PART G: SPECIAL ASSESSMENTS

G.1 Conococheague Creek High pH Assessment

Introduction

Conococheague Creek segments (2016 Integrated Report of Surface Water Quality in Maryland Assessment Unit IDs: MD-02140504-Multiple_segments_1 and MD-02140504-Multiple_segments_2) were originally listed in Category 5 for high pH on the 2002 303(d) list, based on data from the 2001 305(b) report. The threshold used to determine impairment, as indicated in MD's IR, is defined as greater than 10% of measurements exceeding a pH of 8.5 during the most recent five year period. Data used for listing was from the DNR CORE/Trend program, which collected monthly pH data from the mainstem Conococheague Creek at two stations, CON0180 and CON0005. The impairment listing was refined in 2012 defining the impaired portion as only the portion downstream of CON0180, since newer data showed that this station was not impaired.

Then, in 2014, an intensive review of studies completed in the Conococheague Creek relating to pH was conducted in order to determine if the high pH was being caused by karst, a natural condition. The Conococheague Creek in Washington County, MD, is located in a region with prevalent karst (limestone) geology. Karst geology is formed by the slow dissolution of calcium and magnesium oxides in limestone, dolomite, or marble bedrock, which leads to increased alkalinity and ultimately pH (Sherwood 2004). Maryland's IR Assessment Methodology for pH stipulates that, "it is undesirable to incorrectly identify a water body as impaired when the observed condition is of a natural origin." Furthermore, it also states that, "certain conditions in close proximity to limestone springs may also have natural pH values outside of the standards." (MDE 2012). The 2014 review included Biological Stressor Identification, a synoptic pH monitoring survey, ion concentration analyses, and karst formation mapping. The conclusion of the review was that the observed high pH measurements were likely due to natural karst conditions.

Based on the intensive study of Conococheague Creek (Assessment Unit: MD-02140504-Multiple_segments_1), in the Draft 2018 IR that was released for public comment, MDE proposed that the local geological conditions (i.e. karst formations) caused the pH for this stream system to frequently go above the upper bound of Maryland's pH criteria (8.5). MDE intended to move this pH listing from Category 5 (impaired waters for which a TMDL is required) to Category 2 (waters attaining some standards) due to the impairment being caused by the natural geology of the area. However, upon further review and discussion with EPA, MDE decided that additional follow-up monitoring and assessment was needed to further evaluate if the high pH levels were caused by the natural geology of the area or another factor like nutrients. Therefore, MD-02140504- Multiple_segments_1 remained on Category 5 for high pH for the 2018 IR.

In response to the conversation with EPA, MDE developed a study in 2019-2020 to further investigate the cause of the high pH impairment in the Conococheague Creek Watershed. This report provides a brief summary of the 2014 review, details on the 2018 IR category change proposal, and new information on the 2019-2020 Conococheague Creek study investigating the high pH.

Summary of 2014 Intensive Review

Figure 1 shows the location of the Conococheague Creek watershed and the monitoring stations evaluated in the 2014 Intensive Review.

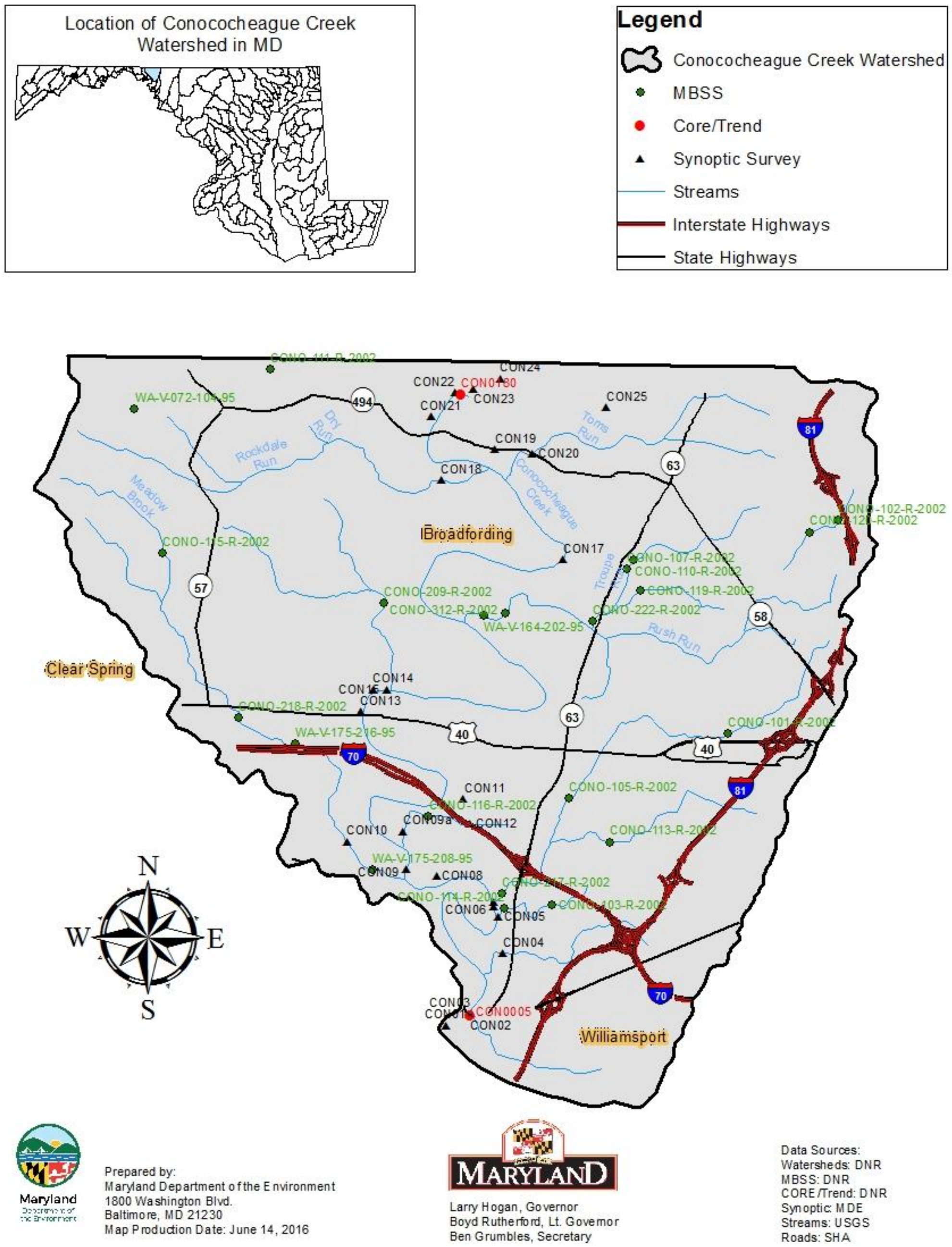

Figure 1: Location of Conococheague Creek Watershed, with pH Sampling Stations

The 2014 intensive review included evaluating the entirety of the CORE/Trend data (1986 – 2019) at both CON005 and CON080 to determine the presence of any seasonal or inter-annual trends as to when exceedances occurred. Over the 31 years, most exceedances occurred in the spring (March-April) and the fall (September – November), which suggested either a bi-modal exceedances pattern or no seasonal pattern at all. A Biological Stressor Identification (BSID) Analysis was also conducted for Conococheague Creek in 2013 since it was listed as impaired for impacts to biological communities in 2004. The BSID analysis did not identify high pH as a cause for biological impairment in the Conococheague Creek. The BSID analysis did identify sediment, nutrients, chlorides, and sulfates as causes of impairment (MDE 2013). A synoptic survey was also conducted given the differing results of the Integrated Report listing analysis and the BSID analysis. In addition, the karst geology of the area was evaluated through maps produced by US Geological Survey, Maryland Geological Survey, Natural Resources Conservation Service, and Western Maryland Resource Conservation & Development Council, Inc. The counties in Maryland most affected by karst are Washington, Carroll, Frederick, and Baltimore, with less extensive areas in Allegany County (Sherwood 2004). Alkalinity and ionic variance were also assessed through water quality samples in Conococheague Creek and the predominant cation was calcium and the predominant anion was bicarbonate, which indicated significant interaction with the limestone bedrock.

Finally, a spatial comparison was performed relating the results from the ion study to mapped karst geology (based on an ongoing survey by MGS) within the state. The analysis compared calcium, alkalinity, and pH, to the prevalence of karst geology in the catchment upstream of the study sites. The results showed a significant correlation between those catchments with greater than 50% karst to high calcium and alkalinity, and higher pH. There were five sites from the ion study in the Conococheague Creek. Of the five, one had no upstream karst, one had 56% karst upstream, and the other three had >85% karst upstream. Based on the information found during this 2014 review, it was determined that the occasionally high pH observations in the mainstem of Conococheague Creek were most likely due to natural conditions, and specifically the karst geology of the watershed. Therefore, it was recommended that the high pH listing for Conococheague Creek should be delisted and moved to Category 2 on the 2018 IR due to the karst geology being a natural condition of the watershed.

Draft 2018 IR

The draft 2018 IR was released for public comment on February 16, 2018 and included a Special Assessment section detailing the results of the 2014 intensive study of Conococheague Creek (Assessment Unit: MD-02140504-Multiple_segments_1) and proposed moving the listing from Category 5 to Category 2 due to local geological conditions (i.e. karst formations) that caused the pH for this stream system to frequently go above the upper bound of Maryland's pH criteria (8.5). EPA commented on the listing change during the 2018 public comment period.

EPA's comment on the 2018 IR: "G.1: The non-tidal Conococheague Creek is listed as impaired for total phosphorus and pH as well as other parameters. MDE proposes to move the pH listing for Conococheague Creek from Category 5 to Category 2 due to the impairment being caused by the natural geology of the area. In addition to geology, other water quality factors can influence pH. For instance, seasonal patterns of high pH during spring and fall may arise from high levels of photosynthesis, which in some cases, is a result of excessive nutrients. MDE's pH assessment method states "Another natural condition which should not be used to identify a water body as pH impaired is an abundance of algae or aquatic plans that elevate pH levels about 8.5 as a result of photosynthetic-drive chemical reaction, unless the condition is being caused by a defined nutrient enrichment source." The BSID analysis identified nutrients as a stressor impacting aquatic life in the Conococheague Creek watershed. To the extent the pH levels may be associated with the identified nutrient enrichment, it may be useful for MDE to explain this link as an additional causative factor, particularly as the phosphorus impairment remains in Category 5. It also may be useful for MDE to compare observed pH and alkalinity values in a biologically unimpaired, reference watershed with 75 to 100 percent karst coverage with observed pH and alkalinity values in the Conococheague Creek."

After further review and discussion with EPA, MDE agreed that additional follow-up monitoring and assessment was needed to further evaluate if the high pH levels were caused by the natural geology of the area or another factor like nutrients. MDE decided to conduct a follow up monitoring study in the Conococheague Creek watershed and kept the MD-02140504- Multiple_segments_1 assessment on Category 5 for high pH for the 2018 IR.

