Forever chemicals: Per- and polyfluoroalkyl substances in the St. Mary's River

St. Mary's county, Maryland

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Introduction

Society advances by incorporating scientific discovery into everyday life by way of new technologies. As is often the case, new technologies are developed for military and industrial uses and then someone envisions a way to incorporate these applications to seemingly improve lives. However, there is always a tradeoff for these advances. Such is the case with per- and polyfluorinated alkyl substances, a group of chemicals comprised of an estimated 4,000 to10,000 separate compounds and collectively referred to as PFAS. This group of chemicals, originally developed in the 1940s as an artillery tank coating have unique properties as surfactants: extremely slick, shedding both water and oil (lipo- and hydrophobic); they are used to manufacture fire-fighting foams, as well as chemical, fire and stain resistant coatings for textiles, and non-stick cookware (Glüge et al. 2020).

PFASs are alkyl chains 4-14 carbon atoms in length whose hydrogen atoms have been replaced with fluoride atoms (Lau, 2015). PFAS with five or fewer carbon atoms in their backbone are known as 'short-chain' compounds; those with six or more are called 'long-chain'. Long chain PFAS have been shown generally to cause the most toxic effects, although no PFAS is considered as safe (Brendel et al. 2018). The carbon-fluorine bond is known as the strongest bond in organic chemistry, and for this reason PFAS compounds are considered 'forever' chemicals (Witt et al. 2020). They cannot be broken down readily by any known environmental, chemical or biologic process. PFAS compounds are primarily released from the stacks of manufacturing facilities and are transported through the air in particulate form, and then settle to Earth's surface. It is by this transport mechanism, which generally follows the hydrogeologic cycle, that PFAS are ubiquitous and found globally in soils, water, air, organisms and even house dust. They are concentrated in biosolids used to fertilize agricultural soils and have been demonstrated to be taken up into food plants (Costello and Lee 2020, Lau 2015). Historically

there have been some documented instances of direct dumping of chemicals into natural surface water bodies, holding ponds and landfills.

PFAS are a class of man-made chemicals that are not currently regulated by the United States Environmental Protection Agency (EPA 2021). PFAS are associated with suppressed immune function, thyroid disease, testicular and kidney disease, cancers, and liver damage. (EPA 2019). Newer short chain and 'GenX' compounds have been studied little but scientists studying them currently are finding that they have similar toxicology to long chain PFAS. (Birnbaum 2020).

Other recent studies have associated perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) with hepatotoxicity, neurotoxicity, reproductive toxicity, immunotoxicity, thyroid disruption, cardiovascular toxicity, pulmonary toxicity, and renal toxicity in laboratory animals and suggest these conditions may affect in-vitro human systems (Zeng et al. 2019).

Materials and Methods

Location

St. Mary's River is located in rural St. Mary's county on Maryland's western shore at 38° 09'N, 76° 27'W. The peninsula is bounded by the Potomac, Patuxent and Wicomico Rivers. The St. Mary's River is a mesohaline tidal tributary feeding the lower Potomac River and Chesapeake Bay. The area of the drainage catchment is approximately 73.78 square miles and features 16 sub-watersheds (St. Mary's River Watershed Organization 2016.) (Appendix 1). The landscape in the watershed is composed of a mixture of agricultural fields with pockets of suburban and concentrations of intensely developed areas. The county remains over 50% forested (St. Mary's county 2010). Of note are two naval installations- Patuxent River Naval Air Station in Lexington Park, Maryland and its annex, Webster Outlying Field in St. Inigoes, Maryland.

The watershed encompasses nearly one-quarter of the land area of St. Mary's county, including its most densely populated and developed areas. Thus, nearly half of the population resides within its borders (St. Mary's Watershed Association (SMRWA) 2016). Webster Field, an aircraft support and testing facility with two airstrips, is in close proximity (250-500 ft.) to the water's edge.

Sample Collection

Sample collection from ten locations for surface water and oyster tissue samples was completed June 4, 2020 in the main stem of the St. Mary's River (appendix A1). Data were collected by boat during ebb tide from the sites that were chosen to represent likely accumulations of the compounds in question, including proximity to the airstrips at the Webster Outlying Field. Decisions were based on likely flow path of water based on bathymetry and geomorphology of the river, as well as known locations of oyster reefs in the river. These locations were mapped out ahead of the actual sampling date; geographic coordinates were recorded at the time of sampling.

