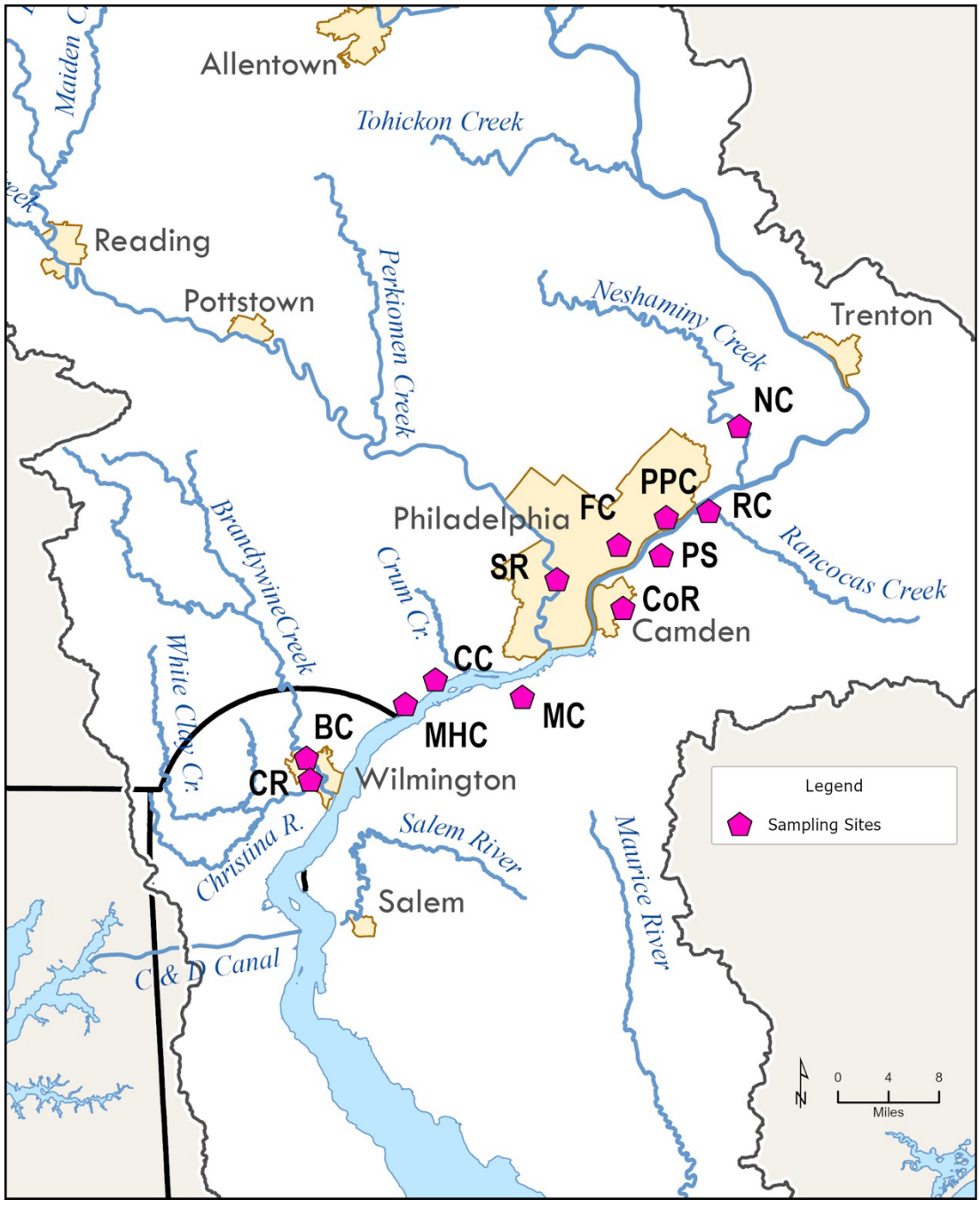

Figure 1. *Map showing the geographic spread of the surface water sampling sites.*

Table 1. *Sampling locations, ordered by decreasing river mile at their confluence with the Delaware.*

Tributary	Location Code	Confluence River Mile	Latitude	Longitude	State
Neshaminy Creek	NC	115.5	40.14156	-74.912438	PA
Rancocas Creek	RC	111.0	40.04434	-74.958270	NJ
Pennypack Creek	PPC	110.0	40.03718	-75.021786	PA
Pennsauken Creek	PS	105.5	39.99378	-75.029359	NJ
Frankford Creek	FC	104.5	40.00545	-75.092486	PA
Cooper River	CoR	101.0	39.93326	-75.086351	NJ
Schuylkill River	SR	92.5	39.96608	-75.184845	PA
Mantua Creek	MC	90.0	39.83125	-75.236045	NJ
Chester Creek	CC	83.0	39.85073	-75.365540	PA
Marcus Hook Creek	MHC	80.0	39.82249	-75.410040	PA
Brandywine Creek	BC	70.5	39.76035	-75.556779	DE
Christina River	CR	70.5	39.73524	-75.551033	DE

3.1 Sample Analysis

Samples were analyzed for the list of target analytes by the methods stated in Table 2 at DRBC's contracted analytical lab, SGS Axys.

Table 2. *Summary of Analytical Parameters used with surface water analysis in this study.*

Analytical Parameter	Method	Sample Volume
PAH (parent and alkylated)	SGS AXYS MLA-021, LRMS	2.5 L
Dioxins/furans	SGS AXYS MLA-217, GC-MS/MS, ATM 16130	2.5 L
OC insecticides	SGS AXYS MLA-228 GC-MS/MS	2.5 L
Insecticides (neonicotinoids and pyrazoles)	SGS AXYS MLA-114, LC-MS/MS	2.5 L
PCB Congeners	SGS AXYS MLA-010, HRMS 1668A/C	2.5 L
PFAS	SGS AXYS MLA-110 HRMS (EPA Method 1633)	0.5 L

3.2 Data Interpretations and Limitations

Data reported by the contract analytical lab was flagged if there were any potential issues. One of the most common is the "J" flag for a detected compound at levels below the limits of quantification. The next most common was "B" when a compound was detected in a blank associated with the sample. When the concentration of a compound in a sample was <10x the concentration in an associated blank, that data is not included in this report but was still uploaded to the Water Quality Portal. If the concentration of a compound in a sample was >10x the concentration in an associated blank, the data is included and discussed in this report. Among the data contained in this report, only one sample, Mantua Creek (N.J.) PAHs, had blank contamination that resulted in data not being included in this report. However, that data was still uploaded to the Water Quality Portal.

This project's experimental design, involving taking a single water sample at each site, provides only a snapshot of the concentrations at the time of sampling and may not represent long-term trends, especially given the high variability of water chemistry over both short and long timescales.

4. Results and Discussion

4.1 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a group of chemicals containing multiple aromatic rings. They naturally occur in fossil fuels but are also generated during the incomplete combustion of organic matter. Therefore, they have many sources from which they can enter the environment. In the Delaware River Basin, a few of the primary contributors include fire, combustion engines and incinerators in the urbanized portion of the river. Therefore, it is expected that tributaries with a large industrial footprint, highly trafficked roads and refineries will have a higher prevalence of PAHs.

