PFAS in Surface Water & Fish

Delaware River

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NEWMOA Webinar

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60 years 1961–2021

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The 1937 Philadelphia Record editorial page cartoon depicted polluted Delaware River

A unified approach to managing, protecting and improving shared water resources with five equal members:

Delaware

New Jersey

Pennsylvania

New York

Federal Government

River of the Year for 2020
"The Delaware River is a national success story," Bob Irvin, President and CEO of American Rivers

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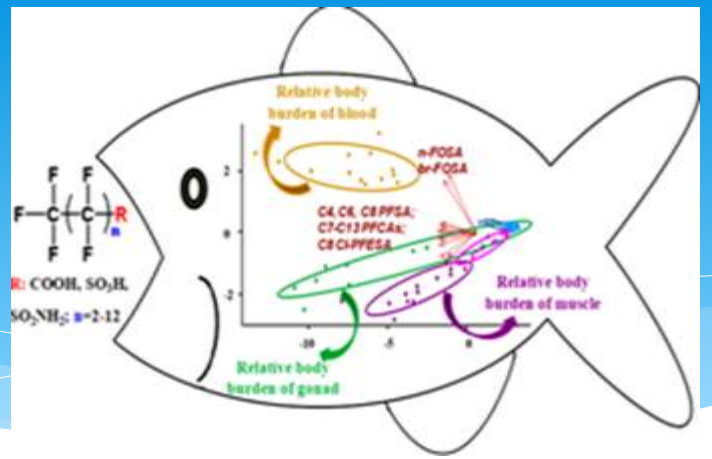
Why are PFAS of Concern?



Shi *et al*, 2018 ES&T

Occurrence, Persistence, Bioaccumulation and Toxicity

Human Health Effects

Association with liver damage, increased cholesterol, thyroid disease, decreased response to vaccines, asthma, decreased fertility and birth weight, pregnancy–induced hypertension

Aquatic Life and Aquatic Dependent Wildlife Effects

Moderately acute and chronically toxic to aquatic organisms (survival, growth and reproduction). Sublethal effects observed (e.g., histopathology, neurological and immune effects) in non-standard tests

Why collect PFAS data in surface water and fish?

What are the occurrences and sources of PFAS?

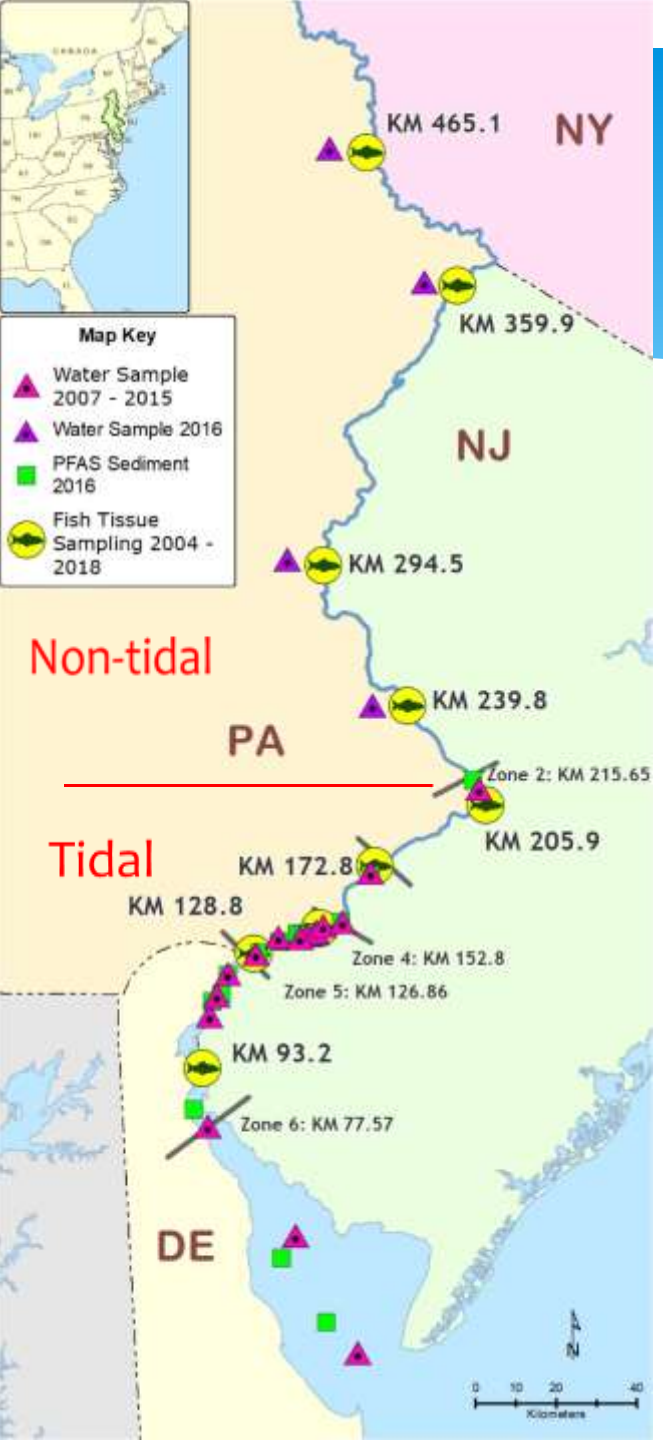
What are the risks to designated uses?

