



# PFAS

## in Delaware Surface Waters Data Summary Report

September 2024

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[de.gov/pfas](https://de.gov/pfas)

### Appendix B

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Plots are available for download at the following link:  
[de.gov/pfas](https://de.gov/pfas)

### Appendix C

#### Laboratory Analytical Report

The full laboratory analytical report and a Microsoft Excel data file are available for download at the following link:  
[de.gov/pfas](https://de.gov/pfas)

# Executive Summary

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The Department of Natural Resources and Environmental Control's Watershed Approach to Toxics Assessment and Restoration (DNREC-WATAR) team collected and evaluated per- and polyfluoroalkyl substances (PFAS) analytical results from 83 surface water samples collected from 33 watersheds across Delaware during the fall of 2022. The purpose of the evaluation was to assess existing concentrations of PFAS in surface waters across the state. The information is being used to inform future actions and prioritize resources available for source identification, control and remediation to the most impacted areas of the state. Tracking and eliminating these chemicals' sources to the environment will have a positive impact on water quality and in maintaining healthy communities in Delaware. Additional Delaware-specific PFAS related information, including summaries of ongoing studies and links to completed studies, can be found on DNREC's PFAS web page [de.gov/pfas](https://de.gov/pfas). An abundance of technical information about PFAS can be found on the Interstate Technology and Regulatory Council (ITRC) webpage [PFAS – Per- and Polyfluoroalkyl Substances \(itrcweb.org\)](https://itrcweb.org). Additional information about the United States Environmental Protection Agency (USEPA) actions related to PFAS can be found on the USEPA PFAS web page [Per- and Polyfluoroalkyl Substances \(PFAS\) | US EPA](https://www.epa.gov/pfas).

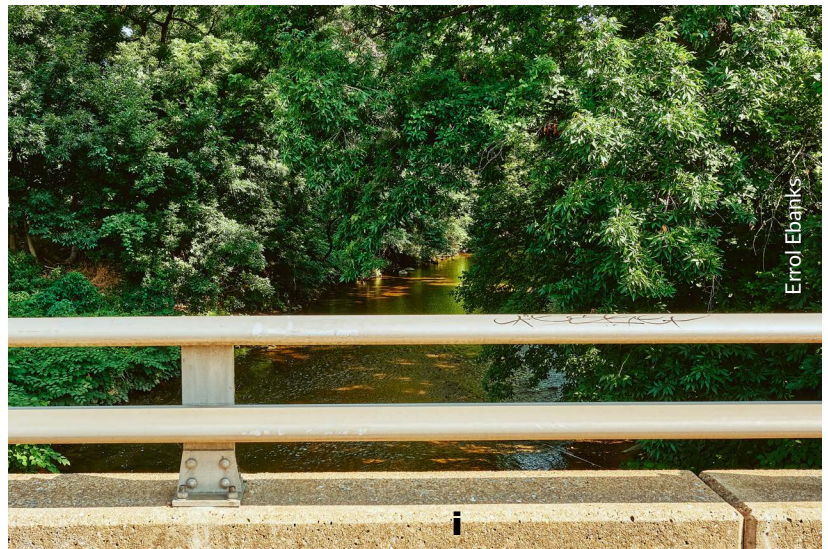


*Red Clay Creek*

As our understanding of PFAS in the environment continues to evolve, the available analytical methods, data reporting structures (e.g., lists of PFAS compounds reported by laboratories) and data analysis techniques are also rapidly changing. As a result, the surface water data collected during this assessment has been summarized and presented in several different ways in hopes that any anomalies or variations will stand out and that they might provide clues to the source(s) of the contamination that can be identified and remediated.

In review of the data presented in this data summary report, several anomalies or differences were identified with regard to the magnitude of PFAS concentration(s), or with the distribution of PFAS family groups and subgroups, that deserve follow-up actions. DNREC is initiating activities to verify and further investigate PFAS in the following water bodies and/or watersheds:

- Red Clay Creek (New Castle County)
- Hershey Run (New Castle County)
- Shellpot Creek (New Castle County)
- Long Branch (New Castle County)
- Little River (Kent County)
- St. Jones River (Kent County)



*Hershey Run*

Follow-up actions will include resampling to verify the data collected during this study and review of any data collected nearby during other studies. If confirmed, additional samples within the water body, general site area or the watershed will need to be collected in an attempt to determine the lateral and/or vertical extent of the impact(s). In some cases, it may be necessary to collect samples from sediment, soil, groundwater, surface water, air and/or aquatic life to fully characterize the impact and to help determine the source(s) of the contamination so that they can be properly addressed.

# Acronyms and Abbreviations

4:2 FTS	1H,1H,2H,2H-Perfluorohexane Sulfonic Acid
5:3 FTCA	5:3 Fluorotelomer Carboxylic Acid
6:2 FTCA	6:2 fluorotelomer Carboxylic Acid
6:2 FTS	1H,1H,2H,2H-Perfluorooctane Sulfonic Acid
6:2 FTUCA	6:2 Fluorotelomer Alpha, Beta-Unsaturated Carboxylate
8:2 FTS	1H,1H,2H,2H-Perfluorodecane Sulfonic Acid
ADONA	4,8-Dioxa-3H-Perfluorononanoic Acid
AFFF	Aqueous Film Forming Foam
COPC	Contaminant of Potential Concern
DNREC	Delaware Department of Natural Resources and Environmental Control
DI	Deionized
DO	Dissolved Oxygen
DW	Division of Water
DWS	Division of Watershed Stewardship
DWHS	Division of Waste and Hazardous Substances
ECF	Electrochemical Fluorination
EDD	Electronic Data Deliverable
ELS	DNREC Environmental Laboratory Section
EQulS	Environmental Quality Information System
ESA	Ether Sulfonic Acid
FASA	Perfluoroalkane Sulfonamide
FCA	Fish Consumption Advisory
FOSA	Perfluorooctane Sulfonamide
FOSAA	Perfluorooctane Sulfonamidocetic Acid
FOSE	Perfluorooctane Sulfonamide Ethanol
FTCA	Fluorotelomer Carboxylic Acid
FTSA	Fluorotelomer Sulfonic Acid
HDPE	High Density Polyethylene
HFPO-DA	Hexafluoropropylene Oxide Dimer Acid (aka Gen-X)
HSCA	Delaware Hazardous Substance Cleanup Act
ITRC	Interstate Technology and Regulatory Council
LC-MS/MS	Liquid Chromatography with Tandem Mass Spectrometry
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
N-EtFOSAA	N-Ethyl Perfluorooctane Sulfonamido Acetic Acid
N-MeFOSAA	N-Methyl Perfluorooctane Sulfonamido Acetic Acid
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List (aka Superfund)
PDF	Portable Document Format
PFAA	Perfluoroalkyl Acid
PFAS	Per and Polyfluoroalkyl Substances
PFBA	Perfluorobutanoic Acid

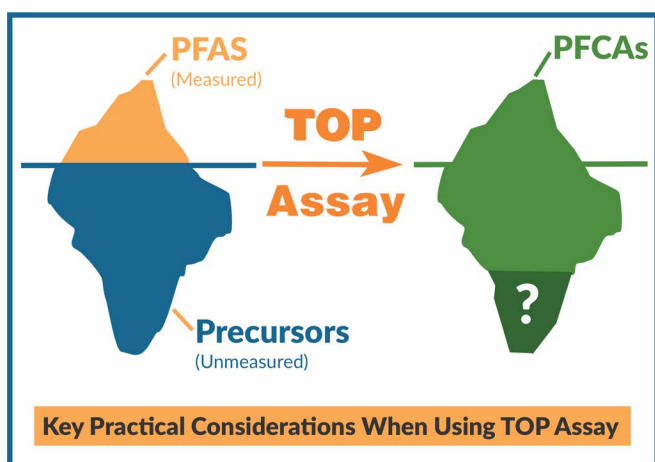
PFBS	Perfluorobutanesulfonic Acid
PFCA	Perfluoroalkyl Carboxylic Acid
PFDA	Perfluorodecanoic Acid
PFDS	Perfluorodecanesulfonic Acid
PFDoA	Perfluorododecanoic Acid
PFECA	Per- and Polyfluoroether Carboxylic Acid
PFECA B	Perfluoro-3,6-dioxahheptanoic Acid (aka NFDHA)
PFEESA	Perfluoro-2-Ethoxyethanesulfonic Acid (aka PES)
PFHpA	Perfluoroheptanoic Acid
PFHpS	Perfluoroheptanesulfonic Acid
PFHxA	Perfluorohexanoic Acid
PFHxS	Perfluorohexanesulfonic Acid
PFMBA	Perfluoro-4-Methoxybutanoic Acid
PFMOAA	Perfluoro-2-Methoxyacetic Acid
PFMPA	Perfluoro-3-Methoxypropanoic Acid
PFNA	Perfluorononanoic Acid
PFO2HxA	Perfluoro-3,5-Dioxahexanoic Acid
PFO3OA	Perfluoro-3,5,7-Trioxaoctanoic Acid
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PFPeA	Perfluoropentanoic Acid
PFPeS	Perfluoropentanesulfonic Acid
PFPrA	Pentafluoropropionic Acid or PFF Acid
PFSA	Perfluoroalkyl Sulfonic Acid
PFTeDA	Perfluorotetradecanoic Acid
PFTrDA	Perfluorotridecanoic Acid
PFUnA	Perfluoroundecanoic Acid
PPB	Parts Per Billion (equivalent to micrograms per liter or µg/L)
PPM	Parts Per Million (equivalent to milligrams per liter or mg/L)
PPT	Parts Per Trillion (equivalent to nanograms per liter or ng/L)
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QAPrP	Quality Assurance Program Plan
QC	Quality Control
RL	Reporting Limit
SOP	Standard Operating Procedure
SPE	Solid Phase Extraction
TMDL	Total Maximum Daily Load
TOP	Total Oxidizable Precursor
USEPA	U.S. Environmental Protection Agency
WATAR	Watershed Approach to Toxics Assessment and Restoration
WWTP	Wastewater Treatment Plant

# Introduction

The Delaware Department of Natural Resources and Environmental Control's Watershed Approach to Toxics Assessment & Restoration (DNREC-WATAR) team is comprised of personnel from DNREC's Division of Watershed Stewardship (DWS), Division of Waste and Hazardous Substances (DWHS) and Division of Water (DW). The team initiated a study in the fall of 2022 to measure concentrations of per- and polyfluoroalkyl substances (PFAS) in the state of Delaware's surface waters as part of early attempts in understanding the nature and extent of PFAS impacts in Delaware. DNREC's intentions were to identify potential contaminant sources (or source areas) within the state and to prioritize future resources to the watersheds that are most impacted by PFAS. Tracking and eliminating these chemicals' sources to the environment will have a positive impact on water quality and in maintaining healthy communities in Delaware. Additional Delaware-specific PFAS-related information, including summaries of ongoing studies and links to completed studies, can be found on DNREC's PFAS web page [de.gov/pfas](https://de.gov/pfas). An abundance of technical information about PFAS can be found on the Interstate Technology and Regulatory Council (ITRC) webpage [PFAS – Per- and Polyfluoroalkyl Substances \(itrcweb.org\)](https://itrcweb.org). Additional information about the United States Environmental Protection Agency (USEPA) actions related to PFAS can be found on the USEPA PFAS web page [Per- and Polyfluoroalkyl Substances \(PFAS\) | US EPA](https://www.epa.gov/pfas).

The state of Delaware contains a total of 45 watersheds, most of which originate in Delaware, and which drain either westward and southward into the Eastern Shore of Maryland and onward into the Chesapeake Bay, or eastward into the Delaware River, Delaware Bay or Inland Bays. **Figure 1** shows a map of these 45 watersheds. During this study, 83 locations were sampled within 33 of Delaware's watersheds. **Figure 2** shows a map of the 83 sample locations.

A total of 39 per- and polyfluoroalkyl substances (PFAS) were analyzed for in each sample collected during this study. A Total Oxidizable Precursor (TOP) assay was also utilized during this study. To use this analytical methodology, two samples were collected at each location for separate analysis. Data from "pre-treatment" samples represents concentrations of the 39 PFAS compounds that were measurable at the time of sample collection. The data from "post-treatment" samples represents concentrations of the 39 measurable PFAS compounds after the sample was put through the TOP assay (an oxidation step) prior to analysis. Effectively, the post-treatment data intends to quantify PFAS concentrations that could exist in the future after unmeasurable PFAS in the sample (referred to as PFAS Precursors) break down, change or otherwise "transform" in the environment into measurable PFAS (most of which transform into perfluoroalkyl carboxylic acids (**PFCAs**)). The graphic below, modified from Ateia et. al. (2023), illustrates this concept.



Although both pre- and post- treatment laboratory analytical results are included in summary tables associated with this report, it is important to note that the TOP analytical methodology and interpretive use of the data is still experimental. No conclusions are presented based upon the post-treatment data. Where noted, some of the data summaries and statistics presented in this report were developed using pre-treatment data only.



The intent of this study is not to evaluate risk to human health or the environment from exposure to concentrations of PFAS detected in Delaware’s waterways. Instead, the intent is to compare the relative degree of PFAS contamination across the state. Doing so allows for prioritization of resources to areas where the highest potential impacts are most likely occurring and where the most positive outcomes can be achieved most efficiently. Further, the surface water data will be considered along with data being collected from other media across the state (e.g., groundwater, soil, biosolids, air, fish and other wildlife) to further refine priorities within watersheds or subwatersheds and to determine potential contaminant sources that are in need of additional investigation, clean-up and restoration. When reviewing this information, it is important to keep in mind that a surface water sample represents a snapshot of conditions at the time of sampling. There are many natural factors that can affect data at any given time. With the understanding that conditions can change regularly, more focused studies may be necessary to determine the extent of any identified localized impacts.

## Project Need

Surface water is withdrawn from several rivers and/or streams in the state for purposes of public water supply. As such, it is a common transport pathway for contaminants that impact human health (through direct contact and/or ingestion). Contaminants in surface water can also be toxic to fish and other aquatic life and to wildlife that drink the impacted surface water. Depending on several factors, some contaminants, including PFAS, can bioaccumulate in the tissue of local fish and other aquatic life. This not only increases the body burden of the chemicals in the organism, potentially causing impacts, but also creates an exposure pathway to organisms at higher trophic levels like piscivorous birds (e.g., kingfishers, great blue heron, osprey, bald eagles), aquatic mammals (e.g., otters) and humans through the consumption of contaminated fish and wildlife.

PFAS and other toxic contaminants can enter surface water through overland flow (i.e., stormwater runoff), through atmospheric deposition and through groundwater discharge. In other words, contaminants detected in surface water likely come from other nearby sources within the watershed. Documentation of the nature, extent, magnitude and distribution of PFAS contamination in surface waters across the state is a good initial step in understanding the overall distribution of PFAS in other environmental media. The data may also provide important forensic clues, or lines of evidence, regarding the source(s) of PFAS and their associated impacts.

