

# **VIRGINIA WATER RESOURCES RESEARCH CENTER**

## **PFAS Monitoring Options to Evaluate Virginia's Surface Waters**

**2022 Report of the Academic Advisory Committee  
for  
Virginia Department of Environmental Quality**



### **SPECIAL REPORT**



**VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY  
BLACKSBURG, VIRGINIA**

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# **PFAS Monitoring Options to Evaluate Virginia's Surface Waters**

## **2022 Report of the Academic Advisory Committee for Virginia Department of Environmental Quality**

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## Acronyms, Abbreviations, and Symbols

°C – degree Celsius

°F – degree Fahrenheit

µg – microgram = one millionth of a gram = 1/1,000,000 gram

µg/kg – microgram per kilogram

µg/L – microgram per liter

# – number

% – percent = 1/100

C<sub>n</sub>F<sub>(2n+1)</sub>-R – per-fluoroalkyl compound

C<sub>n</sub>F<sub>(2n+1)</sub> – per-fluoroalkyl moiety

Σ – sum of

\$ – United States dollar

AAC – Academic Advisory Committee to Virginia Department of Environmental Quality

AFFF – aqueous film-forming foam

AOF – adsorbable organofluorines

ATSDR – Agency for Toxic Substances and Disease Registry

BAF – bioaccumulation factor; refers to the net accumulation of a chemical by an aquatic organism as a result of uptake from all environmental sources (e.g., water, food, sediment, soil). It is the ratio of the concentration of a contaminant in an organism to its concentration in the surrounding environment (e.g., water, sediment, soil).

BCF – bioconcentration factor; refers to the net accumulation of a chemical by an aquatic organism as a result of uptake directly from the ambient water, through gill membranes or other external body surfaces. It is the ratio of the concentration of a contaminant in an organism to its concentration in the surrounding water.

BMF – biomagnification factor; compares tissue concentrations within an organism with respect to tissue concentrations in the prey of the organism.

BSAF – biota-sediment accumulation factor; the ratio of the contaminant concentration in tissue to the contaminant concentration in sediment.

C7–C10 PFSA – perfluorooctanesulfonic acids (PFSA) with a chain length of 7 to 10 carbon atoms

C9–C14 PFCA – perfluorocarboxylic acids (PFCA) with a chain length of 9 to 14 carbon atoms

<sup>14</sup>C-PFOA – radiolabeled perfluorooctanoic acid (carbon-14 is a radioactive isotope of carbon with an atomic nucleus containing 6 protons and 8 neutrons)

CAS – Chemical Abstracts Service

CCL 4 – Contaminant Candidate List 4 = Currently not subject to any proposed or promulgated national primary drinking water regulations but are known or anticipated to occur in public water systems. EPA announced the Final CCL 4 on November 17, 2016.

CCL 5 – Contaminant Candidate List 5 = Currently not subject to any proposed or promulgated national primary drinking water regulations but are known or anticipated to occur in public water systems. EPA published the draft CCL 5 on July 19, 2021.

CDC – United States Centers for Disease Control and Prevention

cm – centimeter = 1/100 of a meter

DCR – Virginia Department of Conservation and Recreation

DOD – United States Department of Defense

dw – dry weight

DWR – Virginia Department of Wildlife Resources

EB – equipment rinse blank; reagent water processed through the sampling equipment in the field in the same manner as the actual water sample to determine if field procedures introduce contaminants into the samples. This is also known as a “rinse blank” or “field equipment blank.”

e.g. – Latin *exempli gratia*; meaning “for example”

EGLE – Michigan Department of Environment, Great Lakes, and Energy

EPA – United States Environmental Protection Agency

etc. – Latin *et cetera*; meaning “and so forth”

EU – European Union

F-53B – chlorinated polyfluorinated ether sulfonate (PFOS substitute)

FAA – United States Federal Aviation Administration

FB – field blank; reagent water exposed to the environment during field sample collection and processed in the laboratory. A field blank is used to document that contamination is not introduced during sample collection.

FOSA – perfluorooctane sulfonamide ( $C_8F_{17}SO_2NH_2$ )

FTOH – fluorinated telomer alcohol

FY – fiscal year

g – gram

GenX chemicals – chemicals used as replacements for perfluorooctanoic acid (PFOA); hexafluoropropylene oxide (HFPO) dimer acid and its ammonium salt are known as “GenX chemicals;” they are the two major chemicals associated with the GenX processing technology used to make high-performance fluoropolymers without the use of PFOA.