2019-2020 Conococheague Monitoring Project

Based on EPA's comment on the 2018 Draft IR, it was agreed to create a joint (EPA/MDE) monitoring project to determine if the reason for high pH readings in the Conococheague Creek Watershed were more likely geological or eutrophication-related. The project team included members from both EPA and MDE and the project team determined that the project should include a water quality study collecting diel pH and nutrient values in the Conococheague Creek and surrounding watersheds, comparisons of the water quality study data with other literature values for evaluating impacts from nutrients, consultations with local geology experts to determine what is unique about the geology and surface water interaction in the Conococheague, a semi-quantitative or qualitative algae survey in the Conococheague Creek Watershed to determine whether algae are present and persistent in the watershed, and research and documentation on the presence of quarries or other significant concentrated sources of alkalinity to the Conococheague Creek Watershed.

Water Quality Study

The main effort of the project was to conduct a water quality monitoring study to collect diel pH data at sites in the Conococheague Creek and surrounding watersheds to determine pH flux and evaluate the impact from nutrients. Ten stations were chosen within the Conococheague Creek, Antietam Creek, and Little Conococheague Creek Watersheds (figure 2) and monitoring began in January 2019. Monitoring was conducted by the MDE Annapolis Field Office. Little Conococheague Creek and Antietam Creek were chosen because of their proximity and similar karst geology/agricultural land use to that of Conococheague Creek. The team was especially interested in learning why the pH in the Conococheague was so much higher than the other two similar watersheds.

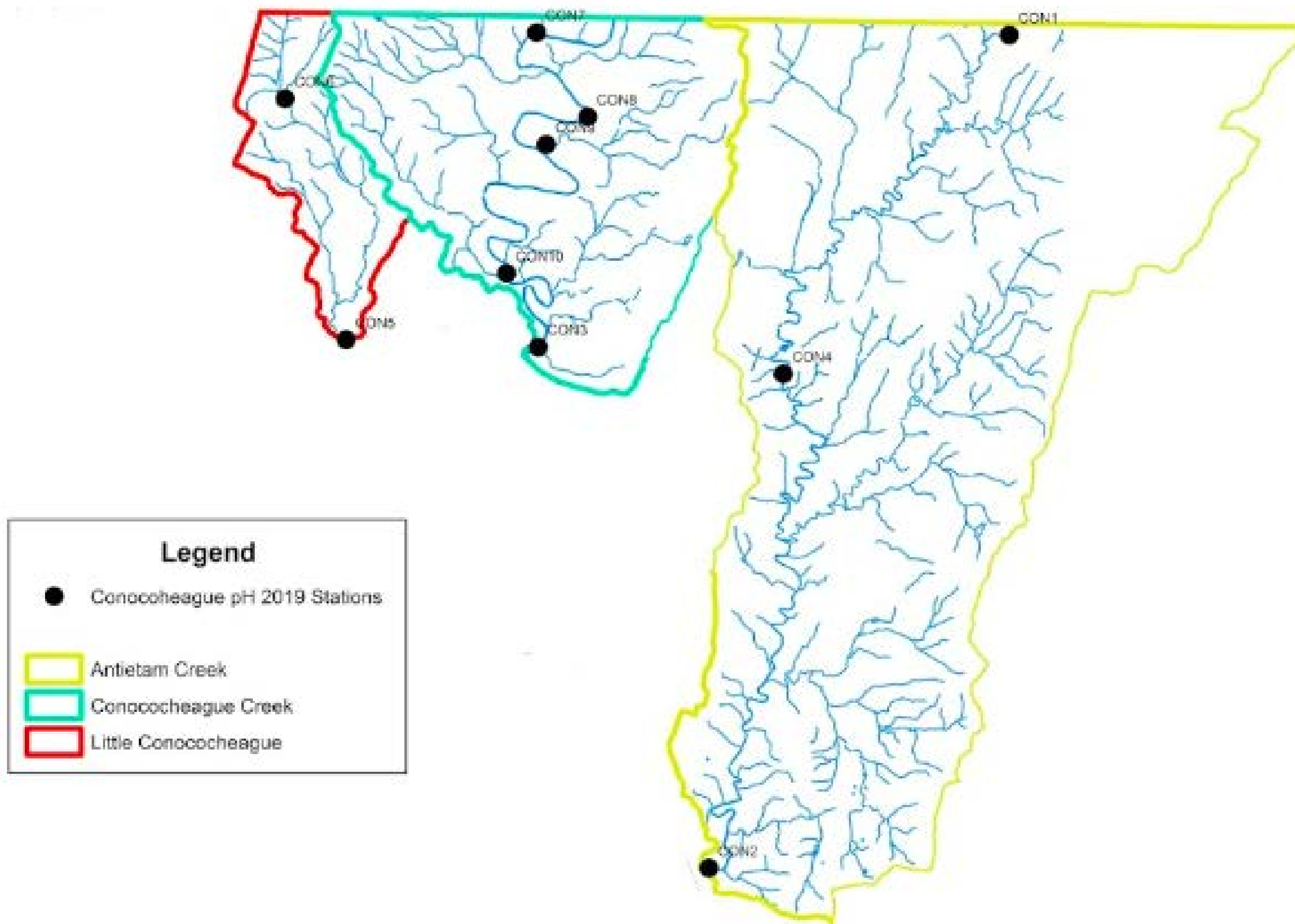

Figure 2: 2019-2020 Monitoring stations

pH Loggers were deployed in January 2019 and set to record pH and temperature every hour. The dates that each logger was deployed are as follows:

- CON1: January 2019 – January 2020
- CON2: January 2019 – January 2020
- CON3: January 2019 – April 2020
- CON4: January 2019 – November 2020
- CON5: January 2019 – January 2020
- CON6: January 2019 – November 2020
- CON7: January 2019 – January 2020
- CON8: January 2019 – January 2020
- CON9: January 2019 – January 2020
- CON10: January 2019 – April 2020

Nutrient samples were also collected monthly at stations CON1 – CON10 from March through November of 2019 for a total of 8 samples per station. Samples were analyzed for total ammonium, nitrate + nitrite, phosphate, total nitrogen and phosphorus, chlorophyll-a (spectrophotometric), phaeophytin (spectrophotometric), alkalinity, and hardness. In addition, a water quality sonde was rotated between 4 sites during the summer months to collect dissolved oxygen. Each sonde was deployed for a full week at CON3, CON8, CON9, and CON10.

In November 2019, 10 months of data was analyzed and CON3 (DNR CORE/Trend station CON005) and CON10 were the only two stations with pH exceedances greater than 10% of the time. Based on this analysis, monitoring stations were changed to more closely focus efforts near CON10 and CON3. CON4 in Antietam Creek and CON6 in Little Conococheague were both dropped since they didn't have any exceedances. Two new stations, CON11 and CON12, were added in the Conococheague Creek, one downstream of CON3 and one in between CON3 and CON10 (Figure 3). pH data was collected at these stations between November 2019 and April 2020.

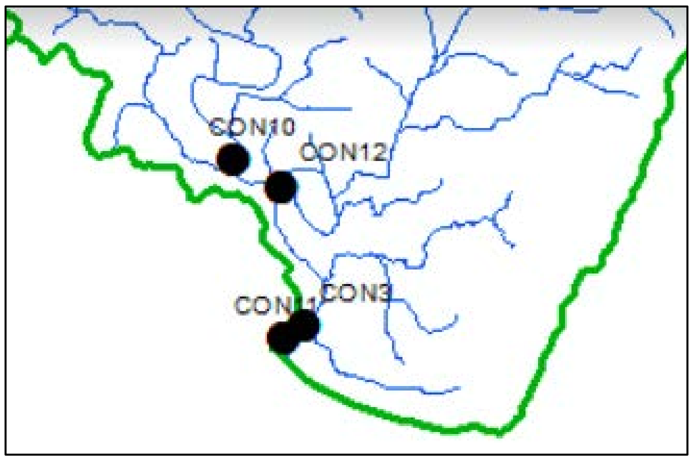

Figure 3: Additional 2019-2020 Monitoring stations

Geological Research

MDE consulted with a geochemist, Chris Gammons, in Montana that has many published studies on pH in streams. He maintained that a karst stream that is in equilibrium with calcium carbonate would have a "resting" pH of about 8.3. In addition, if the stream is even moderately productive, with low turbidity the stream could have a pH swing of one unit. In karst streams the diel pH would range from 7.8 to 8.8, which is a similar range to what was observed in the Conococheague pH logger data.

Additionally, several abiotic factors can limit the pH swing and cause the instream pH to only exceed 8.5 pH criteria for a relatively short period of time. For example, higher flow and gradient areas in streams will have more rapids and riffles. This will reduce the pH swing because the dissolved CO_2 and oxygen would equilibrate with the air more rapidly. Lower flow streams are expected to have large pH swings. Turbidity is also a factor and clearer areas of streams are expected to have larger pH swings because the macrophytes have a greater access to sunlight and therefore can absorb more CO_2 during the day. More turbid streams will have smaller pH swings.

Furthermore, bicarbonate data from the Maryland Biological Stream Survey strongly suggests that the Conococheague mainstem is saturated in calcium carbonate, and this is pushing the pH to around 8.1 to 8.3. The time series data seems to show that photosynthesis was pushing the pH over the 8.5 criteria exactly at the expected time.

Additional geological information was provided by the MDE Field Office. Based on GIS analysis, there is a large amount of crop agriculture with very little tree buffer in the Conococheague Creek Watershed. While it seems that the karst geology is a large factor in the pH exceedances, there is also a nutrient factor, due to the amount of agricultural land. The nutrients increase algae production which in turn pushes a higher pH in an already elevated system. Additionally, the entire creek is a slow run with very little riffle/rapid areas that could counteract the other factors driving the high pH. There is also a dam below station CON10 that causes the river to be very wide and slow moving above station CON10 and may be a contributing source to the pH exceedances around CON10.

Algae Research

MDE field office staff did not observe a significant amount of algae at any of the water quality monitoring stations. Therefore, a standardized algae survey was not completed. The field office staff took qualitative notes on any algae present when they calibrated the logger sensors or collected samples. Chlorophyll-a and periphyton were also analyzed with the nutrient samples.

Concentrated Sources of Alkalinity

MDE staff also researched the presence of quarries and permitted point sources that might contribute to the high pH impairment in the Conococheague Creek Watershed. The MDE Water Permits Interactive Search Portal and ICIS were used to identify locations and possible pH data. There is one quarry near monitoring station CON8 and two WWTPs located near CON1 (Waynesboro WWTP) and CON4 (Funkstown WWTP). Funkstown WWTP had two pH exceedances, one in 1996 and one in 2004. No other point source pH exceedances were found.

Water Quality Data Analysis

Due to resource constraints at MDE, EPA offered assistance with a more robust analysis of the monitoring data through their Wheeling, WV office, led by Leah Ettema and Greg Pond. Their analysis focused on the diel fluctuations in pH to determine if nutrients were a driving force. The team provided a comprehensive analysis of the nutrients, DO, and other parameters collected in a station by station format. Based on their analysis, the Wheeling EPA office concluded that the elevated pH in the Conococheague is primarily due to nutrients. The highest pH levels of all the monitored sites are in the Conococheague Creek mainstem sites (see Table 1 and Figure 4). EPA agreed that the Karst geography does create naturally high levels of pH, so that there is low assimilative capacity. However, alkalinity and hardness are not higher in the Conococheague Creek compared to Antietam Creek. The site with the highest alkalinity and hardness was a tributary to Conococheague Creek mainstem (CON9), and it had lower pH than the Conococheague mainstem (see Figure 5). They also determined that chlorophyll a and phaeophyton are elevated in the Conococheague Creek Watershed; the increased primary production and decomposition amplify pH (and DO) diel fluxes and maximum values (See figure 6). In addition, there is a dam just below CON10. The dam coupled with high nutrient inputs are likely causing the highest levels of primary production on Conococheague (and therefore highest pH and pH daily flux values) to occur directly upstream of the dam at CON10. However, other sites on the Conococheague mainstem exhibit similar pH fluxes, indicating that the issue is not isolated to the area upstream of the dam, just amplified at CON10 (See figure 7, 8, and 9). Finally, all Conococheague Creek sites with DO monitoring had DO saturation levels above the BSID threshold of 115%, resulting from increased primary productivity and decomposition from elevated nutrient levels (See Figure 10). DO saturation was greater than 180% at CON10.