- **Source Water Protection**
- **Fish Consumption Advisories**
- **Maintenance and propagation of fish and other aquatic life**

What actions can be identified to minimize PFAS impacts?

- **Evaluate the efficacy of regulatory and management strategies in reducing exposure and risks**

Sampling Sites



- **Surface water**
- Six tidal sites in 2007, 2008, 2009
- Fifteen tidal sites in 2015
- Four non-tidal sites in 2016
- **Fish**
- Four non-tidal and five tidal sites in 2004, 2005, 2006, 2007, 2010, 2012, 2015 and 2018
- **Sediment**
- Fifteen tidal sites in 2016

Sampling

- Two tidal species white perch, *Morone americana* and channel catfish, *Ictalurus punctatus*
- Two non-tidal species smallmouth bass, *Micropterus dolomieu* and white sucker, *Catostomus commersonii*
- Composites of 5 fillet for each species from fish of similar length and weight
- Surface water sampling and sediment sampling was conducted opportunistically not concurrent with fish collection
- Mid-channel subsurface water grab directly sampled into 2L HDPE
- Surficial sediment collected by Ponar stainless-steel grab
- Field blanks and duplicates with water and sediment sampling

Analytical Methods

- 13 PFAS were analyzed in fish tissue (2g wet), water (1L) and sediment (5g dry) by SGS AXYS Analytical Services Ltd. (Sidney, B.C., Canada).
- Analytical methods included Solid Phase Extraction (SPE) with weak anion exchange sorbent cartridges and LC-MS/MS with isotope dilution.

# of carbons

Carboxylates

# of carbons	
4	Perfluorobutanoate (PFBA)
5	Perfluoropentanoate (PFPeA)
6	Perfluorohexanoate (PFHxA)
7	Perfluoroheptanoate (PFHpA)
8	Perfluorooctanoate (PFOA)
9	Perfluorononanoate (PFNA)
10	Perfluorodecanoate (PFDA)
11	Perfluoroundecanoate (PFUnA)
12	Perfluorododecanoate (PFDoA)

Sulfonates and Sulfonamide

# of carbons	
4	Perfluorobutanesulfonate (PFBS)
6	Perfluorohexanesulfonate (PFHxS)
8	Perfluorooctanesulfonate (PFOS)
8	Perfluorooctane sulfonamide (PFOSA)

Occurrence in Water 2015

Below regional and national guidelines for PFAS in areas designated as drinking water sources.

Zone 1 Concentrations generally below DL

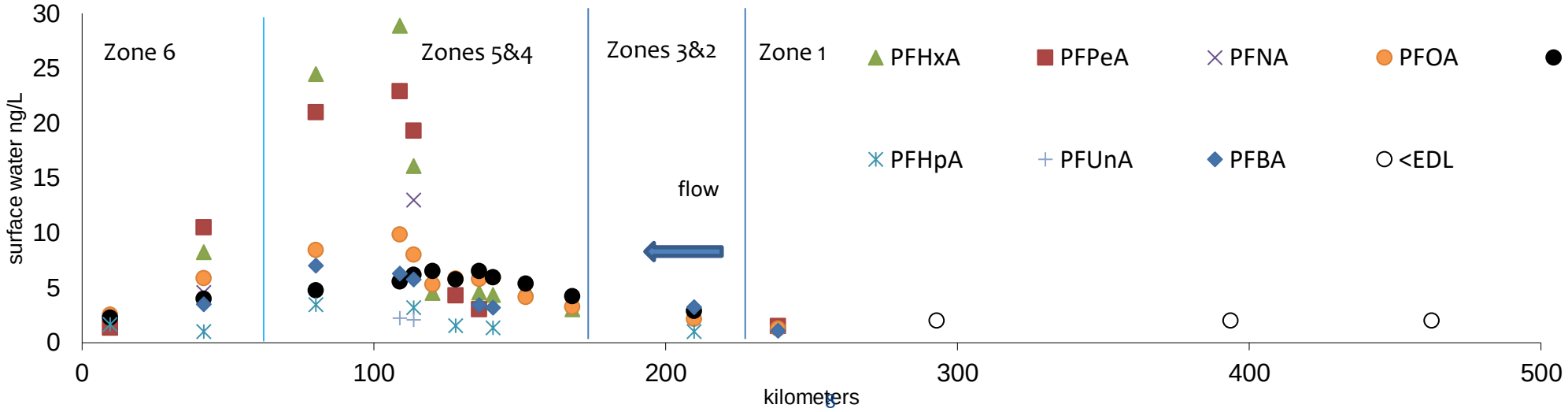
Zones 2 and 3 Below NJ MCLs of PFNA 13 ng/L, PFOS 13 ng/L and PFOA 14 ng/L

