## Health & Ecological Risk Assessment

# Temporal Trends of Per- and Polyfluoroalkyl Substances in Delaware River Fish, USA

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### ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are found in a variety of industrial and household products. Human and wildlife exposure to PFAS is widespread. Increasing evidence suggests adverse effects of PFAS to human health and the environment. Human health risks from exposure through drinking water and fish consumption are areas of concern. Therefore, understanding occurrence and exposure risk is important to protect water resources. PFAS was investigated in fish fillet from the Delaware River over a 15-y period (2004–2018). The sample period coincided with actions to reduce or eliminate the release of certain PFAS to the environment. Elevated levels of perfluorononanoate (PFNA) and perfluoroundecanoate (PFUnA) were initially observed in tidal fish fillet. While significant decreases in PFNA and PFUnA concentrations were observed in fish fillet from the tidal river during the timeframe of the study, changes in concentrations of other PFAS in tidal and nontidal fish were less substantial. In 2018, fish fillet continued to be contaminated with perfluorooctanesulfonate (PFOS) at levels exceeding recommended regional risk advisory limits on fish consumption. *Integr Environ Assess Manag* 2021;17:411–421. © 2020 SETAC

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## INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are found in a variety of industrial and household products such as stain-repellant textiles, firefighting foams, and paper coatings (Conder et al. 2008; Buck et al. 2011; Kotthoff et al. 2015). Perfluorinated chains have unique properties to repel both water and oil (Ding and Peijnenburg et al. 2013; Krafft and Riess 2015). They are a diverse group of compounds that display varying degrees of persistence, toxicity, and bioaccumulation in the environment (Beach et al. 2006; Ding and Peijnenburg et al. 2013; Cousins et al. 2019a, 2019b). The sources of PFAS in the environment include direct emissions from the manufacturing, use, and disposal of surfactants and other materials containing PFAS as well as indirect emissions by transformation of precursor substances such as fluorotelemer alcohols (Prevedouros et al. 2006; Buck et al. 2011; Butt et al. 2014). The PFAS discharges to rivers can arise from waste treatment facilities, especially wastewater treatment facilities receiving industrial waste (Sinclair et al. 2006; Konwick et al. 2008; Castiglioni et al. 2015; Filipovic and Berger 2015; Valsecchi et al. 2015), landfill leachates (Busch et al. 2010; Eggen et al. 2010; Benskin et al. 2012; Allred et al. 2014;

Hamid et al. 2018), land application of waste (Skutlarek et al. 2006), release of aqueous firefighting foams (Kwadijk et al. 2014), stormwater runoff (Kim and Kannan 2007; Xiao et al. 2012), and street runoff (Murakami et al. 2008). A large portion of PFAS emissions are released to surface water (Prevedouros et al. 2006; Ahrens and Bundschuh 2014).

Perfluoroalkyl acids (PFAAs), the class of PFAS that are the focus of this study, persist in aquatic environments (Banjac et al. 2015). Overall, PFAAs with longer perfluorinated carbon chains have greater potential to bioaccumulate. Furthermore, perfluoroalkyl sulfonic acids are reported to be more bioaccumulative than perfluoroalkyl carboxylic acids with the same number of carbons (Conder et al. 2008). Short-chain PFAAs (7 fluorinated carbons or less) are generally more hydrophilic and mobile in water (Ahrens and Bundschuh 2014).

Concentrations of PFAAs in rivers have been correlated with population density in Japan (Murakami et al. 2008) and in Europe where perfluorooctanesulfonate (PFOS) correlated with river basin populations while perfluorooctanoate (PFOA) was strongly influenced by point source emissions from industrial facilities (Pistocchi and Loos 2009). The PFAAs were found in water, fish, and birds in New York waters with elevated concentrations of PFOA in the Hudson River (Sinclair et al. 2006). However, no correlation between PFAAs and land use was evident in a study in New Jersey, USA (Post et al. 2013).

Wildlife and human exposure to many PFAAs have been reported (Giesy and Kannan 2001; Yu et al. 2020). The PFAAs have been detected in fish tissue and other biota (Martin et al. 2013; Chu et al. 2016; Taylor and Johnson 2016; Simmonet-Laprade et al. 2019; Fauconier et al. 2020). Bioaccumulation of PFAAs varies by fish species and does not necessarily increase with trophic position (Martin et al. 2013; Munoz et al. 2017a; Khairy et al. 2019). There is a wide range of PFAA contamination reported in fish (Delinsky et al. 2010; Stahl et al. 2014; Chu et al. 2016; Fakouri Baygi et al. 2016; Taylor and Johnson 2016; Fair et al. 2019). However, PFOS is generally the most frequently detected PFAA in fish with a maximum concentration of PFOS reported at 127 ng/g in fish from US urban rivers (Stahl et al. 2014). The PFOS and other long-chain PFAAs have been reported to bioaccumulate in fish with concentrations much higher than concentrations in surrounding surface water (Sinclair et al. 2006). Bioavailability of PFAAs is also reported to be greater in higher salinity waters (Jeon et al. 2010; Munoz et al. 2017a). The relationship between PFAS and covariates such as lipids, length, weight, age, or sex of fish are not fully understood (Gewurtz et al. 2012; Schultes et al. 2019). The PFAAs have an affinity for phospholipids and/or protein with higher concentrations of PFAAs often found in blood serum and liver of fish than in fish muscle tissue (Martin et al. 2013; Fliedner et al. 2018; Valsecchi et al. 2020). There is increasing awareness of adverse effects to humans from PFAAs (Post et al. 2013, 2017; Grandjean and Clapp 2015; Grandjean 2018; Ritscher et al. 2018). Fish consumption is a major source of exposure to PFAAs with subsequent health risks (Berger et al. 2009; Murakami et al. 2011; Pan et al. 2014; Squadrone et al. 2015; Bhavsar et al. 2016; Fair et al. 2019).