SGS Axys method MLA-021 was used to extract and analyze PAHs. The results for each compound by sampling site are shown in Figure 2. PAH concentrations were quantifiable at all sampling sites. Across the 12 sites, 26 of the 50 target analytes were detected, with an average of 13.1 ± 7.2 (average ± standard deviation) detections, with a minimum of 3 (Marcus Hook Creek, Pa.) and a maximum of 22 (Christina River, Del.). While only methylnaphthalene was quantified at all 12 sites, four compounds, methylfluorene, naphthalene, phenanthrene and pyrene, were found at 11 sites. The average (± standard deviation) Σ_{PAH} (sum of all PAHs quantified in a sample) was 78.61 ± 65.91 ng L^{-1} with a low of 6.2 ng L^{-1} (Marcus Hook Creek) and a maximum of 222.9 ng L^{-1} (Mantua Creek, N.J.). The compounds with the highest average concentrations across the sites were fluoranthene (12.1 ± 8.5 ng L^{-1}), pyrene (10.2 ± 9.0 ng L^{-1}) and naphthalene (8.9 ± 6.1 ng L^{-1}). The compound detected at the highest concentration was pyrene in Mantua Creek at 34.0 ng L^{-1}. Among the 26 PAHs detected, there were 31 instances where four compounds exceeded the USEPA or both the USEPA and DRBC's water quality criteria for human health (Table 3) across eight sites. For DRBC criteria, the Human Health Criteria for water and organisms apply to freshwater zones (1-3), while organism only applies to brackish zones (4-6).

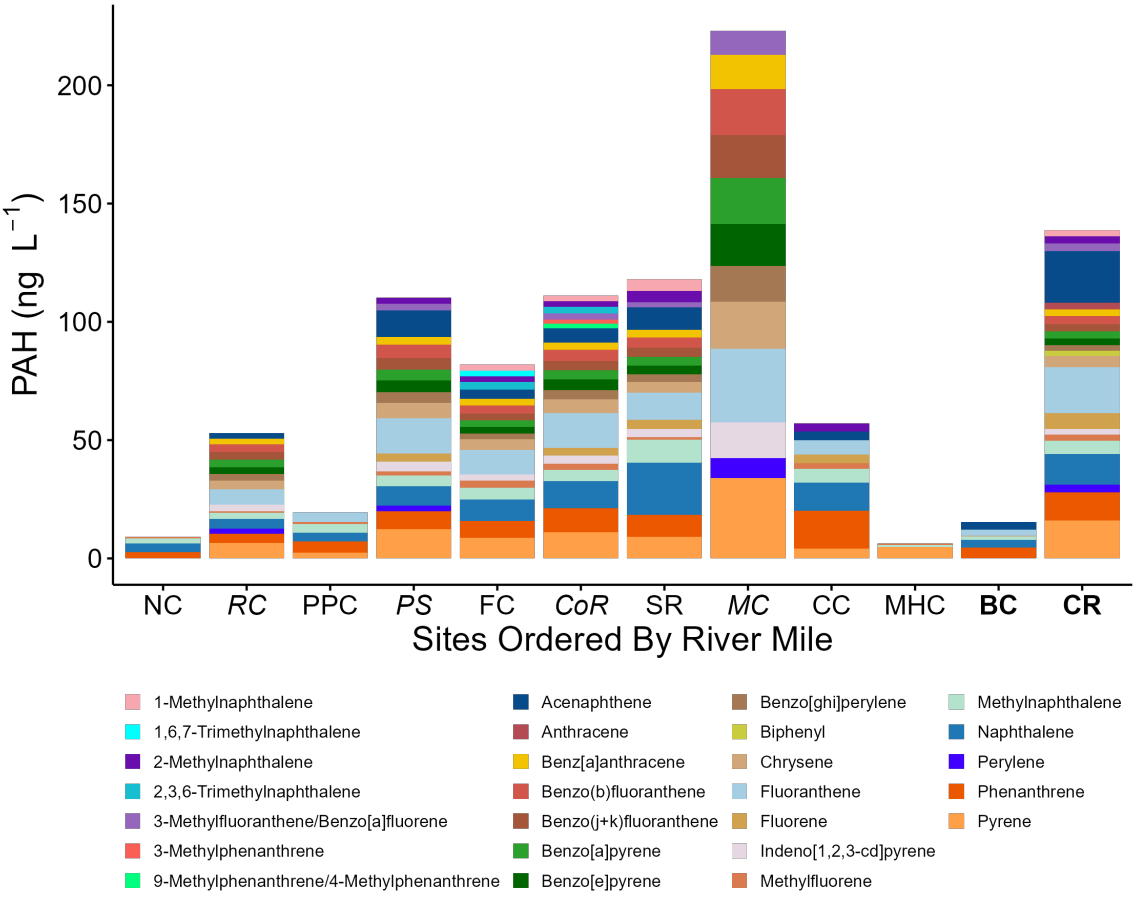

Figure 2. *Aqueous concentrations of PAHs in tributary samples. A normal x-axis label font represents Pennsylvania tributaries, while bold represents* ***Delaware*** *and italicized represents New Jersey.*

Table 3. *PAH compounds where there was at least one exceedance of either or both DRBC and USEPA water quality criteria for human health. Italicized site concentrations exceed USEPA criteria, while those in bold exceed DRBC criteria.*

PAHs with at least 1 criteria exceedance	Human Health Criteria				Site Concentrations (ng L^{-1})											
	Consumption of water & organism (ng L^{-1})		Consumption of organism only (ng L^{-1})													
	USEPA	DRBC	UESPA	DRBC	NC	RC	PPC	FC	PS	CoR	SR	MC	CC	MHC	BC	CR
Benzo(a)anthracene	1.2	3.8	1.3	180		*2.41*		*2.81*	*3.18*	*2.85*	*3.19*	*14.50*				*2.96*
Benzo(b)fluoranthene	1.2	38	1.3	180		*3.39*		*3.33*	*5.75*	*4.76*	*4.35*	*19.40*				*3.47*
Benzo[a]pyrene	0.12	3.8	0.13	18		*3.26*		*2.79*	***4.65***	***3.90***	*3.67*	***19.40***				*2.86*
Indeno[1,2,3-cd]pyrene	1.2	38	1.3	180		*2.81*		*2.47*	*4.29*	*3.41*	*3.32*	*15.30*				*2.43*

4.2 Dioxins and Furans

Dioxins and furans are unwanted byproducts of chemical processes used to make chlorinated intermediates and the combustion of chlorinated materials. They can be released to the environment from various sources, including waste incineration, fuel combustion for heat and power generation, foundries, scrap metal melting, paper production and more.[8] Fortunately, environmental releases of dioxins and furans have declined since the 1970s, largely due to the implementation of air quality regulations, even though these regulations did not specifically target these compounds.[9] However, dioxins and furans remain a long-term environmental concern because they are highly persistent and hydrophobic chemicals that accumulate at particularly high concentrations in sediments.[10] SGS Axys analytical method MLA-217 (EPA Method 16130) was used to extract and analyze dioxins and furans. The results are reported two ways. The first results reported are for the targeted analysis of 17 individual compounds that mediate chemical toxicity (Figure 3). The second result reported is total sum of categories of dioxins and furans: hepta-, hexa-, penta- and tetra- (Figure 4). Of the 17 individual dioxins and furans, only three were detected and quantified (Figure 3). HpCDD (1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin) and OCDF (1,2,3,4,6,7,8,9-Ocachlorodibenzofuran) were only detected three times and one time, respectively, while OCDD (1,2,3,4,6,7,8,9-Ocachlorodibenzo-p-dioxin) was detected in every sample, with concentrations ranging from 30.7 to 251.0 pg L^{-1} with an average of 95.6 ± 74.8 pg L^{-1}. The sources of this compound at the sites studied are unknown, but it is a byproduct of paper bleaching, drinking and wastewater chlorination and waste incineration.[11] It could also form due to forest fires. Neither