HASP – Health and Safety Plan

HB – House bill (Virginia House of Delegates)

HDPE – high-density polyethylene

HFPO – hexafluoropropylene oxide

HFPO-DA – hexafluoropropylene oxide dimer acid

i.e. – Latin *id est*; meaning “that is”

ITRC – Interstate Technology and Regulatory Council

kg – kilogram = 1,000 grams

km – kilometer = 1,000 meters

$K_{ow}$  – octanol-water partition coefficient; it indicates the tendency of an organic compound to adsorb to soil and living organisms; it is usually expressed as  $\log K_{ow}$ ;  $\log K_{ow}$  tends to be inversely related to water solubility and directly proportional to the molecular weight of a substance;  $K_{ow}$  = concentration in octanol/concentration in water

L – liter

LDPE – low-density polyethylene

L/kg – liter per kilogram

LOQ – limit of quantification = The lowest concentration of a substance determined by a given analytical procedure with the established accuracy, precision, and uncertainty.

MCL – maximum contaminant level = The legal threshold limit on the amount of a substance that is allowed in public water systems under the Safe Drinking Water Act.

MDEQ – Michigan Department of Environmental Quality (now Michigan Department of Environment, Great Lakes, and Energy or EGLE)

MDHHS – Michigan Department of Health and Human Services  
mg – milligram = one thousandth of a gram = 1/1,000 gram  
mg/kg – milligram per kilogram = 1 part per million  
mg/L – milligram per liter = 1 part per million  
mm – millimeter = one thousandth of a meter = 1/1,000 meter  
MRL – minimum reporting level; the smallest measured concentration of a substance that can be reliably measured using a given analytical method.  
n – sample size  
NFDHA – nonafluoro-3,6-dioxaheptanoic acid ( $C_5HF_9O_4$ )  
ng – nanogram = one billionth of a gram = 1/1,000,000,000 gram  
ng/kg – nanogram per kilogram = 1 part per trillion  
ng/L – nanogram per liter = 1 part per trillion  
NPDES – National Pollutant Discharge Elimination System  
NQ – not quantifiable  
NTN – nontidal network  
OBS – sodium p-perfluorooctanesulfonate ( $C_8F_{17}OC_6H_4SO_3Na$ )  
PDEP – Pennsylvania Department of Environmental Protection  
PFAA – perfluoroalkyl acid ( $C_8HF_{17}O_3S$ )  
PFAS – per- and polyfluoroalkyl substances ( $C_nF_{(2n+1)}-R$ )  
PFBA – perfluorobutanoic acid ( $C_4HF_7O_2$ )  
PFBS – perfluorobutane sulfonic acid ( $C_4HF_9O_3S$ )  
PFBuA – perfluorobutanoic acid ( $C_4HF_7O_2$ )  
PFC – perfluorinated compound  
PFCA – perfluoroalkyl carboxylic acid ( $C_nF_{(2n+1)}CO_2H$ )  
PFDA – perfluorodecanoic acid ( $C_{10}HF_{19}O_2$ )  
PFDaA – perfluorododecanoic acid ( $C_{12}HF_{23}O_2$ )  
PFDS – perfluorodecane sulfonic acid ( $C_{10}HF_{21}O_3S$ )  
PFHpA – perfluoroheptanoic acid ( $C_7HF_{13}O_2$ )  
PFHxA – perfluorohexanoic acid ( $C_6HF_{11}O_2$ )  
PFHxS – perfluorohexane sulfonic acid ( $C_6HF_{13}O_3S$ )  
PFNA – perfluorononanoic acid ( $C_9HF_{17}O_2$ )  
PFOA – perfluorooctanoic acid ( $C_8HF_{15}O_2$ )  
PFOS – perfluorooctane sulfonic acid ( $C_8HF_{17}O_3S$ )  
PFSA – perfluoroalkane sulfonates  
PFTeDA – perfluorotetradecanoic acid ( $C_{14}HF_{27}O_2$ )  
PFUnDA – perfluoroundecanoic acid ( $C_{11}HF_{21}O_2$ )  
pH – Describes the acidity or alkalinity of a solution on a logarithmic scale on which 7 is neutral, lower values are more acidic, and higher values more alkaline.  
pK<sub>a</sub> – acid dissociation constant; pK<sub>a</sub> is the negative log of the acid dissociation constant (K<sub>a</sub>) value. The more positive the value of pK<sub>a</sub>, the smaller the extent of dissociation at any given pH (Henderson–Hasselbalch equation) – that is, the weaker the acid. A weak acid has a pK<sub>a</sub> value in the approximate range of -2 to 12 in water.  
POCIS – polar organic chemical integrative sampler  
POTW – publicly owned treatment works  
ppb – parts per billion = 1/1,000,000,000 = µg/L or µg/kg  
ppm – parts per million = 1/1,000,000 = mg/L or mg/kg

ppt – parts per trillion =  $1/1,000,000,000,000 = \text{ng/L or ng/kg}$

PQL – practical quantitation level; the minimum concentration of an analyte that can be measured with a high degree of confidence that the analyte is present at the reported concentration.