Zones 4 and 5 Concentrations of PFNA (maximum 976 ng/L) in 2007 with most sites below DL by 2015.

PFOA and PFOS frequently detected but below 10 ng/L by 2015.

Short chain PFAS frequently detected with PFHxA and PFPeA maxima of 28.9 ng/L and 22.9 ng/L respectively in 2015

Zone 6 Lower concentrations with a maximum of 38 ng/L for seven analytes combined



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Occurrence in Sediment 2016

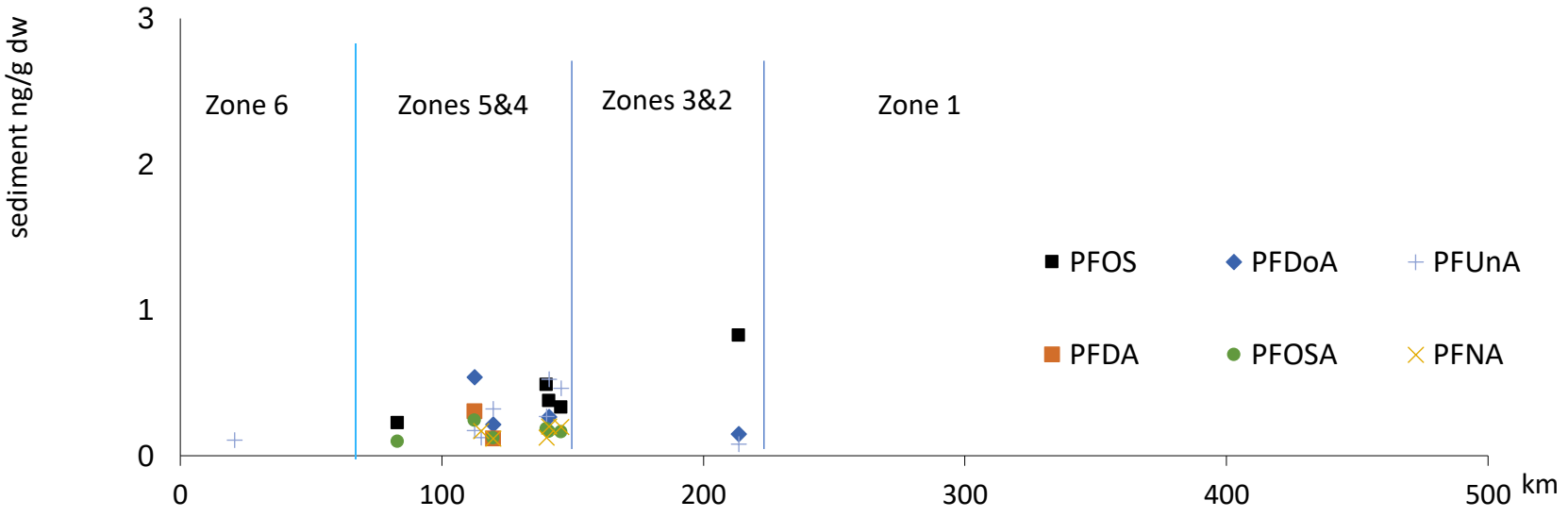
Sediments of the Delaware River are reported to have varied frequency of detection and wide range of concentrations with PFUnA and PFNA frequently detected (Integral 2015; Goodrow et al. 2020).

Zone 1 Sediment samples were not collected in predominantly gravel-and cobble-bed.

Zones 2 and 3 Highest concentration observed was PFOS at 0.8 µg/kg.

Zones 4 and 5 Long chain PFAS were detected at low concentrations (< 1 µg/kg dry wt). Most frequently detected were PFUnA, PFNA and PFOS.

Zone 6 Only PFUnA reported just above the DL at a single site.