Preparations for sampling and our sampling protocol (Appendix A3) were based upon best available guidance from Environmental Protection Agency (EPA), Department of Defense (DoD), the Interstate Technology and Regulatory Council (ITRC), and EPA certified laboratories (pers. comm.) (DoD 2017, EPA 2020, ITRC 2020). These precautions were necessary because PFAS compounds are ubiquitous in both the environment as well as consumer goods and textiles. They posed a very real risk of cross contamination from the environment, our clothes, and our sampling equipment to our samples. For this reason, fresh 40 cm nitrile gloves were worn for each sample and duplicate, the boat was oriented so water flowed toward it and samples were collected 30cm below the surface from the bow of the boat.

Duplicate oyster samples were collected (n=2) from Church Point (#6) and Raleys Shore sites (#1) on September 10, 2020. An additional field blank was completed and submitted to validate our field collection methods. All oysters from both dates

were composite samples of tissues from three organisms. Shells were rinsed with PFAS-free certified water supplied by the laboratories, and separate cleaned and rinsed oyster knives were used to first open and subsequently extract the oyster tissue. The total mass of the tissues collected was approximately 20 grams per site. It is worth noting that due to a prolonged anoxic event in the summer prior to our duplicate sampling, oysters in >2 m water experienced 100% mortality. All samples were packed on ice in glass bottles supplied by the laboratories, and chain of custody was maintained on both sampling days from sampling to the shipping company relinquishing the samples to the lab personnel.

Laboratory Analysis

United States EPA only certifies three test methods at this time for the detection of PFAS in drinking water- EPA Methods 533, 537, and 537.1 (EPA 2020). EPA method 8327, for fluorinated hydrocarbon determination in other liquids such as waste water and solids such as soils and animal tissues, is expected to be certified for use in labs in the near future. Labs that have demonstrated proficiency in these laboratory methods are certified by EPA to conduct these analyses the results of which will be accepted by EPA as proof positive of their veracity. All of these tests are based upon a liquid chromatography separation of compounds which are detected using two mass spectrometers in tandem, known as LC/MS/MS.

Both labs (RTI Labs: Livonia, MI, and Eurofins Lancaster Laboratories: Lancaster, PA) utilized EPA 537 for PFAS quantitation. Quality control/quality assurance protocols met or exceeded criteria for EPA. In addition, RTI labs met or exceeded guidance specified in the Department of Defense's Quality System's Manual for Environmental Laboratories (DoD 2019). PFAS quantitation reporting levels (RL) at RTI were on the order of 3.5-5 ng/L and 600-2,000 ng/kg for Eurofins. Sample analyses quality control measures included a method blank, matrix spikes and duplicates, laboratory control samples and duplicates, and other requirements of the quality control protocols.

Results

Compounds of interest were detected in the surface waters in eight of the ten sampling locations from June 4. There were no compounds of interest noted in the tissue samples from the June sampling date (Table 1). There were however, significant detections in the duplicate oyster tissue sent to Eurofins lab (Table 2). Many of these compounds from both dates were detected at levels above the method detection limit (MDL) but below the reporting level (RL) established for the analyte. Therefore, these values, known as J-values and indicated with an asterisk in tables 1 and 2, are considered to be non-zero estimates. All other positive results are considered to be firm values above the established RL.

Table 1. PFAS levels in surface water of the St. Mary's River, St. Mary's county, Maryland, USA.