The PFOS was listed on Annex B of the Stockholm Convention in 2009 (UNEP-POPS 2009). PFOA was listed on Annex A of the Stockholm Convention in 2019 (UNEP-POPS 2019) and perfluorohexane sulfonate (PFHxS) has been proposed for listing under Stockholm Convention and is under review (UNEP-POPS 2017). The PFOS and PFOA manufacturing and use have been reduced or eliminated in the USA through a voluntary stewardship agreement between the US Environmental Protection Agency and major manufacturers. The Significant New Use Rules (SNUR) of the Toxic Substances Control Act (TSCA) have also been exercised in complement with the stewardship program. The 4 states within the Delaware River drainage basin (New Jersey, New York, Pennsylvania, and Delaware) also have initiatives to manage PFAS exposure.

## MATERIALS AND METHODS

### Sampling procedures

Fish were collected from 5 stations in the tidal portion of the river (Salem River, NJ, USA to Crosswick Creek, NJ, USA) and 4 stations in the nontidal river (Lambertville, NJ, USA to Narrowsburg, NY, USA) in 2004, 2005, 2006, 2007, 2010, 2012, 2015, and 2018 (Figure 1 and Supplemental Data Table S1). Two tidal species, white perch, *Morone*

*americana* and channel catfish, *Ictalurus punctatus* and 2 nontidal species, smallmouth bass, *Micropterus dolomieu* and white sucker, *Catostomus commersonii* were collected by electrofishing or hook-and-line by the New Jersey Department of Environmental Protection or the New York Department of Environmental Conservation staff in coordination with jurisdictional agencies to determine there were no potential impacts to threatened and endangered or special concern species and resources within the collection areas. These resident fish represent benthic and variable depth dwellers as well as trophic level 3 (omnivorous diet primarily of fish and invertebrates) and trophic level 4 (top predator almost exclusively piscivorous) used in fish consumption guidance. Fish samples were stored frozen (−20 °C) until
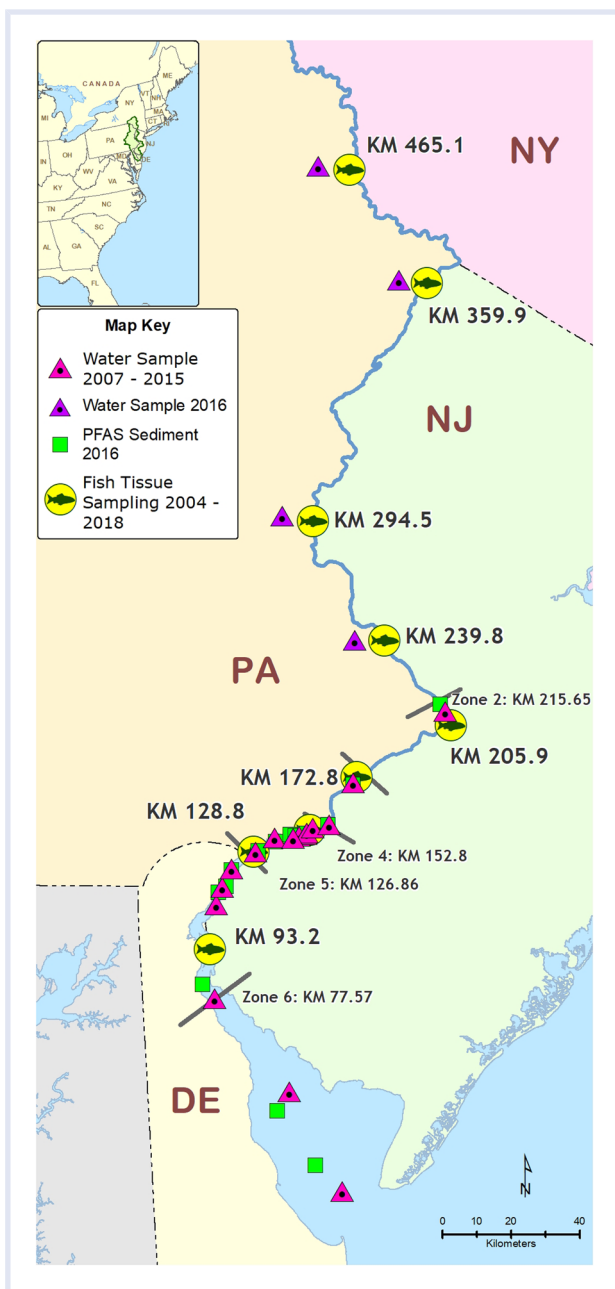


**Figure 1.** Delaware River Basin map with sample sites.

processing in the laboratory. A composite of 5 fillets for each species from fish of similar length and weight at each location was prepared at the laboratory (Supplemental Data Table S2). Fillets included the skin for white perch, smallmouth bass, and white sucker. Fillets did not include the skin for channel catfish. Percent moisture and percent lipids of fish fillet composites were measured in the laboratory (Supplemental Data Table S3).