Occurrence in Fish Fillet 2015

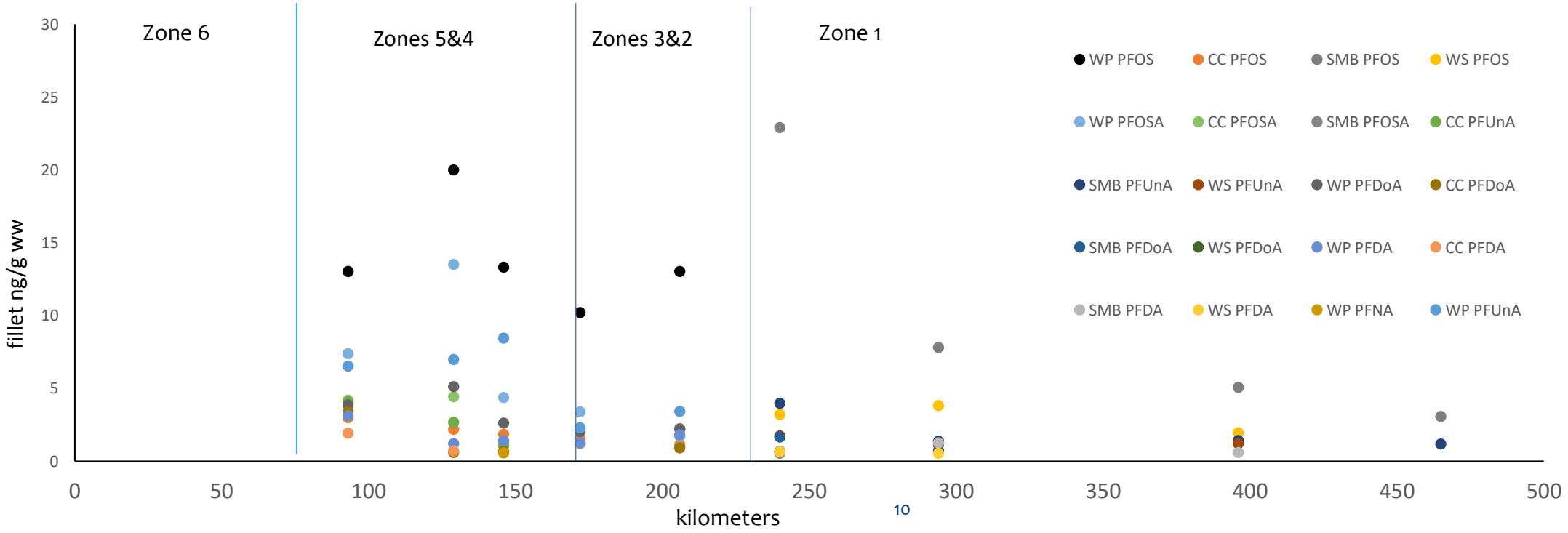
Of the thirteen analytes included in the study, six were detected in fish fillets (PFOS, PFNA, PFDA, PFUnA, PFDoA, PFOSA).

Concentrations varied by species and location.

Zone 1 Concentrations in non-tidal fish species were lower than tidal species except for smallmouth bass at the most downstream non-tidal collection site

Zones 2, 3, 4 and 5 Long chain PFAS were detected in tidal fish

Zone 6 Fish collection and analysis in the bay is conducted by a different agency