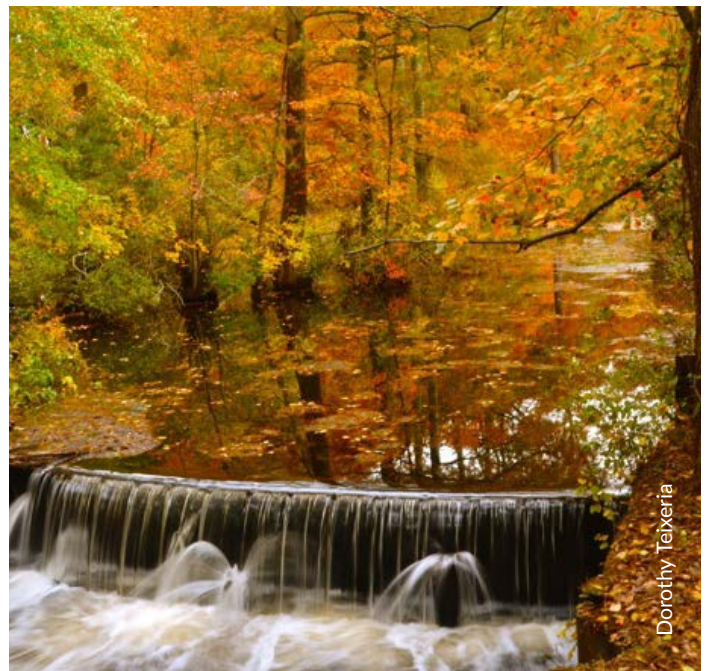


## Purpose and Scope (Experimental Design)

This PFAS in surface water study covered the entire state of Delaware, in both tidal and non-tidal portions of select watersheds. In an attempt to isolate potential PFAS sources to geographic drainage areas, surface water sampling sites were chosen at accessible locations at or just above a body of water's head of tide (defined as the furthest point where tidal effects can be measured) and near the body of water's discharge point to another major waterway (i.e., a river mouth). DNREC considered multiple other sources of information prior to selecting final sampling sites, including existing and readily available data on other toxic compounds in surface water, sediments and biota; Maryland's Clean Water Act Section 303(d) Lists of Impaired Waters for toxics and associated Total Maximum Daily Loads (TMDLs) (MDE, 2022a), and Delaware's 2022 Combined Watershed Assessment Report (305(b)) and Determination for the Clean Water Act Section 303(d) List of Waters Needing TMDLs (DNREC, 2022a); fish consumption advisories (FCAs) in both Maryland (MDE, 2022b) and Delaware (DNREC, 2018); the type and location of permitted (NPDES) point source surface water discharges; and the location of Federal Superfund (National Priorities List or NPL) sites and Delaware Hazardous Substance Cleanup Act (HSCA) regulated waste sites. Finally, some surface water sampling sites were chosen based upon their proximity to jurisdictional boundaries (i.e., state lines). Critical factors in station selection, regardless of the watershed sampled, were accessibility and safety.

**Table 1** presents the watersheds that were sampled and the specific sample locations within those watersheds. **Figure 2** shows the spatial distribution of the sampling sites across the state. A total of 83 individual locations (sites) were sampled across 33 of Delaware's watersheds.

Sampling was conducted during the fall (2022) under low flow conditions. Such conditions are not likely to represent a worst case for contaminant transport, but they often represent a worst case for contaminant bioavailability, toxicity and bioaccumulation. Storms of large magnitude, low duration and high frequency are less common in the fall following the Atlantic hurricane season. Stream flows tend to be lower and steadier; sediment resuspension tends to be less; and importantly, the magnitude and duration of dissolved phase contamination in the water column can be elevated due to diffusive exchange with the sediments and a high contribution from groundwater, both of which could contain PFAS. Coupled with other stressors such as higher water temperature, lower dissolved oxygen and lower water volume, the added stress associated with toxic contaminants can make aquatic communities especially vulnerable to impact in the fall. For the above reasons, the sampling under this study targeted the fall.



*Trussum Pond, Laurel*

# Field Collection and Laboratory Analysis Methods

DNREC personnel collected all of the field samples and prepared them for courier pickup by the state of Delaware's contract laboratory, Eurofins Environmental Testing Northeast, LLC (Eurofins Edison). The samples were subsequently shipped to a Eurofins laboratory facility in Sacramento, California, for specialized analysis. Details about the field sampling and the specialized analyses are provided below.

## Field Methods

Between October 18 and November 9, 2022, surface water samples were collected for this study from both land and from a boat, depending on the sampling site's accessibility. The DNREC-ELS sampling team utilized standard operating procedures (SOPs) for all surface water sample collection and handling activities (DNREC, 2023c). The policies, procedures, and documentation practices followed by DNREC-ELS are further described in the ELS Quality Manual (QM) (DNREC, 2019). The SOPs are included in ELSs Quality Assurance Program Plan (QAPrP) (DNREC, 2024) and were described in DNREC's project specific Quality Assurance Project Plan (QAPP) (DNREC, 2022b).



Overpass sampling

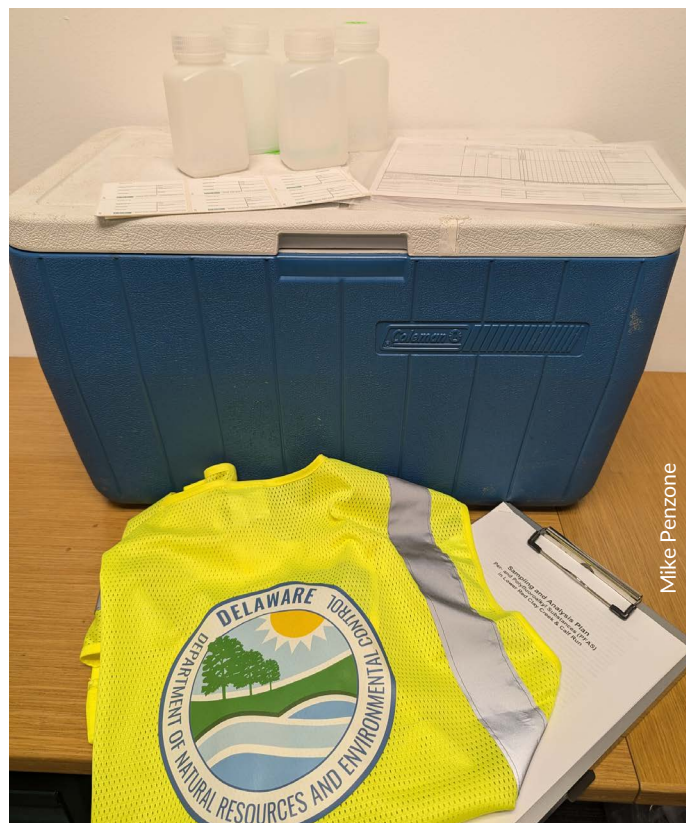
## Sampling Procedures

The primary pieces of equipment utilized to collect the water samples from land or boat was a specially designed sampling pole and collection vessel. In cases where the extendable pole was not long enough to reach the water surface (greater than 24 feet), for example from a tall overpass, the sampling team used a stainless-steel bucket tied to a nylon cord that could be lowered to the water surface. If sampling from the water, the boat was positioned and anchored as close as possible to the target coordinates, and the same sampling pole and collection vessel was utilized to collect a representative sample. Due to the methodology used for analysis, the water sample collection required the filling of two 250ml High Density Polyethylene (HDPE) bottles (one bottle for pre-treatment analysis and one for TOP assay and post-treatment analysis). Once collected, the samples were properly labeled and placed on ice for transport back to the ELS Laboratory in Dover where they were repackaged into coolers with ice and picked up weekly by a Eurofins Edison courier for analysis.

In addition to collecting PFAS samples, field measurements were collected at each sample site at the time of sampling using a hand-held multi-meter. These measurements, which included water temperature, dissolved oxygen (DO), dissolved oxygen saturation (%), pH, specific conductance and salinity, provide an indication of general water quality at each location at the time of sampling.

## Equipment Decontamination Procedures

As noted in the QAPP for the project, decontamination of sampling equipment between sampling sites was necessary to ensure that contamination was not inadvertently introduced into field samples as a result of dirty equipment or as carry over (cross contamination) from another site (DNREC, 2022b). During this study, the key pieces of equipment that needed to be decontaminated included the stainless-steel bucket and the sampling pole/vessel. The bucket and the sampling tools were decontaminated with Alconox™ detergent or equivalent, followed by six deionized (DI) water rinses, a methanol rinse and another DI water rinse prior to going into the field and between sampling locations. Once at the sampling site, the equipment received three rinses with ambient (surface) water prior to collecting the sample.



*PFAS sample bottleware*

## Laboratory Methods

Specialty analyses of PFAS in surface water were provided by Eurofins Edison under contract with DNREC. Samples were analyzed by USEPA Method 537 (Modified) for a DNREC-defined list of specific PFAS analytes (DNREC REM list) using liquid chromatography – tandem mass spectrometry (LC-MS/MS). As noted previously, two samples were analyzed at each sample location: a pre-treatment sample was analyzed following a solid phase extraction (SPE) step, while the post-treatment sample was first processed by the TOP assay prior to SPE and analysis. Although not the focus of this study, analytical results for each sample are being compared pre- and post-TOP assay to assess the presence of additional PFAS compounds (aka Precursors) that cannot be directly quantified by the analytical methods available for use. In general, a greater PFAS analyte concentration measured in post-TOP assay (or post-treatment) samples suggest more extensive total PFAS contamination at the corresponding site. According to researchers, “the application of the TOP assay to samples from PFAS-contaminated sites has generated several new insights, but it has also presented various technical challenges...” (Ateia et al, 2023). Regardless of the challenges, the hope was that the data might provide additional insight into PFAS impacts (or future measurable impacts) across the state, especially as more data are collected and evaluated over time.

Additional details about the analytical method(s), TOP assay, compound reporting lists, etc. are provided in the QAPP developed for the project (DNREC, 2022b). All analytical results were supplied to DNREC as both electronic data deliverables (EDDs) that were subsequently loaded into DNREC’s Environmental Quality Information System (EQIS) database, and in Portable Document Format (PDF).

## Quality Control

For sample collection and laboratory analyses associated with this project, all of the Quality Assurance/Quality Control (QA/QC) policies and procedures detailed in the QAPP prepared in advance of the sampling event were followed.

As such, and upon receipt and review of the analytical data package from Eurofins Edison on February 7, 2023, it was determined that the data did not conform to Delaware HSCA contract protocols, specifically the notation of Method Detection Limits (MDLs) in reports and EDDs. As a result, the data package needed to be revised by the laboratory. The corrected/updated data package was received by DNREC on May 5, 2023. The data were subsequently determined to be acceptable for use by the project's quality control team and were uploaded to DNREC's EQulS database. The laboratory also performed a corrective measure per DNREC's contract in order to eliminate this error in the future.

The team planned for duplicate sample collection and analysis, equipment blank sample collection and analysis, and field blank sample collection and analysis as part of this study.

Duplicate samples were collected at a rate of approximately one per every seven samples during the sampling event. A "duplicate sample" is one that is collected at the same location and time as another sample (referred to as the "parent sample"). Both samples are handled separately, submitted to the laboratory separately and analyzed separately. By comparing laboratory analytical results between the parent and duplicate samples, one can evaluate the variability of the total sample collection and analysis processes, which may help to add context to other sample results during data evaluation.

Equipment blanks were collected after equipment decontamination to demonstrate that decontamination procedures were adequate. To collect the equipment blanks, PFAS-free water from Eurofins Edison was used to rinse the decontaminated equipment. The rinse water was collected and analyzed for PFAS compounds like every other surface water sample collected and analyzed during this study. Elevated equipment blank samples (pre-treatment data) would indicate that decontamination procedures were not adequate and that cross-contamination between sample locations would have been possible.

Field blanks were collected by exposing PFAS-free water from the laboratory to ambient field conditions during sampling. Once sampling was complete, the field blank container was sealed and analyzed. Field blank data allows for the evaluation of "other" non-sampling related sources of cross-contamination, for example from the air.

## Data Evaluation and Presentation Methods

As our understanding of PFAS in the environment continues to evolve, the available analytical methods, data reporting structures (e.g., lists of PFAS compounds reported by laboratories) and data analysis techniques are also rapidly changing. As a result, the surface water data collected and analyzed during this assessment have been summarized and presented in several different ways, in hopes that any anomalies or variations will stand out and that they might provide clues to the source(s) of the impact that can be identified and remediated. Results will also help to direct resources towards areas in need of further investigation and/or evaluation.

**Tables 2 and 3** present the analytical results from each sample site, including duplicate samples, for each of the 39 reported PFAS compounds. As noted previously, each sample location has a "pre-treatment" result as shown in **Table 2** and a "post-treatment" result as shown in **Table 3**. While the "pre-treatment" data are most appropriate for use in evaluating the current nature and extent of

surface water impacts from PFAS in Delaware, because it represents the condition of the surface water at the time the sample was collected, for completeness both pre- and post-treatment are included in the summary report.

In general, laboratories have a “lowest concentration” that can be confidently measured in a sample using the available analytical instruments and methods. This value is called the Reporting Limit (RL). A Method Detection Limit is lower than the RL and is a statistical calculation of the lowest concentration that can be detected by the instruments and methods. Typically, each compound that is part of analysis has its own RL and MDL, which are different from the RL and MDL of other compounds in the same analysis. When laboratories detect a compound in a sample, but the concentration is between the RL and the MDL, the result is marked with a letter “J” to indicate it is an approximate value. In these cases, the laboratory is confident that the compound is present in the sample because the result is greater than the MDL, but the laboratory cannot say exactly how much of that compound is present because the result is less than the RL. When compounds are not detected in a sample, the laboratory will still report the result as the MDL concentration (and sometimes the RL concentration, as was the case for this study) but will mark it with a letter “U” to show that “the analyte was analyzed for, but not detected.” In these cases, the compounds may be present in a sample, but if so, they are at concentrations that are too low to detect. Therefore, results marked with a “U” should more realistically be reported as “> MDL.” However, for this report, any result that was reported by the laboratory and marked with a “U” was assigned a concentration of zero for purposes of data display and computations. This was done for ease of public understanding of the large quantity of data summarized in this report and because the intent of data evaluation is to identify anomalies when data are compared to each other.

## **Individual Compounds**

Concentrations from eight specific PFAS compounds were extracted from the dataset and evaluated individually because there are currently state and/or federal criteria for these compounds in groundwater and/or drinking water, and because they have been the subject of the most research to date. Those eight compounds include HFPO-DA (Gen X), PFBS, PFBA, PFHxS, PFHxA, PFNA, PFOS and PFOA.

## **Summed Compounds**

Concentrations of each of the previously identified eight individual compounds were summed (“sum of eight compounds”) to represent another point of comparison between sample locations. Concentrations of each of the 39 reported PFAS compounds were also summed (“sum of 39 compounds”) to represent the total magnitude of measured and reported PFAS in the samples.

## **Family Groups and Subgroups**

Data were also aggregated further to compute and compare total concentrations of the specific PFAS family groups/subgroups described below. Classification of PFAS into specific family groups/subgroups is primarily based on shared chemical structure characteristics. PFAS within these groups tend to act similarly and by looking at them together, scientists may be able to better determine sources and the potential impacts. More general PFAS information and information about each of the families of PFAS can be found on the Interstate Technology and Regulatory Council (ITRC) webpage, under their Available Resources heading [www.itrcweb.org/PFAS](http://www.itrcweb.org/PFAS).

**Perfluoroalkyl carboxylic acids (PFCAs):** PFCAs are one of two major subgroups of perfluoroalkyl acids (PFAAs), and one of the most commonly researched PFAS (ITRC, 2020). PFAAs do not degrade under ambient conditions and are called terminal PFAS or terminal transformation products. PFCAs are grouped together based on a shared chemical structure: a chain of two or more fully fluorinated carbon atoms (the “tail”) connected to a carboxylic acid group (the “head”). PFCAs in particular are commercially used as surfactants and are manufactured through Electrochemical Fluorination (ECF) or fluorotelomerization (ITRC, 2023). The most frequently detected PFCA is PFOA (NEMA, 2020).

**Perfluoroalkyl sulfonic acids (PFSAs):** PFSAs are the second of two major subgroup of PFAAs, and one of the most commonly researched PFAS (ITRC, 2020). PFAAs do not degrade under ambient conditions and are called terminal PFAS or terminal transformation products. PFSAs are grouped together based on a shared chemical structure: a chain of two or more fully fluorinated carbon atoms (the “tail”) connected to a sulfonic acid group (the “head”). PFSAs in particular are commercially used as surfactants and manufactured by ECF. The most frequently detected PFSA is PFOS (NEMA, 2020).

**Fluorotelomer sulfonic acids (FTSAs):** FTSAs are polyfluoroalkyl substances produced through the fluorotelomerization process. Polyfluoroalkyl substances, unlike perfluoroalkyl substances, do not contain fully fluorinated chains of carbon atoms in the “tail.” Instead, some of the carbon atoms in the “tail” of polyfluoroalkyl substances are more weakly connected to hydrogen atoms. FTSAs contain a sulfonic acid “head” group and are examples of PFAS precursors that may degrade or transform into terminal PFAS in the environment. FTSAs are especially prone to degradation at the weak carbon-to-hydrogen bonds in the “tail.” The transformation of fluorotelomer-based substances is a potential source of PFCAs in the environment (ITRC, 2020). FTSAs are commonly detected at sites where Aqueous Film-Forming Foam (AFFF) is a primary source, in wastewater treatment plant (WWTP) effluent and in landfill leachate (NEMA, 2020).