Surface water sampling and sediment sampling were conducted opportunistically with other scheduled field activity and were nonconcurrent with fish collection. Water samples in the tidal portion of the river and bay were collected at slack tide at 6 locations in 2007, 2008, and 2009 and at 15 locations in 2015 (Figure 1 and Supplemental Data Table S6). Midchannel subsurface ambient water was directly sampled into 2 L HDPE (high density polyethylene) prewashed bottles obtained from the analytical laboratory. Surface water samples were also collected at 4 nontidal sites in a single sampling event in 2016 (Figure 1 and Supplemental Data Table S6). Quality assurance steps included collection of field blanks and duplicates. The water samples were placed on ice in coolers to maintain a temperature of $4 \pm 2\,°C$ while transported and shipped to the laboratory for analyses. Grab samples were collected on 17 October 2007, 6 August 2008, 22 October 2009, and 3 August 2015 (tidal) and 20 September 2016 (nontidal) when the mean daily average flows for Delaware River at Trenton, New Jersey, USA were at 152.63, 129.97, 141.58, 183.49, and $99.11\,m^3/s$, respectively. The river flows at sampling were below the harmonic mean flow of $184.06\,m^3/s$ used to calculate protection of human health criteria for carcinogens and above the 30-d flow with a 5-y recurrence interval (30Q5) of $79.29\,m^3/s$ used with human health criteria for systemic toxicants. The flows at sampling were also above the minimum flows for aquatic life protection based on a 7Q10 flow of $70.79\,m^3/s$. Water samples were collected over a narrow range (61%–76% exceedance) of the tidal Delaware River hydrograph that are typical of late summer and autumnal conditions. Flows did not correlate with or strongly influence contaminant concentrations.

Sediment samples were collected at 15 sites on 7 September 2016 by a decontaminated Ponar stainless-steel grab (Figure 1 and Supplemental Data Table S8). The sediment was discharged into a large decontaminated stainless-steel bowl and a prewashed stainless-steel spoon was used to collect a sample for analysis. To minimize the potential of cross-contamination, samples were collected from the middle of the sediment sample, an area unlikely to have been in direct contact with the sampler itself. Samples were kept cool in the field and during shipment to the laboratory. Sediment total organic carbon (TOC), bulk and dry weight, bulk and dry density, and percent moisture were measured in the laboratory (Supplemental Data Table S9).

*Analytical methods*

The PFAS were analyzed in fish tissue (2 g wet), water (1 L) and sediment (5 g dry) using SGS AXYS Analytical Services Ltd. Methods (Sidney, BC, Canada). After spiking with isotopically labeled quantification standards, fish fillet homogenates were extracted in methanolic KOH solution. The supernatant of fish samples was centrifuged and diluted in water. Sediment samples were extracted with acetic acid solution and then methanolic $NH_4OH$ solution. The supernatant of sediment samples was further combined in ultrapure carbon powder and diluted with water. All samples had a cleanup by solid phase extraction (SPE) cartridges with weak anion exchange sorbent and elution procedures chosen to meet analysis requirements. The extracts were further spiked with labeled recovery (internal) standards and were analyzed by LC-MS/MS. Final sample concentrations were determined by isotope dilution/internal standard quantification against extracted calibration standards processed through the analysis procedure alongside the sample (Supplemental Data Tables S10 and S11). Samples were analyzed for perfluorobutanoate (PFBA) 45048-62-2, perfluoropentanoate (PFPeA) 45167-47-3, perfluorohexanoate (PFHxA) 92612-52-7, perfluoroheptanoate (PFHpA) 120885-29-2, perfluorooctanoate (PFOA) 45285-51-6, perfluorononanoate (PFNA) 72007-68-2, perfluorodecanoate (PFDA) 73829-36-4, perfluoroundecanoate (PFUnA) 196859-54-8, perfluorododecanoate (PFDoA) 171978-95-3, perfluorobutanesulfonate (PFBS) 45187-15-3, perfluorohexanesulfonate (PFHxS) 108427-53-8, perfluorooctanesulfonate (PFOS) 45298-90-6, and perfluorooctane sulfonamide (PFOSA) 754-91-6. Additional details on the analytical methods are described in Sedlak et al. (2017). All PFAS data were reported to the lowest calibrated standard concentration prorated to sample size. Sample analyte concentrations were not blank corrected. During the more than a decade of analysis, the analytical quantification methodologies and instrumentation used did not change significantly. Additionally, the use of isotopically labeled quantification standards (surrogates) yields recovery corrected results, so accuracy (trueness and precision) tends to be independent of the actual recovery of target compounds through the analytical procedure (i.e., the methods are not prone to accuracy shifts due to minor procedural changes). The regular method quality control (QC) included independent verification of the accuracy of analytical standards by comparative analysis of standards from multiple independent sources. Each analysis batch included a spiked sample that was fortified with the validated standards. The consistency of QC recovery limits across the method versions used reflected the consistency of method performance observed. Since Certified Reference Materials (CRMs) are limited for these analytes (with the exception of NIST SRM 1947 for which good agreement with this PFOS reference value was found in tissue), method interlaboratory comparison studies, rather than CRMs, were the primary means of checking and monitoring laboratory and method performance against external standards. The analytical laboratory regularly participated in external accuracy assessment studies.