Site no.	Compound	Detection amount (ng/L)*	Number of carbon atoms	J value
1	Perfluorpentanoic acid	7.6	5	
4	Perfluorooctanesulfonic acid (PFOS)	2.2	8	*
4	Perfluorpentanoic acid	3.8	5	*
5	1H,1H,2H,2H-Perfluorodecanesulfonate	9.1	10	
5	Perfluorobutanesulfonic acid	1.2	4	*
5	Perfluorobutanoic acid (HFBA)	1.5	4	*
5	Perfluorooctanesulfonic acid (PFOS)	1.5	8	*
5	Perfluorooctanoic acid (PFOA)	1.3	8	*
6	1H,1H,2H,2H-Perfluorodecanesulfonate	8.6	10	
6	Perfluorooctanesulfonic acid (PFOS)	1.5	8	*
7	1H,1H,2H,2H-Perfluorodecanesulfonate	5.4	10	
7	Perfluorobutanesulfonic acid	0.96	4	*
7	Perfluoroheptanoic acid	0.91	7	*
7	Perfluorooctanesulfonic acid (PFOS)	1.4	8	*

8	1H,1H,2H,2H-Perfluorodecanesulfonate	7.3	10	
8	Perfluorobutanoic acid (HFBA)	3.2	4	*
9	1H,1H,2H,2H-Perfluorodecanesulfonate	5.1	10	
9	Perfluorohexanoic acid	2.1	6	*
9	Perfluorooctanesulfonic acid (PFOS)	1.5	8	*
10	Perfluorooctanesulfonic acid (PFOS)	1.3	8	*
10	Perfluorooctanoic acid (PFOA)	1.3	8	*
10	Perfluorpentanoic acid	3.1	5	*

**1ng/L= 1part per trillion*

Table 2. PFAS levels in oyster tissue in the St. Mary's River, St. Mary's county, Maryland, USA.

Site no.	Compound	Detection amount (ng/kg)*	Number of carbon atoms	J value
1	Perfluorobutanoic acid (HFBA)	800	4	*
1	Perfluoropentanoic acid	220	5	*
8	6:2 Fluorotelomer sulfonic acid	1100	6	*

1 ng/kg = 1 part per trillion

Discussion

The St. Mary's River is on the US Environmental Protection Agency's 'impaired waters' list, or 303(d) list - so named because regulations are contained in that section of the U.S. Clean Water Act - for low oxygen levels in the main stem of the river, usually during the summer months (EPA 1972). The results of this study and those noted below suggest that there is a far more insidious reason about which to be concerned. The river is unusual from a regulatory sense in that its entire catchment is located within the borders of St. Mary's county. This suggests, in a regulatory context, that this is ideal for a number of reasons. Locally, St. Mary's county, Maryland government is the first line of defense regarding environmental control, and the local government has a decent track record of respecting the environment. Secondly, from a state

standpoint, much less coordination of competing interests and jurisdictions need to be navigated for environmental regulations. This is not to say that locally and at the state level, there are not competing political or stakeholder interests; there are.

All local and state regulations flow logically and of necessity from federal guidance. EPA issued a health advisory for two compounds, PFOA and PFOS which suggests a lifetime exposure limit of 70 parts per trillion combined. However, EPA approved methods test for a total of 29 separate PFAS compounds. Many states have followed this guidance in recent history to develop guidelines. Fourteen states have developed or are currently developing maximum contaminant levels (MCLs) of 10-47 parts per trillion. MCLs are enforceable regulations, unlike advisories. Some states including several previously referred to have combined limits of 70 parts per trillion, likely based on the federal advisory. North Carolina has set an advisory of 140,000 parts per trillion. Thirty-four states, including Maryland have no regulations in place nor have they set health advisory recommendations.

Maryland has started to monitor and develop plans to address PFAS in drinking water, surface water and seafood to protect human health. Between 2012 and 2015, 42 water systems in Maryland were monitored for PFOA and PFOS. All but one well tested above the federal advisory of 70 parts per trillion. Since then, a more robust plan has started to be implemented, starting with the testing of the St. Mary's River, in which the activity described in this report provided a quality control check of the state's efforts. Both sets of results are consistent.

The development of stringent MCLs will also provide de facto protection to the environment and wildlife as well. Care must be taken to protect the natural world and its inhabitants. While effects on wildlife have not been thoroughly explored, many wild aquatic animals are harvested for human consumption. Some of these animals have shown varying levels of bioaccumulation, which is the accumulation of substances in tissues over time. For example, recent research has demonstrated varying levels of PFAS compounds in both farmed and wild fin-

and shellfish in the Netherlands (Zafeiraki et al. 2019). In addition, high levels of PFAS were found in both sportfish species and diamondback terrapins off the Atlantic coast of North America (Gewurtz et al. 2014, Bangma et al. 2019). Most recently, the NGO Public Employees for Environmental Responsibility (PEER) conducted a study of seafood commonly harvested and consumed from the Potomac and St. Mary's Rivers. They found that oysters had levels exceeding 2,000 parts per trillion, consistent with the findings of this study, and crabs contained over 600 parts per trillion. Striped bass, a migratory species harvested from the mouth of the Potomac river, were determined to contain over 23,000 parts per trillion PFAS. The number of compounds ranged from five to nine.