ProbMon – probabilistic monitoring

PVC – polyvinyl chloride

QAPP – quality assurance project plan

QA/QC – quality assurance and quality control

QSM – Quality Systems Manual

RfD – reference dose

SPE – solid-phase extraction

TB – trip blank; reagent water collected in the same type of container used for the analytical test. It is meant to remain unopened and to accompany the sample containers throughout the sampling and shipping process.

TMDL – total maximum daily load

TMF – trophic magnification factor; the change in contaminant concentrations per trophic level.

TOP – total oxidizable precursors

TSV – tissue screening value

TV – tissue value

TWV – time-weighted average

UCMR 3 – Third EPA Unregulated Contaminant Monitoring Rule

UCMR 5 – Fifth EPA Unregulated Contaminant Monitoring Rule

UNEP-OECD – United Nations Environment Programme-Organisation for Economic Co-operation and Development

UPLC/MS/MS – ultrahigh performance liquid chromatography/tandem mass spectrometer

U.S. – United States

USAF – United States Air Force

USDON – United States Department of the Navy

USFAA – United States Federal Aviation Administration

USGS – United States Geological Survey

VA – Virginia

VBC – Virginia Biosolids Council

VDEQ – Virginia Department of Environmental Quality

VDH – Virginia Department of Health

VIMS – Virginia Institute of Marine Science

VMRC – Virginia Marine Resources Commission

VPDES – Virginia Pollution Discharge Elimination System

ww – wet weight

WWTP – wastewater treatment plant



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# 1. Introduction

## 1.1. Purpose

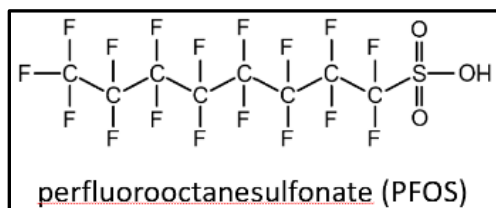
In response to emerging awareness and concern regarding the presence of per- and polyfluoroalkyl substances (PFAS) in Virginia's freshwaters, the Virginia Department of Environmental Quality (VDEQ) requested the Academic Advisory Committee (ACC) develop options for a VDEQ action plan on ambient monitoring of PFAS. The study aims to help the agency best determine how to evaluate water quality for the Commonwealth's surface freshwaters with regard to PFAS. This report details activities and findings of the ACC in fiscal year (FY) 2022.

The structure of this report follows the outline submitted to VDEQ in the AAC's FY 2022 work plan. Section 1 of this report describes the purpose of the work, defines PFAS, and provides background information on designated uses of Virginia's waters. Section 2 offers an overview of PFAS, including major sources of PFAS, how these substances move through the environment, and their impact on the environment and human health. Section 2 also describes current and recommended regulations and thresholds. Section 3 of the report highlights known occurrences of PFAS in Virginia's aquatic environment. The final section, Section 4, focuses on ambient monitoring of PFAS and methods of sample collection and analysis. The report summarizes monitoring approaches utilized by other states and describes ways to prioritize where and how frequently to monitor PFAS. The report concludes with recommendations for VDEQ.

## 1.2. Per- and poly-fluoroalkyl substances (PFAS)

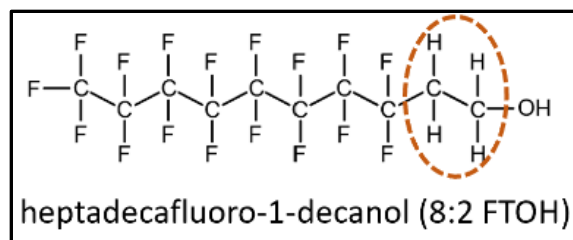
The acronym PFC represents two groups of fluorine-containing organic compounds:

- 1) Perfluorinated (perfluoro) compounds, in which all carbons, except those associated with functional groups, are fully fluorinated (all hydrogens attached to a carbon are substituted with fluorine atoms; see example in Figure 1);



**Figure 1.** Example of a perfluorinated compound, where all carbons are fully fluorinated unless associated with a functional group.