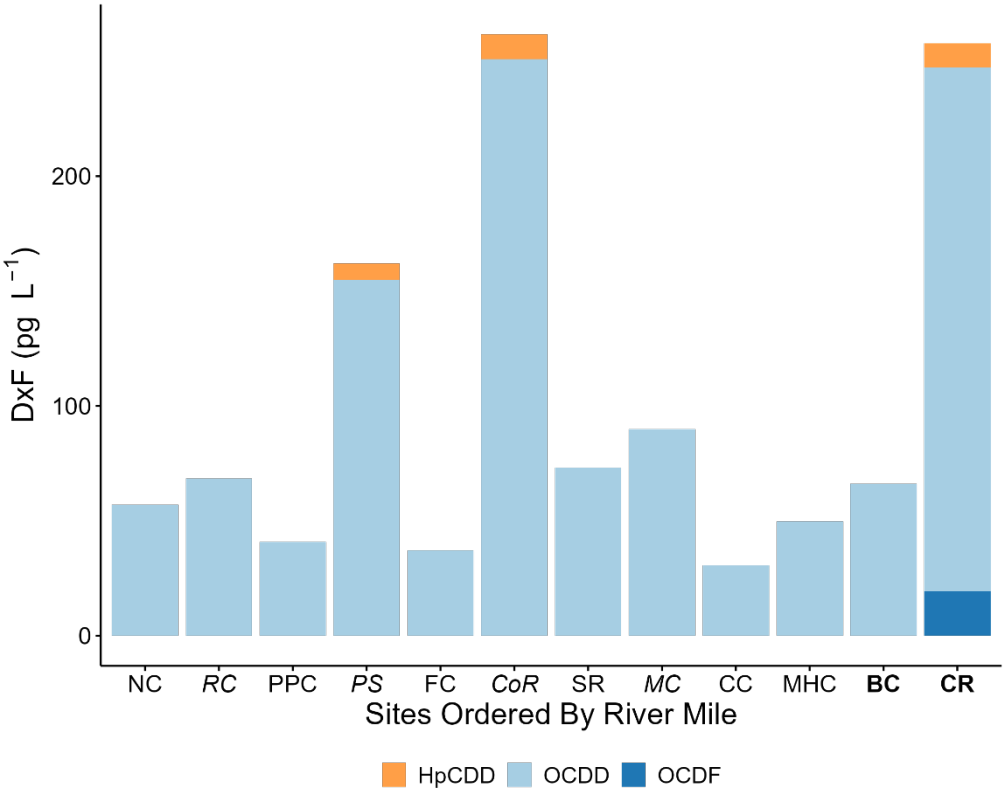

Figure 3. *Individual dioxins and furans quantified in samples. A normal x-axis label font represents Pennsylvania tributaries, while bold represents* ***Delaware*** *and italicized represents New Jersey.*

of the three targeted DxF compounds has water quality criteria in the Delaware River Basin from the Basin states, USEPA or DRBC. The one dioxin that has criteria in the Basin, 2,3,7,8-TCDD, was not detected in the samples above the analytical detection limit (0.13 ± 0.03 pg L^{-1}), which is above the human health criteria for water and organisms at 0.005 pg L^{-1}.

Total dioxin and furan results are the sum of individual hepta-, hexa-, penta- and tetra- congeners quantified above reporting limits. The total dioxin and furan values shown below do not include the concentrations of the 18 individual compounds presented in Figure 3. These individual total concentration categories were between 0.1 and 23.8 pg $L^{-1,}$ with total hepta-dioxins, hepta-furans and hexa-furans being found in all samples (Figure 4). The total categories were dominated by hepta-dioxins, followed by hepta-furans.

The tributaries with the highest total and individual concentrations of dioxins and furans are the Christina River (Del.), Pennsauken Creek (N.J.) and Cooper River (N.J.). A more detailed discussion of individual tributaries and their pollutant profiles is discussed below in section 4.7.

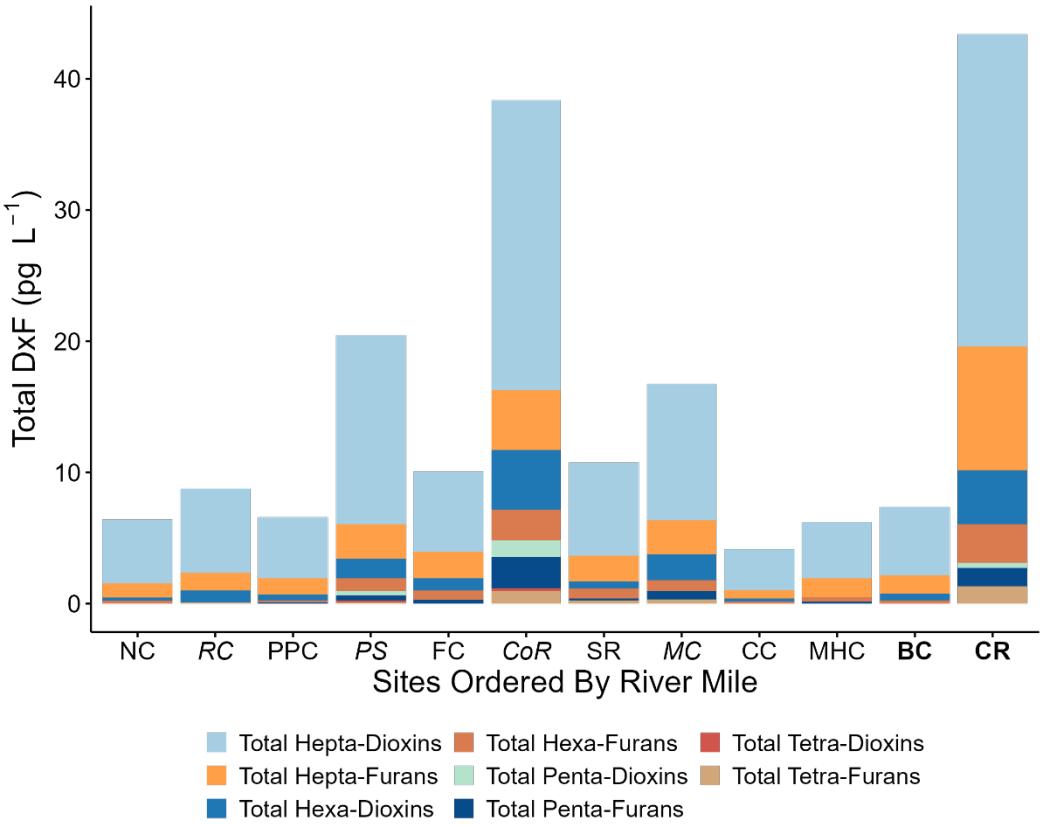

Figure 4. *Concentrations of totals dioxins or furans. Normal x-axis labels represent A normal x-axis label font represents Pennsylvania tributaries, while bold represents* ***Delaware*** *and italicized represents New Jersey.*

4.3 Organochlorine Insecticides

Use of organochlorine insecticides rapidly expanded after WWII to control mosquitoes and other insects in agriculture. Their broad application continued until the late 1960s when organochlorine effects on non-target organisms became evident. Organochlorines have not been produced since

the early 1970s, yet their resistance to degradation allows them to persist in sediment and water, remaining detectable after more than 50 years since they were banned.

SGS Axys method MLA-228 was used to extract and analyze 29 organochlorine insecticides. Despite their low solubility, these insecticides were quantified in water samples across the 12 tributary sites. The average number of compounds quantified at a given site was 11.6 ± 3.1, ranging from five to 16. Three compounds (dieldrin, hexachlorobenzene and cis-chlordane) were quantified at each site, while six were quantified at 10 or 11 sites. Despite being banned from production for >40 years, these highly persistent insecticides remain in many Delaware River tributaries.