These results as well as documented human health effects highlight the need for regulation. Many of these detrimental effects have been known for years. Local jurisdictions, like St. Mary's county are tied to state and federal regulations. When there is no principle guidance in place, there can be no teeth to local regulations. This is especially true when a large part of the county is made of state lands, and there are two federal military installations which have been documented to use fire fighting foams, the primary ingredient which is PFAS. The local government has limited to no jurisdiction over these entities.

In addition, local government does not have jurisdiction over consumer goods brought into the county which may contain potentially toxic substances. The regulation of consumer goods manufacturing standards is by necessity mandated at the federal level. Firm, realistic, and stringent MCLs need to be established to support any regulations promulgated to limit or eliminate PFAS use and importation. This starts with federal regulation which should be informed by the best possible science.

More research needs to be done to mitigate exposure to animals or animal products already contaminated with PFAS. Barring that, regulatory agencies may have to put temporary moratoria on the harvest of select species. This, of course is not an ideal, or even palatable

solution and has not proven popular in the past no matter how successful. Many families in coastal communities like St. Mary's depend on fishing as the primary means of economic support. Indeed, there will have to be backing from local, state and federal authorities to develop new aquaculture technologies, to say nothing of convincing traditional fishers to change their ingrained culture.

While filtering with reverse osmosis, charcoal, and ion exchange resins have been shown to be effective means of removal from water sources, widespread use is not in place and it is costly. Still, development grants could be made available along with enhanced onshore, closed aquaculture facilities to raise and harvest uncontaminated seafood. While it will prove to be challenging to isolate from such ubiquitous compounds, by using a thoughtful combination of regulation, new technologies, education regarding new economic models of opportunity we can start to ease back from the environmental precipice that has been threatening us for the past eighty years.

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Appendix and Supplemental Materials