- 2) Polyfluorinated (polyfluoro) compounds, in which at least one carbon is fully fluorinated (see example in Figure 2; the carbons in the red dotted circle are not fluorinated).<sup>1, 2</sup>

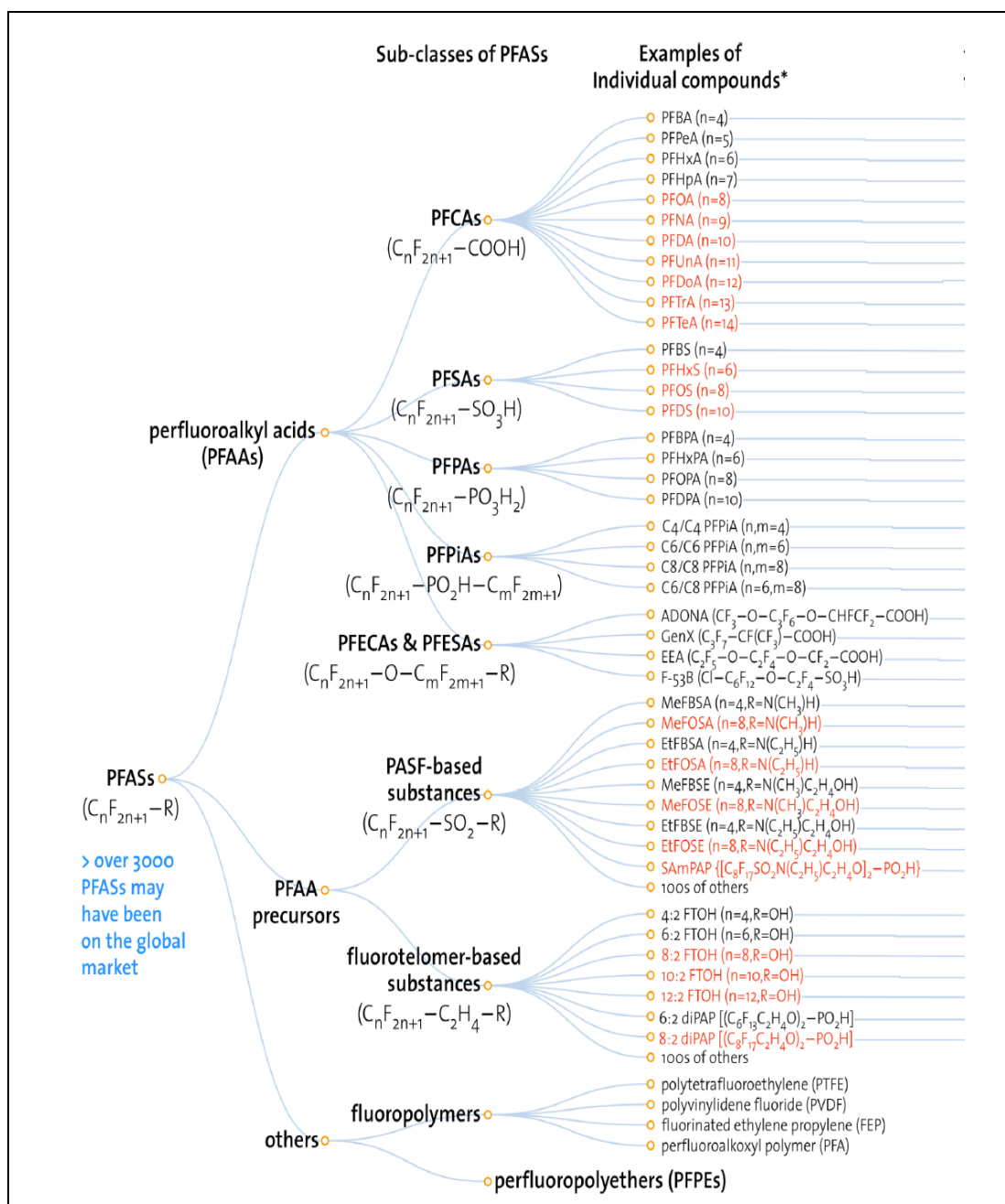


**Figure 2.** Example of a polyfluorinated compound, where at least one carbon is fully fluorinated. In this example, all carbons are fully fluorinated except the two in the red dotted circle.