Concentrations of individual organochlorine insecticides were predominantly <1 ng L^{-1}, except for dieldrin, which was detected in every sample. Of the 12 detections, eight were >1 ng L^{-1} and two were >20 ng L^{-1} (Figure 5). All detections of dieldrin were above USEPA and DRBC human health criteria for both "organisms only" and "water and organisms" (Table 4). While dieldrin was the compound found in the highest concentration, even without it, Marcus Hook Creek and Frankford Creek would still have higher Σ_{OC} (sum of all organochlorine compounds quantified in a sample) than the other 12 sites. Additional compounds that exceeded DRBC and/or USEPA water quality criteria were p,p'-DDE (11 sites), p,p'-DDT (nine sites), p,p'-DDD (five sites), heptachlor (two sites) and hexachlorobenzene (one site).

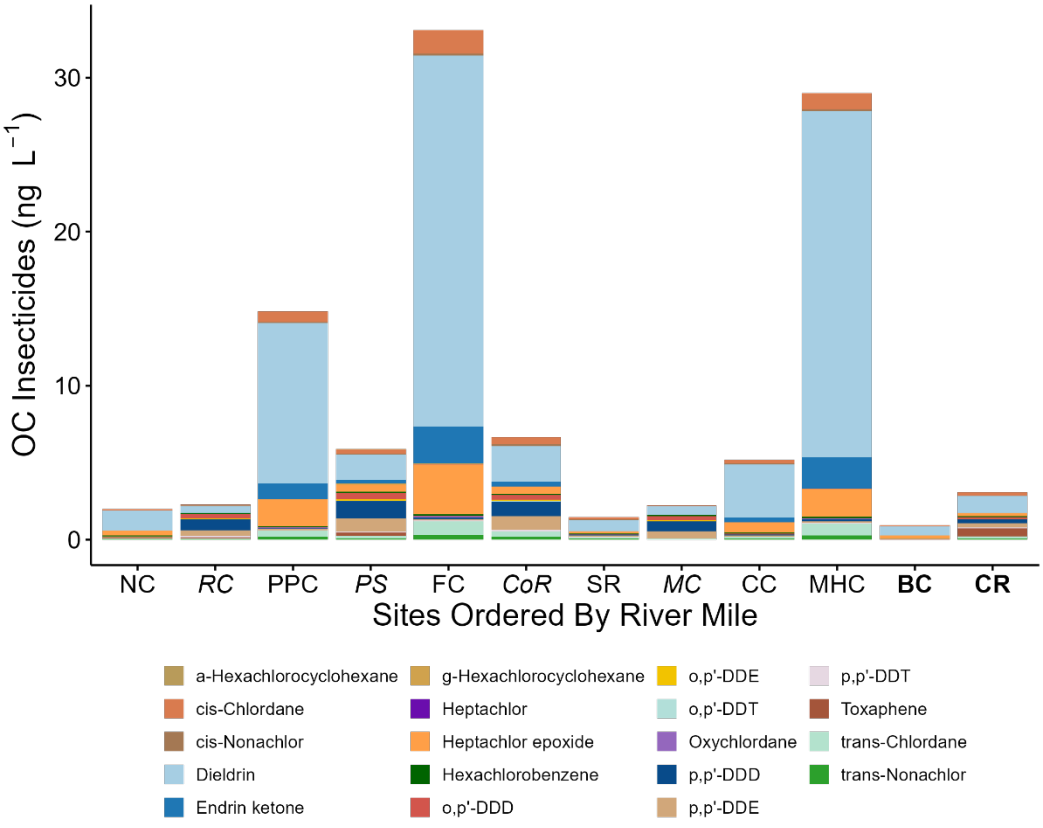

Figure 5. *Concentrations of organochlorine insecticides. A normal x-axis label font represents Pennsylvania tributaries, while bold represents* ***Delaware*** *and italicized represents New Jersey.*

Table 4. *Organochlorine insecticides where there was at least one exceedance of either or both DRBC and USEPA water quality criteria for human health. Italicized site concentrations exceed USEPA criteria, while those in bold exceed DRBC criteria.*

Organochlorine Insecticides with at least 1 criteria exceedance	Human Health Criteria				Site Concentrations (ng L^{-1})											
	Consumption of water & organism (ng L^{-1})		Consumption of organism only (ng L^{-1})													
	USEPA	DRBC	UESPA	DRBC	NC	RC	PPC	PS	FC	CoR	SR	MC	CC	MHC	BC	CR
Heptachlor epoxide	0.032	0.039	0.032	0.039	***0.317***		***1.73***	***0.473***	***3.25***	***0.484***	***0.139***		***0.684***	***1.81***	***0.16***	***0.204***
Dieldrin	0.0012	0.052	0.0012	0.054	***1.29***	***0.457***	***10.4***	***1.63***	***24.1***	***2.31***	***0.723***	***0.535***	***3.44***	***22.5***	***0.63***	***1.09***
Hexachlorobenzene	0.079	0.28	0.079	0.29	0.051	0.045	0.076	0.074	0.072	0.053	0.045	*0.087*	0.065	*0.082*	0.042	0.072
α-Hexachlorocyclohexane	0.036	2.6	0.39	4.9				*0.047*								
Heptachlor	0.0059	0.079	0.0059	0.079					*0.024*					*0.029*		
p,p'-DDE			0.018	0.22	*0.051*	***0.359***	*0.069*	***0.836***	*0.101*	***0.892***		***0.47***	*0.077*	*0.121*	*0.038*	***0.272***
p,p'-DDD			0.12	0.31	0.022	***0.726***	0.042	***1.14***	*0.083*	***0.96***	0.055	***0.639***	0.078	0.114		*0.266*
p,p'-DDT			0.03	0.22		*0.086*	*0.037*	*0.069*	*0.05*	*0.098*	*0.03*	*0.036*		*0.051*		*0.051*

4.4 Current Use Insecticides

4.4.1 Neonicotinoids

These insecticides are among the most heavily used globally and are highly effective in controlling and preventing insect infestations. These chemicals can be applied prophylactically as seed coatings or directly to plants. Unlike most insecticides, neonicotinoids are water-soluble, which allows them to be absorbed by plants to control boring insects.[12] Despite their effectiveness, neonicotinoids have low toxicity to vertebrates, making them relatively safe for human use. A major concern with neonicotinoids is their potential adverse impacts on non-target species, particularly pollinators, which remains an open area of research.

SGS Axys analytical method MLA-114 was used to extract and analyze 16 neonicotinoids. Of these, nine are insecticides, six are metabolites of those insecticides and one is an adjuvant added to formulations to enhance insecticide efficacy. Across our 12 sites, the average number of neonicotinoid detections was 3.9 ± 2.9, with 11 of the 12 sites between two and four detections. Frankford Creek was the outlier, with 13 detections and the highest Σ_{NN} (sum of neonicotinoids