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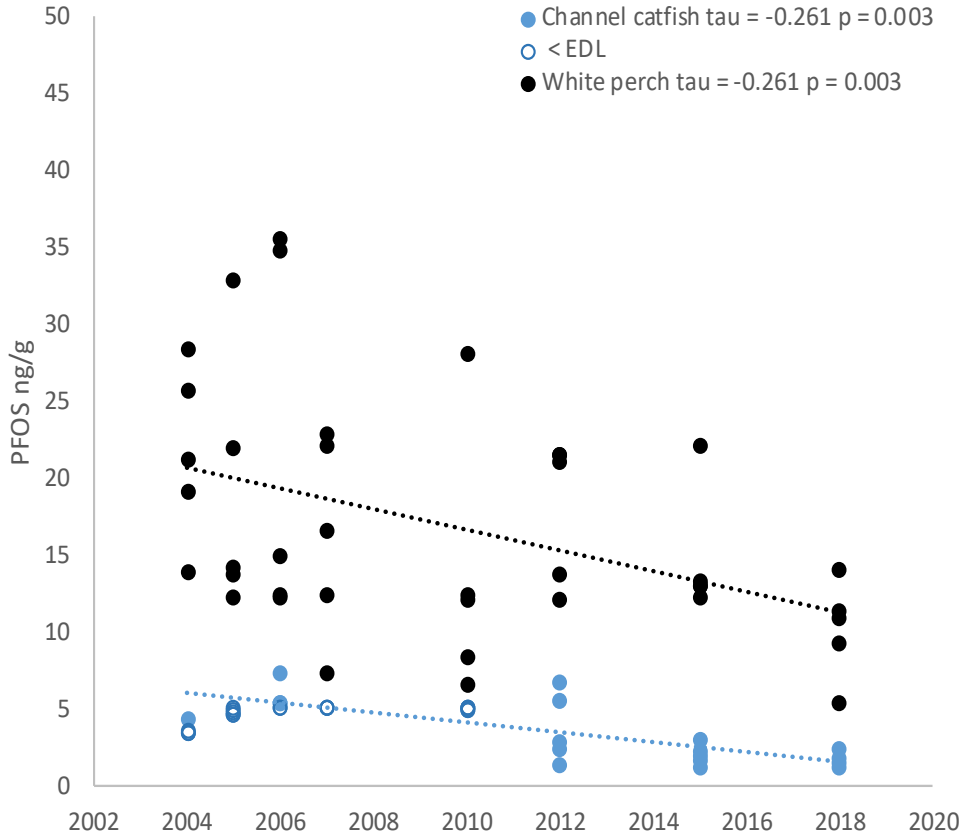
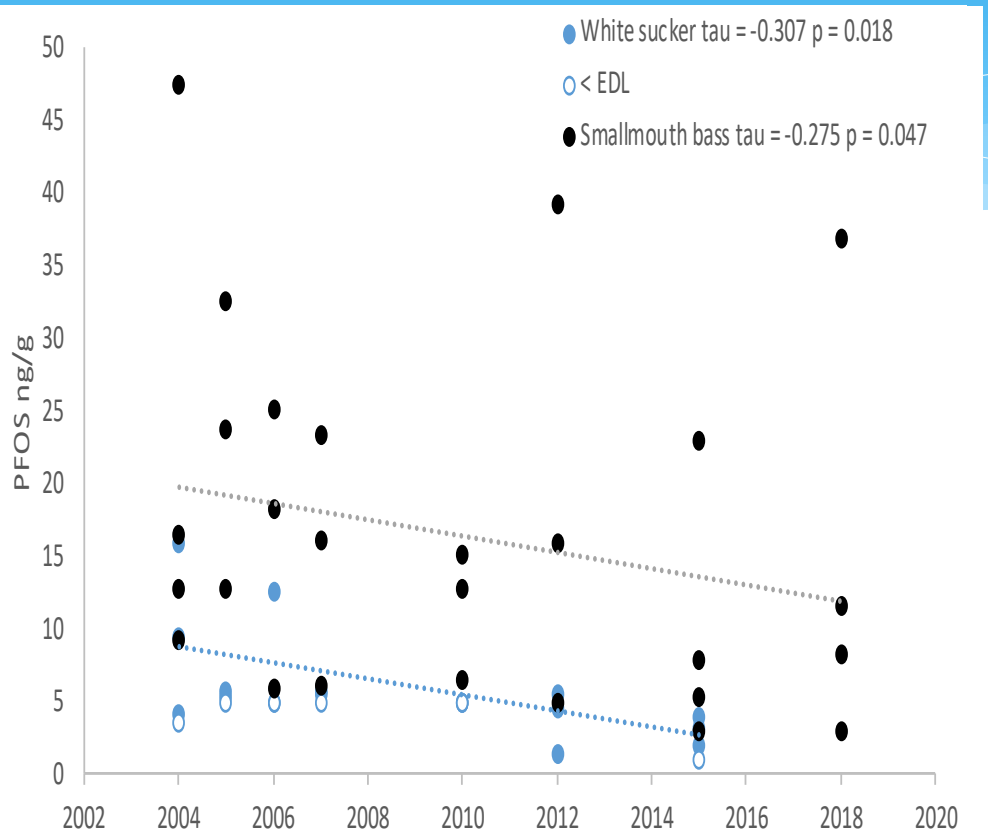
Temporal Trends in Fish





PFOS concentrations in fish fillet of four species tested appear to be slowly decreasing.
PFOS in fish fillet is currently estimated to trigger restrictive fish consumption advisories.