Per- and polyfluoroalkyl substances (PFAS) are manufactured, fluorinated aliphatic (carbon chain) compounds, which are a subgroup of PFCs.<sup>3,4</sup> Examples of perfluoroalkyl substances are illustrated in Figure 3. Detailed information on PFAS terminology and classification can be found in a 2011 review paper by Buck and co-workers.<sup>3</sup> More information on chemical names and structures for PFAS is available in a 2020 document prepared by the Interstate Technology and Regulatory Council (ITRC).<sup>5</sup> Briefly, a per-fluoroalkyl compound is expressed by  $C_nF_{(2n+1)}-R$ , where,  $C_nF_{(2n+1)}$  represents the per-fluoroalkyl portion of the molecular structure. A poly-fluoroalkyl compound contains at least one per-fluoroalkyl moiety ( $C_nF_{(2n+1)}$ ) in its molecular structure. A poly-fluoroalkyl compound has the potential to be transformed abiotically or biotically into a per-fluoroalkyl compound by cleaving off the none-fluorinated portion from its structure.<sup>3</sup> For example,  $C_nF_{2n+1}SO_2NHCH_2CH_2OH$  (a polyfluoroalkyl compound) may degrade in the environment to  $C_nF_{2n+1}SO_3H$  (a perfluoroalkyl compound).

Substances having perfluoroalkyl chains with  $\geq 7$  carbons are termed long-chain PFAS.<sup>3</sup> Perfluoroalkyl carboxylic acids with  $\geq 8$  carbons and perfluoroalkane sulfonates with  $\geq 6$  carbons are also called long-chain PFAS.<sup>6</sup> Many PFAS are acids (perfluoroalkyl acids or PFAA, e.g., perfluoroalkyl carboxylic, sulfonic, sulfinic, phosphonic, and phosphinic acids). The PFAA may be present in protonated or anionic forms, or as a mixture of both, depending on the pH of the environmental matrix and the compound's acid dissociation constant ( $pK_a$ ). However,  $pK_a$  values for many PFAS are unknown.<sup>3,7</sup> Protonated and anionic forms of PFAA have very different physicochemical properties from their unprotonated forms. For example, protonated forms have higher water solubilities and lower vapor pressures compared to their unprotonated forms. These distinct characteristics result in different environmental behaviors and bioavailability.

Hexafluoropropylene oxide dimer acid (HFPO-DA) and its ammonium salt have been used in the manufacture of high-performance fluoropolymers, a specific class of PFAS. These substances are known as GenX chemicals because they are the two major chemicals associated with the GenX processing technology<sup>8,9</sup> that makes high-performance fluoropolymers without the use of perfluorooctanoic acid (PFOA). Similarly, perfluorobutane sulfonic acid (PFBS) and its potassium salt are a replacement for perfluorooctane sulfonic acid (PFOS), a chemical that was voluntarily phased out by its U.S. manufacturers.<sup>10</sup>



**Figure 3.** “Family tree” of per-fluoroalkyl substances, including examples of individual PFAS. Red text indicates PFAS that have been restricted under the national/regional/international regulatory or voluntary frameworks with or without specific exemptions.<sup>4</sup>

### 1.3. Designated uses of Virginia’s waters

Virginia Law (Administrative Code: 9VAC25-260-10) defines designation of uses of Virginia’s waters as the following:

*A. All state waters, including wetlands, are designated for the following uses: recreational uses, e.g., swimming and boating; the propagation and growth of a balanced,*

*indigenous population of aquatic life, including game fish, which might reasonably be expected to inhabit them; wildlife; and the production of edible and marketable natural resources, e.g., fish and shellfish.*

*B. Subcategories of the propagation and growth of a balanced indigenous population of aquatic life, including game fish designated use for waters in the Chesapeake Bay and its tidal tributaries are listed in this subsection including: 1) Migratory Fish Spawning and Nursery Designated Use; 2) Shallow-water Submerged Aquatic Vegetation Designated Use; 3) Open Water Aquatic Life Designated Use; 4) Deep Water Aquatic Life Designated Use; and 5) Deep Channel Seasonal Refuge Designated Use.*

The VDEQ's current statewide Water Quality Monitoring Program<sup>11</sup> consists of an integrated network of subprograms that vary in purpose and regional emphasis. The VDEQ's ambient water quality monitoring program is designed to produce representative data that support evaluation, restoration, and protection of the quality of the Commonwealth's waters for fishing, swimming, boating, drinking, and supporting healthy wildlife and aquatic organisms. Virginia's comprehensive water quality monitoring strategy integrates fixed-site (i.e., conventional) and probabilistic monitoring techniques, and both complement each other.