**Perfluorooctane sulfonamides (FOSAs):** FOSAs are a subgroup of the family of fully fluorinated perfluoroalkane sulfonamides (FASAs) which are used as raw material to make surfactants and surface treatment/protection products. They are also products and intermediates of the ECF process (ITRC, 2020). FASAs including FOSA can be precursors and can transform into PFAAs such as PFOS. (NEMA, 2020).

**Perfluorooctane sulfonamidoacetic acids (FOSAAs):** FOSAAs are a subgroup of the family of perfluoroalkane sulfonamido substances. Although perfluoroalkane sulfonamido substances have fully fluorinated carbon chain “tails”, these compounds are considered polyfluoroalkyl substances because some carbon atoms in the “head” group are bonded to hydrogen atoms. FOSAAs are perfluoroalkane sulfonamido substances that contain acetic acid as the “head” group. FOSAAs can be raw materials for the production of surfactant and surface treatment products (ITRC, 2020). They are also typically present as intermediate environmental transformation products of other PFAS compounds (NEMA, 2020).

**Per- and Polyfluoroether carboxylic acids (PFECAs):** PFECAs are a combined subgroup of per- and polyfluoroalkyl ether acids that each contain a carboxylic acid “head.” These compounds were “developed as replacements for other PFAS that have been phased out of production and use (e.g. GenX or ADONA)” (ITRC, 2020). They are surfactants and polymerization aids used in production of other products.

**Ether sulfonic acids (ESAs):** ESAs are another combined subgroup of per- and polyfluoroalkyl ether acids that each contain a sulfonic acid “head” and include some fluoropolymer polymerization aids “developed as replacements for other PFAS” (ITRC, 2020). ESAs include some fluoropolymer polymerization aids that were developed to replace PFOS (NEMA, 2020).

**Fluorotelomer carboxylic acids (FTCAs):** FTCAs are a subgroup of polyfluoroalkyl substances that are produced by the fluorotelomerization process (ITRC, 2023) and contain carboxylic acid “head” groups. FTCAs can be biotransformation products of fluorotelomer alcohols, which are used to make plastics. Some FTCAs are present in carpet and therefore may end up in landfill leachates (NEMA, 2020).

## **Family Group Fingerprints**

Building on the previous aggregation of data into family groups and subgroups, DNREC’s final data evaluation technique calculated the percent contribution of each of the eight family group and subgroups to the total measured PFAS concentration (sum of 39) for each sample. This represents a sort of “family group fingerprint,” which removes any bias caused by the magnitude of PFAS concentrations, directing focus to the chemical makeup of each sample instead. This evaluation could allow DNREC scientists to determine whether a source of PFAS might be present within a watershed that is contributing to a localized concentration of a particular family group, even if it isn’t at a significant concentration.



# Results

## Field Parameters

**Table 4** presents the field measurements collected at each sample location, including water temperature, dissolved oxygen (DO), dissolved oxygen saturation (%), pH, specific conductance and salinity. The salinity of the water determines if it is freshwater or marine water (saltwater). According to DNREC's Surface Water Quality Standards (DNREC, 2023a), marine water has a salinity of five parts per thousand or greater.

## QA/QC Samples

Duplicate samples were collected at 12 sites during this study. Data for each of the parent and duplicate samples (both pre-treatment and post-treatment) are included in **Tables 5 and 6**, respectively. The data were arranged into family groups and subgroups.

Summary data for the five equipment blank samples and five field blank samples collected during this study (both pre-treatment and post-treatment) are included in **Tables 7 and 8**, respectively. The data were arranged into family groups and subgroups.

## Surface Water Samples

To meet the objectives of the study, data were tabulated, evaluated utilizing the methods described in **Data Evaluation and Presentation Methods** and graphed for comparison. To make identification of different family groups easier, a standardized color scheme was generated by the DNREC team that is carried throughout this evaluation and data display (e.g. all PFCAs are colored a shade of green; all PFSA's are colored a shade of blue). Analytical results for each of the 39 measured compounds, including pre-treatment and post-treatment data is included in **Tables 2 and 3**, respectively. The data were arranged into family groups and subgroups.



Sarah Silves

*Delaware's surface water*

## Summary Statistics

Statistical calculations help scientists to identify trends or clusters of information within data sets that might not be readily apparent otherwise. **Table 9** presents a summary of the detection frequency of the compounds (or sums of compounds) and family groups that are highlighted in this study. The table also includes the minimum, median, mean and maximum concentration of each compound or family group evaluated. Minimum and maximum concentrations represent the lowest and highest concentration, respectively, of each compound in the data set. The mean concentration is the average concentration, derived by summing all of the concentrations of each compound and dividing by the total number of samples in the data set. The median concentration is the middle value of the data set when concentrations are ordered from least to greatest (e.g., the 50th value in a list of 100 values). The median concentration is useful to consider when one is dealing with a wide range of values or when there are outliers in the data set (a very high or low number compared to the rest) which would skew the calculation of the mean concentration.

## Individual PFAS Compounds

Pre-treatment and post-treatment PFAS data are presented for all compounds in **Tables 2 and 3**. Figures showing the distribution of HFPO-DA (GenX), PFBS, PFBA, PFHxS, PFHxA, PFNA, PFOS and PFOA across the state are shown on **Figure 3, Figure 4, Figure 5, Figure 6, Figure 7, Figure 8, Figure 9, and Figure 10**. Graphs comparing the magnitude of concentration of the select PFAS from samples collected during this study are included in **Appendix A (Graphs A.1-A.14)**.

In some cases, the same data are shown at different scales in order to highlight variation when one or more elevated detection(s) “dampens” the smaller scale distribution patterns. In general, the data were arranged and plotted from north on the left side of the graph (Brandywine River at Smith Bridge) to south on the right side of the graph (The Ditch under Fenwick Island Bridge). Post-treatment data are shown next to the pre-treatment data, and is a lighter shade of the same color.

## Sum of 8 PFAS and Sum of 39 PFAS

Pre-treatment and post-treatment PFAS data are presented for all compounds in **Tables 2 and 3**. Figures showing the distribution of the “sum of 8 compounds” and the “sum of 39 compounds” across the state are shown on **Figure 11 and Figure 12**. Graphs comparing the magnitude of concentration of the sum of eight compounds and sum of 39 compounds from samples collected during this study are included in **Appendix A (Graphs A.15-A.18)**.

In some cases, the same data are shown at different scales in order to highlight variation when one or more elevated detection(s) “dampens” the smaller scale distribution patterns. In general, the data have been arranged and plotted from north on the left side of the plot (Brandywine River at Smith Bridge) to south on the right side of the plot (The Ditch under Fenwick Island Bridge). Post-treatment data are shown next to the pre-treatment data, and is a lighter shade of the same color.

## PFAS Family Groups and Subgroups

Pre-treatment and post-treatment PFAS data are presented for all compounds in **Tables 2 and 3**. Figures showing the distribution of PFCAs, PFSAs, FTSA, FOSAs, ESAs and FTCAs across the state are shown on **Figure 13, Figure 14, Figure 15, Figure 16, Figure 17, Figure 18, Figure 19 and Figure 20**. Graphs comparing the magnitude of concentration of each of the family groups and subgroups from

samples collected during this study are included in [Appendix A \(Graphs A.19-A.29\)](#). Graphs comparing the sum of 39 compounds represented as family groups and subgroups for each sample (pre-treatment data only) are also included in [Appendix A \(Graphs A.30 - A.32\)](#).

In some cases, the same data are shown at different scales in order to highlight variation when one or more elevated detection(s) “dampens” the smaller scale distribution patterns. In general, the data have been arranged and plotted from north on the left side of the plot (Brandywine River at Smith Bridge) to south on the right side of the plot (The Ditch under Fenwick Island Bridge). Post-treatment data are shown next to the pre-treatment data and is a lighter shade of the same color.

## PFAS Fingerprints

Pre-treatment data are presented in [Table 2](#) for all compounds. The data were used to generate a PFAS Family Group fingerprint as described in [Family Groups Fingerprints](#). The fingerprint data are summarized in [Table 10](#). A graph comparing the fingerprints between all sampling stations is included in [Appendix A \(Graph A.33\)](#).

## Comparison to existing criteria

DNREC’s intentions with this study were to identify the most impacted water bodies within the state, to identify potential contaminant sources (or source areas) within the state and to prioritize future resources to the watersheds that are most impacted by PFAS. This assessment was not conducted to evaluate human health or ecological risk from exposure to PFAS compounds or to make any final conclusions about sources. Additional human health and/or ecological risk characterization was not conducted and presented as part of this study because there are very few established Delaware or federal criteria for PFAS compounds to provide adequate perspective. More importantly, the improper interpretation and application of criteria can lead to incorrect conclusions.

It is important, however, to have some context for framing the data presented in this data summary report. To ensure that all evaluators of this data are comparing information consistently, below are the existing or proposed water-based criteria that have been established/adopted by the USEPA and/or the state of Delaware at the time of report publication. Close attention should be paid to the description of how the criteria are meant to be applied and what exceedances of the criteria represent.

## USEPA Drinking Water Standards

Compound	Maximum Contaminant Level (MCL)
PFOA	4 ng/L (ppt)
PFOS	4 ng/L (ppt)
PFNA	10 ng/L (ppt)
PFHxS	10 ng/L (ppt)
HFPO-DA	10 ng/L (ppt)
Mixture of two or more: PFNA, PFHxS, HFPO-DA and PFBS	Hazard Index of 1

Maximum Contaminant Levels (MCLs) for drinking water are established under the USEPA National Primary Drinking Water Regulations (USEPA, 2009). MCLs for several PFAS compounds were set by the USEPA in April 2024 (USEPA, 2024a). These criteria are applicable to finished drinking water only (after treatment) in regulated public drinking water systems and not to “raw” water samples collected from a surface water body or from groundwater. The MCLs for PFNA, PFHxS, PFBS and/or HFPO-DA are to be combined and used in the calculation of a Hazard Index as noted on EPA’s website (USEPA, 2024b) to determine if an exceedance of the criterion has occurred.

Of Delaware’s surface waters, only six water bodies are designated as a source of public drinking water (raw water). Those include the freshwater segments of the Brandywine Creek, Red Clay Creek, White Clay Creek, Christina River, Red Lion Creek and Dragon Run Creek (DNREC 2023a).

### HSCA Screening Levels for Groundwater

Compound	HSCA Groundwater Screening Value	
	ug/L (ppb)	ng/L (ppt)
Hexafluoropropylene oxide dimer acid (HFPO-DA)	0.006	6
Perfluorobutanesulfonic acid (PFBS)	0.6	600
Perfluorobutanoic acid (PFBA)	1.8	1,800
Perfluorohexanesulfonic acid (PFHxS)	0.039	39
Perfluorohexanoic acid (PFHxA)	0.61	610
Perfluorononanoic acid (PFNA)	0.0059	5.9
Perfluorooctanesulfonic acid (PFOS)	0.004	4
Perfluorooctanoic acid (PFOA)	0.006	6

According to criteria contained in Delaware’s **HSCA Screening Level Table (DNREC, 2023b)**, the screening levels should be used for screening purposes only for the protection of human health and the environment. The screening levels are not to be construed as site specific clean up levels. The HSCA Screening Level Table combines background, risk-based and regulatory values in soil, groundwater, soil gas, sediment, and surface water. The screening levels should be used to determine the contaminants of potential concern (COPCs) in the risk assessment process.

**Note:** An exceedance of any value in the HSCA screening level table only means that the compound should be retained for further risk assessment as defined by DNREC regulations and guidance and is applicable only to sites that are being regulated under Delaware’s HSCA program.

## USEPA Draft Recommended Freshwater Aquatic Life Water Quality Criteria for PFOA and PFOS

Criteria Component	Acute Water Column (CMC)	Chronic Water Column (CCC)
PFOA	49 mg/L (ppm) or 49,000,000 ng/L (ppt)	0.094 mg/L (ppm) or 94,000 ng/L (ppt)
PFOS	3.0 mg/L (ppm) 3,000,000 ng/L (ppt)	0.0084 mg/L (ppm) 8,400 ng/L (ppt)
Duration	1-hour average	4-day average
Frequency	Not to be exceeded more than once in three years, on average.	Not to be exceeded more than once in three years, on average.

### Notes:

mg/L Milligrams per liter

ng/L Nanograms per liter

CMC Criterion Maximum Concentration

CCC Criterion Continuous Concentration

These criteria have been proposed by the USEPA to protect aquatic life from direct harm related to exposure from these chemicals above the noted concentrations (USEPA, 2022). The criteria do not account for bioaccumulation in aquatic organisms, like fish, and the subsequent risk posed to human health through consumption. Again, note that these criteria are “Draft Recommendations” and are not approved and adopted by DNREC or USEPA. They are provided here because they are available for public review and provide additional context for comparing measured concentrations from this study.

# Conclusions

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After reviewing the data presented in this summary report, it was determined that follow up actions were required in several watersheds to examine anomalies or differences that were identified with regard to the magnitude of PFAS concentration(s), or with the distribution of family groups and subgroups. DNREC has initiated, or is the process of initiating, activities to verify and further investigate PFAS in the following water bodies and watersheds:

- Red Clay Creek
- Shellpot Creek
- Hershey Run
- Long Branch
- Little River
- St. Jones River



*Shellpot Creek*

DNREC has resampled or plans to resample sites from these watersheds to verify data collected during the initial study. If results support the initial findings, additional samples within the water body and/or general site area will need to be collected in an attempt to determine the lateral and/or vertical extent of the impact. In some cases, it may be necessary to collect samples from sediment, soil, groundwater, surface water, air and/or aquatic life to fully characterize the impact, and to help determine the source(s) of the contamination so that they can be properly addressed.

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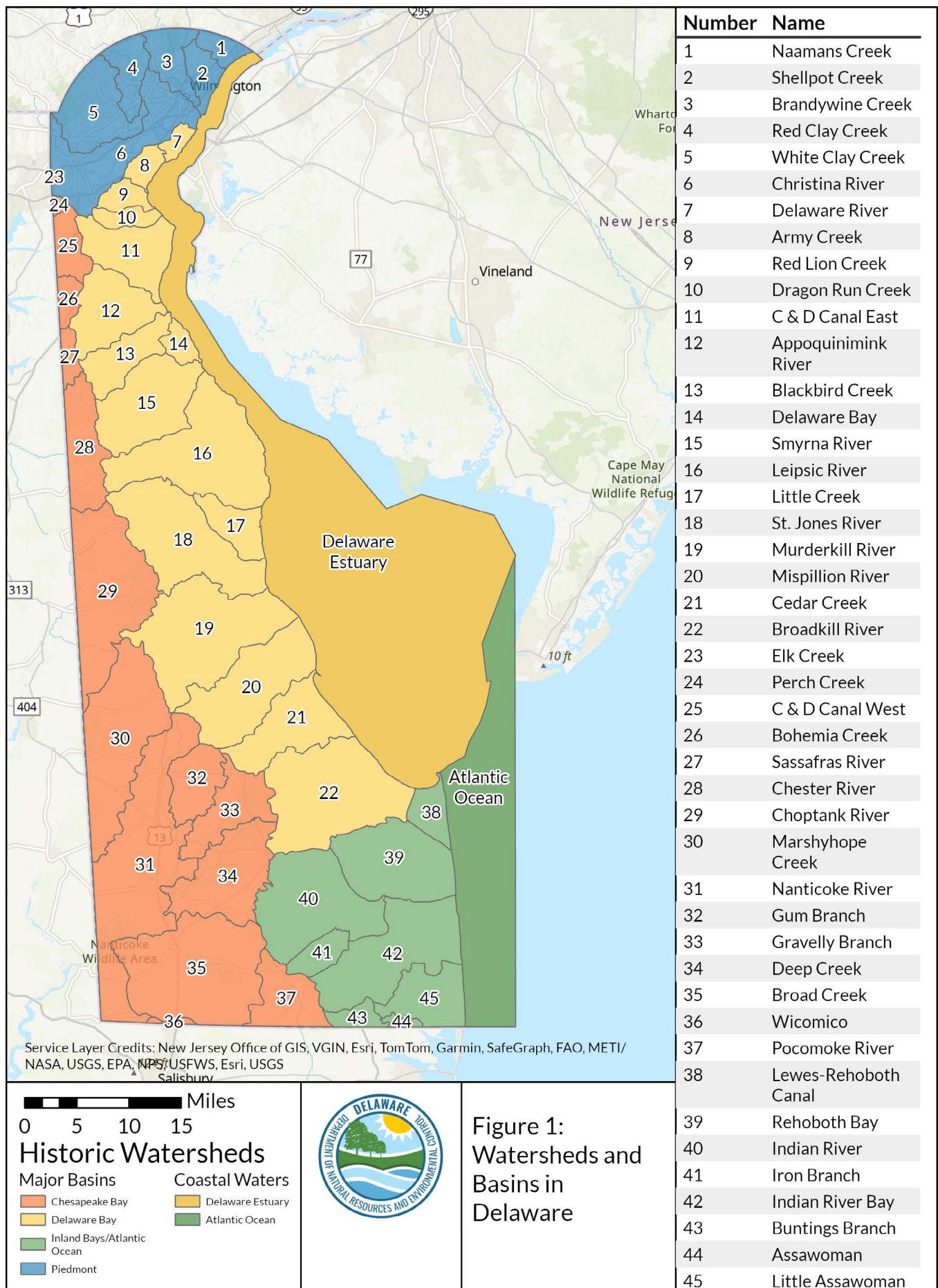
[epa.gov/system/files/documents/2024-04/pfas-ncpdwr\\_fact-sheet\\_general\\_4.9.24v1.pdf](https://epa.gov/system/files/documents/2024-04/pfas-ncpdwr_fact-sheet_general_4.9.24v1.pdf).