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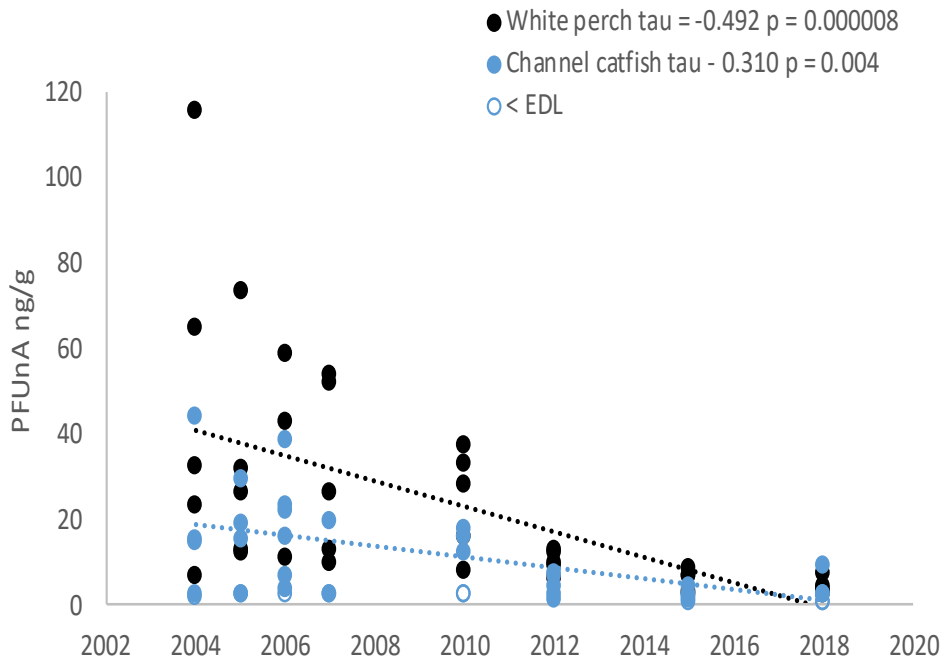
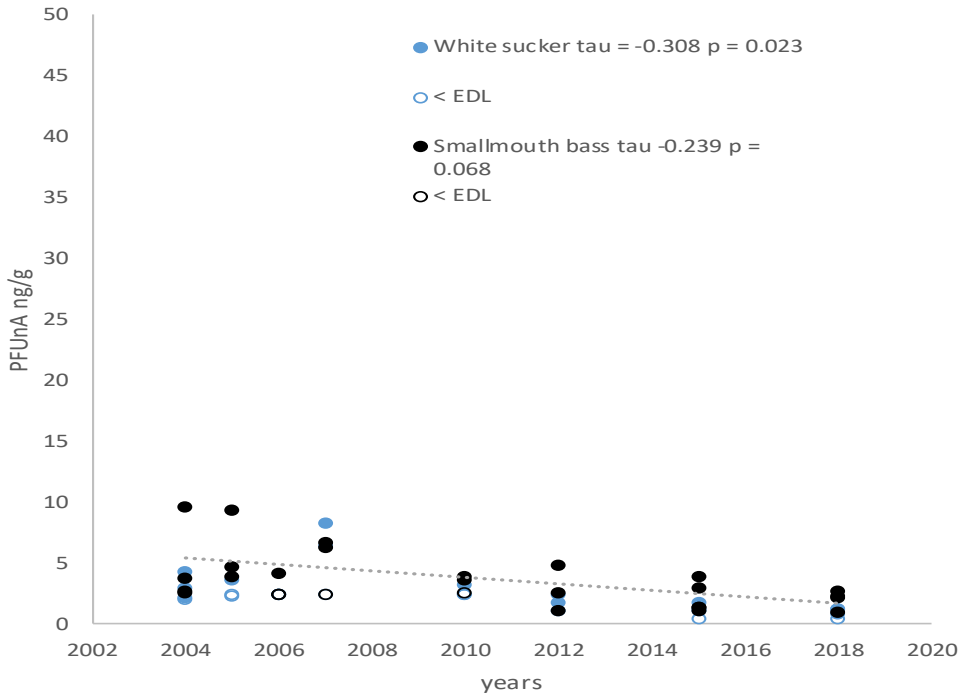
Temporal Trends in Fish





PFUnA concentrations highest in tidal fish with a known local industrial discharge, both tidal species showing significant decreases by 2018. In non-tidal river, PFUnA in smallmouth bass also showed decreases in concentration overtime, white sucker without a clear decreasing trend.