*Statistics*

Trends over time in PFAS concentrations by fish species were computed by nonparametric regression programs in R Software (R Core Team 2019). If the data did not contain censored data (nondetects), a Mann-Kendall (MK) trend test was run (Helsel 2012). If censored data (nondetects) were present, an Akritas-Thiel-Sen (ATS) slope was estimated (Helsel 2012). Duplicate samples were not included in the estimate of trends. Data for each trend test were plotted to confirm a monotonic pattern. A trend was considered significant if the *p*-value was less than 0.05.

## RESULTS AND DISCUSSION

*Spatial distribution*

The Delaware River is divided into 6 major zones for water quality management (DRBC 2013). The zones differ in land use and anthropogenic impacts (DRBC 2019). Starting at the confluence of the East and West Branches of the Delaware

River, nontidal Zone 1 (532.2–214.7 km) with a catchment dominated by forests is a high-quality source for drinking water and is managed as Special Protection Waters (DRBC 2008). In this zone of the river, PFAAs concentrations were below detection limits in surface water with the exception of PFBA and PFPeA measured just above detection limits at the most downstream nontidal site (Figure 2 and Supplemental Data Table S7). Concentrations in nontidal fish species were lower than tidal species with the exception of smallmouth bass at the most downstream collection site (Figure 2 and Supplemental Data Table S4). Sediment samples were not collected in this zone with predominantly a gravel- and cobble-bed.

Zones 2 and 3 (214.7–153 km) are tidal freshwater with a more urbanized catchment and are designated as a source for drinking water after reasonable treatment. Source water protection is a critical component of risk management in this segment of the river (PWD 2007). In areas designated as drinking water sources, the highest concentrations observed in limited sampling were 7.5 ng/L PFOS and 5.8 ng/L PFOA
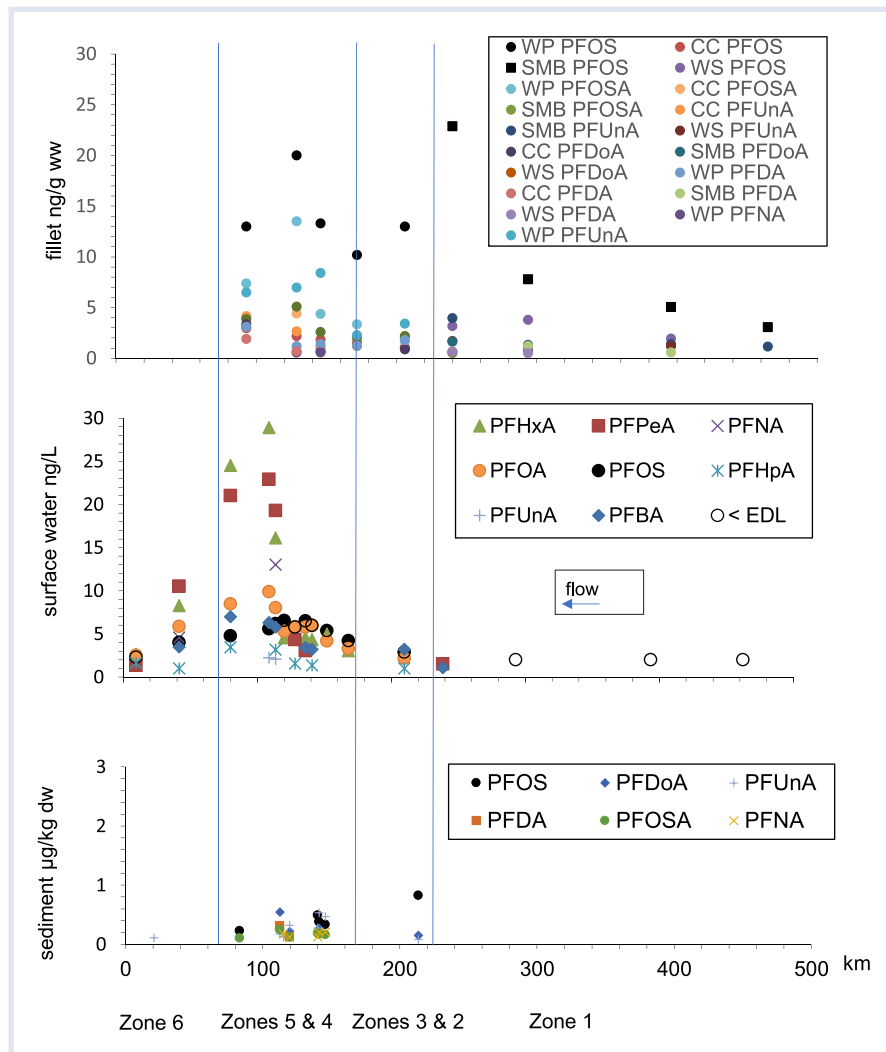


**Figure 2.** The PFAAs in 2015 to 2016 samples. CC = Channel Catfish; dw = dry weight; SMB = Smallmouth Bass; WP = White Perch; WS = White Sucker; ww = wet weight; nonconcurrent sampling, sediment not sampled >km 214, fish not collected <km 93.

in 2007 and 4.3 ng/L PFNA in 2008, which are below maximum contaminant level (MCL) drinking water recommendations by the New Jersey Department of Environmental Protection (NJDEP) for PFNA at 13 ng/L, PFOS at 13 ng/L, and PFOA at 14 ng/L, or US Environmental Protection Agency (USEPA) Health Advisory (HA) of 70 ng/L for PFOA and PFOS combined. The highest concentration of PFAAs in sediment, observed in this study, was PFOS at 0.8 ng/g in an upstream Zone 2 site, near the head of tide at 214 km (Figure 2 and Supplemental Data Table S8). Long-chain PFAAs were also detected in tidal fish species in Zones 2 and 3 (Figure 2 and Supplemental Data Table S4).