Table 1: Site Summary of pH Metrics

Site	Watershed	n	Max pH	Max pHFlux	% of all pH points >8.5	CDF percentile at 8.5 pH	% of days with pH values >8.5
CON-10	Conococheague Creek	9141	9.05	1.15	14.9%	84.3	44%
CON-3	Conococheague Creek	8619	8.85	0.9	10.2%	89.3	23%
CON-8	Conococheague Creek	8493	8.95	0.89	8.3%	91.4	25%
CON-12	Conococheague Creek	2169	8.77	0.9	7.4%	92.3	17%
CON-11	Conococheague Creek	2563	8.73	1.31	7.3%	92	19%
CON-7	Conococheague Creek	8726	8.93	0.91	5.6%	94.1	21%
CON-1	Antietam Creek	8031	8.9	0.99	2%	97.8	15%
CON-9	Rush Run	8276	8.72	0.67	1.9%	97.8	7%
CON-5	Little Conococheague Creek	8622	8.73	0.95	0.2%	99.8	1%
CON-2	Antietam Creek	8837	8.58	0.82	0.1%	99.8	1%
CON-4	Antietam Creek	7383	8.26	0.51	0%	100	0
CON-6	Little Conococheague Creek	7303	7.67	0.7	0%	100	0

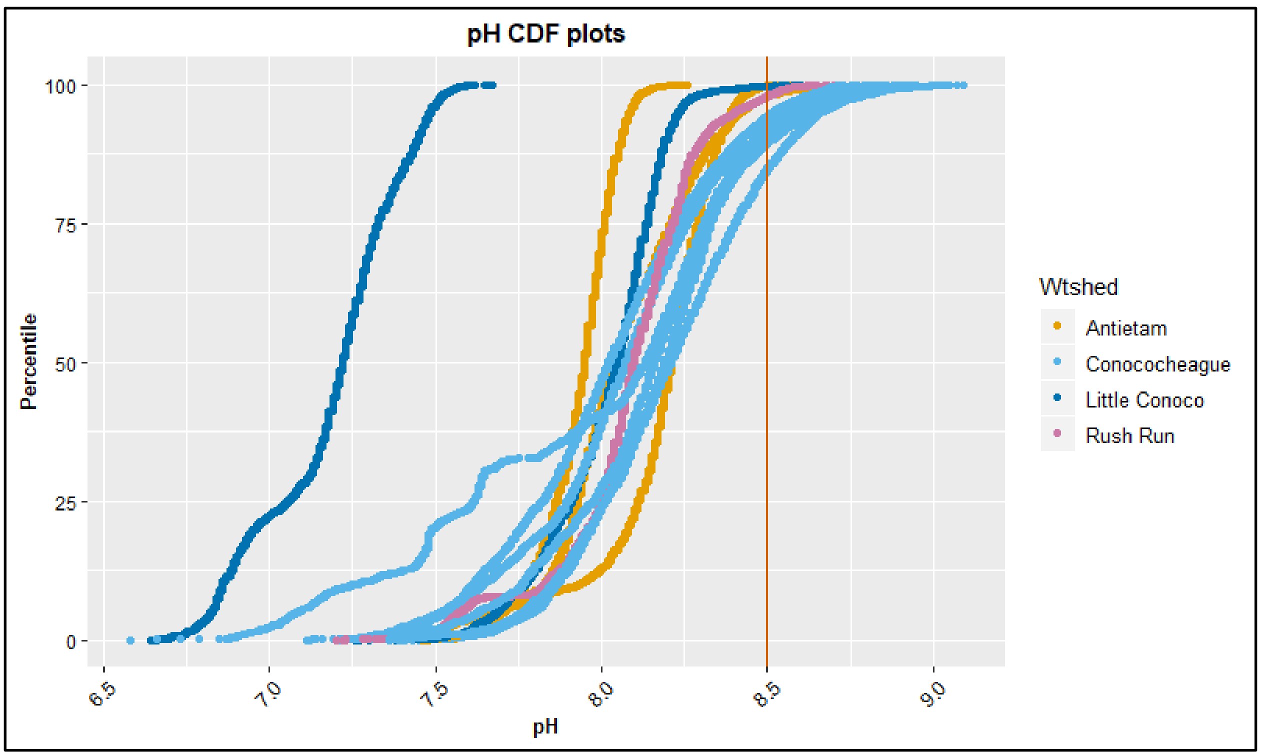

Figure 4: Cumulative Distribution Function plot of pH data

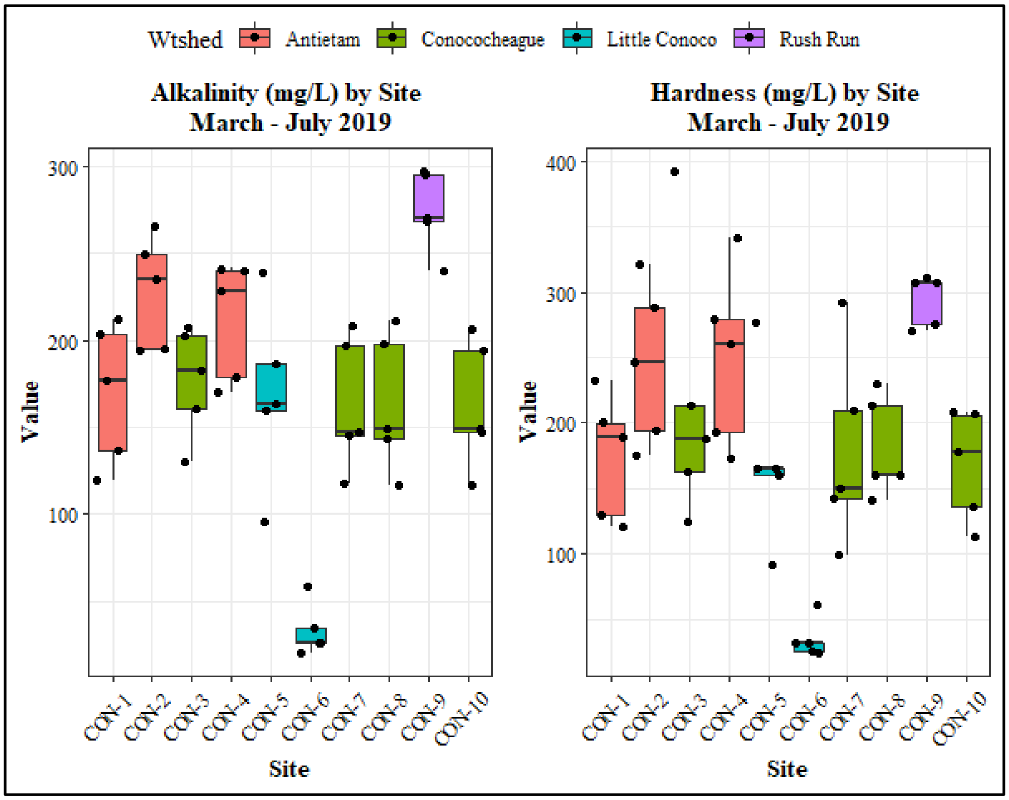

Figure 5: Hardness and Alkalinity Box Plots

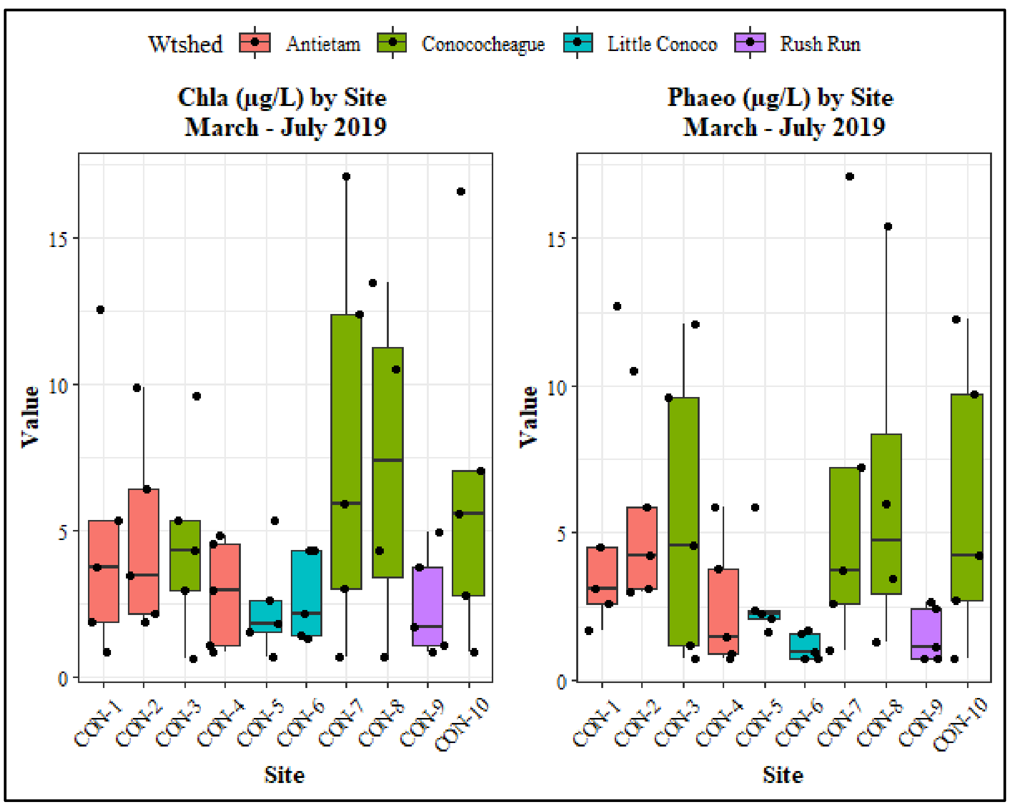

Figure 6: Chlorophyll a and Phaeophyton Box Plots

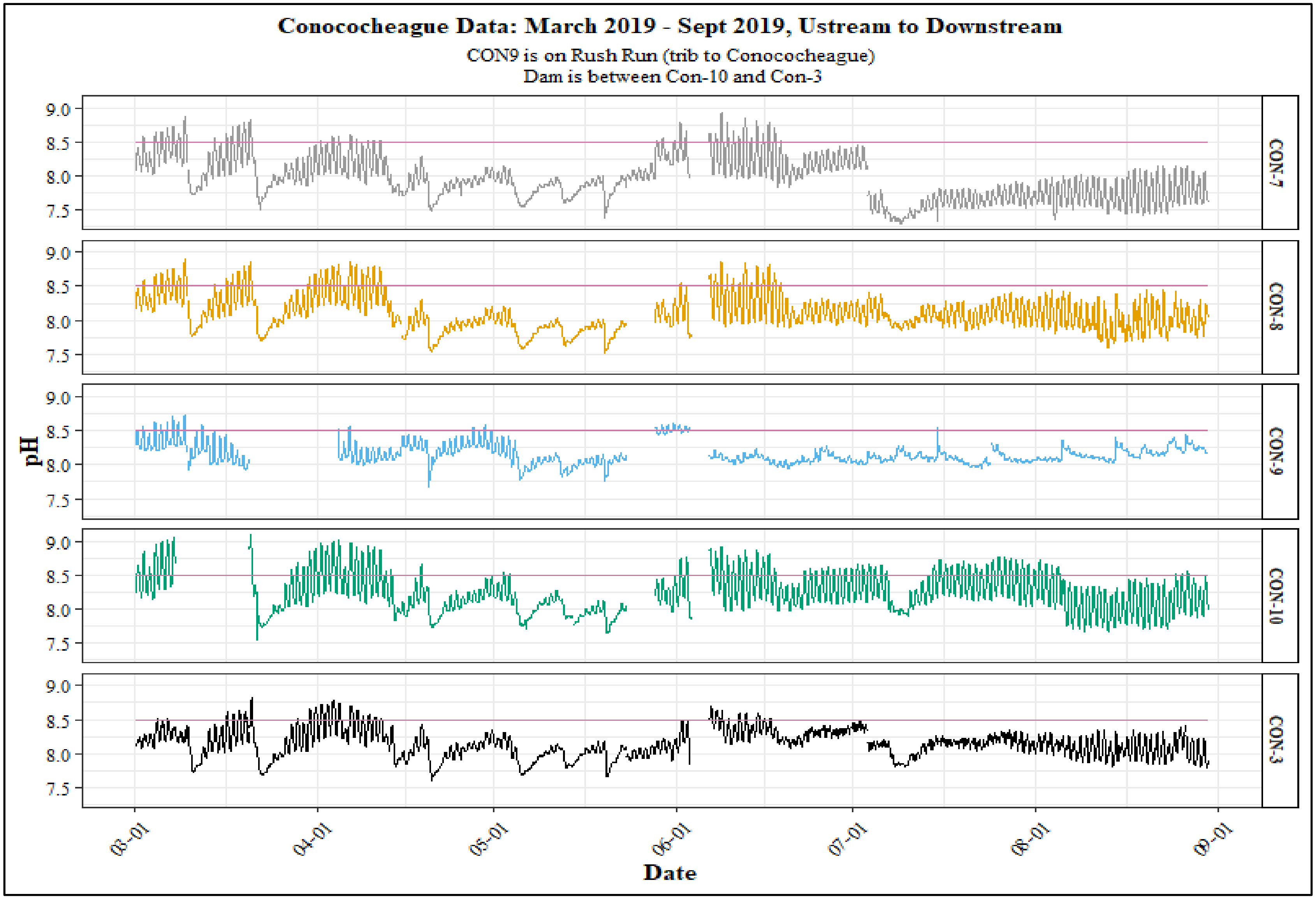

Figure 7: Summer Conococheague Creek pH Data

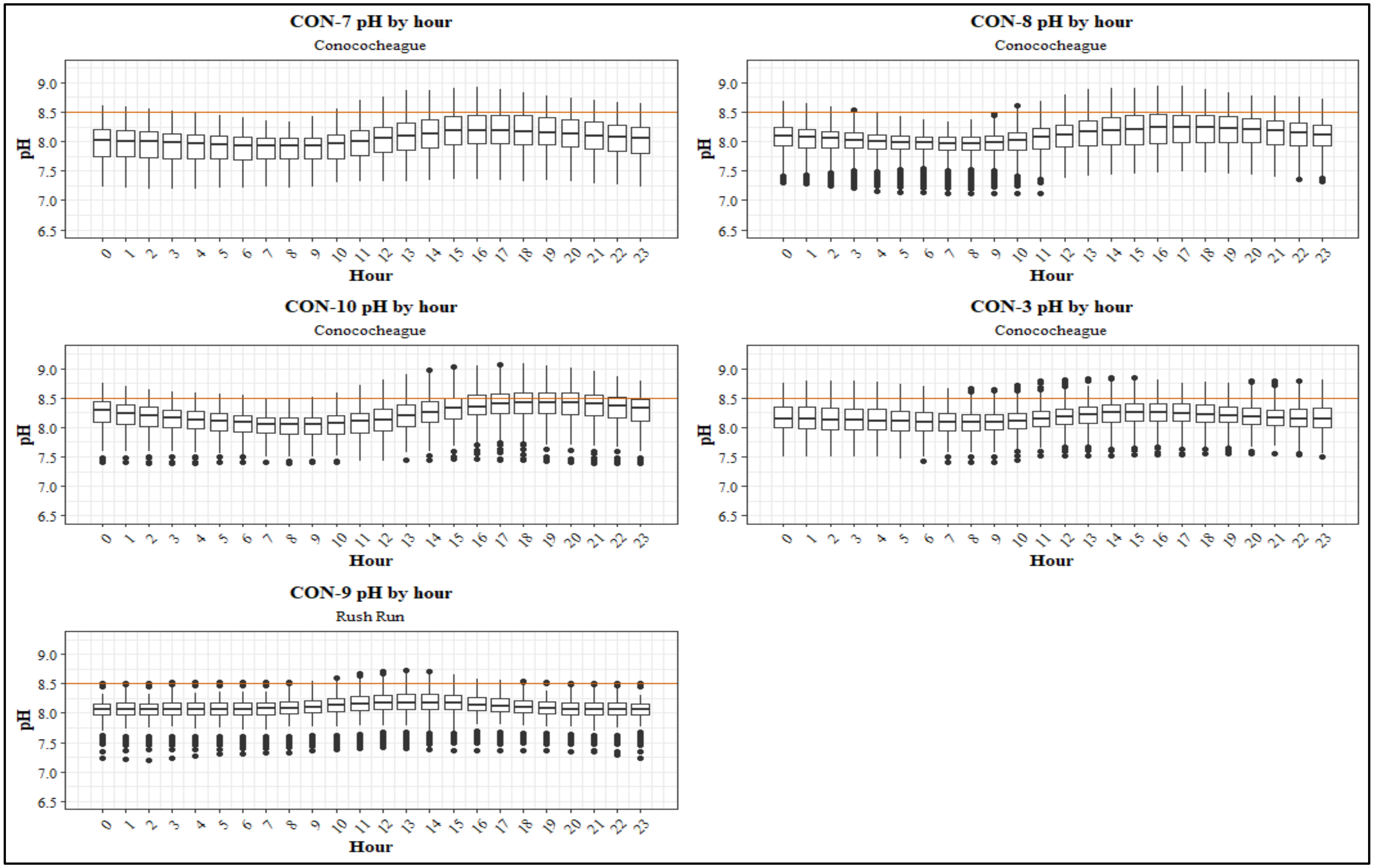

Figure 8: Conococheague Creek pH Data by Hour

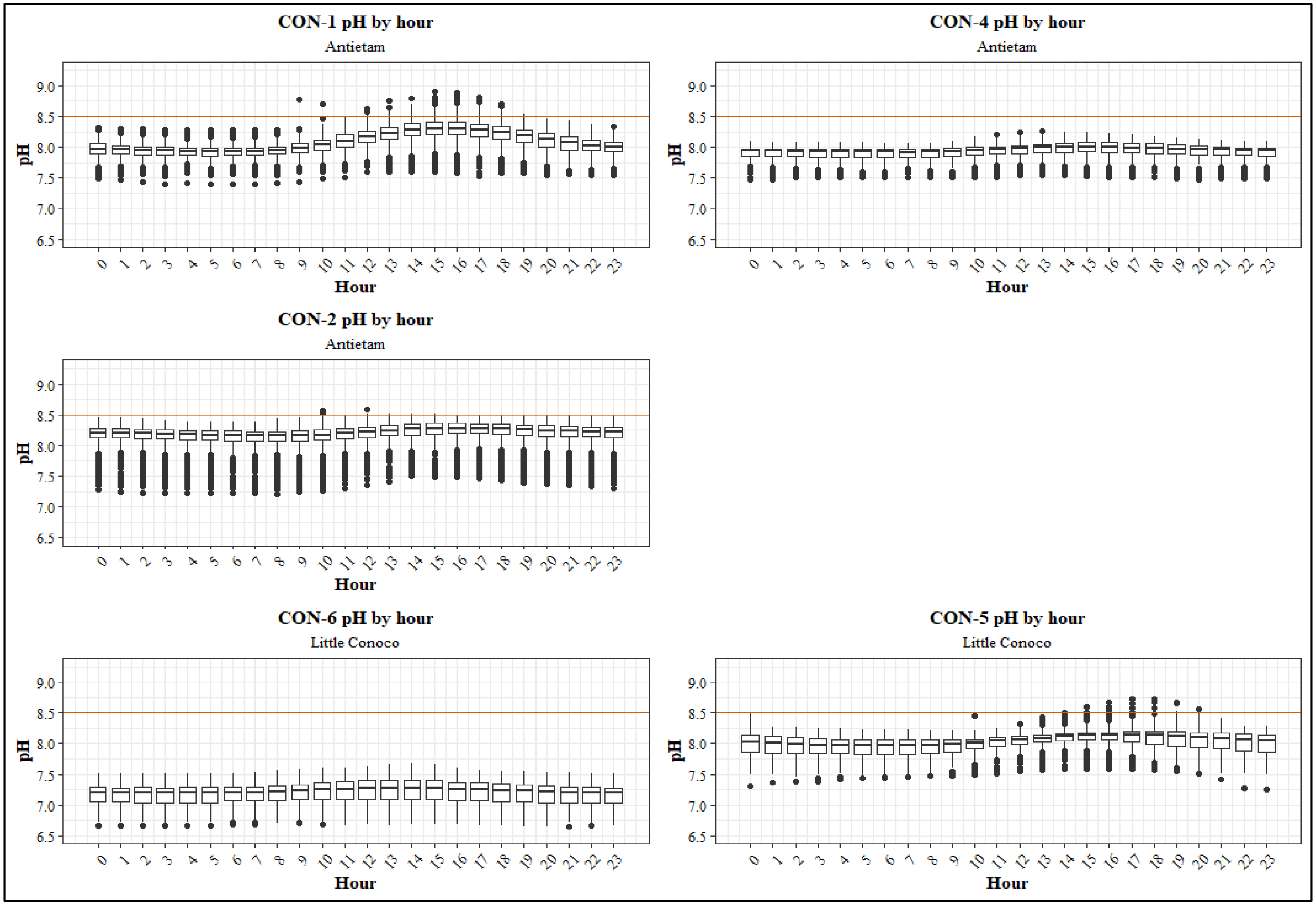

Figure 9: Antietam Creek and Little Conococheague pH Data by Hour

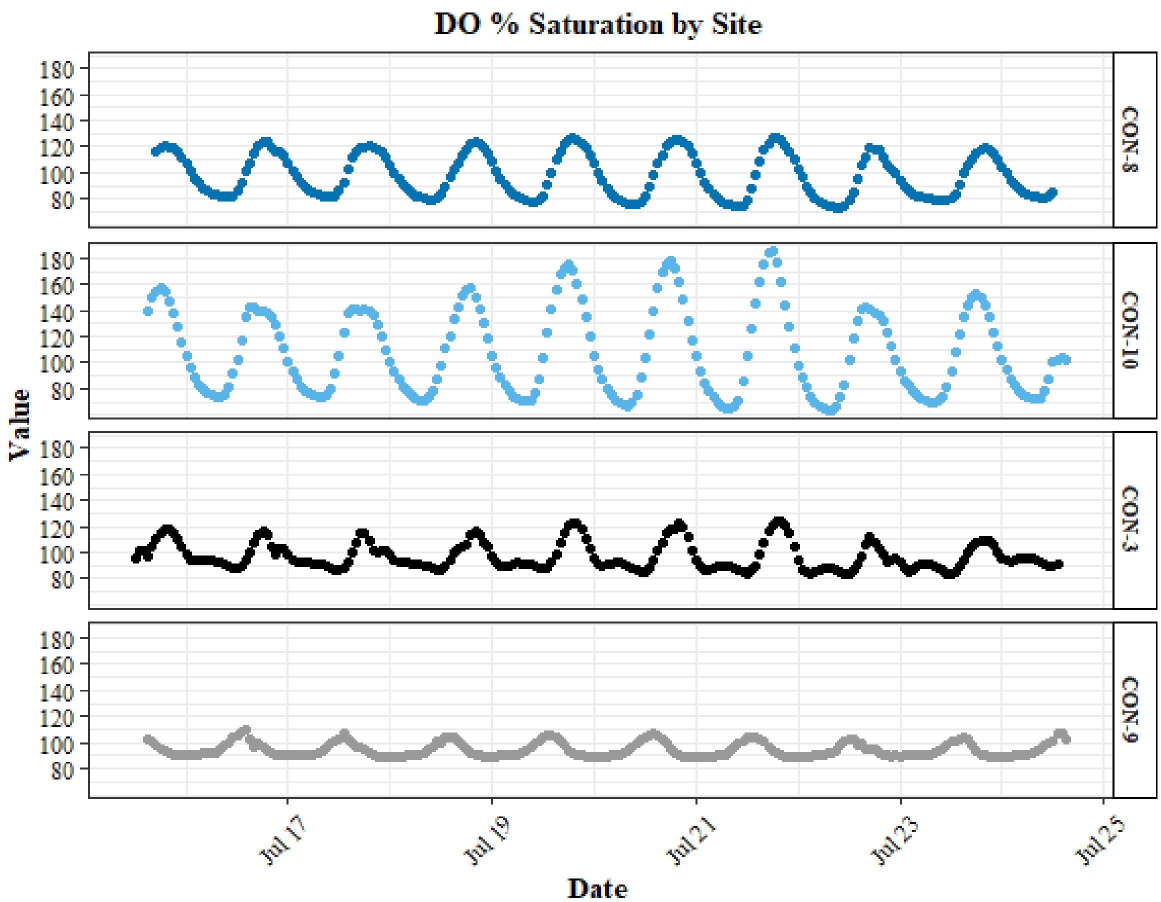

Figure 10: DO Percent (%) Saturation per Site

Water Quality Monitoring Conclusion

EPA and MDE discussed the results provided by the Wheeling team, with a focus on the geographic extent of the high pH problem in the Conococheague Creek Watershed since the main exceedances were shown around CON10. Based on the analysis, the pH exceedances were concentrated at CON10 because of the dam below the station that causes the river to be very wide and slow moving. However, the daily pH fluxes that occurred throughout the Conococheague Creek Watershed indicate that the nutrient input and pH increases were not isolated to the area around CON10 and existed throughout the entire watershed.

In summary, MDE and EPA agree that the high pH in the Conococheague Watershed is due to a combination of the Karst geography, the high nutrient input, and the dam around CON10. Since the entire 8-digit watershed MD-02140504 was already listed for Phosphorus, and the nutrients and pH are linked, along with karst and the dam, the entire MD-02140504 Conococheague Creek watershed should remain on Category 5 for phosphorus and also be placed on Category 5 for pH. When the TMDL is completed for phosphorus, it will also include the high pH listing for the same 8-digit watershed and both can be moved to Category 4a together.