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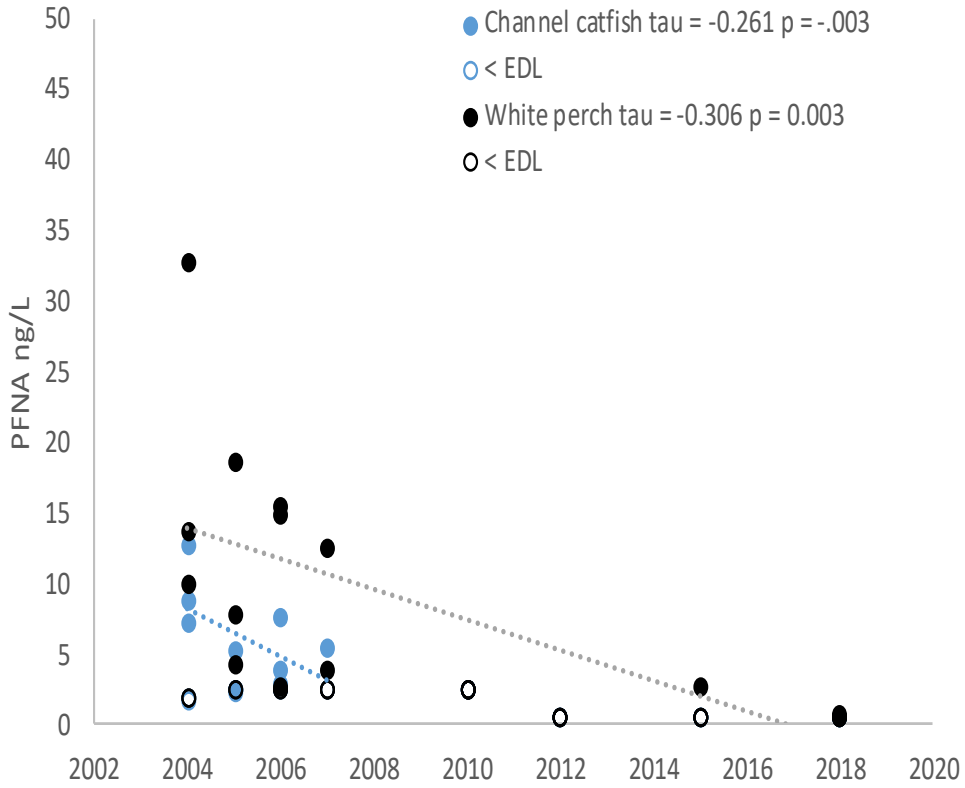
Temporal Trends in Fish

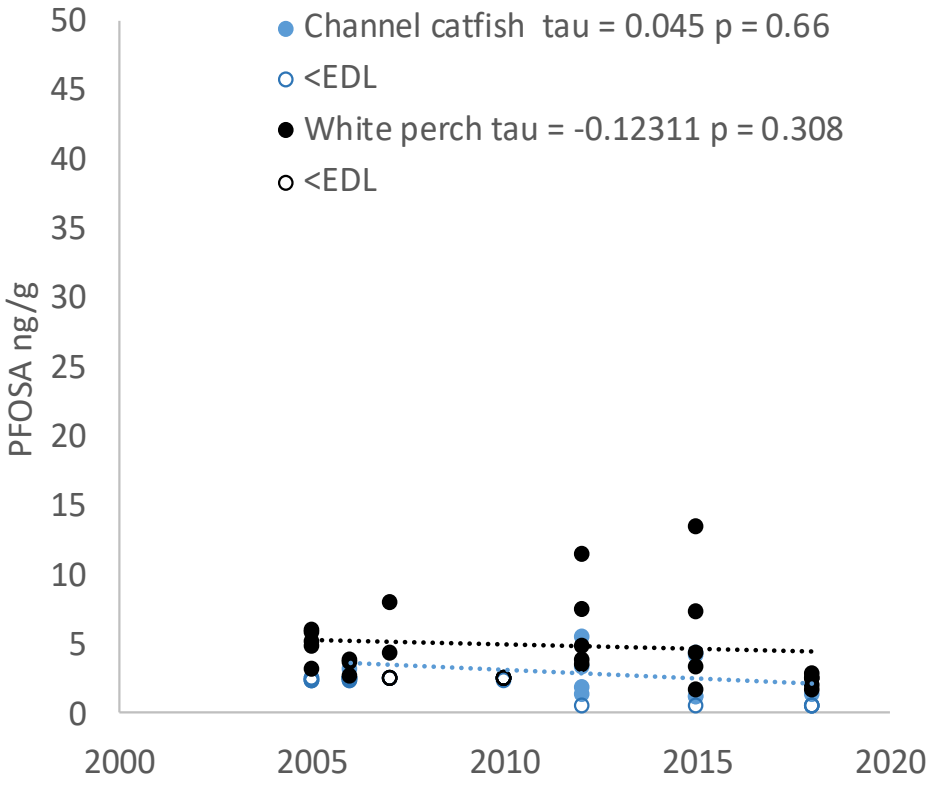


PFNA detected in tidal fish decreasing to below or near DL (1.0 ng/g) by 2018.