Zones 4 and 5 (153 to 77.6 km) are the most urbanized and industrialized zones of the river. With salinity transitioning from freshwater to brackish, designated use does not include sources for drinking water. The highest concentration of PFAS was observed in this segment of the river. A notable finding near an industrial discharge was the concentrations of PFNA (maximum 976 ng/L) in 2007 and the marked decrease in concentrations of PFNA to a maximum of 13 ng/L at 114 km and most sites below detection limits for PFNA by 2015 (Figure 2 and Supplemental Data Table S7). The PFNA is used as a processing aid in the manufacturing of fluoropolymers and is also a product of precursor transformation. The PFNA has been detected in stormwater, river water, oceans, and biota at levels higher than PFOA and PFOS at some locations (Houde et al. 2005; Wilkinson et al. 2016). The PFUnA was also detected in tidal surface water with a maximum of 26 ng/L at 129 km in 2007 declining to a maximum of 2.2 ng/L at 109 km with most other sites below the detection limits for PFUnA in 2015 (Figure 2 and Supplemental Data Table S7). The PFUnA is an impurity in fluoropolymer manufacturing and a breakdown product of stain- and grease-proof coatings on food packaging, couches, and carpets (Bach et al. 2017). In 2010, a local industry phased out use of a fluorosurfactant product that is a known source of PFNA and PFUnA. In Zones 4 and 5, PFOA and PFOS were frequently detected with the highest concentrations in 2008 of 48 and 12 ng/L, respectively. By 2015, the highest concentrations were 10 ng/L PFOA and 7 ng/L PFOS at 109 km (Figure 2). The PFDA was detected in 2007, 2008, and 2009 decreasing to below detection limits at all sites by 2015. The PFDoA was not detected in Zones 4 and 5 surface water samples or in any zone of the river.

Of the short chain PFAS analyzed, PFHxA and PFPeA were frequently detected with maxima of 28.9 ng/L and 22.9 ng/L respectively in 2015 (Figure 2 and Supplemental Data Table S7). This is consistent with shifts in production to short chain PFAS and observations in other locations (Codling et al. 2014; Zhao et al. 2015). Concerns are increasing regarding short chain PFAS occurrence in the environment and potential impacts (Brendel et al. 2018). Other short chain compounds PFHpA, PFHxS, PFBA, and PFBS were measured in surface water at <6 ng/L in 2015 (Figure 2 and Supplemental Data Table S7).

Long-chain PFAS were detected at low concentrations (<1 µg/kg dry wt) in sediments of Zones 4 and 5. The most

frequently detected were PFUnA (53%), PFNA (33%), and PFOS (33%) with their highest concentrations at 0.5, 0.2, and 0.8 µg/kg, respectively. Also detected at low concentrations were PFOSA, PFDoA, and PFDA. Other shorter chain PFAAs were not found above detection limits (Figure 2 and Supplemental Data Table S7). Unlike many locations where PFOS is the most frequently observed PFAS in sediment (Codling et al. 2014; White et al. 2015; Munoz et al. 2017b), sediment from the tidal Delaware River and some of its tributaries have PFUnA and PFNA detected more frequently and at higher concentrations than PFOS and other long-chain PFAS (Goodrow et al. 2020).

Zone 6 (77.6 to 0 km) of the Delaware Bay has a less urbanized catchment than the tidal river with abundant fringing wetlands. Surface water is estuarine transitioning from brackish to marine salinity. The tidally influenced hydrodynamics of the bay facilitates mixing and dilution. In this zone, the more upstream sample, at 42 km, had a total concentration of 38 ng/L for 7 analytes combined (PFPeA, PFHxA, PFOA, PFNA, PFOS, PFBA, and PFHpA) with PFPeA at 11 ng/L being the largest contributor to the total. In the more downstream sample, at 10 km, a total concentration of 12 ng/L for 6 analytes combined (PFPeA, PFHxA, PFOA, PFOS, PFBA, and PFHpA) was detected with PFHpA at 2.7 ng/L the largest contributor to the total (Figure 2 and Supplemental Data Table S7). The PFAAs were not detected in Zone 6 sediment with the exception of PFUnA reported just above the detection limit at a single site (Figure 2 and Supplemental Data Table S8). Fish collection and analysis in the bay is conducted by a different agency and data were not available to be included in this study.

The spatial variability of PFAAs in the Delaware River followed patterns observed by other anthropogenic contaminants with higher concentrations generally in the more urbanized Zones 2 to 5 of the river (Vilimanovic et al. 2020). Concentrations of PFNA and PFUnA in early surface water and fish samples, PFHxA and PFPeA in later surface water samples, PFOS in smallmouth bass, and PFOS in upper Zone 2 sediment point toward putative site-specific releases.