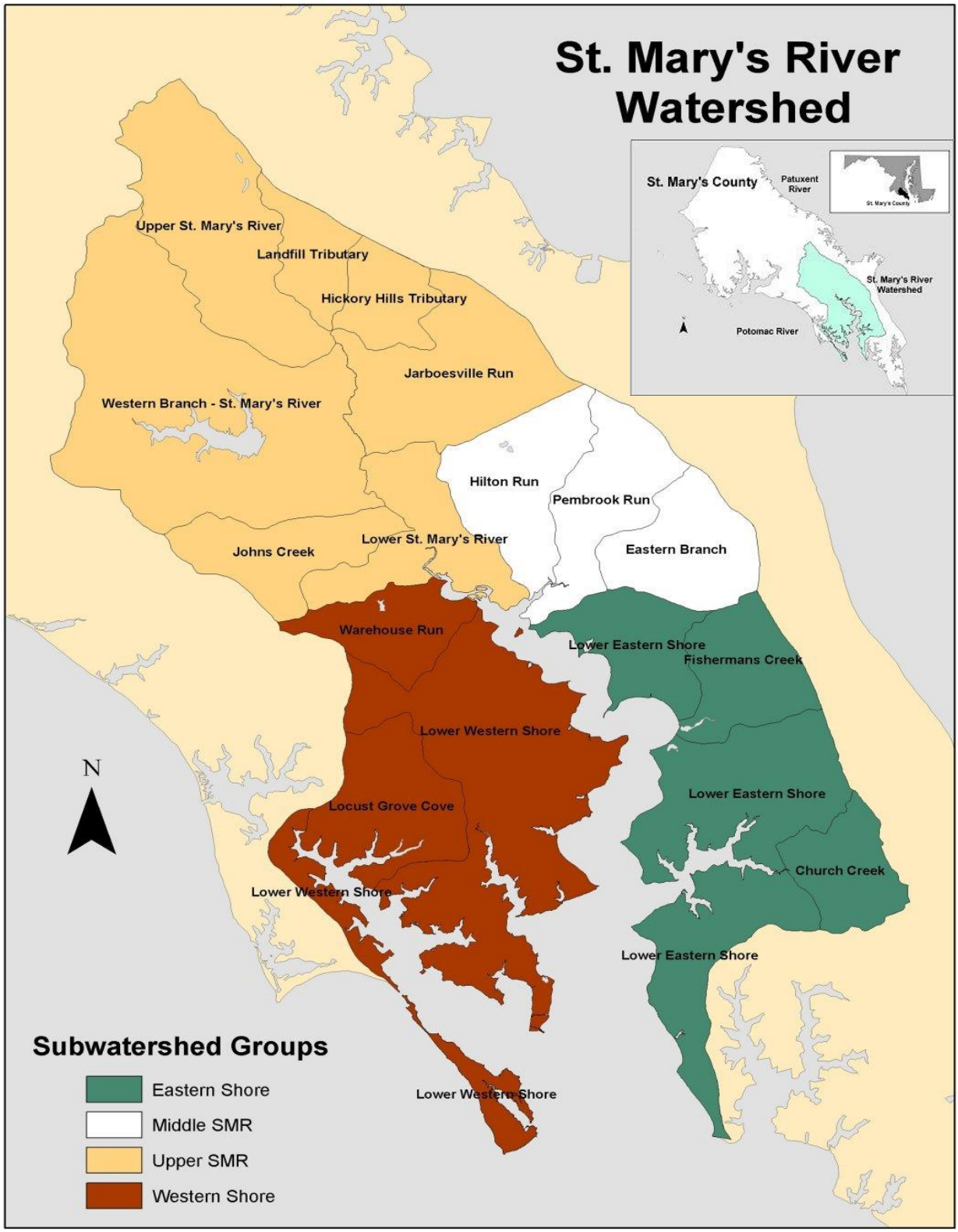

Figure A 1. St. Mary's River sub watersheds. (SMRWA.org)

Figure A 2. Sampling locations, PFAS determination, St. Mary's River, St. Mary's county, Maryland USA

Table A1. Sample site coordinates.

Site No	Site Name	Latitude	Longitude	Sampled Surface Water	Sampled Oyster Tissue
1	Raleys Shore	38.15663	-76.43018	yes	yes
2	End of Runway or Langley	38.14037	-76.43680	yes	no
3	Goad	38.13078	-76.43543	yes	no
4	Molls Cove	38.15279	-76.42484	yes	yes
5	Church Creek	38.16267	-76.40736	yes	no
6	Broom Cove	38.17226	-76.41414	yes	yes
7	Windmill Point	38.15705	-76.44800	yes	no
8	Seminary or St. Mary's Hall	38.18863	-76.43688	yes	yes
9	Horse Shoe Point	38.19648	-76.46667	yes	yes
10	Nacht	38.20838	-76.45206	yes	yes
11	Breton Bay (Control)	38.27250	-76.64083	no	yes

Table A2. PFAS Compounds tested for in water and tissue samples. RTI Labs Lancaster