2020-2022 IR Listing

Because the entire Conococheague Creek Watershed has new data showing daily pH fluxes in all sites, and the entire watershed is already listed for phosphorus, MDE proposes combining MD-01240504_Multiple_segments_1 and MD-02140504_Multiple_segments_2 as MD-02140504 and placing it in Category 5 for high pH for the combined 2020-2022 IR. The data also shows that the high pH is linked to the high nutrients and both Category 5 listings for the Conococheague Creek Watershed, for phosphorus and high pH, will be incorporated together when a TMDL is completed for phosphorus. The changes between the 2018 listing and the proposed 2020-2022 listings are shown in Tables 2 and 3 below.

Table 2: Summary of 2018 IR Listing

Assessment Unit	Size	Units	Listing Category	Cause	Indicator	Cause Grouping
MD-02140504	132.17	Miles	5	Phosphorus, Total	Fish and Benthic IBIs	Nutrients
MD-02140504-Multiple_segments_1	127.46	Miles	5	pH, High	Direct Measurement	pH
MD-02140504-Multiple_segments_2	4.7	Miles	2	pH, High	Direct Measurement	pH

Table 3: Proposed 2020-2022 IR Listing

Assessment Unit	Size	Units	Listing Category	Cause	Indicator	Cause Grouping
MD-02140504	132.17	Miles	5	Phosphorus, Total	Fish and Benthic IBIs	Nutrients
MD-02140504	132.17	Miles	5	pH, High	Direct Measurement	pH

The note associated with the proposed 2020-2022 listing specifically says "MD-02140504-Multiple_segments_1 and MD-02140504-Multiple_segments_2 were merged in 2020. A 2020 study showed that the entire watershed is impaired for pH due to high nutrient input and natural karst geology. This listing will be incorporated into a future nutrient TMDL for phosphorus."

G.2 Piscataway Creek Elevated PFOS Listing

MDE's WSA recommends listing the Piscataway Creek (tidal and non-tidal waters) as impaired in Maryland's Combined 2020-2022 Integrated Report of Surface Water Quality for elevated levels of PFOS in fish tissue. This memo describes the rationale for the proposed listing.

Background

PFAS are a family of thousands of human-made chemicals that are found in a wide range of products used by consumers and industry since the 1940's. PFAS have been used in a variety of applications including in stain- and water-resistant fabrics and carpeting, cleaning products, paints, and fire-fighting foams due to their resistance to grease, oil, water and heat. Due to the strength of the carbon-fluorine bond, many PFAS may bioaccumulate in the food chain and remain persistent in the environment. Understanding the occurrence of PFAS compounds in various environmental compartments (e.g., air, surface water, groundwater, and land) and the routes of human exposure (e.g., in drinking water or in foods such as seafood) is a growing area of science, as environmental and public health professionals seek to better understand the risks to human health posed by PFAS.