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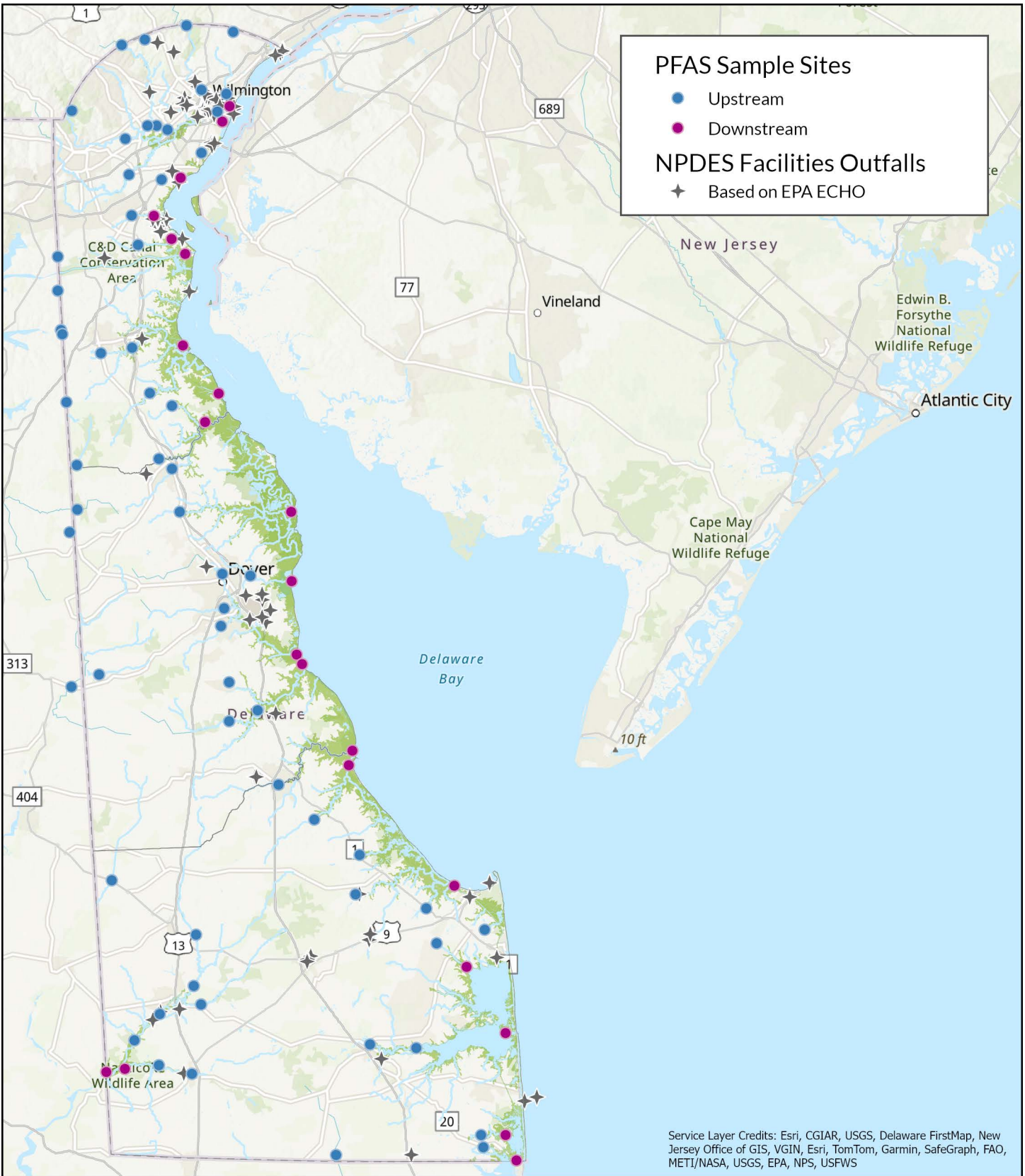
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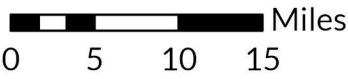
# Figures



Number	Name
1	Naamans Creek
2	Shellpot Creek
3	Brandywine Creek
4	Red Clay Creek
5	White Clay Creek
6	Christina River
7	Delaware River
8	Army Creek
9	Red Lion Creek
10	Dragon Run Creek
11	C & D Canal East
12	Appoquinimink River
13	Blackbird Creek
14	Delaware Bay
15	Smyrna River
16	Leipsic River
17	Little Creek
18	St. Jones River
19	Murderkill River
20	Mispillion River
21	Cedar Creek
22	Broadkill River
23	Elk Creek
24	Perch Creek
25	C & D Canal West
26	Bohemia Creek
27	Sassafras River
28	Chester River
29	Choptank River
30	Marshyhope Creek
31	Nanticoke River
32	Gum Branch
33	Gravelly Branch
34	Deep Creek
35	Broad Creek
36	Wicomico
37	Pocomoke River
38	Lewes-Rehoboth Canal
39	Rehoboth Bay
40	Indian River
41	Iron Branch
42	Indian River Bay
43	Buntings Branch
44	Assawoman
45	Little Assawoman



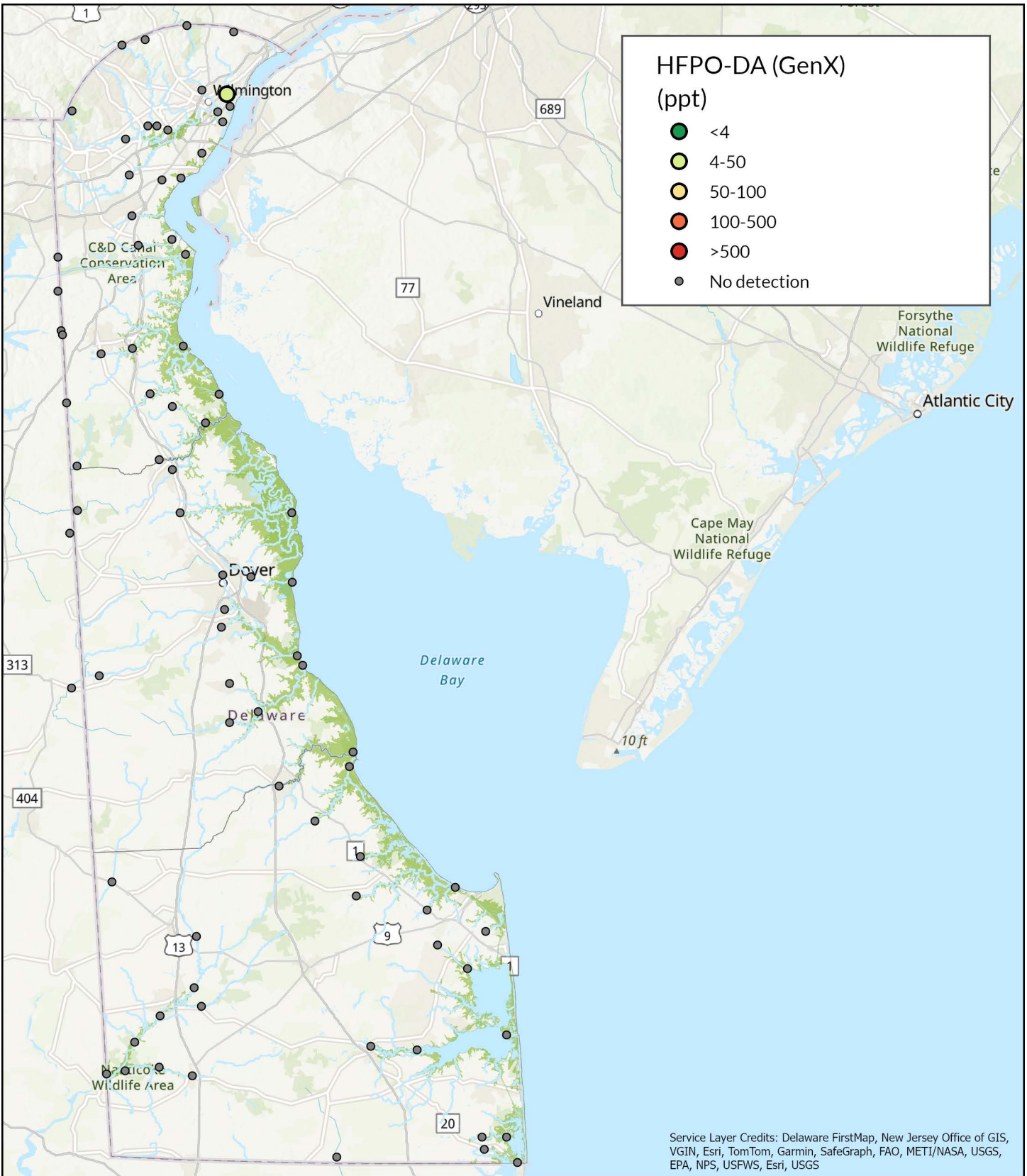
Service Layer Credits: Esri, CGIAR, USGS, Delaware FirstMap, New Jersey Office of GIS, VGIN, Esri, TomTom, Garmin, SafeGraph, FAO, METI/NASA, USGS, EPA, NPS, USFWS



- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 2:  
PFAS Sample Locations in Delaware Surface Water - Fall 2022