*Temporal trends in fish*

Of the 13 analytes included in the study, 6 were detected in fish fillets (PFDoA, PFUnA, PFDA, PFNA, PFOS, and PFOSA) and 7 were not detected (PFOA, PFHpA, PFHxA, PFHxS, PFpeA, PFBA, and PFBS) (Supplemental Data Table S4). The highest concentrations found were PFUnA in fish collected at a tidal site (146 km) near a known industrial discharge. At that location, white perch collected in 2004 had a maximum concentration of 116 ng/g PFUnA and channel catfish had a maximum of 44 ng/g PFUnA with both species showing significant decreases to 7.6 ng/g and 9.4 ng/g, respectively, by 2018 (Figure 3 and Supplemental Data Table S5). In the nontidal river, the highest PFUnA concentration was in smallmouth bass at 9.7 ng/g collected in 2004 with a significant decrease in concentration overtime and a maximum of 8.3 ng/g in white sucker collected in 2007
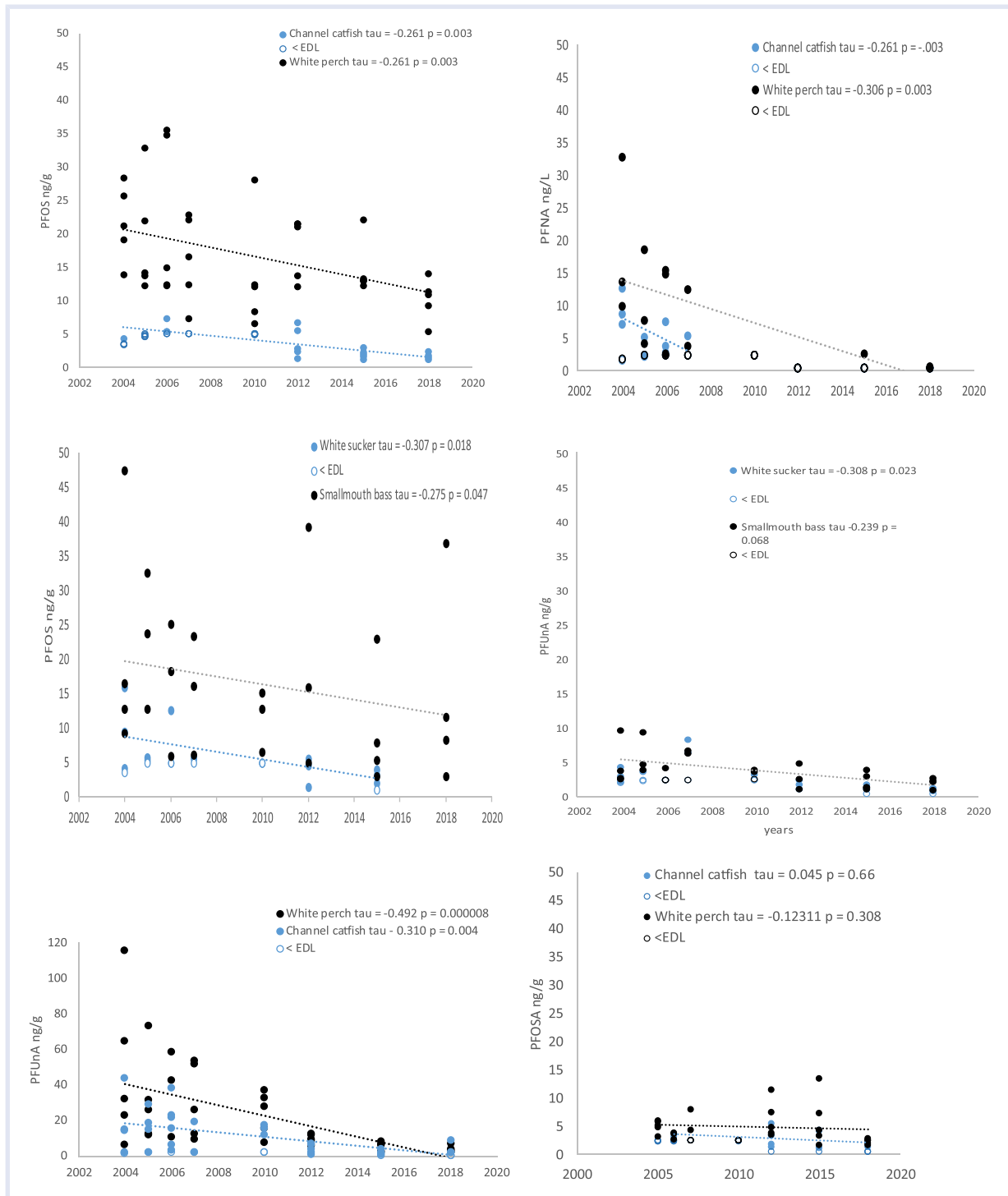
**Figure 3.** Temporal trends in fish.

without a clear decreasing trend in concentration through 2018 (Figure 3 and Supplemental Data Table S5). In addition to site-specific releases of PFUnA to the river, atmospheric oxidation of 10:2 fluorotelomer alcohol may lead to the predominance of persistent and bioaccumulative PFUnA in biota. The PFNA in white perch and channel catfish were 31 ng/g and 11 ng/g, respectively, in tidal fish collected in 2004 decreasing to below or near detection limits by 2018

(Figure 3). The PFNA concentrations and trends are presumed to reflect early site-specific releases and subsequent actions to reduce industrial discharges of PFNA to the tidal portion of the river. In contrast, PFNA levels in nontidal fish were below detection limits (1.0 ng/g) throughout the study (Supplemental Data Table S4).