In fall 2020, MDE began its effort to sample fish tissue for PFAS by including PFAS analytes in its fish tissue sampling program, which at the time was focused on sampling of fish tissue in the Eastern Shore Region. In late 2020 and early 2021, MDE also initiated a targeted study of the occurrence of PFAS compounds in surface water and fish tissue in the Piscataway Creek area since there were two potential PFAS sources upstream. The Piscataway Creek PFAS study included monitoring for PFAS in surface waters and fish tissue in the tidal and non-tidal waters of Piscataway Creek. Nanjemoy Creek was also sampled and was used as a reference site with tidal and non-tidal sampling locations similar to and south of Piscataway Creek with no known PFAS sources. MDE determined that it would be beneficial to sample PFAS levels in surface water and fish tissue in Piscataway Creek in order to better understand human health risk and potential sources of PFAS. MDE was also aware of a discharge of firefighting foam and the resulting fish kill investigation (on July 31, 2020, from Joint Base Andrews) and data concerning PFAS releases to surface water discussed in the 2018 Site IR of the Fire Fighting Foam usage at Joint Base Andrews, Prince George's County, Maryland (https://mde.maryland.gov/Documents/PFC%20Final%20Joint%20Base%20Andrews%20SI%20Report%2007%20May%202018.pdf).

Piscataway Creek Location

Piscataway Creek is located off the Potomac River in Prince George's County. There are two potential PFAS sources upstream from Piscataway Creek. The first is Joint Base Andrews (JBA) that has two tributaries on the southwest side that join to form Tinkers Creek, the major tributary to Piscataway Creek. The second source is Prince George's County Multi Agency Training Center which is located directly adjacent to Piscataway Creek. Please see Figure 1 below.

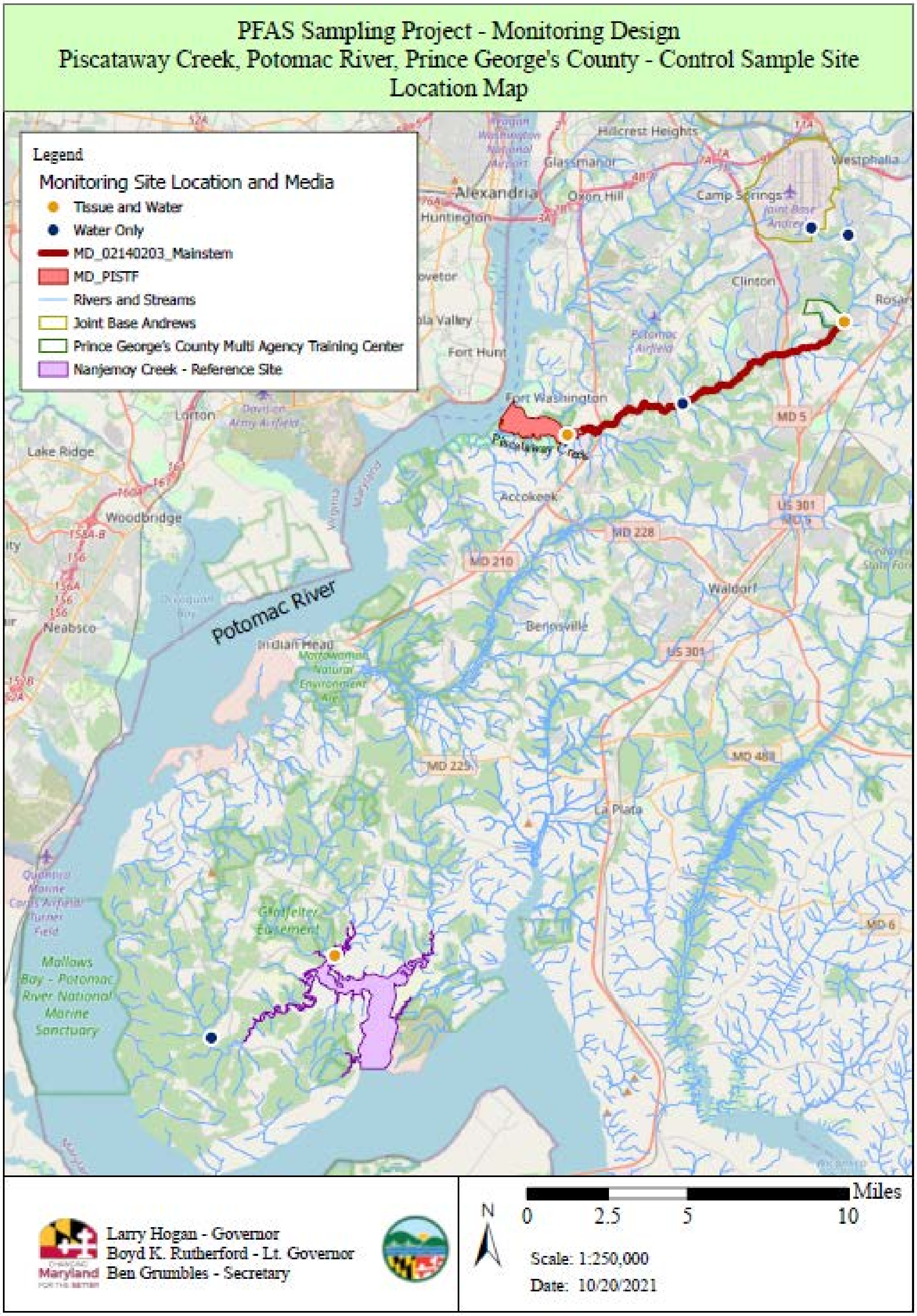

Figure 1: Piscataway Creek Sampling Area Locator Map

The Piscataway Creek watershed encompasses 69 square miles in Prince George's County. Headwaters originate to the west and east of JBA (in the vicinity of Camp Springs, Clinton and Woodyard). On the southwest side of JBA two branches join to form Tinkers Creek, the major tributary to Piscataway Creek. Surface water runoff flows into Tinkers Creek, to Piscataway Creek, and eventually into the Potomac River. From the southeast of JBA, the mainstem receives drainage from nearly 1,500 acres of the base and is partially redirected to a man-made lake (Base Lake) on base.