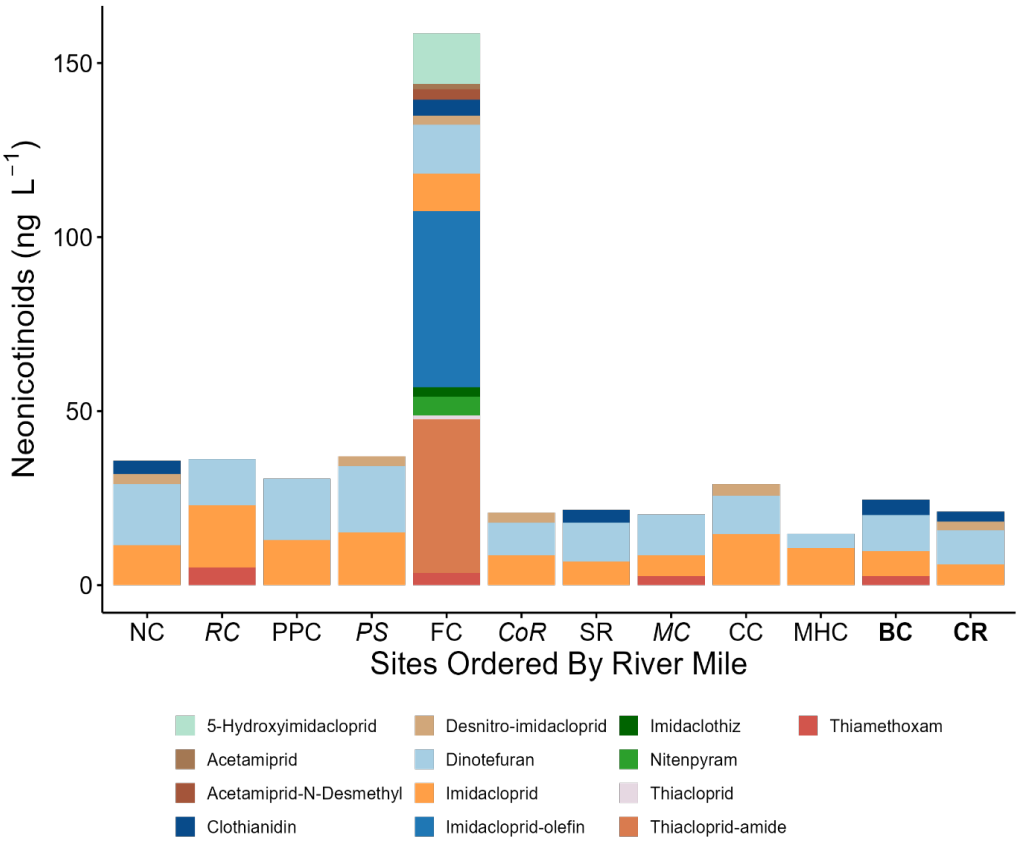

Figure 6. *Aqueous neonicotinoid concentrations in tributary surface waters. Normal x-axis labels represent Pennsylvania tributaries, while bold represents* ***Delaware*** *and italicized represents New Jersey.*

quantified in a sample) at 158.5 ng L^{-1}, whereas the other 11 sites ranged from 14.8 to 37.0 ng L^{-1} (Figure 6). Among the compounds quantified in Frankford Creek (Pa.), imidacloprid-olefin and thiacloprid-amide, which are metabolites of imidacloprid and thiacloprid, had the highest concentrations of all neonicotinoids at 50.5 and 44.2 ng L^{-1}, respectively. The presence of metabolites suggests that a source of these insecticides in the watershed is actively degrading. The most prevalent neonicotinoid insecticides are dinotefuran. Imidacloprid was quantified at all 12 sites and had the highest average concentrations across the sites at 12.4 ± 4.2 and 10.7 ± 3.9 ng L^{-1}. Currently, it is unknown why Frankford Creek is an outlier compared to the other 11 tributaries (see Section 4.7.1 for further discussion).

4.4.2 Pyrazoles

Fipronil is a pyrazole insecticide used to control pests on crops and golf courses as well as fleas on pets. Like neonicotinoids, it has high toxicity to insects but low toxicity to vertebrates. Fipronil, however, has a lower solubility than neonicotinoids[13] , making it less mobile in the environment and, consequently, more persistent.

SGS AXYS analytical method MLA-114 was also used to extract and analyze five pyrazole compounds, including the insecticide fipronil and four of its metabolites. Fipronil was detected at 11 of the 12 sites, with only the Christina River (Del.) being below detection. The most common metabolites in the samples were fipronil sulfone (10 sites) and fipronil desulfinyl (five sites). Notably, fipronil sulfone was quantified in the Christina River, indicating that while fipronil itself was not found above

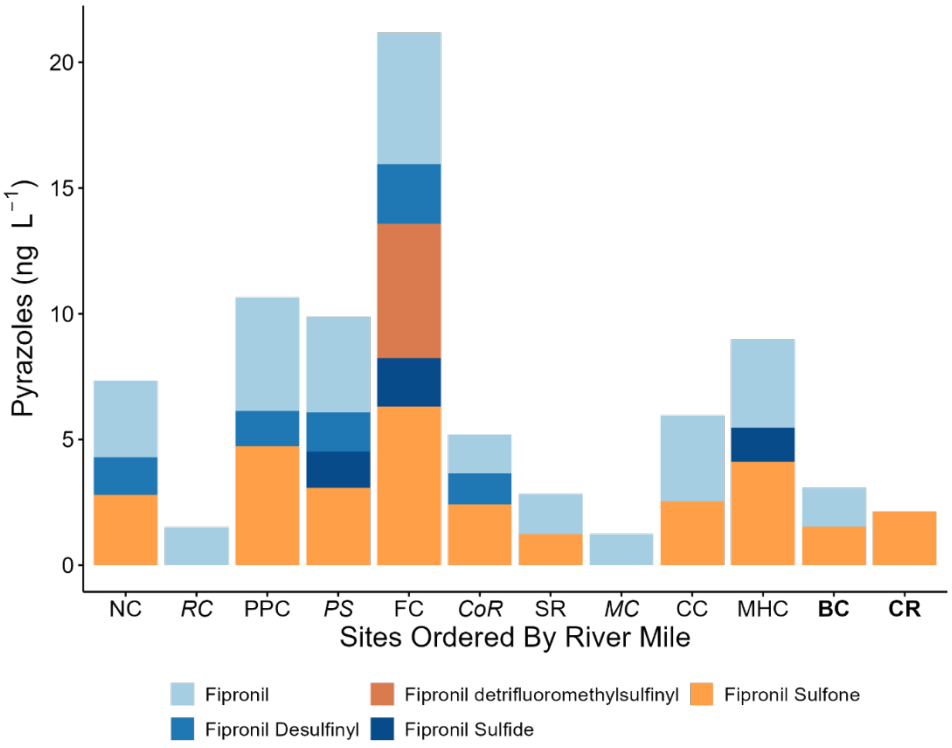

Figure 7. *Aqueous concentrations of fipronil and its metabolites in surface waters of Delaware River tributaries. A normal x-axis label font represents Pennsylvania tributaries, while bold represents* ***Delaware*** *and italicized represents New Jersey.*

detection limits, it is still being used in the watershed. Concentrations of Fipronil averaged 2.8 ± 1.4 ng L^{-1}, while the metabolites, when quantifiable in a sample, were similar (Figure 7). Like with other classes of insecticides, Frankford Creek (Pa.) had the highest number of detections and total fipronil concentrations (sum of all targeted analytes).

4.5 Polychlorinated Biphenyls (PCBs)

PCBs are among the most well-known legacy environmental pollutants, manufactured from 1929 until their ban in 1979. These chemicals were valued for their long-term stability, non-flammability, high boiling point and electrical insulating properties, making them suitable for use in a wide range of applications,[14] including as a dielectric material in electrical transformers, as plasticizers in paints, plastics and rubber and as pigments, dyes and additives in carbonless copy paper.[14] Due to their broad use and limited toxicological knowledge at the time, PCBs were mass-produced and frequently mishandled, resulting in widespread environmental releases. Because of their long-term stability and hydrophobicity, PCBs—banned for ~45 years—remain nearly ubiquitous in sediment and are found at low concentrations in water.

PCBs were analyzed using the SGS AXYS MLA-010 analytical method for 159 features (individual and multiple congeners that cannot be chromatographically separated), which account for all 209 congeners. Of those 159 features, 93 were detectable in at least one sample. The number of PCBs detected in each tributary ranges from three to 66, averaging 29.6 ± 21.3. This indicates that despite a manufacturing ban since 1979 (45 years ago), a broad suite of these compounds is pervasive in Delaware River Basin estuarine tributaries.