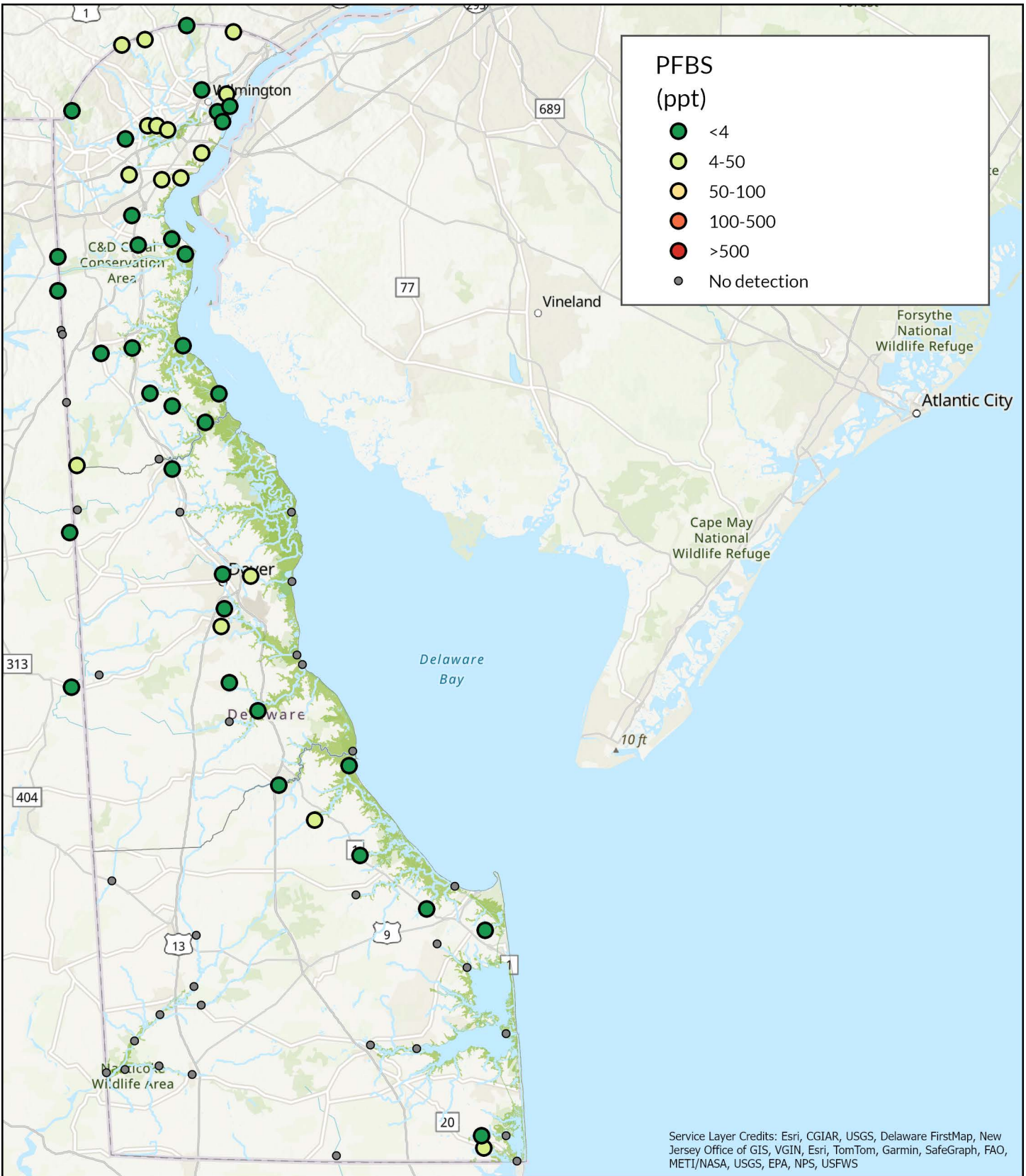


0 5 10 15 Miles

- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



**Figure 3:**  
HFPO-DA (GenX) in  
Delaware Surface Water -  
Fall 2022



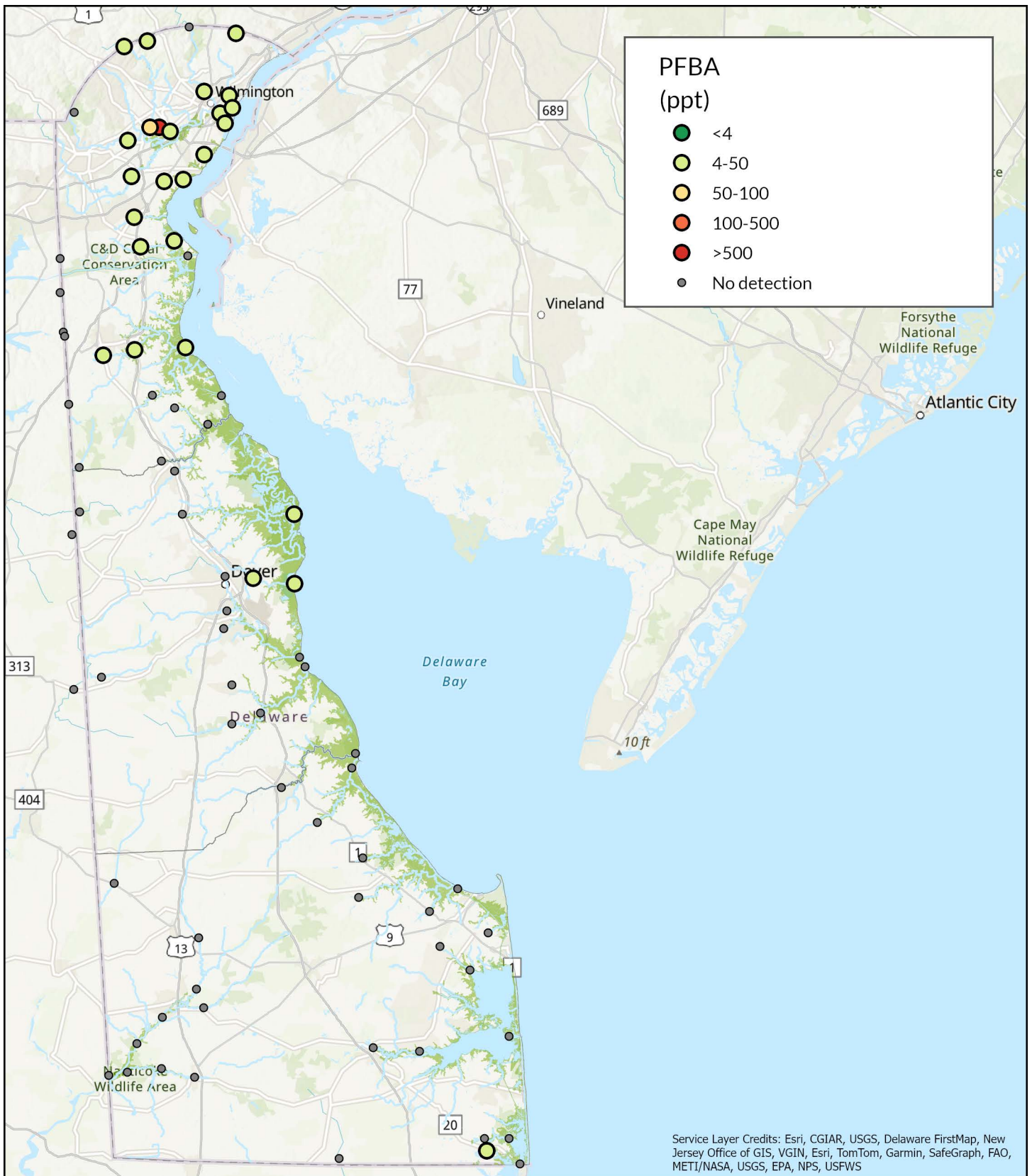
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0 5 10 15 Miles

- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



**Figure 4:**  
PFBS in Delaware Surface Water - Fall 2022

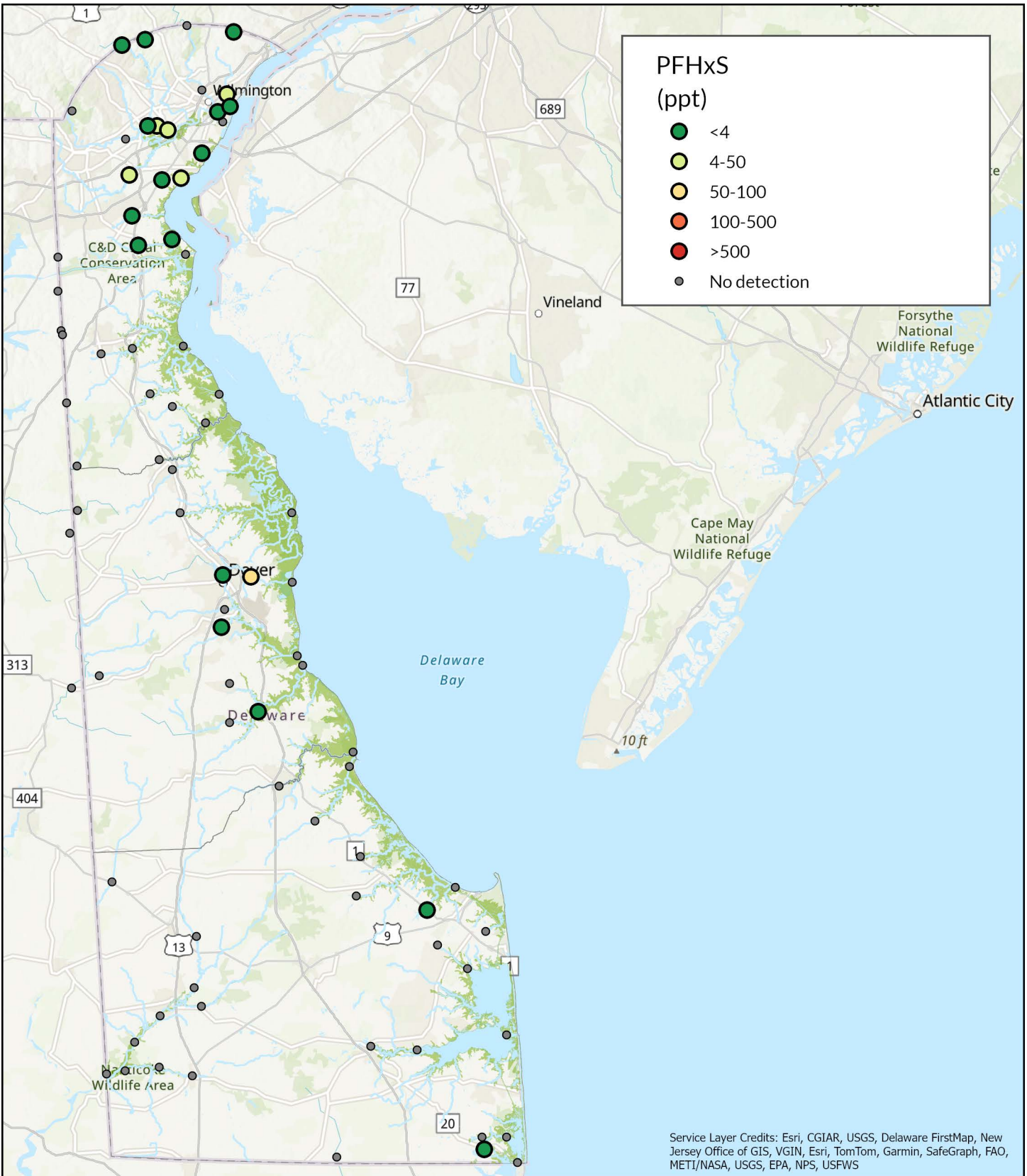


0 5 10 15 Miles

- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 5:  
PFBA in Delaware Surface  
Water - Fall 2022



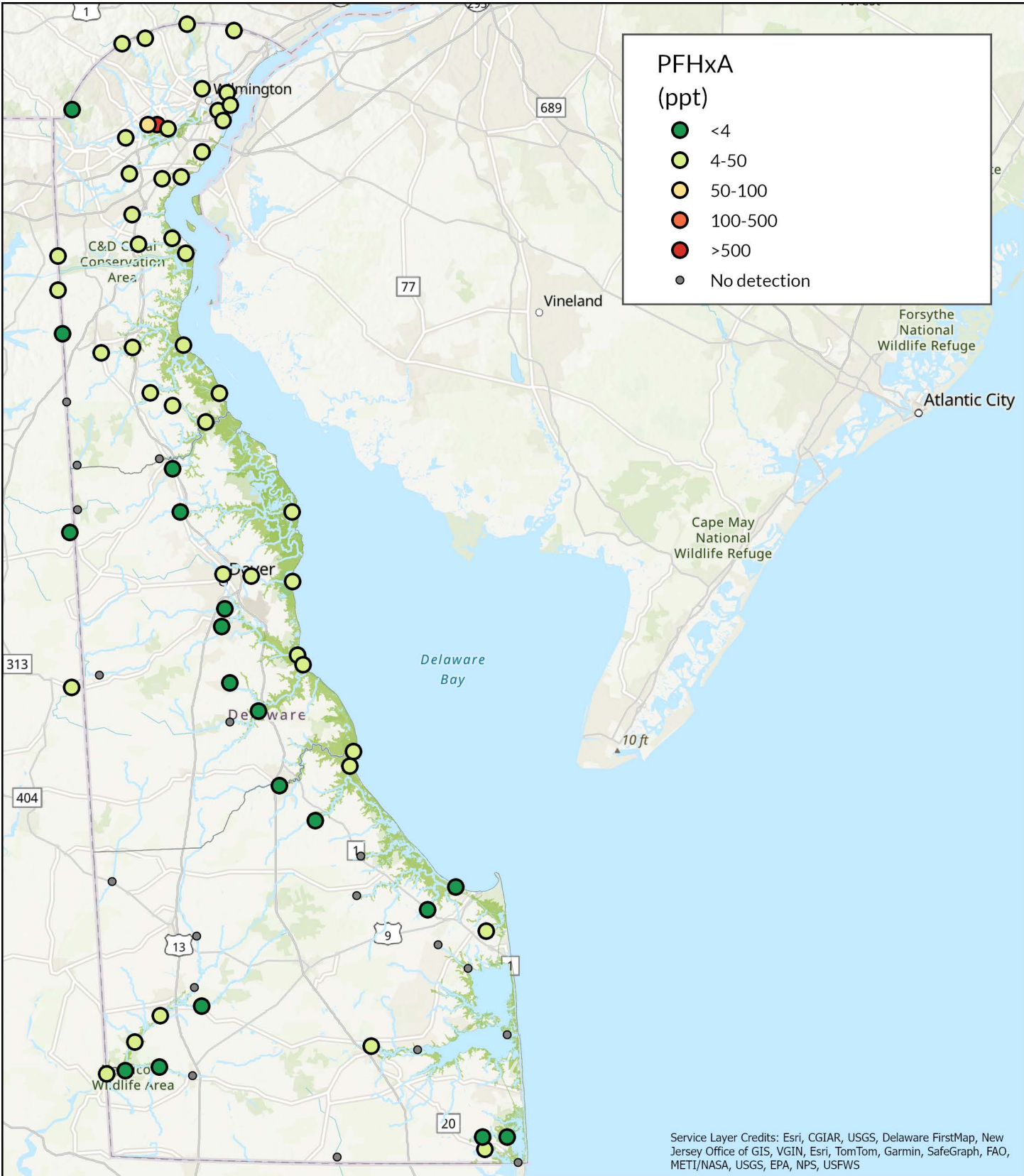
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0 5 10 15 Miles

- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 6:  
PFHxS in Delaware Surface  
Water - Fall 2022



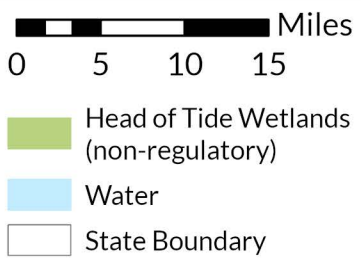
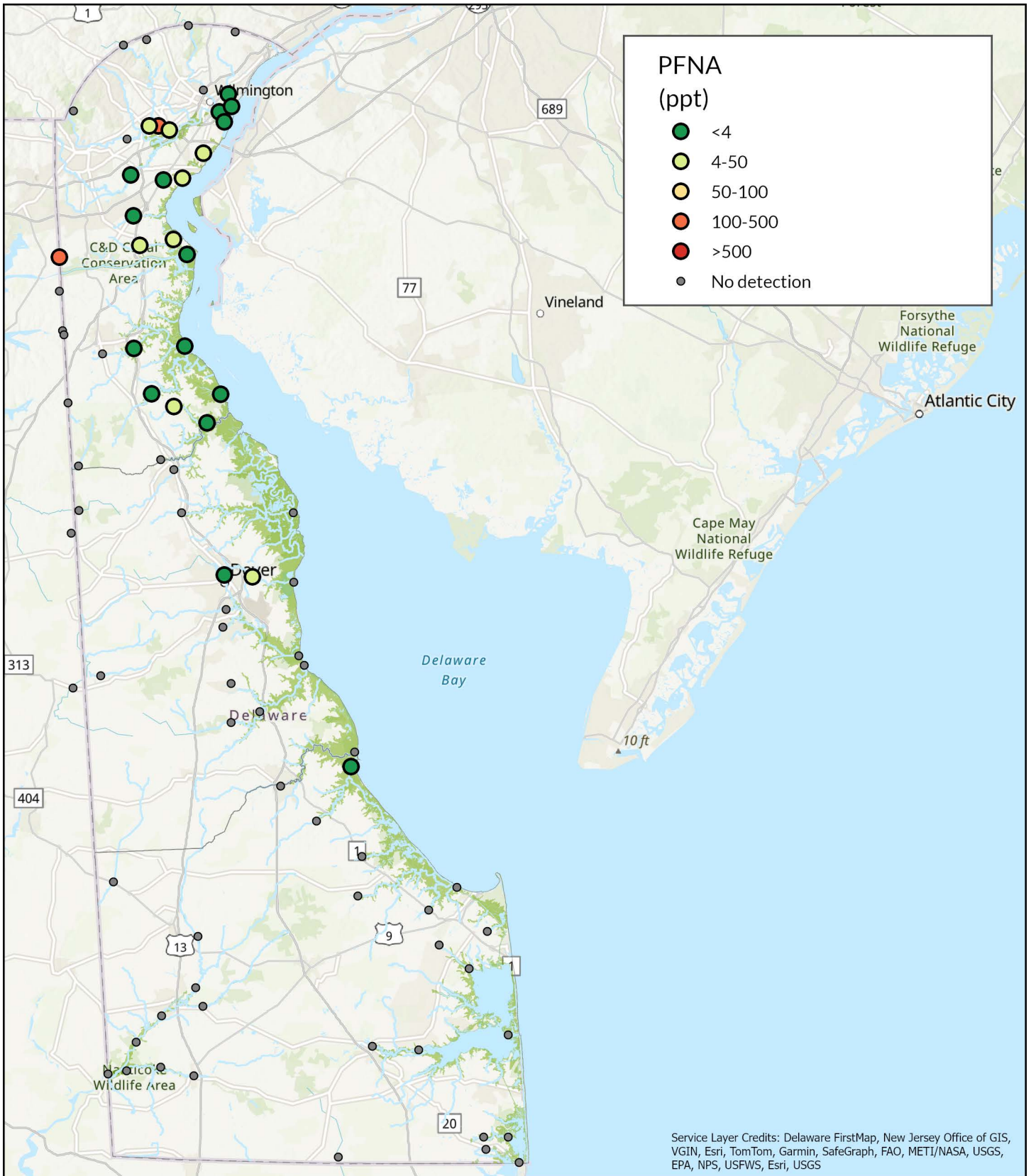
Service Layer Credits: Esri, CGIAR, USGS, Delaware FirstMap, New Jersey Office of GIS, VGIN, Esri, TomTom, Garmin, SafeGraph, FAO, METI/NASA, USGS, EPA, NPS, USFWS

0 5 10 15 Miles

- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 7:  
PFHxA in Delaware Surface Water - Fall 2022