The northern region of the Piscataway Creek between JBA and Louise F. Cosca Regional Park is more developed. The major land use in this region is JBA. The base sits atop a north-south drainage divide, in the vicinity of the runways, that separates the Potomac River Basin to the west and the Patuxent River Basin to the east. The area surrounding JBA to the east is residential, commercial, light and heavy industrial, agricultural and some open land. The land used to the west is residential, commercial, and industrial. The area to the north is commercial and light industrial. The population density here is high.

The southern region comprises the area between Louise F. Cosca Regional Park to Piscataway Creek drainage. The land use to the south is mostly forested, some open and row-crop agricultural land, residential, commercial, and light industrial. Butler Branch (tributary to Piscataway Creek) flows through Louise F. Cosca Regional Park, and it forms a lake within the park. This Park has extensive facilities: shelters, grills, restrooms, athletic fields, tennis courts, and nature trails. To the south the land is more forested and agricultural with the encroachment of rural development and many new home estates. Along Accokeek Road (Route 373) between Dyson Road and Bealle Road there are older homes with septic systems. To the south along Indian Head Highway (Route 210) there is extensive urban development and homes with septic systems.

PFAS Fish Tissue and Ambient Water Quality Monitoring in the Piscataway Creek

In late 2020 and early 2021, MDE initiated the targeted study of the occurrence of PFAS compounds in surface water and fish tissue in the Piscataway Creek area. The Piscataway Creek was selected in part based on findings in the 2018 JBA Site Investigation report. The report indicates that "groundwater generally flows radially outward from these areas toward the streams and base boundaries." Also, the report states that "The relationship between groundwater and surface water drainage suggests that a portion of the groundwater discharges as base flow to six streams discharging from JBA. Finally, there are a number of places in the report under the various areas investigated where the report indicates that recreational fishing occurs in one or more of these streams and that there is a potentially complete pathway for human exposure to surface water from discharges from PFAS in groundwater. The Report includes the following statement: "Piscataway Creek is used for recreational fishing by residents of nearby communities and could provide an exposure pathway to humans through dermal contact and ingestion of fish". MDE was also aware of a discharge of firefighting foam and the resulting fish kill investigation (on July 31, 2020, from JBA).

On October 26, 2020, MDE collected fish tissue samples at Commo road in the Piscataway Creek to determine the occurrence and levels of 14 PFAS analytes, including PFOA and PFOS. Yellow-bullhead catfish and redbreast sunfish were collected in the non-tidal portion of Piscataway Creek, west of Rt. 210, off Commo Road. The results indicated elevated concentrations of PFOS in redbreast sunfish, compared to similar species collected and analyzed for PFAS during the annual fish tissue core station collection. Yellow-bullhead catfish were also collected at the same location but the results were not as elevated as redbreast sunfish. The elevated levels of PFOS in redbreast sunfish suggested that further investigation was warranted.

MDE completed a more detailed study of the Piscataway in May 2021, including the collection of surface water samples, an additional fish tissue collection in the Piscataway Creek tidal waters, and a tidal and non-tidal water and fish collection at reference locations in Nanjemoy Creek (a reference site with tidal and non-tidal sampling locations similar to and south of Piscataway Creek with no known PFAS sources). Water samples were collected at five locations along the Piscataway Creek downstream to the tidal headwaters. Fish tissue samples were collected at two locations, one in tidal headwaters of Piscataway Creek and the other in the non- tidal portion of Piscataway Creek off of Commo Road. Figure 2 shows the location of the Piscataway Creek sampling area and the monitoring stations evaluated in the 2020-2021 Intensive Review. Figure 3 shows the location of the Nanjemoy Creek Reference Site sampling area and the monitoring stations evaluated in the 2021 portion of the Piscataway Creek Intensive Review.

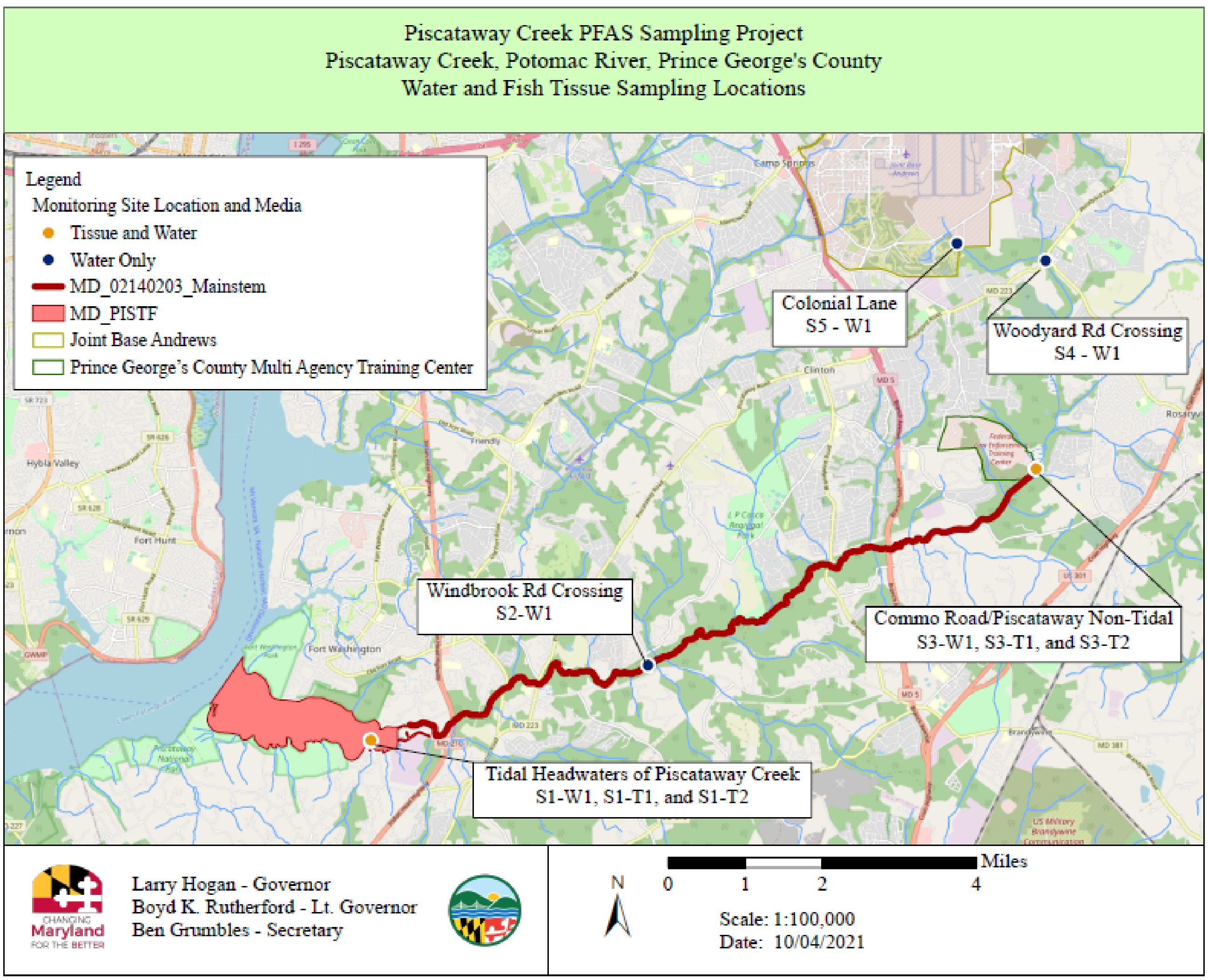

Figure 2: Piscataway Creek Sampling Area Monitoring Stations evaluated in the 2020-2021 Intensive Review

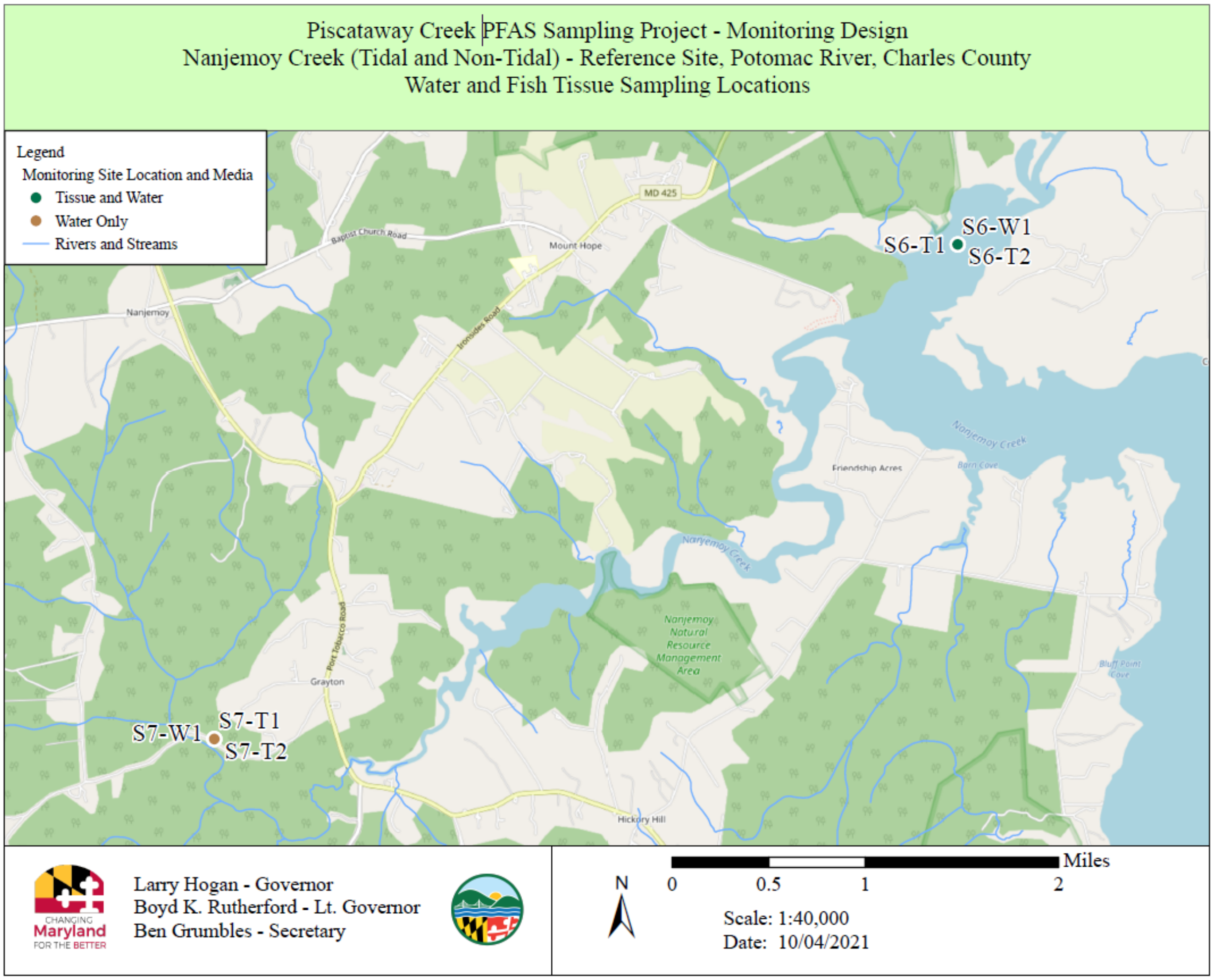

Figure 3: Nanjemoy Creek - Reference Site Sampling Area Monitoring Stations evaluated in the 2021 Intensive Review