The concentrations of PCB_{TOTAL} (the sum of all quantifiable PCB features in an individual sample) ranged from 124 to 6,541 pg L^{-1}, with an average of 2,037 ± 2,169 pg L^{-1} (Figure 8). The highest detection of any individual PCB was for decachlorobiphenyl at 824 pg L^{-1} in the Christina River (Del.) sample. There was also a detection at 812 pg L^{-1} for decachlorobiphenyl at Marcus Hook Creek (Pa.). While the source of decachlorobiphenyl in these samples is unknown, the DuPont Edgemoor facility, located slightly upstream from the mouth of the Christina River, was a known source of this congener in the past.

The lowest concentration for an individual compound, other than those below detection limits, was 16.2 pg L^{-1}. DRBC's human health water quality criteria for both "organisms only" and "water and organisms" are set at 16 pg L^{-1} for PCB_{TOTAL} within a sample. Therefore, each of the 355 instances in which an individual PCB was quantified across the 12 sites exceeded DRBC's human health water quality criteria. Furthermore, PCB_{TOTAL} concentrations across the 12 tributaries were 7.7 to 409 times higher than DRBC's human health water quality criteria.

PCB_{TOTAL} at all sites greatly exceeded DRBC's water quality criteria, with Marcus Hook Creek (6,541 pg L^{-1}) and the Christina River (5,583 pg L^{-1}) having the highest PCB_{TOTAL} concentrations, while Neshaminy Creek (Pa.), had the lowest at 124 pg L^{-1}.

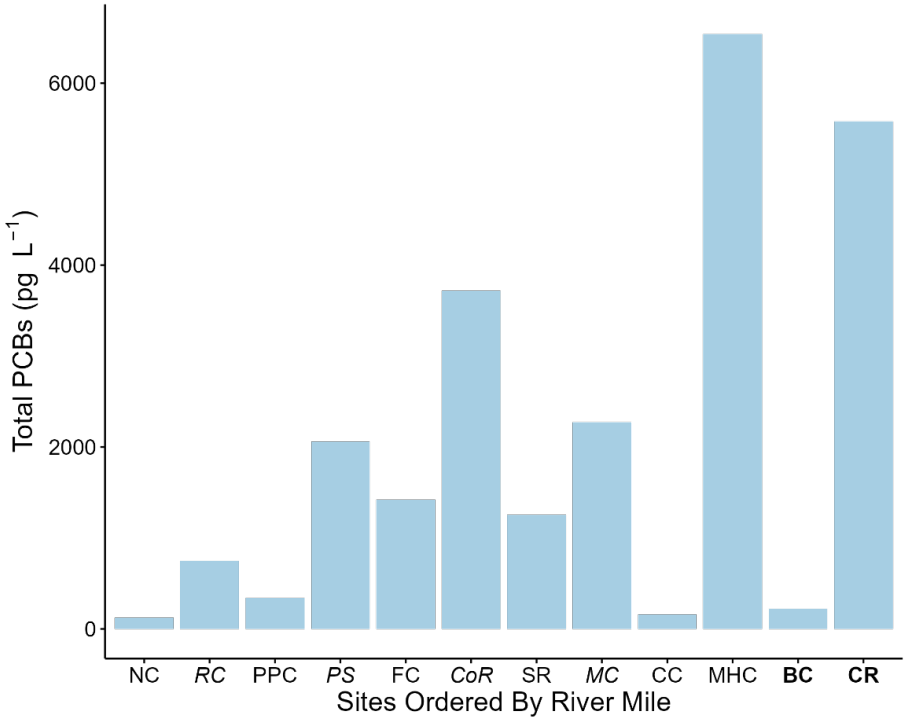

Figure 8. *Total aqueous PCB concentrations in tributaries of the Delaware River. A normal x-axis label font represents Pennsylvania tributaries, while bold represents* ***Delaware*** *and italicized represents New Jersey.*

4.6 Per and Polyfluoroalkyl Substances (PFAS)

The first commercially produced PFAS compound, PTFE (Teflon), was accidentally discovered at the DuPont Chambers Works facility in Deepwater, N.J., on the banks of the Delaware River in 1938.[15] Since then, the number of PFAS compounds has surged to nearly 15,000.[16] These chemicals are used in countless products, many of which are known to consumers, including non-stick cookware, stain-resistant furniture, waterproof clothing and grease-resistant food packaging, to name a few. Generally, PFAS are highly persistent and range from mildly to highly soluble. Unlike many legacy pollutants, PFAS have a stronger affinity for binding to proteins rather than lipids. Due to these unique characteristics, the specific PFAS compounds in the environment vary across each environmental media (water, sediment, soils, plants, animal tissues, etc.). Sources include PFAS manufacturers, industry (users of PFAS), military installations (largely AFFF firefighting foams), landfill leachate, stormwater runoff (leaching from exterior materials containing PFAS) and treated wastewater effluent.

SGS AXYS MLA-110 (EPA Method 1633) was used to extract and analyze water samples for 40 PFAS compounds. Of these, 10 of the 40 compounds were found at concentrations above quantification limits. Five (PFBS, PFHxA, PFOS, PFOA and PFPeA) of these 10 compounds were detected at all 12 sites, and two (PFHpA, PFNA) were found at 11 sites, indicating the widespread presence of these seven compounds in tributary waters of the Delaware River Estuary (Figure 9). The average number of detections per sample was 8.1 ± 1.1, with a maximum of 10 detections in the Christina River in Del. and a minimum of 6 detections in Mantua Creek in N.J. The Σ_{PFAS} (sum of all PFAS that are

quantifiable in a sample) concentration across all sites averaged 57.3 ± 34.2 ng L^{-1}, with a maximum in the Christina River (131.2 ng L^{-1}) and a minimum in Mantua Creek (20.9 ng L^{-1}).

Recent DRBC PFAS sampling (mostly in the mainstem Delaware River) has demonstrated that Σ_{PFAS} concentrations increase with decreasing river mile (from Trenton, N.J. to Pea Patch Island, Del.), with peak values at Pea Patch Island ranging from 40-50 ng L^{-1}.[17] Tributary sites have Σ_{PFAS} concentrations generally near or well above the high end of values observed in the mainstem, with 7 of the 12 sites >40 ng L^{-1}. While the discharge volumes of these tributaries are relatively low compared to the mainstem, the mass of PFAS they deliver to the river contributes to the concentration increases as water flows downstream.

In December 2024, the USEPA released draft National Human Health Ambient Water Quality Criteria for PFOA, PFOS and PFBS, which are shown in Table 5 with the concentrations of each compound across the sites sampled. At the time of this publication, these criteria remain draft and are subject to change. PFBS Surface water concentrations did not exceed the draft criteria for any sites, while PFOA and PFOS concentrations did exceed the draft criteria at all sites. Additionally, the new USEPA Maximum Contaminant Level (MCL) values for PFOA, PFOS and PFNA in drinking water are shown, which are several orders of magnitude higher than the human health criteria. PFOA exceeded the 4 ng L^{-1} MCL at each site, while PFOS exceeded its 4 ng L^{-1} MCL at nine sites. PFNA only exceeded its 10 ng L^{-1} MCL at the Chester Creek (Pa.) site. The human health criteria, while still in draft form, are designed to "protect the general population from adverse health effects due to ingesting water, fish and shellfish from inland and nearshore water bodies." Therefore, water concentrations that exceed these criteria could lead to adverse health effects in humans.