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.

PFNA levels in non-tidal fish were below DL throughout the study.

Temporal Trends in Fish



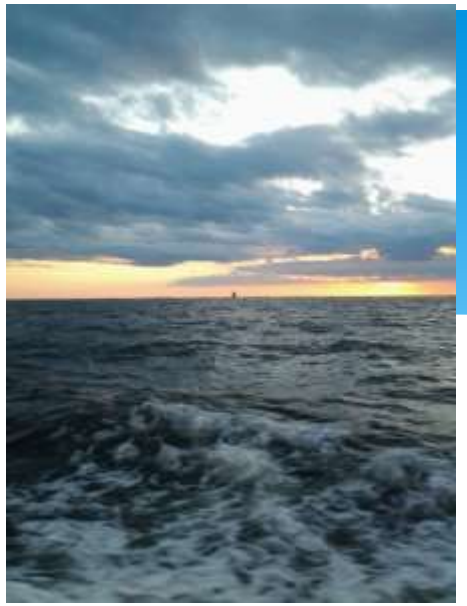
Occurrence of co-occurring precursors may influence bioaccumulation and trends in fish

PFOSA had highest concentrations in tidal fish collected in 2012 with no significant trends observed through 2018

PFOSA was at or below DL in non-tidal fish

Summary

- Levels of PFOS in fish fillet are estimated to trigger restrictive fish consumption advisories in the Delaware River.
- PFOS concentrations in fish fillet of the four species tested appear to be slowly decreasing.
- PFAS observed in fish and surface water indicate that further evaluation of risk to human health, aquatic life 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 for PFOS and PFOA in areas designated as drinking water sources.



Planned for 2021

- Concurrent sampling of surface water, sediment and fish in tidal and non-tidal river
- Extended list of 40 PFAS analytes (including precursors and replacement products)

Perfluoroalkyl carboxylates	Perfluoroalkyl sulfonates	Perfluorooctane sulfonamidoacetic acids	Ether sulfonates
Perfluorobutanoate (PFBA)	Perfluorobutanesulfonate (PFBS)	N-Methylperfluorooctanesulfonamidoacetic acid (N-MeFOSAA)	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-PF3ONS)
Perfluoropentanoate (PFPeA)	Perfluoropentanesulfonate (PFPeS)	N-Ethylperfluorooctanesulfonamidoacetic acid (N-EtFOSAA)	11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS)
Perfluorohexanoate (PFHxA)	Perfluorohexanesulfonate (PFHxS)	**Perfluorooctane sulfonamides**	**Leachate**
Perfluoroheptanoate (PFHpA)	Perfluoroheptanesulfonate (PFHpS)	N-Methylperfluorooctanesulfonamide (N-MeFOSA)	3:3 perfluorohexanoic acid (3:3 FTCA)
Perfluorooctanoate (PFOA)	Perfluorooctanesulfonate (PFOS)	N-Ethylperfluorooctanesulfonamide (N-EtFOSA)	5:3 perfluorooctanoic acid (5:3 FTCA)
Perfluorononanoate (PFNA)	Perfluorononanesulfonate (PFNS)	Perfluorooctanesulfonamide (PFOSA), a.k.a FOSA	7:3 perfluorodecanoic acid (7:3 FTCA)
Perfluorodecanoate (PFDA)	Perfluorodecanesulfonate (PFDS)	**Perfluorooctane sulfonamidoethanols**	**EPA 533**
Perfluoroundecanoate (PFUnA)	Perfluorododecanesulfonate (PFDoS)	N-Methylperfluorooctanesulfonamidoethanol (N-MeFOSE)	Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA)
Perfluorododecanoate (PFDoA)	**Fluorotelomer sulfonates**	N-Ethylperfluorooctanesulfonamidoethanol (N-EtFOSE)	Perfluoro-4-methoxybutanoate (PFMBA)
Perfluorotridecanoate (PFTrDA)	4:2 fluorotelomersulfonate (4:2 FTS)	**Ether carboxylates**	Perfluoro-3-methoxypropanoate (PFMPA)
Perfluorotetradecanoate (PFTeDA)	6:2 fluorotelomersulfonate (6:2 FTS)	Perfluoro-2-propoxypropanoate (HFPO-DA)	Perfluoro-3,6-dioxaheptanoate (NFDHA)
	8:2 fluorotelomersulfonate (8:2 FTS)	4-dioxa-3H-perfluorononanoate (ADONA)	

40 Analytes in 2021

SGS AXYS

MLA-110

SPE-WAX

LC-MS/MS

Isotope Dilution

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