While nontidal species generally had lower concentration of PFAS when compared to tidal fish, the highest

Table 1. Fish consumption risk

| Sample location | Latitude | Longitude | River kilometer | Species | ng/g | PFOS triggers | Estimated FCA[a] |
|---|---|---|---|---|---|---|---|
| Narrowsburg, NY | 41.60948 | −75.06382 | 465 | Smallmouth bass | 2.95 | >0.56 but ≤3.9 | Weekly |
| Narrowsburg, NY | 41.60948 | −75.06382 | 465 | White sucker | <0.917 | >0.56 but ≤3.9 | NA[b] |
| Milford, PA/Montague, NJ | 41.30757 | −74.79845 | 396 | Smallmouth bass | 8.15 | >3.9 but ≤17 | Monthly |
| Milford, PA/Montague, NJ | 41.30757 | −74.79845 | 396 | White sucker | 1.38 | >0.56 but ≤3.9 | Weekly |
| Easton, PA/Phillipsburg, NJ | 40.69086 | −75.20395 | 294 | Smallmouth bass | 11.6 | >3.9 but ≤17 | Monthly |
| Easton, PA/Phillipsburg, NJ | 40.69086 | −75.20395 | 294 | White sucker | 4.4 | >3.9 but ≤17 | Monthly |
| Lambertville, NJ | 40.36273 | −74.94834 | 240 | Smallmouth bass | 37 | >17 but ≤51 | Once/3 mo |
| Lambertville, NJ | 40.36273 | −74.94834 | 240 | White sucker | 3.51 | >0.56 but ≤3.9 | Weekly |
| Crosswicks Creek, NJ | 40.14909 | −74.71808 | 206 | Channel catfish | <0.943 | >0.56 but ≤3.9 | NA[b] |
| Crosswicks Creek, NJ | 40.14909 | −74.71808 | 206 | White perch | 14 | >3.9 but ≤17 | Monthly |
| Tacony Palmyra Br./ Pennsauken Ck. | 39.99097 | −75.05559 | 172 | Channel catfish | 1.43 | >0.56 but ≤3.9 | Weekly |
| Tacony Palmyra Br./ Pennsauken Ck. | 39.99097 | −75.05559 | 172 | White perch | 10.9 | >3.9 but ≤17 | Monthly |
| Woodbury Creek, NJ | 39.86677 | −75.19666 | 146 | Channel catfish | 1.1 | >0.56 but ≤3.9 | Weekly |
| Woodbury Creek, NJ | 39.86677 | −75.19666 | 146 | White perch | 11.3 | >3.9 but ≤17 | Monthly |
| Raccoon Creek, NJ | 39.80795 | −75.37387 | 129 | Channel catfish | 1.68 | >0.56 but ≤3.9 | Weekly |
| Raccoon Creek, NJ | 39.80795 | −75.37387 | 129 | White perch | 9.23 | >3.9 but ≤17 | Monthly |
| Salem River, NJ | 39.57603 | −75.49406 | 93 | Channel catfish | 2.34 | >0.56 but ≤3.9 | Weekly |
| Salem River, NJ | 39.57603 | −75.49406 | 93 | White perch | 5.33 | >3.9 but ≤17 | Monthly |

FCA = fish consumption advisory; PFOS = perfluorooctanesulfonate.
[a] For general population with an additional advisories for high risk populations (infants, children, pregnant women, nursing mothers and women of childbearing age) (Goodrow et al. 2020).
[b] Advisory trigger is less than the laboratory estimated detection limit.

concentration of PFOS in the 4 species tested, at 48 ng/g in 2004 and 37 ng/g in 2018, were found in nontidal smallmouth bass (Supplemental Data Table S4). Smallmouth bass had a relatively high geometric mean for PFOS at 29 ng/g and the least change in concentration of the species tested in the Upper Mississippi River (Newsted et al. 2017). The PFOS concentrations in fish fillet of the 4 species tested appear to be slowly decreasing (Figure 3 and Supplemental Data Table S5). A review by Land et al. (2018) of time trends in biota found insignificant changes in PFOS concentrations in North America.

Occurrence of additional co-occurring precursors may influence bioaccumulation and trends in fish. Similar to the precursor to PFOS ratios reported by Munoz et al. (2017b), the average PFOSA to PFOS concentration ratios were <1 and varied by species with the tidal species having average ratios of 0.9 for channel catfish and 0.3 for white perch. The PFOSA had maximum concentrations of 11.5 ng/g in white perch and 5.6 ng/g in channel catfish collected in 2012 with no significant trends observed in tidal fish through 2018 (Figure 3 and Supplemental Data Tables S4 and S5). The PFOSA was at or below detectable levels in nontidal

smallmouth bass and white sucker fillet (Supplemental Data Table S4).

The PFDA was detected in the 4 species tested. The highest concentration observed was 8.2 ng/g in 2004 in tidal white perch. The PFDA concentrations showed a significant decrease in white perch but no significant trends were observed in the other species (Supplemental Data Tables S4 and S5). The PFDoA was also detected in the 4 species tested. The highest concentration observed was 9.5 ng/g in tidal white perch collected in 2012. No trends in PFDoA concentrations were observed in any of the species tested (Supplemental Data Tables S4 and S5).