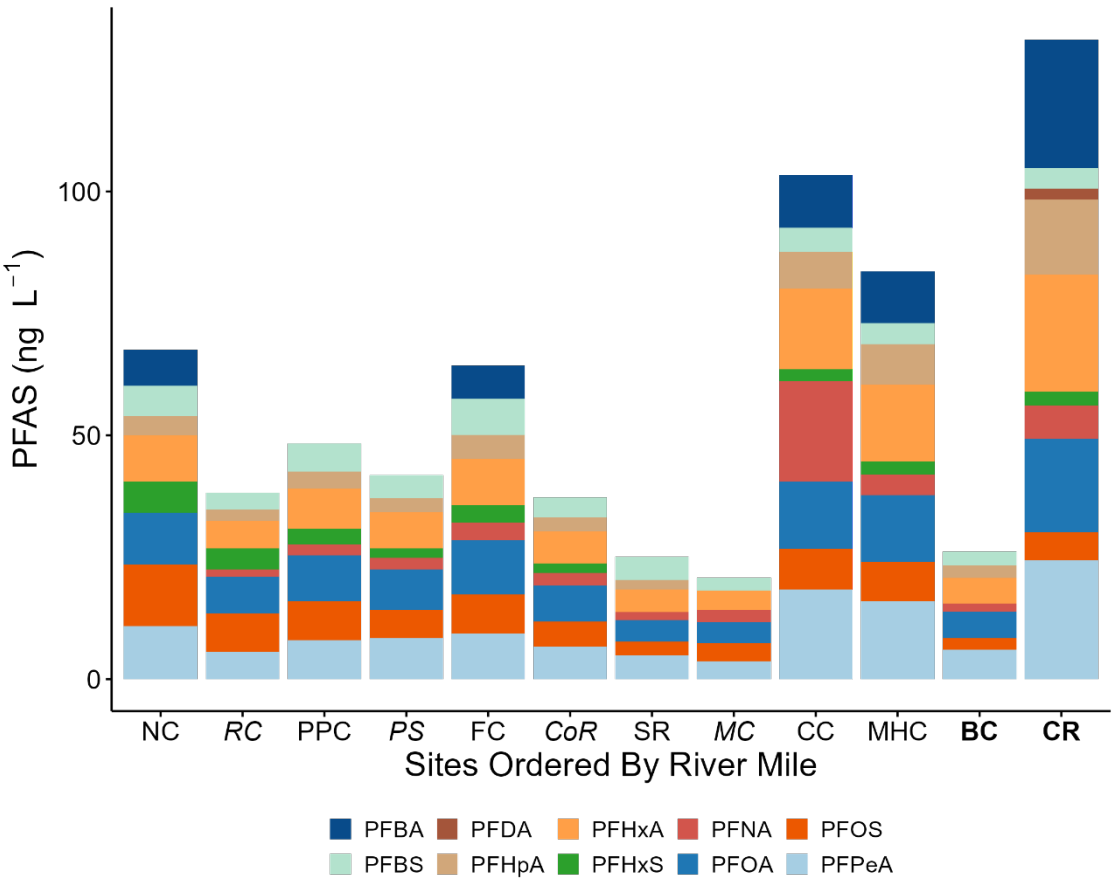

Figure 9. *Aqueous concentrations of PFAS in tributary surface waters, arranged by decreasing river mile at its confluence with the Delaware River. A normal x-axis label font represents Pennsylvania tributaries, while bold represents* ***Delaware*** *and italicized represents New Jersey.*

Table 5. *PFAS compound concentrations that exceeded USEPA Draft surface water human health criteria (**bold**) and USEPA Maximum Contaminant Levels (italicized).*

PFAS with at least 1 criteria exceedance	USEPA Draft Surface Water Human Health Criteria		USEPA Drinking Water	Sites											
	Consumption of water & organism	Consumption of organism only	Maximum Contaminant Level	NC	RC	PPC	PS	FC	CoR	SR	MC	CC	MHC	BC	CR
				ng L^{-1} or ppt											
PFOA	0.0009	0.0036	4	***10.6***	***7.5***	***9.4***	***8.3***	***11.1***	***7.4***	***4.4***	***4.3***	***13.8***	***13.7***	***5.5***	***19.1***
PFOS	0.06	0.07	4	***12.6***	***7.9***	***8.0***	***5.7***	***8.1***	***5.2***	**2.8**	**3.7**	***8.3***	***8.0***	**2.3**	***5.7***
PFNA			10									*20.6*			
Mixture			1 (unitless)									*2.3*			

4.7 TRIBUTARY COMPARISON ACROSS POLLUTANT CLASSES

All tributaries sampled were contaminated with chemicals from each of the targeted pollutant classes. Even tributaries with low concentrations relative to the others still exceed water quality criteria, particularly for PCBs. Tributaries that stood out due to one or more compounds, classes of pollutants or trends in pollutants are briefly discussed in the sections below.

4.7.1 Frankford Creek

Frankford Creek flows through densely populated neighborhoods, with a large semi-natural buffer including parks and golf courses in its floodplain, before entering industrial areas in North Philadelphia, Pa. The presence and concentration of legacy and current-use insecticides in Frankford Creek are notably higher than the other tributaries examined. It had the highest Σ_{OC}, driven by heptachlor epoxide and endrin ketone, both of which exceeded DRBC and USEPA water quality criteria in the analyzed samples. In terms of current-use insecticides, neonicotinoids and pyrazoles, the contrast is even more stark: Frankford Creek had the highest occurrence and concentrations of neonicotinoids and pyrazoles, which were ~2 and >3 times higher, respectively, than the second most polluted tributaries. The use of insecticides in the greenspace surrounding Frankford Creek may explain the presence of current-use insecticides. However, the reason for the presence of organochlorine insecticides, which have been banned from manufacture for >50 years, is currently unknown.

4.7.2 Christina River

The Christina River flows through Wilmington, Del. It is lined by marshes immediately upstream of the city before giving way to tree-lined buffers as it drains from residential sprawl. The Christina River is a hotspot for legacy pollution, including dioxins and furans, PCBs and PAHs, and also for the emerging contaminant PFAS. For dioxins and furans, it has the second highest concentrations of the individual toxic compounds and is the highest for total dioxins and furans. PCB_{TOTAL} concentrations also stand out on the Christina River at 5,583 pg L^{-1}, behind Marcus Hook Creek, but well above the 3rd tributary (Cooper River) at 3,719 pg L^{-1}. The Christina River also had the second-highest Σ_{PAH} concentration at 139 ng L^{-1}. The presence of legacy pollutants in the Christina River is well-documented, and ongoing efforts are focused on reducing pollutant loading and remediating contaminated sites.[18] For PFAS, the Christina River had the highest Σ_{PFAS} concentration at 131 ng L^{-1}, even higher than the 76 ng L^{-1} measured by DRBC at the same exact location in the fall of 2021.[19] It should be noted that the 2021 sample was collected near the middle of a rising tide, which would have diluted the concentration in the river water, compared to the more recent sample, which was collected during low tide. The presence and impact of PFAS is a relatively new issue, but numerous lawsuits against manufacturers are pending, efforts to regulate their use are underway and water quality criteria are actively being examined.

4.7.3 Marcus Hook Creek

The headwaters of Pennsylvania's Marcus Hook Creek flow through greenspace with densely populated areas nearby. However, a large part of its watershed contains heavy industrialization that

dates to the 1800s. While much of the watershed's industrial footprint is from the petrochemical industry, the creek has the lowest concentration of Σ_{PAH} at 6.22 ng L^{-1}. However, it has some of the highest concentrations of other legacy pollutants. Marcus Hook Creek had the highest PCB_{TOTAL} concentration at 6,540 pg L^{-1}, which, for perspective, was almost 1,000 pg L^{-1} higher than the second highest concentration recorded in the Christina River. It also had similar levels of organochlorine insecticides (~29 ng L^{-1}) to Frankford Creek. Lastly, this watershed also stands out with the 3rd highest Σ_{PFAS} concentration.