**Figure 8:**  
PFNA in Delaware Surface Water - Fall 2022



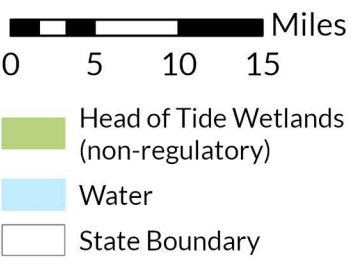
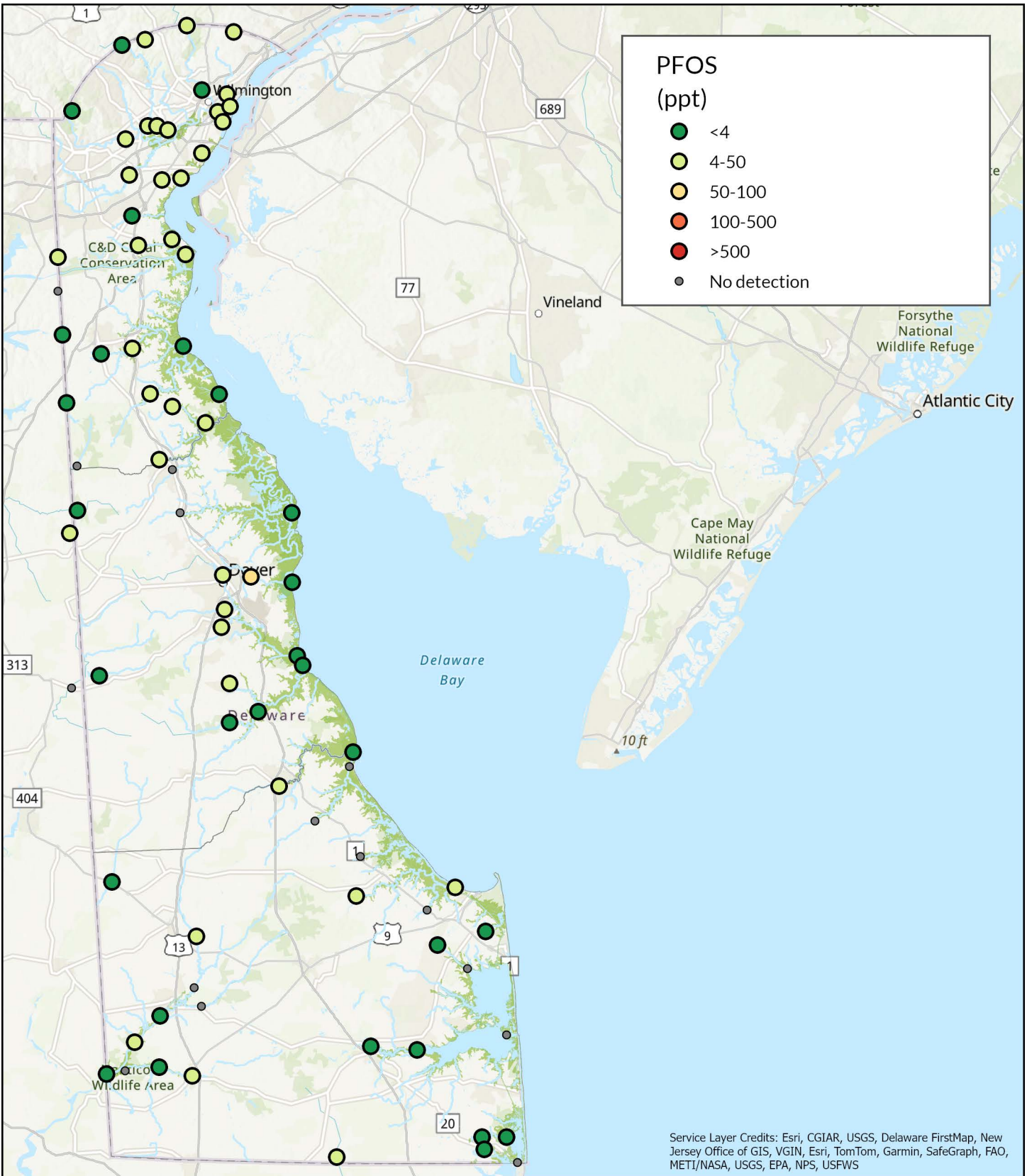
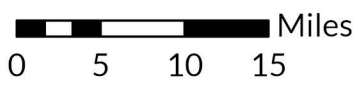
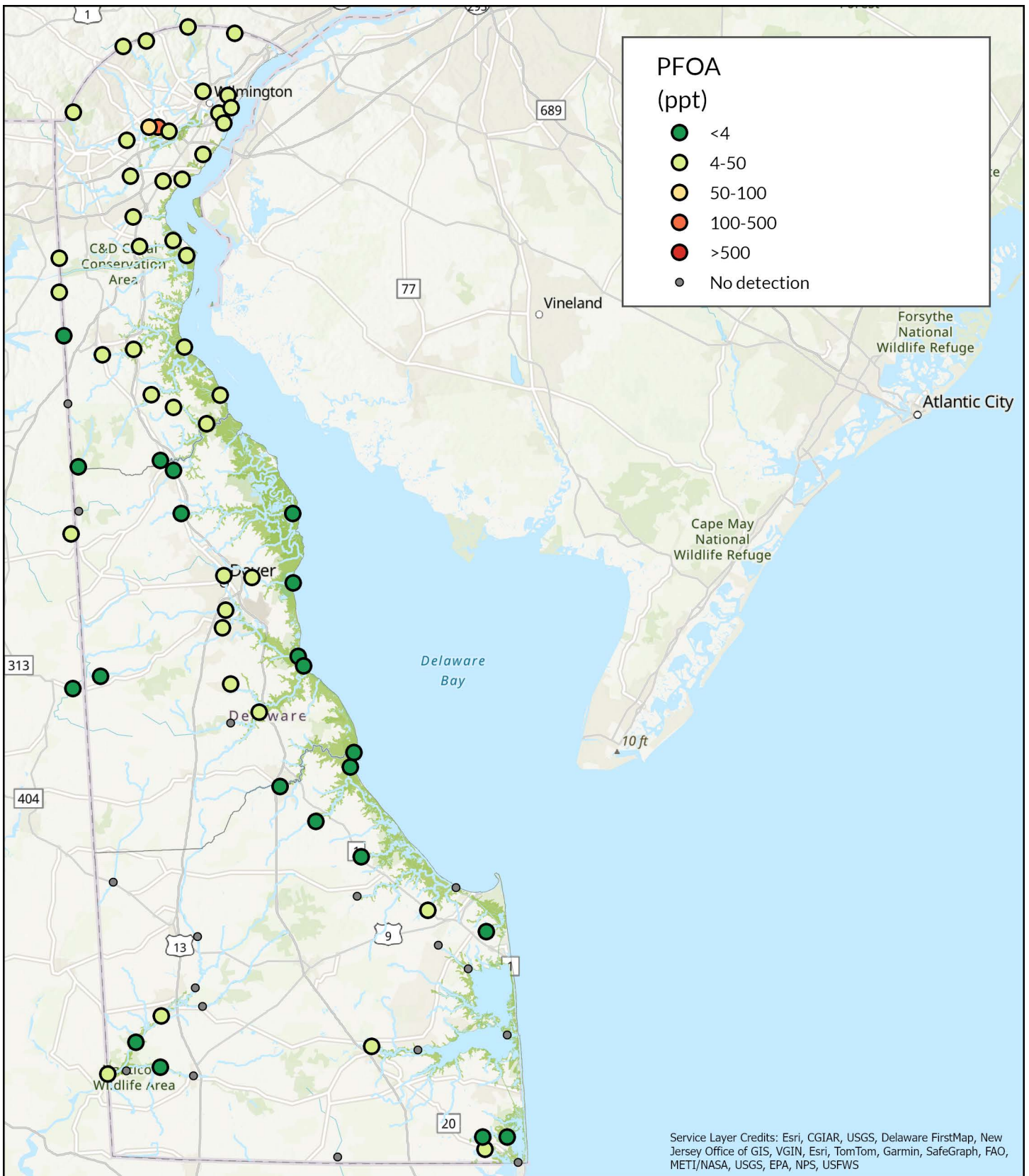


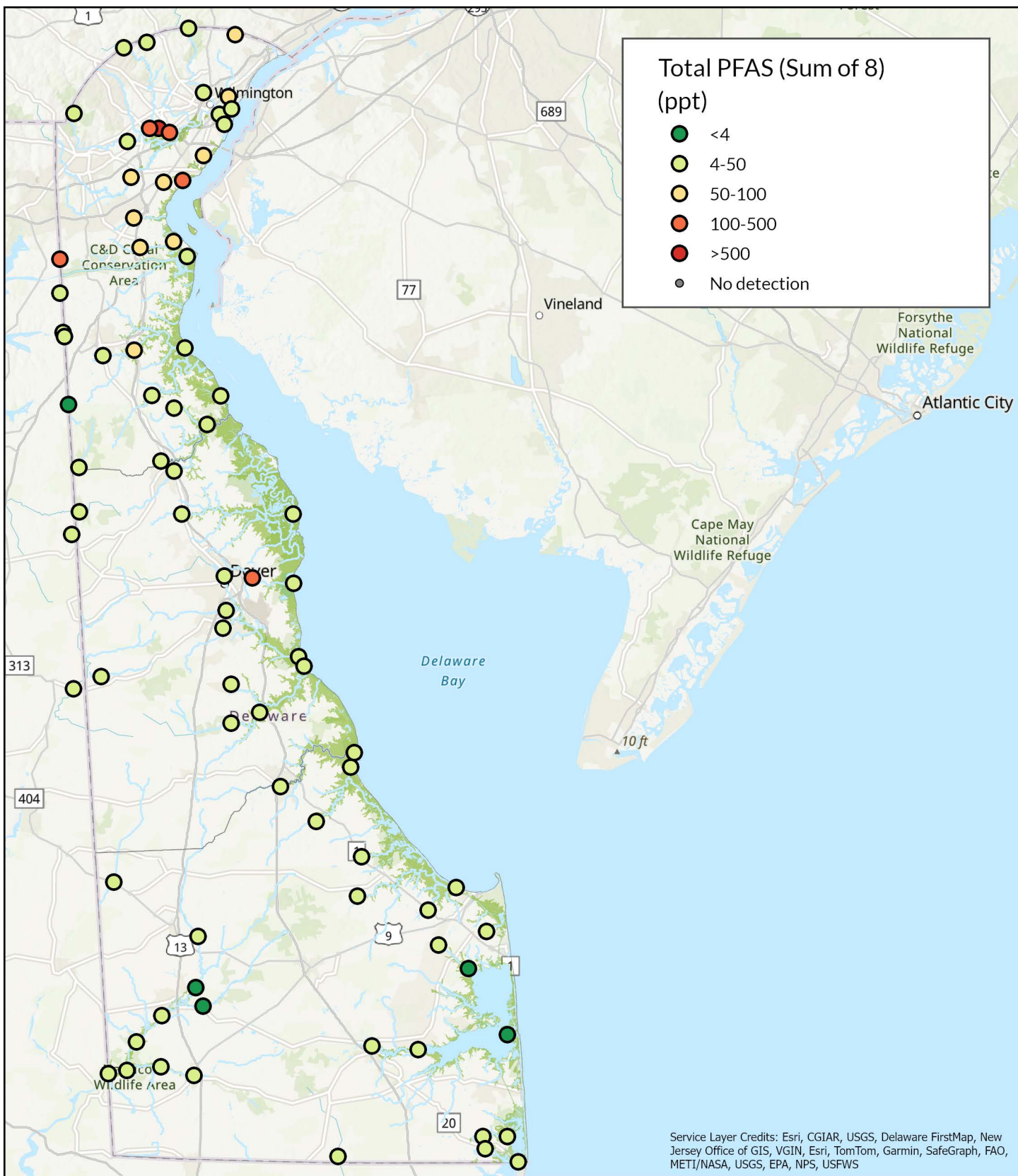
Figure 9:  
PFOS in Delaware Surface  
Water - Fall 2022



- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 10:  
PFOA in Delaware Surface  
Water - Fall 2022



0 5 10 15 Miles

- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 11:  
Total PFAS (Sum of 8) in  
Delaware Surface Water -  
Fall 2022

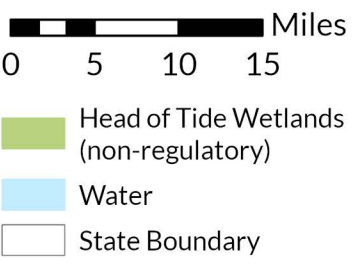
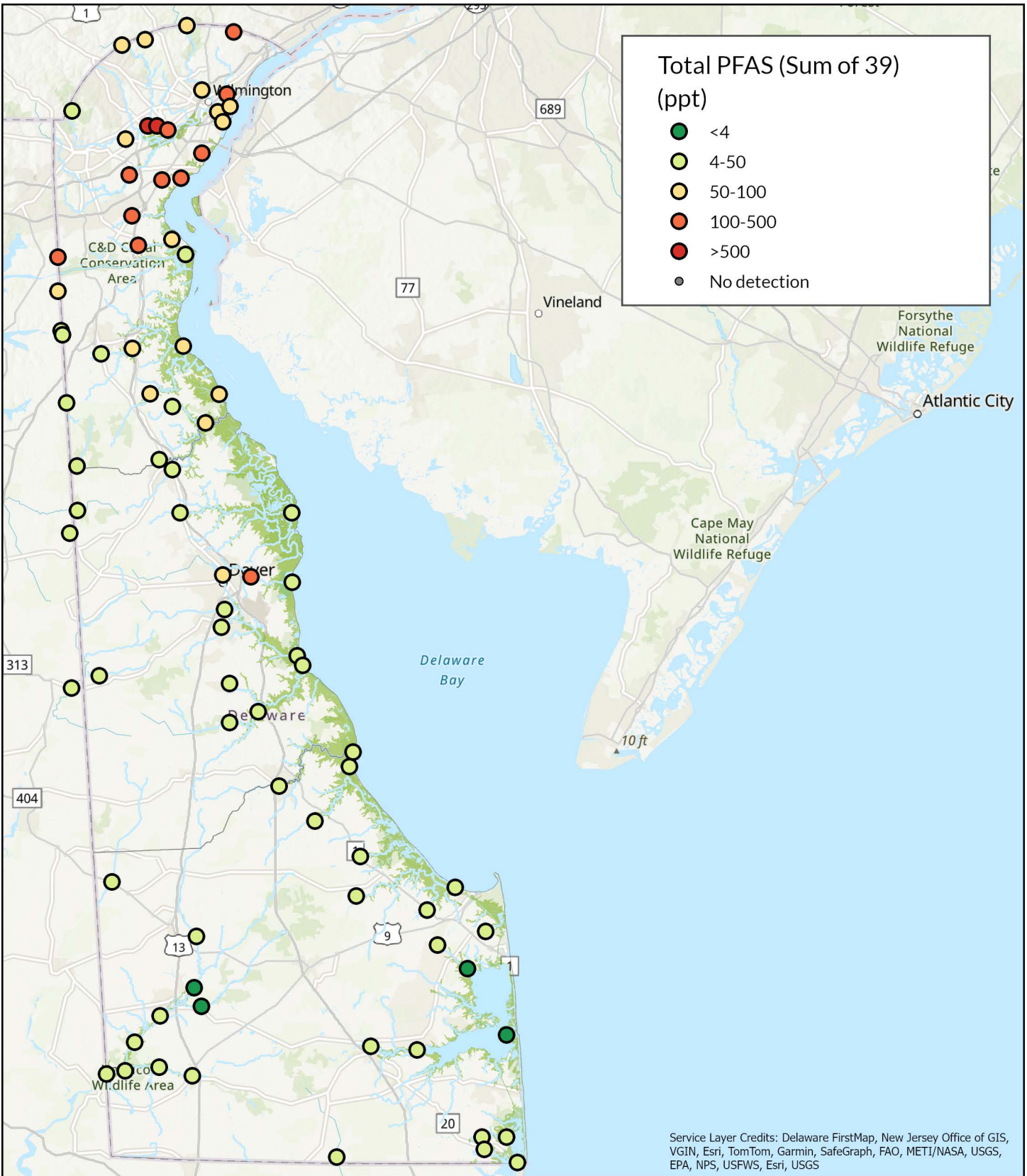
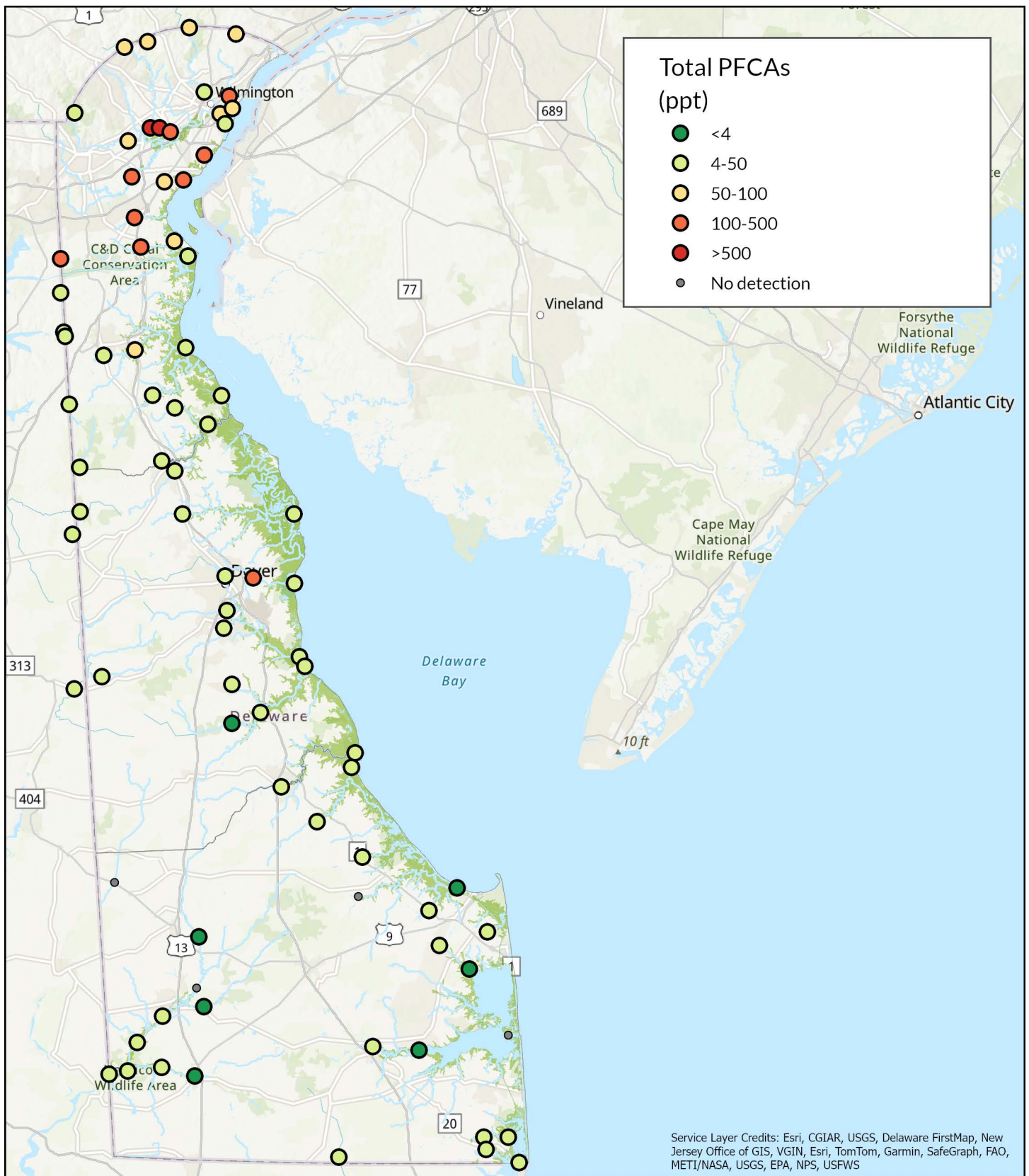