Monitoring for toxic pollutants in fish tissue is the most direct way that VDEQ assesses safety concerns regarding toxic pollutants in the waters of the Commonwealth. However, VDEQ may provide occasional support for cases of potential drinking water contamination, which is largely the responsibility of the Virginia Department of Health (VDH). Fish tissue monitoring can also be used to determine whether pollutants might pose potential risk to humans. The VDEQ uses a tiered approach in its Fish Tissue and Sediment Monitoring Program.<sup>11</sup> When financial support is sufficient, the program starts with Tier I screening that studies a relatively large number of sampling stations. Tier I screening is used to identify sites where concentrations of chemical contaminants in stream sediments and/or edible portions of commonly consumed fish species indicate potential aquatic ecosystem impairment and/or significant health risks to human consumers. When results from Tier I monitoring indicate contamination, a second more-intensive Tier II study is initiated to determine magnitude, geographical extent, and potential source(s) of contamination in the sediments and/or fish. If there is a budget constraint, the Tier II study (i.e., follow-up monitoring in areas with known contamination) is used more than the Tier I study.

According to VDEQ's water quality monitoring strategy,<sup>11</sup> criteria used to select Tier I sampling stations include the following:

- 1) Correspondence with VDEQ programs and offices to identify contaminated waste sites that may impact tissue and sediments in aquatic environments,
- 2) Regional office recommendations,
- 3) Extensive literature searches,
- 4) Important recreational and/or commercial fisheries,
- 5) Proximity to point source discharges,
- 6) Spatial distribution among sample stations, and
- 7) Requests from VDH.

Personnel with VDEQ report that stations could also be selected based on requests of the VDEQ Total Maximum Daily Load (TMDL) Program to provide data for TMDL development and implementation monitoring. In addition, stations could be selected based on correspondence with and monitoring requests made by agencies other than VDH, including Virginia Department of Wildlife Resources (DWR), Virginia Department of Conservation and Recreation (DCR), Virginia Marine Resources Commission (VMRC), Virginia Institute of Marine Science (VIMS), and EPA (D. Garey, personal communication, May 22, 2022). The final selection of Tier I sampling sites, however, can only be confirmed once field reconnaissance has been conducted.

According to the VDEQ's "Quality Assurance/Quality Control Project Plan for the Fish Tissue and Sediment Monitoring Program,"<sup>12</sup> Tier I sample stations are selected on a rotational river basin approach among the fourteen river basins or sub-basins in Virginia. State law requires a minimum of 24 fish tissue and sediment sample stations per year. Approximately 24-35 stations are usually selected among two river basins per year to provide adequate basin coverage.

If tissue values (TVs) or tissue screening values (TSVs) from Tier I monitoring exceed established water quality standards and measures of quality assurance and quality control (QA/QC) were achieved, then an intensive Tier II investigation may be conducted. Unique features of Tier II investigations include the following: 1) sample replication to increase statistical confidence around data points; and 2) multiple station sampling to characterize the contaminant's spatial distribution. As with Tier I data analyses, results from Tier II monitoring are compared to the risk-based TVs and/or TSVs calculations, and appropriate QA/QC procedures are followed.

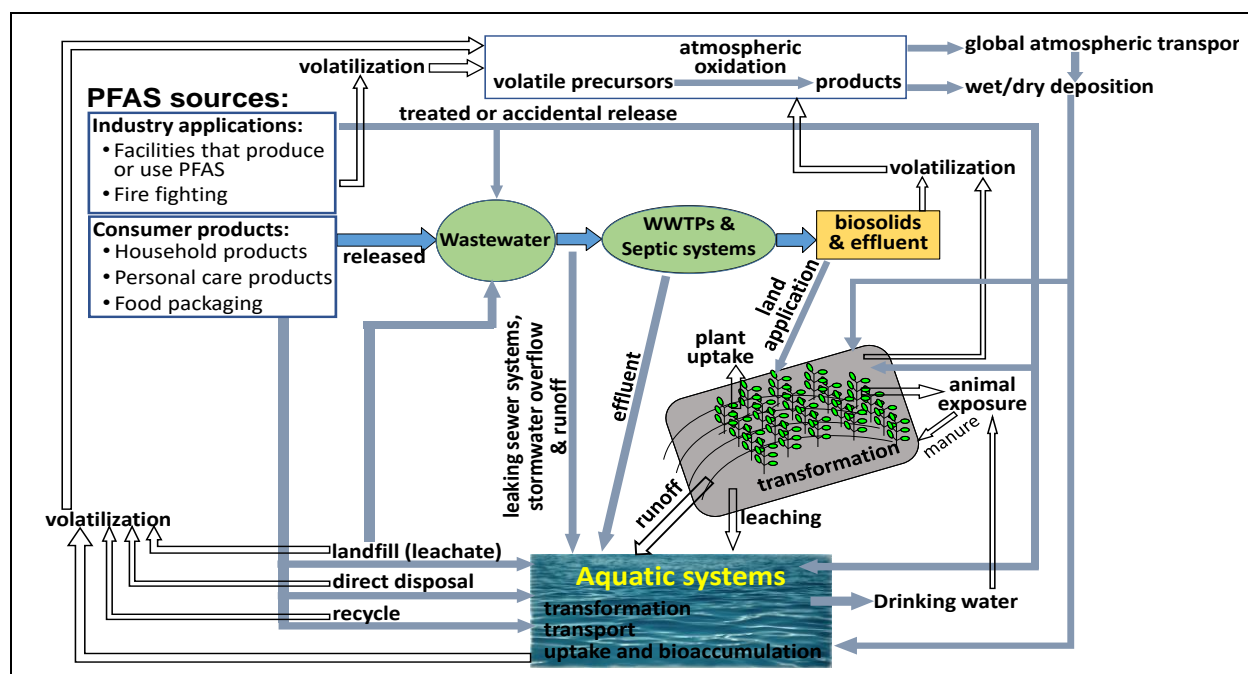
Since the late 1970s, VDEQ's tiered approach has been successfully used by its Water Quality Monitoring Program<sup>11</sup> to identify potential pollution concerns for organic and metal contaminants and to evaluate human health issues.<sup>13</sup> With adequate financial support, the same tiered approach would be appropriate for assessing occurrences of PFAS in Virginia's waters.