4.7.4 Mantua Creek

The Mantua Creek Watershed in N.J. is dominated by high-density suburban sprawl followed by warehouses and petrochemical facilities near its mouth at the Delaware River. The petrochemical presence could be why this watershed has Σ_{PAH} concentrations of 222.9 ng L^{-1}, almost double the tributary with the second highest value. No other target analyte group stood out for Mantua Creek.

4.7.5 Cooper River

The Cooper River Watershed in N.J. is comprised of suburban neighborhoods and commercial properties, with a lower industrial presence than many of the other tributaries sampled. Upstream of the sampling location, the river features a large impoundment called Cooper River Lake (circa 1940), which likely traps sediment- and particulate-bound pollutants while increasing contact times that enhance sorption and degradation. This impoundment may explain why the Cooper River has a relatively higher concentration of legacy pollutants. It had the highest sum concentration of the individual toxic DxF compounds appearing in Figure C (261 pg L^{-1}), primarily due to OCDD accounting for 251 pg L^{-1}. It also had the second-highest concentration of total dioxins and furans, just behind the Christina River. The Cooper River was also a hotspot for PCB_{TOTAL} at 3,719 pg L^{-1}.

5. Conclusions

The Delaware River Estuary from Trenton, N.J., to Lewes, Del. is a densely populated region with a long history of industrialization, resulting in pollution from a wide range of land uses along this stretch. The results from the tributaries sampled reflect this history, showing a mixture of legacy pollutants—such as PCBs, PAHs, organochlorine insecticides, dioxins and furans—and more recent compounds, including PFAS, neonicotinoids and pyrazoles. While the sources of these pollutants in each tributary may not be known, connections can generally be made to current or past land use within each watershed. Of particular concern are the exceedances of EPA and DRBC water quality criteria, notably for legacy pollutants such as PCB_{TOTAL}, along with four PAHs and eight organochlorine insecticides. Despite being banned for over 40 years, PCBs and organochlorines persist in the Delaware River Basin. Emerging contaminants, including neonicotinoids and pyrazoles, are also present, although they do not have any water quality criteria. Similarly, PFAS is a growing concern and was often present at higher concentrations in the tributaries measured compared to the Delaware River mainstem. Several PFAS compounds are being investigated as candidates for water quality criteria in the coming years to limit their environmental discharges or even use in consumer products.

6. Project Overview

This project was undertaken by DRBC, and all sample analyses were carried out by our contract analytical lab, SGS Axys. No major problems occurred during this project, and therefore, the only change made to the original work plan was an extension to allow for more time to process the data and write the final report.

REFERENCES

(1) DRBC. *Polychlorinated Biphenyls (PCBs)*. Delaware River Basin Commission. https://www.nj.gov/drbc/programs/quality/pcb.shtml (accessed 2025-01-07).
(2) DuPont. *DuPont Delaware River Study Phase I Characterization of Ecological Stressors In the Delaware Estuary*; 2007.
(3) Fischer, J. M.; Riva-Murray, K.; Hickman, R. E.; Chichester, D. C.; Brightbill, R. A.; Romanok, K. M.; Bilger, M. D. *Water Quality in the Delaware River Basin, Pennsylvania, New Jersey, New York, and Delaware, 1998-2001*; Circular; 2004. https://pubs.usgs.gov/circ/2004/1227/ (accessed 2023-01-18).
(4) Hickman, R. E. *Pesticide Compounds in Streamwater in the Delaware River Basin, December 1998-August 2001*; Scientific Investigations Report; Scientific Investigations Report; 2004. https://www.usgs.gov/publications/pesticide-compounds-streamwater-delaware-river-basin-december-1998-august-2001.
(5) Haaf, L.; Demberger, S.; Kreeger, D.; Baumbach, E. *Technical Report for the Delaware Estuary and Basin 2017*; 17–07; Partnership for the Delaware estuary, 2017; p 379. https://www.delawareestuary.org/wp-content/uploads/2018/01/TREB-2017-complete.pdf.
(6) DRBC. *Delaware River and Bay Water Quality Assessment*; 2023–1; Delaware River Basin Commission, 2023. https://www.nj.gov/drbc/library/documents/WQAssessmentReport2022.pdf.
(7) NYSDEC. *Sampling, Analysis, and Assessment of per and Polyfluoroalkyl Substances (PFAS)*; 2022. https://www.dec.ny.gov/docs/remediation_hudson_pdf/pfassampanaly.pdf (accessed 2023-01-18).
(8) USEPA. *Locating and Estimating Air Emissions from Sources of Dioxins and Furans*; EPA-454/R-97-003; USEPA: Research Triangle Park, North Carolina. https://www3.epa.gov/ttnchie1/le/dioxin.pdf.
(9) Hites, R. A. Dioxins: An Overview and History. *Environ. Sci. Technol.* **2011**, *45* (1), 16–20. https://doi.org/10.1021/es1013664.
(10) Wenning, R. J.; Martello, L. B. Dioxin. In *Encyclopedia of Ecology*; Jørgensen, S. E., Fath, B. D., Eds.; Academic Press: Oxford, 2008; pp 921–930. https://doi.org/10.1016/B978-008045405-4.00385-2.
(11) PubChem. *Octachlorodibenzo-p-dioxin*. https://pubchem.ncbi.nlm.nih.gov/compound/18636 (accessed 2025-01-09).
(12) *REVIEW: An overview of the environmental risks posed by neonicotinoid insecticides - Goulson - 2013 - Journal of Applied Ecology - Wiley Online Library*. https://besjournals.onlinelibrary.wiley.com/doi/full/10.1111/1365-2664.12111 (accessed 2025-01-03).
(13) Bonmatin, J.-M.; Giorio, C.; Girolami, V.; Goulson, D.; Kreutzweiser, D. P.; Krupke, C.; Liess, M.; Long, E.; Marzaro, M.; Mitchell, E. A. D.; Noome, D. A.; Simon-Delso, N.; Tapparo, A. Environmental Fate and Exposure; Neonicotinoids and Fipronil. *Environ. Sci. Pollut. Res.* **2015**, *22* (1), 35–67. https://doi.org/10.1007/s11356-014-3332-7.
(14) US EPA, O. *Learn about Polychlorinated Biphenyls*. https://www.epa.gov/pcbs/learn-about-polychlorinated-biphenyls (accessed 2025-01-03).
(15) E.I. du Pont de Nemours & Company. The Discovery. An “Accident” Derived from Solid Research. *The wide world of teflon*. 1963, p 20.

(16) *CompTox Chemicals Dashboard*. https://comptox.epa.gov/dashboard/chemical-lists/PFASSTRUCT (accessed 2025-01-03).
(17) Conkle, J. *PFAS Water Quality and Fish Tissue Assessment Study - Year 2*; 2024–2; Delaware River Basin Commission: West Trenton, NJ, 2024; p 35. https://www.nj.gov/drbc/library/documents/DRBC_PFASYear2Study_DWCF_march2024.pdf.
(18) *Chemical Contaminants*. Christina Conservancy. https://www.christinaconservancy.org/issues/chemical-contaminants/ (accessed 2025-01-07).
(19) Conkle, J.; MacGillivray, R. *PFAS Water Quality and Fish Tissue Assessment Study - Year 1*; 2023–6; Delaware River Basin Commission: West Trenton, NJ, 2023; p 19. https://www.nj.gov/drbc/library/documents/DRBC_PFAS-Year1Study_DWCF_July2023.pdf.