Figure 12:  
Total PFAS (Sum of 39) in  
Delaware Surface Water -  
Fall 2022

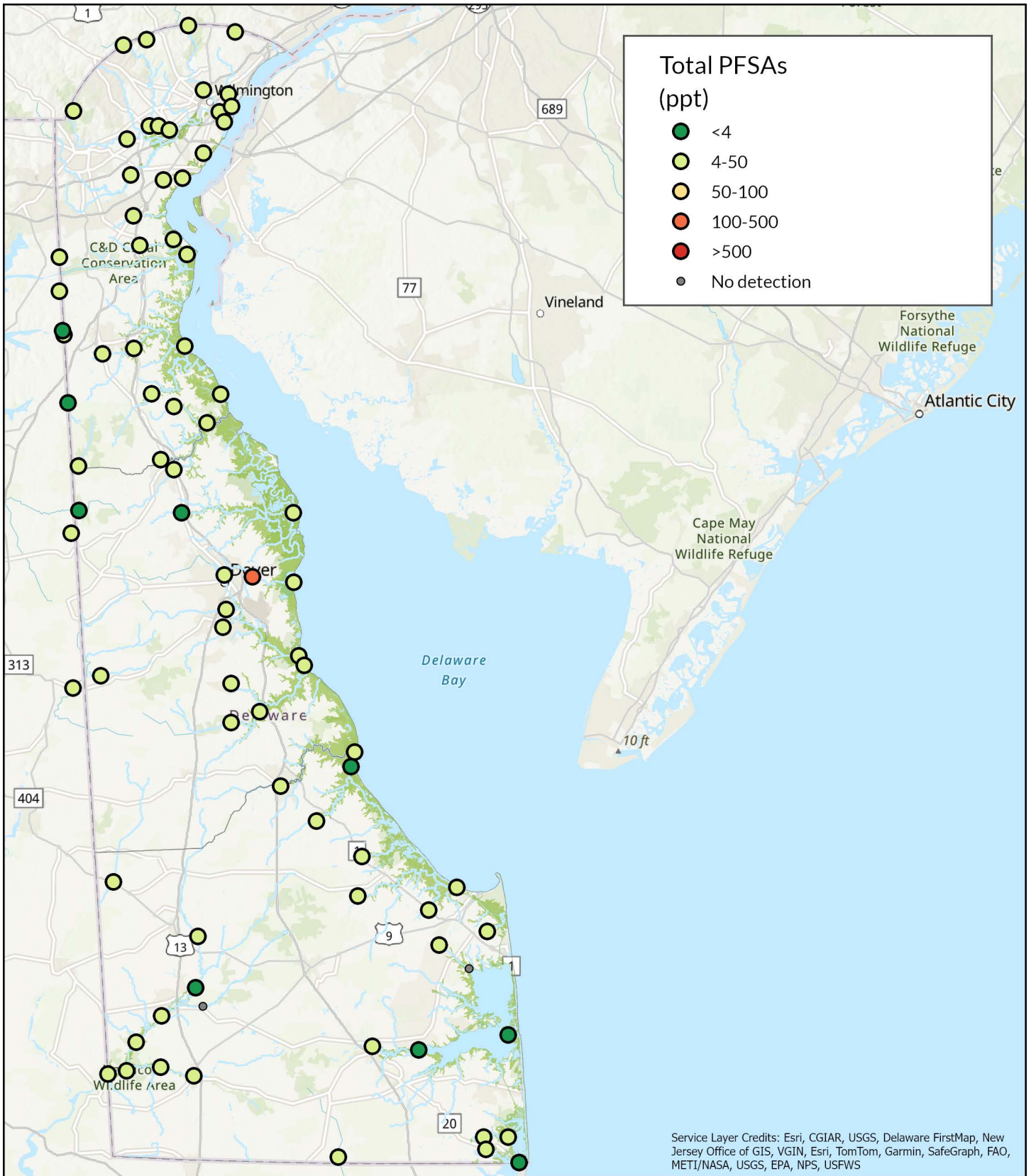


0 5 10 15 Miles

- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 13:  
Total PFCAs in Delaware  
Surface Water - Fall 2022

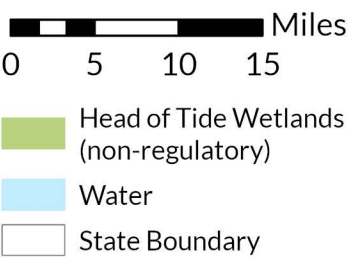
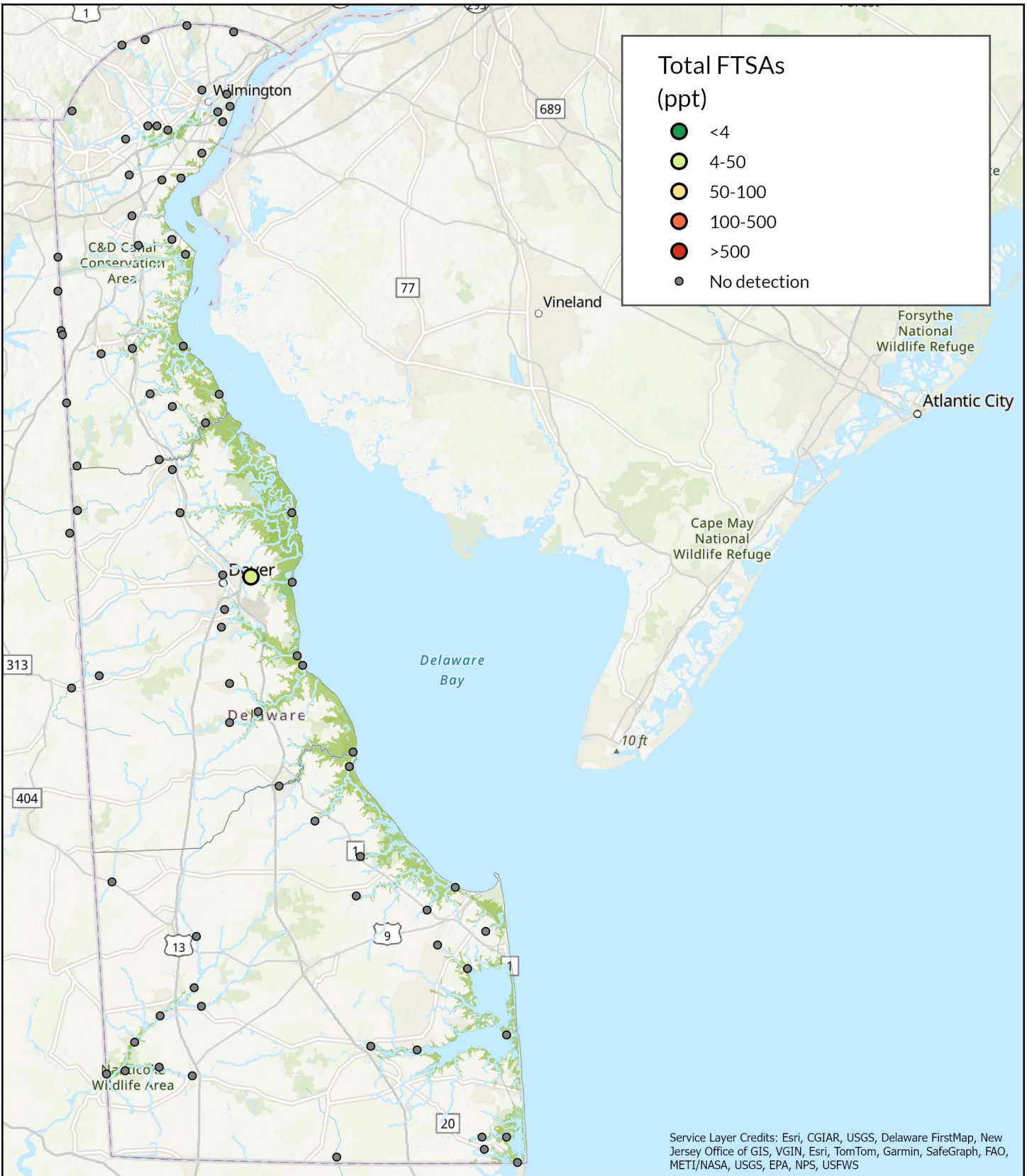


0 5 10 15 Miles

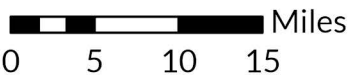
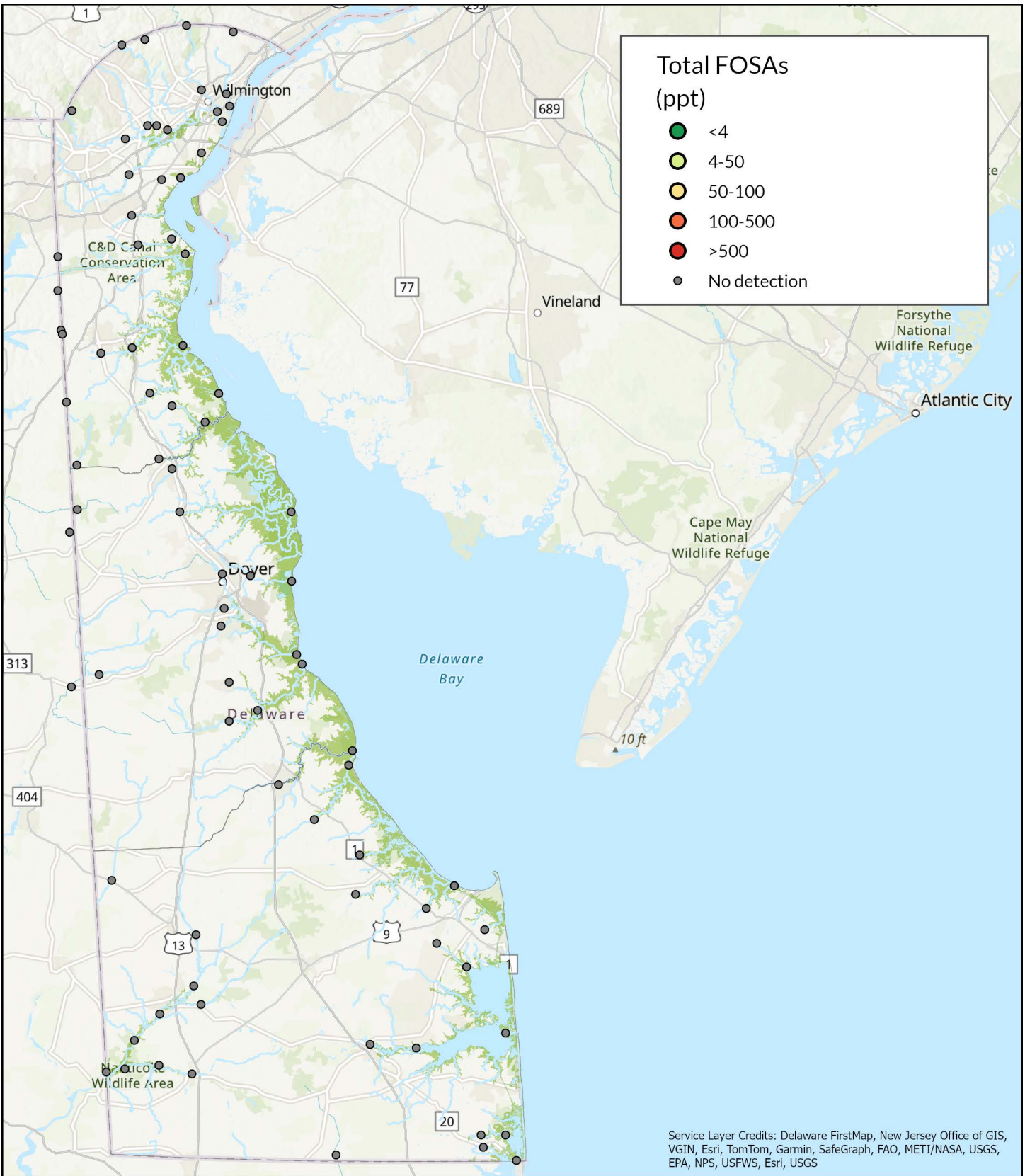
- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 14:  
Total PFSA in Delaware  
Surface Water - Fall 2022



**Figure 15:**  
**Total FTSAs in Delaware**  
**Surface Water - Fall 2022**



- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 16:  
Total FOSAs in Delaware  
Surface Water - Fall 2022