Analyte	CAS #	MDL	LOQ/RL	Units
1H,1H,2H,2H-Perfluorodecanesulfonate	39108-34-4	0.0007	0.004	ug/L
1H,1H,2H,2H-Perfluorohexanesulfonate	757124-72-4	0.0006	0.004	ug/L
1H,1H,2H,2H-Perfluorooctanesulfonate	27619-97-2	0.0008	0.004	ug/L
N-ethyl perfluorooctanesulfonamidoacetic acid	2991-50-6	0.0014	0.004	ug/L
N-methyl perfluorooctanesulfonamidoacetic acid	2355-31-9	0.0009	0.004	ug/L
Perfluorobutanesulfonic acid	375-73-5	0.0012	0.004	ug/L
Perfluorobutanoic acid	375-22-4	0.0009	0.004	ug/L
Perfluorodecanesulfonic acid	335-77-3	0.0005	0.004	ug/L
Perfluorodecanoic acid	335-76-2	0.0006	0.004	ug/L
Perfluorododecanoic acid	307-55-1	0.0009	0.004	ug/L
Perfluoroheptanesulfonic acid	375-92-8	0.0007	0.004	ug/L
Perfluoroheptanoic acid	375-85-9	0.0006	0.004	ug/L
Perfluorohexanesulfonic acid	355-46-4	0.0005	0.004	ug/L
Perfluorohexanoic acid	307-24-4	0.0009	0.004	ug/L
Perfluorononanesulfonic acid	68259-12-1	0.0004	0.004	ug/L
Perfluorononanoic acid	375-95-1	0.0005	0.004	ug/L
Perfluorooctanesulfonic acid	1763-23-1	0.0005	0.004	ug/L
Perfluorooctanoic acid	335-67-1	0.0015	0.004	ug/L
Perfluorooctansulfonamide	754-91-6	0.0015	0.004	ug/L
Perfluoropentanesulfonic acid	2706-91-4	0.0007	0.004	ug/L
Perfluoropentanoic acid	2706-90-3	0.0007	0.004	ug/L
Perfluorotetradecanoic acid	376-06-7	0.0021	0.004	ug/L
Perfluorotridecanoic acid	72629-94-8	0.0007	0.004	ug/L
Perfluoroundecanoic acid	2058-94-8	0.0005	0.004	ug/L

Table A3. PFAS Compounds tested tissue samples. Eurofins lab

Analyte	MDL	RL	Units
Perfluorohexanoic acid	0.20	0.60	ng/g
Perfluoroheptanoic acid	0.20	0.60	ng/g
Perfluorooctanoic acid	0.20	0.60	ng/g
Perfluorononanoic acid	0.20	0.60	ng/g
Perfluorodecanoic acid	0.20	0.60	ng/g
Perfluorotridecanoic acid	0.20	0.60	ng/g
Perfluorotetradecanoic acid	0.20	0.60	ng/g
Perfluorobutanesulfonic acid	0.40	2.00	ng/g
Perfluorohexanesulfonic acid	0.20	0.06	ng/g
Perfluorooctanesulfonic acid	0.20	0.06	ng/g
NEtFOSAA	0.20	2.00	ng/g
NMeFOSAA	0.20	2.00	ng/g
10:2 FTS	0.60	2.00	ng/g
Perfluoropentanesulfonic acid	0.20	0.60	ng/g
Perfluoroheptanesulfonic acid	0.20	0.60	ng/g
Perfluorononanesulfonic acid	0.20	0.60	ng/g
Perfluorodecanesulfonic acid	0.20	0.60	ng/g
Perfluorododecanesulfonic acid	0.02	2.00	ng/g
Perfluorooctanesulfonamide	0.20	0.60	ng/g
Perfluorohexadecanoic acid	0.20	0.60	ng/g
Perfluorooctadecanoic acid	0.20	0.60	ng/g
Perfluorobutanoic acid	0.80	2.00	ng/g
Perfluoropentanoic acid	0.20	0.60	ng/g
NMeFOSE	0.50	2.00	ng/g
NMeFOSA	0.50	2.00	ng/g
NEtFOSE	0.50	2.00	ng/g
NEtFOSA	0.50	2.00	ng/g
HFPODA	0.40	2.00	ng/g
DONA	0.20	3.00	ng/g
9Cl-PF3ONS	0.20	2.00	ng/g
11Cl-PF3OUdS	0.20	0.60	ng/g
Perfluorododecanoic acid	0.20	0.60	ng/g
4:2 Fluorotelomer sulfonic acid	0.60	2.00	ng/g
Perfluoroundecanoic acid	0.20	0.60	ng/g
6:2 Fluorotelomer sulfonic acid	0.60	2.00	ng/g
8:2 Fluorotelomer sulfonic acid	0.60	3.00	ng/g

Detailed Sample Collection and handling protocol

COVID-19 distancing will be adhered to. Team members will remain at least six feet apart and wear face masks and eye protection. Nitrile gloves will be worn. No food will be on the work vessel. Potable water will be from artesian wells and in aged stainless-steel bottles and used for drinking only. While hand sanitizer will be onboard for use at any time, it will be kept in a dry box throughout the sample collections, only to be used after all samples are triple secured; the sample bottle is closed and labeled, and placed into doubled Ziploc bags.