## **2. Per- and Poly-fluoroalkyl Substances – An Overview**

This section describes how PFAS were and continue to be used. Major sources of PFAS are identified, and investigative studies on the fate and transport of PFAS in water, biosolids, soils, atmosphere, and organisms are highlighted. Owing to the negative impacts of PFAS to human health and the environment, advisory thresholds and regulations are being developed by various states, the EPA, and other government agencies. This PFAS overview also provides information on the rapidly evolving subject of threshold and regulation development.

### **2.1. Major sources**

Since the 1940s, more than 4,000 PFAS<sup>3, 4</sup> have been produced and used within the global market in a wide range of industrial applications and consumer products (Figure 4).<sup>5</sup> Examples of industrial uses of PFAS include stain repellents for textiles, additives to paper products, and materials in aqueous film-forming foams (AFFFs) used to control electrical fires. Consumer products containing PFAS include cookware, food packaging, textile, furniture, cosmetics, cleaning products, etc.



*Figure 4. Sources and environmental pathways of PFAS.*

The major sources of PFAS are assumed to be localized and associated with industrial facilities where PFAS were/are produced or used to manufacture other products. Other sources include oil refineries (none in Virginia), airfields, closed and active military installations, industrial facilities, or other locations where PFAS were used for firefighting with AFFF.<sup>14-18</sup> The 2019 record by the Federal Aviation Administration (FAA) lists 81 active airfields in Virginia, 11 of which are for military use.<sup>19</sup> There are a total of 26 military installations in Virginia, several of which have identified potential contamination of PFAS in nearby groundwater.<sup>20, 21</sup> There are 16 firefighting training facilities in Virginia. To date, the focus has been on facilities where PFAS-containing products have been directly manufactured or used. The EPA has identified PFAS contamination at these five Virginia sites:<sup>22</sup> Fentress Air Base (Fentress), Oceana Naval Air Station (Virginia Beach), Northwest Annex (Chesapeake), NASA Wallops Island, and DuPont Spruance (Richmond).

Investigations have suggested that septic systems,<sup>23</sup> wastewater treatment plant (WWTP) effluents,<sup>24</sup> biosolids,<sup>25-27</sup> and legacy or current landfills<sup>28-30</sup> are other important sources of PFAS (Figure 4). Such sources contribute PFAS to aquatic systems, many of which are drinking water supplies. A 2012 survey estimated that municipal WWTPs throughout Virginia treated approximately 671 million gallons of wastewater per day and served more than 5.85 million Virginians.<sup>31</sup> The remaining 30% of Virginia's population uses septic systems. In 2016, a total of 64,508 dry tons of biosolids were spread on approximately 43,000 acres of farmland and forestland in Virginia, with additional usage for urban landscapes.<sup>32</sup> With increasing economic development and urban population growth in Virginia, the volume of WWTP effluent and the mass of biosolids generated are expected to increase. Such increases in WWTP effluent and biosolids would result in increased potential input of PFAS to Virginia's waters. Aging urban sewer distribution systems as well as stormwater overflow and runoff could be important routes



for PFAS to enter the aquatic environment,<sup>33</sup> especially for urban waters.<sup>34</sup> Furthermore, recycling and direct disposal of PFAS-containing consumer products may significantly contribute to the exposure and presence of PFAS in the environment.<sup>35-41</sup>