PFAS Threshold

MDE developed risk-based swimming criteria for Perfluorooctanoic Acid (PFOA), Perfluorooctanesulfonic Acid (PFOS) and Perfluorobutanesulfonic Acid (PFBS) and risk-based fish tissue screening criteria for PFOA and PFOS in order to interpret the sampling results from the perspective of potential risk to human health. Both PFOA and PFOS have EPA-established reference doses (i.e. toxicity values) which were used by EPA to develop EPA's 2016 PFAS Health Advisory for PFOA and PFOS in drinking water. PFOA and PFOS currently have the same EPA reference doses and MDE used these reference doses and the EPA PFBS reference dose to develop its risk-based screening criteria for use in interpreting surface water and fish tissue sampling results.

Maryland, as well as most states, do not have numeric PFAS water quality criteria. EPA is developing human health as well as aquatic life criteria and is expected to release draft criteria for review in the next 1-2 years.

Maryland regulations addressing narrative criteria to protect aquatic life and human health from toxic materials in toxic amounts are addressed in the Code of Maryland Regulations:
26.08.01.01B. (93)
26.08.02.03B. General Water Quality Criteria
26.08.08.03-3
(7) Toxic Substance Criteria. All toxic substance criteria to protect:
(a) Freshwater aquatic organisms apply in waters designated as fresh water in Regulation .03-1B;
(b) Estuarine or saltwater aquatic organisms apply in waters designated as estuarine or salt waters as specified in Regulation .03-1B; and
(c) The wholesomeness of fish for human consumption apply in fresh, estuarine, and salt waters.

EPA advocates that both numeric and narrative criteria are useful in WQS, because they help protect a water body from the effects of specific chemicals as well as from the effects of pollutants that are not easily measured, such as chemical mixtures and floatable debris. Narrative criteria are also helpful when numeric criteria are not available or are under development, but the substance is known to be toxic. Most importantly, narrative criteria should be adopted based on biological monitoring and assessment methods to supplement numerical criteria. In accordance with 40 CFR 131.11(b)(2), in adopting water quality criteria, states and authorized tribes should "establish narrative criteria or criteria based on biomonitoring methods where numeric criteria cannot be established or to supplement numeric criteria." In the case of PFAS compounds, fish tissue and water column PFAS levels will be compared to health endpoint recommendations provided by EPA.

PFAS "Standards", Toxicity Values and Uncertainty Analyses

Health-based guidance values in specific environmental media for some PFAS have been developed by federal, state, and international agencies using a variety of critical studies, endpoints, methods, and policy choices. This study focuses specifically on assessing human health risk associated with measured levels of PFOA, PFOS and PFBS in surface water, and PFOS in fish taken from Piscataway Creek. PFOS was the predominant PFAS detected in fish tissue and the only detected PFAS with peer reviewed toxicity values, therefore, fish tissue consumption risks were evaluated only for PFOS. MDE used peer reviewed reference doses (RfDs) for PFOA and PFOS which were developed by EPA (and used by EPA in developing its 2016 Drinking Water Health Advisory Levels) and an MDE estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime (with uncertainty factors generally applied to reflect limitations of the data used). The PFBS RfD was a Provisional Peer-Reviewed Toxicity Value (PPRTV) primarily derived for use in EPA's Superfund Program. RfDs are generally used in noncancer health assessments and the RfDs utilized in this assessment are approved by EPA and detailed within the Regional Screening Level User's Guide, (May, 2021), https://www.epa.gov/risk/regional-screening-levels-rsls-users-guide. The MDE-developed health based guidance values for swimming and for fish consumption are estimates of a daily exposure dose that is not expected to lead to a non-cancer health risk over a set period of time. These guidance values are used to identify exposures (and levels in surface water and fish) that could potentially pose an unacceptable risk to human health. However, exposure above a guidance value does not mean that health problems will occur. MDEs quantitative assessment addresses only PFOA, PFOS, and PFBS, three of the most studied PFAS which both have RfDs.

The MDE risk threshold for noncarcinogens is set at a hazard quotient of 1 which is the ratio of the potential exposure to a substance and the level at which no adverse effects are expected (calculated as the exposure divided by the appropriate chronic or acute value) which means adverse noncancer effects are unlikely at this level, and thus can be considered to have negligible risk. For hazard quotients greater than 1, the potential for adverse effects increases, but we do not know by how much. For toxins that affect the same target organ or organ systems that can cause similar adverse health effects, combining hazard quotients from different toxics is often appropriate. The sum of hazard quotients is a hazard index (HI) which was utilized for PFOA, PFOS and PFBS in this evaluation. An HI of 1 or lower means toxics are unlikely to cause adverse noncancer health effects over a lifetime of exposure. However, an HI greater than 1 doesn't necessarily mean adverse effects are likely.

As stated previously, PFAS compounds have been in use since the 1940s and PFAS are found in a wide array of consumer and industrial products. Other than for PFOA, PFOS and PFBS, the vast majority of PFAS compounds in the marketplace have little to no toxicity information or RfDs. As greater knowledge of the toxicity of other PFAS compounds advances, MDE will re-visit prior assessments to ensure that appropriate actions are taken to address any unacceptable human health risk. Currently, MDE, EPA and other organizations are collaborating to generate and review research and consider new scientific information as it becomes available on the bioaccumulation potential and toxicity of additional PFAS. Developing toxicity values or oral reference doses, RfDs, for other PFAS, including GenX chemicals are a priority for EPA and will be considered by MDE as the research becomes available.

Surface Water Results

Surface water samples were collected on May 14th and 18th of 2021 in and around the non-tidal and tidal waters of Piscataway creek and the reference sites in the tidal and non-tidal waters of Nanjemoy Creek south of Piscataway Creek. A total of 10 field blanks containing PFAS-free water supplied by the contract laboratory were utilized during sampling. The number of samples, sample locations and quality control samples are detailed in Tables 1 and 2.

Table 1: Piscataway Creek Intensive Survey Sampling Information

Location	Position	Collection Reference	Site Reference	Sample ID	Sample Type	Field Blanks	Avg Length (cm)	Avg Weight (g/lbs.)	Collection Date	Deliver to Lab
Tidal headwaters of Piscataway Creek	38.69522, -77.00623	Water Sample		S1-W1	Water	S1-FB1			5/14/2021	5/21/2021
Tidal headwaters of Piscataway Creek	38.69522, -77.00623	Composite Species 1 - Largemouth Bass		S1-T1	Tissue	S1-FB1	39.9	910.8	5/14/2021	5/21/2021
Tidal headwaters of Piscataway Creek	38.69522, -77.00623	Composite Species 2 - Blue Catfish		S1-T2	Tissue	S1-FB1	47.38	1081	5/14/2021	5/21/2021
Windbrook Road Crossing	38.70933, -76.93954	Water Sample		S2-W1	Water	S2-FB1				5/21/2021
Commo Road - Non Tidal	38.74618, -76.84636	Composite Species 1 - Redbreast Sunfish		S3-T1	Tissue	S3-FB1	15.5	72.8	5/17/2021	5/21/2021
Commo Road - Non Tidal	38.74618, -76.84636	Composite Species 2 - Yellow Bullhead Catfish		S3-T2	Tissue	S3-FB1	17.7	75.8	5/17/2021	5/21/2021
Commo Road - Non Tidal	38.74618, -76.84636	Water Sample		S3-W1	Water	S3-FB1			5/17/2021	5/21/2021
Woodyard Road Crossing	38.78536, -76.84388	Water Sample		S4-W1	Water	S4-FB1			5/18/2021	5/21/2021
Colonial Lane	38.78866, -76.86529	Water Sample		S5-W1	Water	S5-FB1			5/18/2021	5/21/2021
Tidal headwaters of Nanjemoy Creek	38.44992, -77.15417	Water Sample	Control	S6-W1	Water	S6-FB1			5/20/2021	5/21/2021
Tidal headwaters of Nanjemoy Creek	38.44992, -77.15417	Composite Species 1 - Bluegill	Control	S6-T1	Tissue	S6-FB1	16.7	107.4	5/20/2021	5/21/2021
Tidal headwaters of Nanjemoy Creek	38.44992, -77.15417	Composite Species 2 - Blue Catfish	Control	S6-T2	Tissue	S6-FB1	48.4	1073.2	5/20/2021	5/21/2021
Non Tidal waters of Nanjemoy Creek	38.42201, -77.21040	Water Sample	Control	S7-W1	Water	S7-FB1			5/26/2021	5/28/2021
Non Tidal waters of Nanjemoy Creek	38.42201, -77.21040	Composite Species 1 - Redbreast Sunfish	Control	S7-T1	Tissue	S7-FB1	14.9	60.2	5/26/2021	5/28/2021
Non Tidal waters of Nanjemoy Creek	38.42201, -77.21040	Composite Species 2 - Yellow Bullhead Catfish	Control	S7-T2	Tissue	S7-FB1	21.1	142.2	5/26/2021	5/28/2021

Field Blanks	One with each site collected	S1-FB1,S2-FB1,S3-FB1,S4-FB1,S5-FB1,S6-FB1,S7-FB1			Water	7
Trip Blanks	One with each "trip"	TB-1,TB-2,TB-3,TB-4			Water	4
Replicates	Done in Lab	Water Sample	Lab Sample		Water	1
Replicates	Done in Lab	Tissue Replicate	Lab Sample		Tissue	1
NIST Water Sample	Done in Lab	Water Sample	Lab Sample		Water	1
NIST Tissue Sample	Done in Lab	Tissue Replicate	Lab Sample		Tissue	1

Media	Count
Tissue	10
Water	20

Table 2: Piscataway Creek Fall 2020 PFAS Sampling

Location	Position	Collection Reference	Site Reference	Sample ID	Sample Type	Field Blanks	Avg Length (cm)	Avg Weight (g/lbs.)	Collection Date
Commo Road - Non Tidal	38.74776, -76.84507	Composite Species 1 - Yellow Bullhead Catfish	PIS0134	2020FTC_PISC_A	Tissue	FB_2020FTC_PISC	20.2	102.2	10/26/2020
Commo Road - Non Tidal	38.74776, -76.84507	Composite Species 2 - Redbreast Sunfish	PIS0134	2020FTC_PISC_B	Tissue	FB_2020FTC_PISC	15.16	54.4	10/26/2020

Surface water concentrations of PFOS ranged from not detected in Nanjemoy Creek to 1.5040 ug/L (parts per billion (ppb)) in the mainstem of Piscataway Creek. All PFOS plus PFOA surface water concentrations were below recreational swimming screening criteria (based on incidental ingestion). Concentrations of PFOS compounds in the nontidal headwaters and tidal headwaters of Piscataway Creek were significantly greater than PFOS surface water concentrations in comparable locations in the Nanjemoy Creek reference site. PFOS surface water concentrations in Piscataway Creek and comparisons to a similar reference site, Nanjemoy Creek, indicate significant ongoing sources of PFOS exist within the Piscataway Creek watershed.