Sampling will be completed by the Association's designated field team made up of one scientist, John, with sample collection training and experience. The second member of the team, Bob, will be an experienced vessel operator who has knowledge of oyster bars, river bathometry, and geomorphology. Sampling will occur on an outgoing or ebb tide, if practical, and be from a work vessel. The time and date for each sample collected will be recorded on the field data sheets.

This team will be provided with sampling containers for all PFAS samples and field blank, quart-size Ziploc bags, chain of custody data sheets, cooler for samples, and field collection instructions provided by RTI Labs. Additional Ziploc bags, 26 inch and elbow-length nitrile gloves, non-waterproof field data sheets, ultra-fine point permanent Sharpie writing utensil will be provided by the team.

Additionally, the team will be provided with a separate set of sampling containers for water quality data collection for use in the SMCM lab. They will also have a separate set of field data collection sheets and carry a YSI PRO 3200 for WQ determination each site: air and water temperature, salinity, and dissolved oxygen.

Instrument will be calibrated prior to use with fresh standards. A GPS with accuracy of +/– 2 meters will also be onboard and coordinates recorded for each sampling site.

The team will follow the sampling sheet instructions provided by RTI Labs in addition to EPA and DoD protocols for the collection of PFAS samples. The team will wear all cotton clothing that has been washed a minimum of 8 times – and laundered without fabric softeners at least 2 times. They will not have bathed in the previous 24 hours and they will not have worn or used since their last bath any deodorants, shaving creams, antiperspirants, cosmetics, antibiotics, sunscreens moisturizers, hand creams, or pesticides. Boots will be PVC rubber or polyurethane. If none, the team member will be barefoot.

FOR EACH SITE: All samples will be collected by John using two pairs of nitrile gloves for each site. Bob will not touch any samples, sampling gear, or containers. Collection at each site will begin with the water sample for RTI Labs – PFAS testing. Water will be collected at the bow of the boat using 26-inch Nitrile gloves from one foot below the surface. If not at slack tide, boat will be oriented down current.

The method will be dip sample bottle remove cover and cap at 12-in depth; pour contents of bottle into pre-labeled sample container containing preservative; cap sample bottle, agitate and place in Ziploc bags; and secure sample in PFAS sample cooler with ice. Two such water samples will be collected into two sample bottles. Next, three large oysters (target 3-inch or larger) will be collected using hand tongs. Using a clean pair of elbow-length nitrile gloves, John will shuck these oysters

allowing the liquor to drain and then place the composite tissue sample (about 20g) into a pre- labeled sample bottle. During this process of sample collection by John, Bob will record, using a pencil, onto the field data sheets GPS coordinates, date and time, and site name and number. After each sample for RTI Labs is collected, water quality sampling will commence. Water will be sampled one foot below the surface. John will verbally transmit water quality data to Bob and Bob will record on field data sheets. John will then collect a sample of surface water for analysis in the College lab. The sample bottle will be rinsed out several times with surface water prior to collecting the sample. He will label this sample and secure it in a separate carrying case, so as to keep RTI Lab samples discrete from in-house (College) samples.

Once completed for a site, John will verify that the data has been recorded accurately. The team will repeat this process for all sites in the sampling plan. Upon returning to the dock, John will take the RTI Labs – PFAS sampling field data sheet and place it along with chain of custody and samples collected into the RTI Labs supplied shipping container. At this point custody of the samples, field data sheets, and chain of custody sheets will go to Bob. Bob will make electronic copies of all sheets. Bob will hold the samples in a refrigerator at 42 degrees F overnight as per directions from RTI. The next morning, Bob will add ice (from well water) to the cooler, place a shipping label on the shipping container (shipped through Bob's Fedex account), and drop the package off at a Fedex pickup site in Lexington Park (Pak Mail). The package will be shipped Fedex Express to RTI Labs in Michigan. In-house samples will be refrigerated until such time that analysis can occur. Bob will make

electronic copies of the water quality field data sheets and provide John with the originals for the addition of lab analysis data, once testing has occurred.