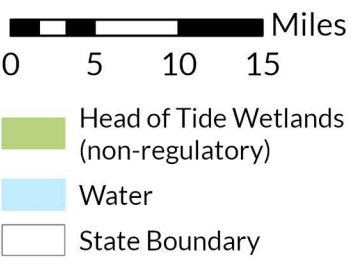
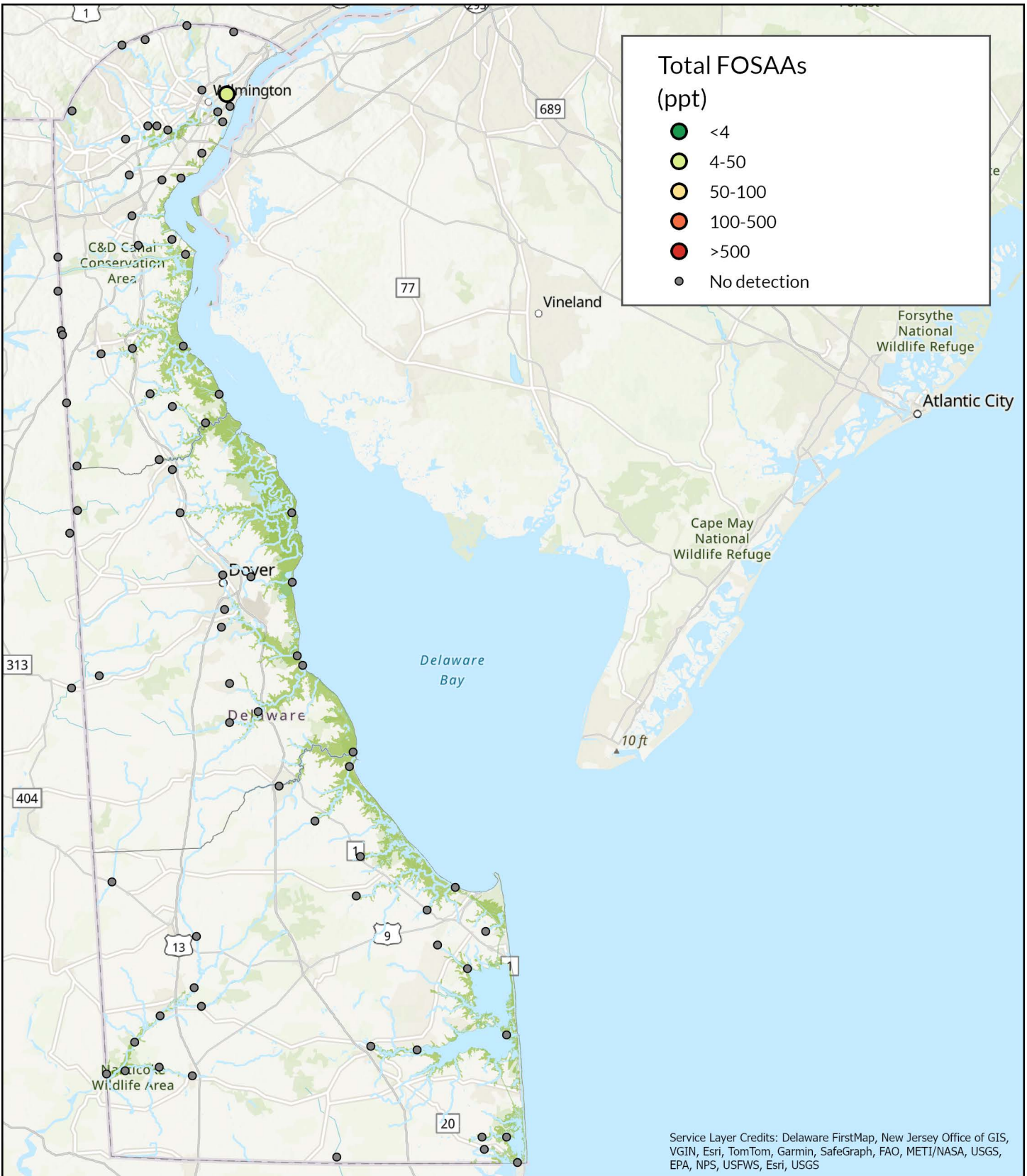
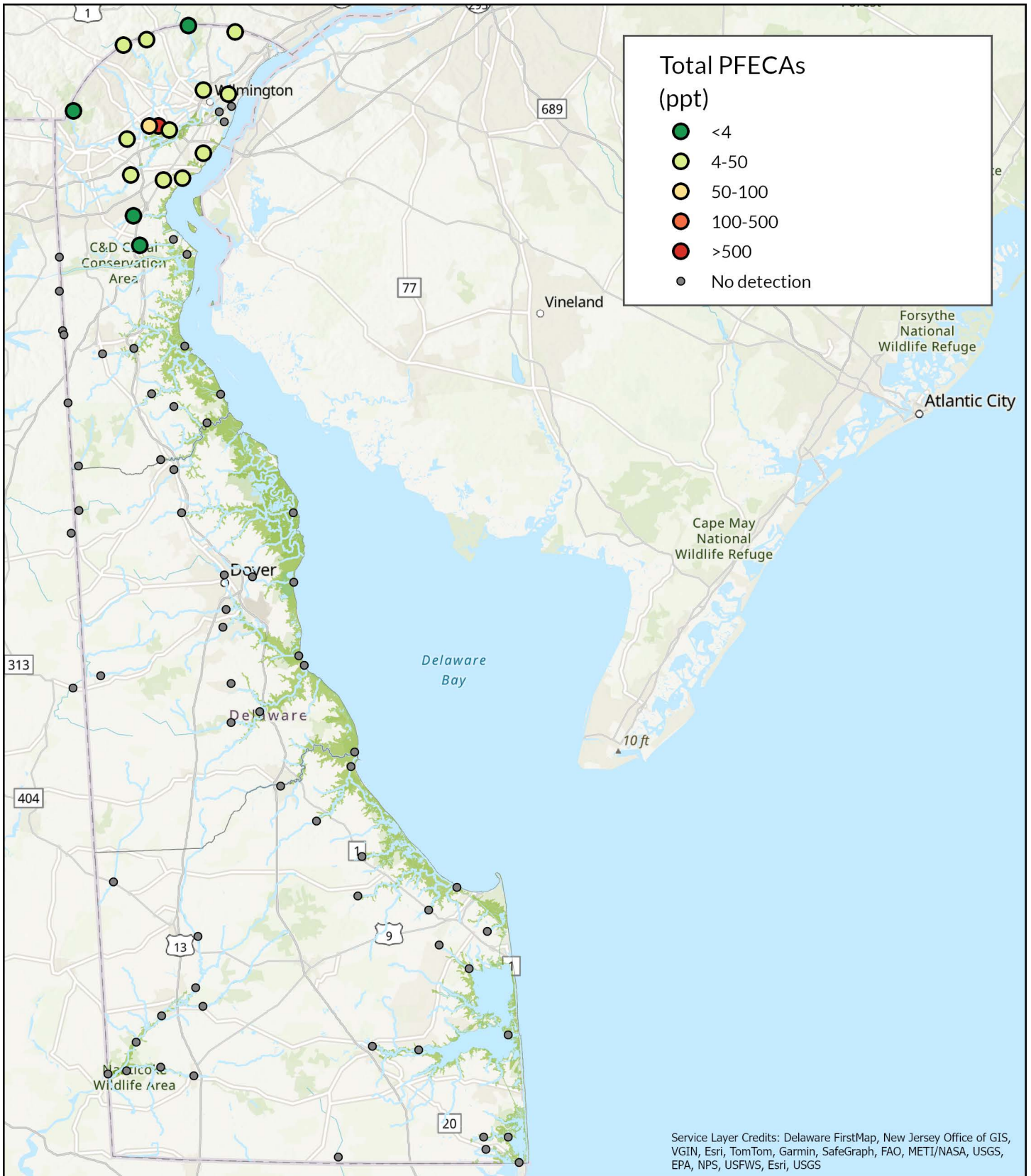


Figure 17:  
Total FOSAA in Delaware  
Surface Water - Fall 2022



**Total PFECAs (ppt)**

- <4
- 4-50
- 50-100
- 100-500
- >500
- No detection

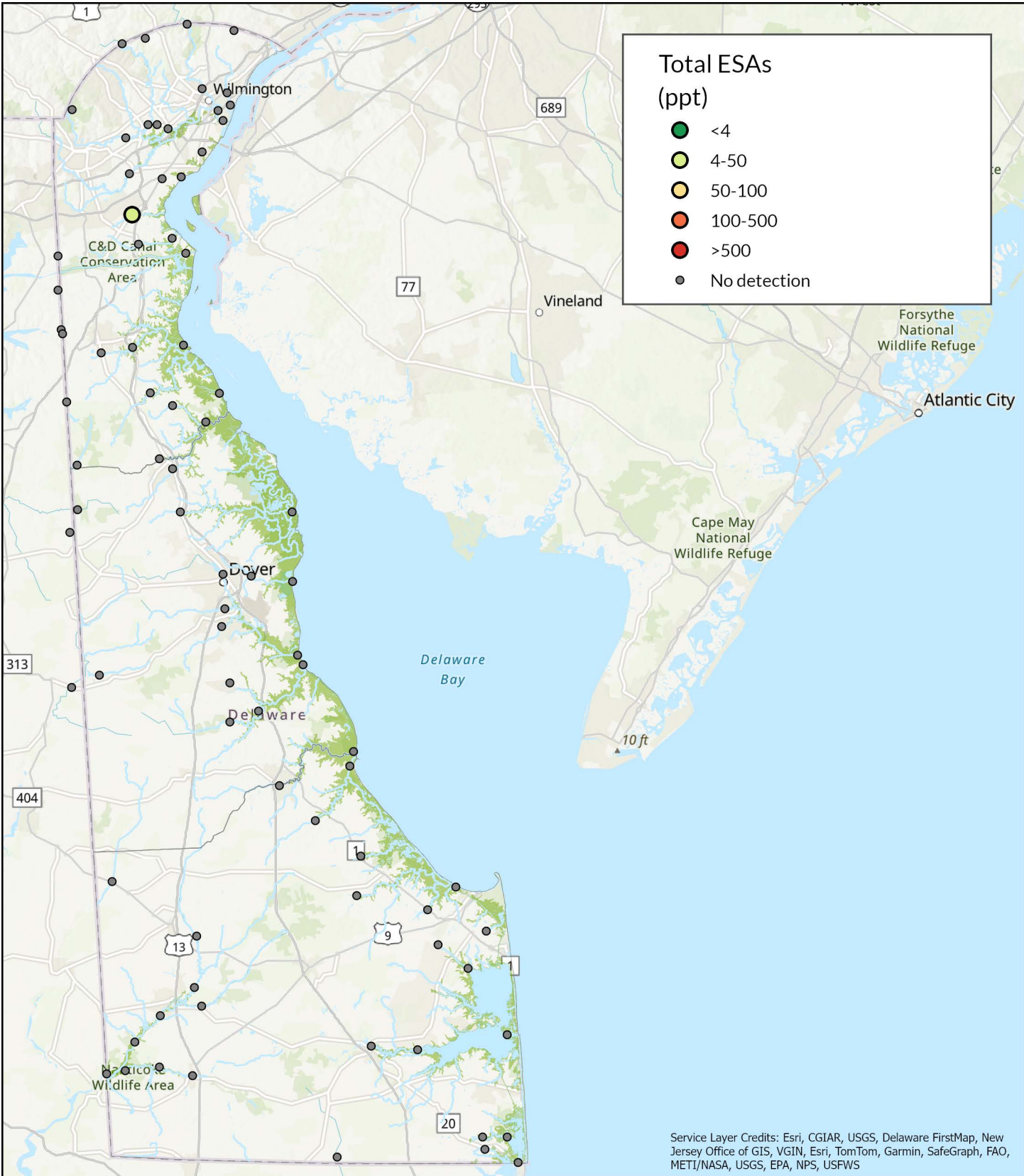
Service Layer Credits: Delaware FirstMap, New Jersey Office of GIS, VGIN, Esri, TomTom, Garmin, SafeGraph, FAO, METI/NASA, USGS, EPA, NPS, USFWS, Esri, USGS

0 5 10 15 Miles

- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



**Figure 18:**  
Total PFECAs in Delaware Surface Water - Fall 2022

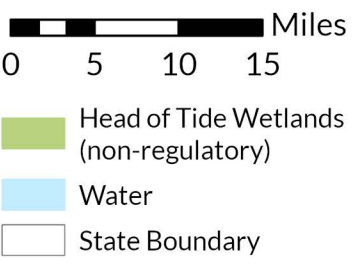
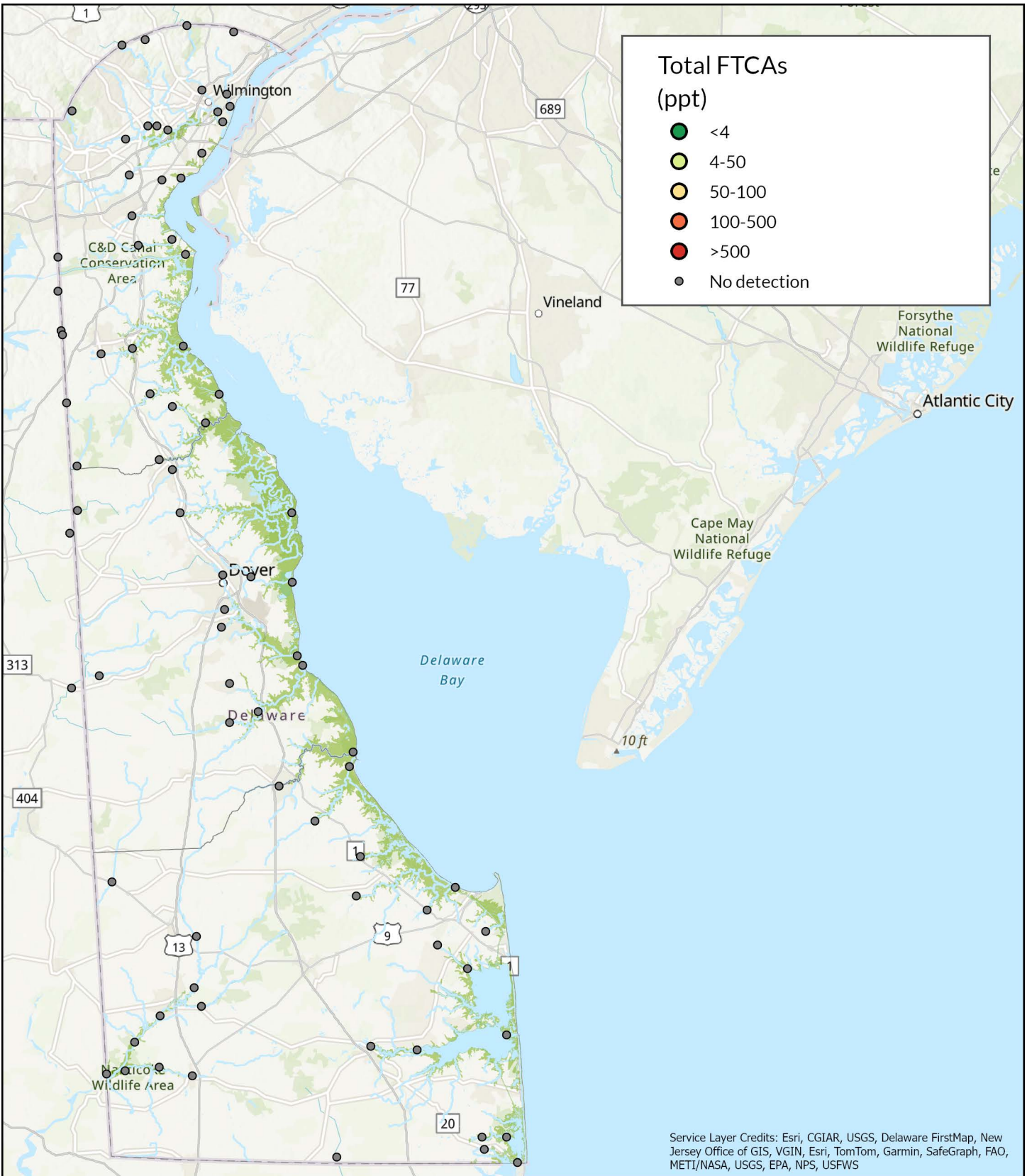


0 5 10 15 Miles

- Head of Tide Wetlands (non-regulatory)
- Water
- State Boundary



Figure 19:  
Total ESAs in Delaware  
Surface Water - Fall 2022



**Figure 20:**  
Total FTCAs in Delaware  
Surface Water - Fall 2022

# Appendix A

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## Appendix A

### PFAS Data Tables

Tables are available for download  
at the following link:  
[de.gov/pfas](https://de.gov/pfas)

# Appendix B

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## Appendix B

### PFAS Data Plots

Plots are available for download  
at the following link:  
[de.gov/pfas](https://de.gov/pfas)

# Appendix C

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## Appendix C

### Laboratory Analytical Report

The full laboratory analytical report and a Microsoft Excel data file are available for download at the following link:  
[de.gov/pfas](https://de.gov/pfas)

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Remediation Section,  
Environmental Laboratory Section,  
and  
Resource Protection Section





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