Table 3: Surface Water Results for Piscataway Creek Intensive Survey Spring 2021 with MDE-calculated risk-based screening criteria for PFOA, PFOS, and PFBS for Recreational Swimming.

Site Description	ID	Collection Date	PFOS + PFOA (ug/L)	Recreational Screening Criteria PFOS+PFOA (ug/L)		PFBS (ug/L)	Recreational Screening Criteria PFBS (ug/L)	
				Moderate	Intensive		Moderate	Intensive
Tidal headwaters of Piscataway Creek	S1-W1	5/14/2021	0.1007	17.5	8.77	0.00689	26.2	13.1
Windbrook Road Crossing	S2-W1	5/18/2021	0.1469	17.5	8.77	0.01060	26.2	13.1
Commo Road - Non-Tidal	S3-W1	5/18/2021	0.6250	17.5	8.77	0.03940	26.2	13.1
Woodyard Road Crossing	S4-W1	5/18/2021	1.2860	17.5	8.77	0.08080	26.2	13.1
Colonial Lane	S5-W1	5/18/2021	1.5040	17.5	8.77	0.10800	26.2	13.1
Tidal Headwaters of Nanjemoy Creek	S6-W1	5/18/2021	0.00453	17.5	8.77	ND	26.2	13.1
Non-Tidal Headwaters of Nanjemoy Creek	S7-W1	5/18/2021	ND	17.5	8.77	ND	26.2	13.1

*Note that PFOS levels at S3, S4, and S5 are a magnitude over 500 times higher than the reference sites (stations S6 and S7).

Fish Tissue Results

MDE collected fish tissue samples at two locations in the tidal and non-tidal waters of Piscataway Creek. Additionally, fish tissue samples were collected from two locations in the tidal and non-tidal waters of the Nanjemoy Creek reference site. On May 14, 2021, May 17, 2021, May 20, 2021, and May 26, 2021, MDE collected fish tissue samples at four sampling locations: the tidal headwaters of Piscataway Creek (5/14/2021), the non-tidal waters of Piscataway Creek at Commo Road (05/17/2021), the tidal headwaters of Nanjemoy Creek (05/20/2021), and the non-tidal waters of Nanjemoy Creek (05/26/2021). All samples were collected according to MDE's fish tissue methodology and were submitted for analysis to determine the levels of 14 PFAS (Table 4).

Table 4: PFAS Parameters

Parameter	Acronym	CAS Number
Perfluorobutanesulfonic Acid	PFBS	375-73-5
Perfluorohexanoic Acid	PFHx A	307-24-4
Perfluoroheptanoic Acid	PFHpA	375-85-9
Perfluorohexanesulfonic Acid	PFHxS	355-46-4
Perfluorooctanoic Acid	PFOA	335-67-1
Perfluorononanoic Acid	PFNA	375-95-1
Perfluorooctanesulfonic Acid	PFOS	1763-23-1
Perfluorodecanoic Acid	PFDA	335-76-2
N-Methyl Perfluorooctanesulfonamidoacetic Acid	NMeFOSAA	31506-32-8
PerfluorouND1ecanoic Acid	PFUnA	2058-94-8
N-Ethyl Perfluorooctanesulfonamidoacetic Acid	NEtFOSAA	1691-99-2
Perfluorododecanoic Acid	PFDoA	16517-11-6
Perfluorotridecanoic Acid	PFTrDA	72629-94-8
Perfluorotetradecanoic Acid	PFTA	376-06-7

MDE's evaluation of the fish tissue samples from Piscataway Creek includes a comparison of measured PFOS fish tissue concentrations to measured concentrations at the reference site and to a range of MDE-calculated risk-based site-specific fish consumption screening concentrations. These human health-based screening concentrations for PFOS assume that all fish are consumed from the same harvesting location. MDE found that fish tissue concentrations in redbreast sunfish in the non-tidal portion of Piscataway Creek off Commo Road were in excess of the PFOS screening criteria and that fish tissue PFOS concentrations in largemouth bass were in excess of screening criteria in the tidal portion of Piscataway Creek. Fish tissue PFOS concentrations from fish sampled from the Nanjemoy Creek control sites were significantly lower than fish tissue PFOS concentrations in fish sampled from Piscataway Creek. Results of the fish tissue consumption evaluation for PFOS indicated consumption of fish tissue within non-tidal and tidal portions of the Piscataway Creek study area are in excess of the MDE site-specific fish consumption screening criteria.

Table 5: Fish Tissue Sample Results from Piscataway Creek Intensive Survey Fall 2020 - Spring 2021 with MDE-calculated risk-based screening criteria for PFOA, and PFOS for Fish Consumption

Site Description	ID	Collection Date	Species Common Name	PFOS (ug/kg)	Fish Tissue (cooked) Screening Concentration (ug/kg)		
					General Population (76 kg)	Women Child-bearing Age (67 kg)	Children (14.5 kg)
Piscataway - Commo Road	2020FTC_PISC_A	10/26/2020	Yellow Bullhead Catfish	20.0	73	64	37
Piscataway - Commo Road	2020FTC_PISC_B	10/26/2020	Redbreast Sunfish	233.0	73	64	37
Tidal headwaters of Piscataway Creek	S1-T1	5/14/2021	Largemouth Bass	94.2	73	64	37
Tidal headwaters of Piscataway Creek	S1-T2	5/14/2021	Blue Catfish	2.5	73	64	37
Commo Road - Non Tidal	S3-T1	5/17/2021	Redbreast Sunfish	231.0	73	64	37
Commo Road - Non Tidal	S3-T2	5/17/2021	Yellow Bullhead Catfish	24.7	73	64	37
Tidal headwaters of Nanjemoy Creek	S6-T1	5/20/2021	Bluegill	5.2	73	64	37
Tidal headwaters of Nanjemoy Creek	S6-T2	5/20/2021	Blue Catfish	1.4	73	64	37
Non tidal waters of Nanjemoy Creek	S7-T1	5/26/2021	Redbreast Sunfish	5.2	73	64	37
Non tidal waters of Nanjemoy Creek	S7-T2	5/26/2021	Yellow Bullhead Catfish	3.3	73	64	37
Consumption Rate (mg-day)					**29,825**	**29,825**	**11,185**
Approximate Meals per Month (8-ounce meal adult, 3-ounce meal child)					**4**	**4**	**4**

*PFOA and PFBS were not detected in any fish tissue samples, therefore, all fish tissue risk-based values are for PFOS.

Results Summary

The study concludes that PFOA and PFOS are present in the non-tidal and tidal waters of Piscataway Creek at concentrations below risk-based recreational use swimming screening criteria. However, PFAS surface water concentrations in both the non-tidal and tidal portions of Piscataway Creek are significantly greater than PFAS concentrations at the Nanjemoy Creek reference sites. PFOA and PFOS are present in fish tissue at levels that exceed human consumption-based screening criteria and fish consumption advisories and additional assessments are warranted in both the tidal and non-tidal waters of Piscataway Creek.

Table 6: Summary of Total PFAS and PFOS Sampling Results for Surface Water

Location	Media	Concentration Range (PFAS) (ug/kg)	Maximum Concentration PFAS (ug/kg)	Maximum Concentration PFOS (ug/kg)
Nanjemoy Creek non-tidal	fish tissue	4 - 10	10	5
Nanjemoy Creek tidal	fish tissue	1 - 6	6	5
Piscataway Creek non-tidal	fish tissue	29 - 247	247	231
Piscataway Creek tidal	fish tissue	4 - 101	101	94

Table 7: Summary of Total PFAS and PFOS Sampling Results for Fish Tissue

Location	Media	Concentration Range (PFAS) (ng/L)	Maximum Concentration PFAS (ng/L)	Maximum Concentration PFOS (ng/L)
Nanjemoy Creek non-tidal	surface water	ND	ND	ND
Nanjemoy Creek tidal	surface water	7	7	3
Piscataway Creek non-tidal	surface water	310 - 3,193	3,193	1,100
Piscataway Creek tidal	surface water	207	207	74

Rationale for Integrated Report/303(d) PFAS Impairment Listing

Following the Assessment Methodology for Determining Impaired Waters by Chemical Contaminants for Maryland's Integrated Report of Surface Water Quality: Fish Tissue Data Use for Integrated Report Listings, when a fish consumption advisory is issued for a waterbody, the designated use of that waterbody is not being supported and usually results in listing a waterbody as impaired for the specific contaminant. According to the methodology, the risk-based screening criteria for PFOS can be used as a listing threshold, and a 4 meals per month advisory of a common recreational fish species for a 76 kg individual (general population) is the threshold used for an impairment listing. Both the tidal and nontidal portions of Piscataway Creek show elevated PFOS levels above the listing threshold and have an advisory at 4 meals per month and therefore, should be listed as impaired (Category 5) on the

Combined 2020-2022 IR of Surface Water Quality. Since the number of meals does not meet the goal of at least four meals per month, MDE has determined that the narrative criterion that provides for the “wholesomeness of fish for human consumption” is not met. The geographic scale of the assessment was shown in figure 2 of this narrative, and the summary of the impairment listings are in Table 8 below.

Table 8: Summary of the 2020-2022 IR Impairment Listings

Assessment Unit	Basin Name	Designated Use	Listing Category	Cause	Sources
MD-02140203-Mainstem	Piscataway Creek	Fishing	5	PERFLUOROOCTANE SULFONATE (PFOS) IN FISH TISSUE	Upstream Source
MD-PISTF	PISTF - Piscataway Creek tidal Fresh	Fishing	5	PERFLUOROOCTANE SULFONATE (PFOS) IN FISH TISSUE	Upstream Source

References

EPA, Regional Screening Levels (RSLs) User’s Guide, May 2020, https://www.epa.gov/risk/regional-screening-levels-rsls-users-guide.

EPA (2000a). Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 1. Fish Sampling and Analysis. In (doi: EPA 823-B-00-0073rd ed.

EPA (2000b). Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 2. Risk Assessment and Fish Consumption Limits. In (doi: EPA 823- B-00-0083rd ed.

MDE (2006) Total Maximum Daily Loads of Fecal Bacteria for the Non-Tidal Piscataway Creek Basin in Prince George’s County, Maryland. Document Version: May 10, 2006

USGS current conditions for USGS 01653600 PISCATAWAY Creek AT PISCATAWAY, MD, https://waterdata.usgs.gov/nwis/uv?site_no=01653600. 09/27/2021