While decreases in PFNA and PFUnA concentrations were observed in fish fillet during the time period of this study, changes in concentrations of other PFAAs were variable. The numerous factors determining the fate, bioaccumulation, and trends of PFAS in the environment are yet to be fully understood (Babut et al. 2017; Taylor et al. 2018; Munoz et al. 2019).

*Fish consumption risk*

While working to reduce toxic contaminants that bioaccumulate, state agencies issue "advisories" containing

meal advice for consumers of recreationally caught fish to minimize the risk to human health. Advisories are not regulatory standards, but are recommendations intended to provide additional information of interest to high-risk groups (USEPA 2020). For risk assessment of bioaccumulative chemicals such as PFAAs, tissues that are consumed by humans (e.g., fillets or muscle tissue) and trophic levels of the fish species of interest (e.g., secondary consumer or top-level predatory fish) are considered. Risk from fish consumption was evaluated based on 9 sampling locations, with 4 species collected and New Jersey preliminary fish consumption advisory triggers for PFOS, PFNA, and PFOA applicable within the Delaware River Basin (Goodrow et al. 2020). In 2018, 6% of fish fillets exceeded 17 ng/g PFOS, 56% exceeded 3.9 PFOS ng/g, and 89% exceeded 0.56 ng/g PFOS, levels that would trigger restrictive consumption advisories of no more than 1 meal every 3 months, no more than 1 meal per month, and no more than 1 meal per week, respectively, for the general population. Eleven percent of the samples were below estimated detection limits (~0.9 ng/g) and advisories were not estimated (Table 1). By comparison, 44% of these fish fillets exceed a Food Standard Australia New Zealand (FSANZ) trigger value for PFOS in fish of 5.2 ng/g (Taylor 2018) or 33% exceed a European Union Environmental Quality Standard (EU EQS$_{biota}$) for PFOS of 9.1 ng/g (Valsecchi et al. 2020). Also in 2018, 1 species (white perch) at 1 site (Woodbury Creek) with 0.6 ng/g PFNA exceeded the most protective risk advisory trigger for that compound (0.23 ng/g) for an estimated advisory of no more than 1 meal per week. Risk advisory triggers were not proposed for PFDoA, PFUnA, PFDA, or PFOSA, the other analytes detected in fish fillet.

Piscivorous wildlife are also at risk from the transport and accumulation of water soluble PFAS with low vapor pressure. The PFAS have been detected in wildlife indicating biomagnification as well as continued exposure of wildlife to a diverse and incompletely characterized suite of PFAS (Martin et al. 2003; Sedlak et al. 2017; Fair et al. 2019). Compared to fish with gills that can relatively rapidly depurate PFOS, wildlife with lungs such as shorebirds and marine mammals are more likely to bioaccumulate PFOS (Larson et al. 2018). In the Delaware Estuary, PFOS has been reported as a contaminant in osprey eggs (Toschik et al. 2005) and bottlenose dolphins (Houde et al. 2005; White et al. 2015). A wildlife risk assessment, based on concentrations in whole fish, was not an objective of the study reported here. The PFAS concentrations have been reported to be higher in the blood and viscera of fish than in fillet muscle (Labadie and Chevreuil 2011; Murakami et al. 2011; Pan et al. 2014; Shi et al. 2018). The PFAS levels observed in fish and other biota indicate that further evaluation of risk to wildlife is warranted in the Delaware River (the present study; Houde et al. 2005; Toschik et al. 2005; Goodrow et al. 2020).

Persistent PFAS contaminants continue to be measured while fluorinated compounds used as alternatives to long-chain PFAS are increasingly being detected in the environment (Wang et al. 2013, 2015; Heydebreck et al. 2015; Pan et al. 2018; Washington et al. 2020). Additional studies are needed in surface waters and in fish to evaluate the efficacy of regulatory and management strategies in reducing exposure and risks from PFAS to human health and aquatic dependent wildlife.

## CONCLUSION

While significant decreases in PFNA and PFUnA concentrations were observed in fish fillet from the tidal river over the sample period, decreases in concentrations of other PFAS in tidal fish were less substantial. Elevated levels of PFOS in fish fillet are estimated to trigger restrictive fish consumption advisories. The PFAS levels observed in fish indicate that further evaluation of risk to human health and wildlife is warranted in the Delaware River. Surface water samples collected from the tidal Delaware River between 2007 and 2015 found elevated levels of PFUnA and PFNA in areas not designated for drinking water sources with apparent decreases over the sample period. Surface water concentrations varied for other PFAS but appear to be below regional and national guidelines in areas designated as drinking water sources. Sediment from the tidal main stem Delaware River had long-chain PFAS detected at low concentrations. The results from this work can inform management approaches to minimize exposure risks to human health and wildlife.

*Disclaimer*—The author has no conflicts of interest to report related to this submittal.

*Open Data Badge*—This article has earned an Open Data Badge for making publicly available the digitally shareable data necessary to reproduce the reported results. The data are available at https://www.waterqualitydata.us/. Learn more about the Open Practices badges from the Center for Open Science: https://osf.io/tvyxz/wiki.

*Data Availability Statement*—Associated metadata and calculation tools are available upon request by contacting Ron MacGillivray (ron.macgillivray@drbc.gov).

## SUPPLEMENTAL DATA

Table S1. Fish collection sites and species
Table S2. Fish length and weight
Table S3. Fish fillet homogenate percent lipid and percent moisture
Table S4. PFAS in fish
Table S5. PFAS trends in fish
Table S6. Surface water sites

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