Although various PFAS were detected at concentrations up to parts per billion (ppb) in 95 leachate samples collected from 18 unnamed U.S. landfills,<sup>30</sup> it is unknown to what extent these compounds are present in the leachate of Virginia's landfills. Additionally, it is not known if PFAS have migrated from leachate into the groundwater or surface water. In 2020, 22.5 million tons of solid waste, approximately 63.5% of which was municipal solid waste and potentially contains PFAS,<sup>42</sup> were received at Virginia's permitted solid waste management facilities. Approximately 72.4% and 11.8% of the solid waste managed in Virginia was landfilled and incinerated onsite, respectively, for the 201 permitted landfill facilities throughout the Commonwealth.<sup>43</sup> Both active and inactive landfills can store decades of consumer wastes with a mixture of PFAS chemicals.<sup>44-46</sup> The extent to which PFAS leach from landfills into Virginia's waters via direct discharge remains unknown. In Virginia, landfill leachate is often hauled or piped to a WWTP for treatment. Landfills with direct discharge of leachate have individual permits. The VDEQ data on permitted landfills was not reviewed for this report. These data should be reviewed for additional information on PFAS.

Atmospheric deposition has recently been proposed as a significant source of PFAS to aquatic systems.<sup>47-51</sup> Although it is believed that the high temperature ( $\geq 1,000$  °C) used for solid waste incineration may completely destroy PFAS molecules, resulting in limited atmospheric contribution of PFAS,<sup>52</sup> a recent report by EPA stated that fate and transport of PFAS during incineration are not yet well understood.<sup>53</sup> Other research has shown evidence that at lower incineration temperatures, a significant portion of PFAS were converted to volatile PFAS,<sup>54</sup> and the specific profiles of volatile PFAS released depend on incineration temperatures and operating conditions.<sup>55, 56</sup> Furthermore, research has demonstrated that certain PFAS and their degradation products are semi-volatile in nature and can emit into the air from landfills. Thus, PFAS from landfills could contribute to additional atmospheric deposition.<sup>46, 57, 58</sup>

## **2.2. Environmental fate and pathways**

Once released into the environment through various pathways (Figure 4), PFAS are highly resistant to physical, chemical, and biological degradation because of the strong structural carbon-fluorine bonds they contain.<sup>59, 60</sup> For example, half-lives of 40 and 90 years in aquatic systems were reported for PFOA and PFOS, respectively.<sup>61</sup> Due to their high octanol-water partition coefficients ( $K_{ow}$ ),<sup>62</sup> many PFAS and their precursors have high partition potential into the solid phase during wastewater treatment processes. This property results in their accumulation in biosolids at levels up to parts per million (ppm) (dry weight, dw),<sup>25, 63</sup> whereas their levels are typically in parts per trillion (ppt, or ng/L) in WWTP effluents.<sup>64-67</sup>

The dominant PFAS in typical municipal biosolids (80–219 ppb, dw) as well as in biosolids-applied soils (2–483 ppb, dw) is PFOS.<sup>26</sup> Reported concentrations of all PFAS in soil increased linearly as the loading rate of biosolids increased. This study also demonstrated that the leaching potential of PFAS decreases with increasing chain length, suggesting higher transport potential for short-chain PFAS in soils amended with biosolids.<sup>26</sup> Furthermore, a variety of precursors in biosolids could be transformed to PFAS over time in soils applied with biosolids. Similar to

biosolids-applied soils, PFAS are also detectable in soils irrigated with WWTP effluent, although their levels are typically at ppt (dw) levels.<sup>68</sup>

A recent comprehensive study on a field with a long record of biosolids applications plus irrigation using treated wastewater<sup>69</sup> reported the presence of PFAS in surface soils, deeper soils into the vadose zone, and in the underlying groundwater. Twelve PFAS homologues were detected (ranging from 73 to 196 ppb, dw) in every near-surface soil sample ranging from 0–30 cm depth. Multiple PFAS (especially short-chain) were found distributed throughout the soil profile. Average measured concentrations of PFAS in these soils suggest the soil burden contained levels of PFOS > perfluorodecanoic acid (PFDA) > PFOA for all substations sampled. This pattern was independent of historical loading rates and agricultural operations at the substations. Measured concentrations of PFOA and PFOS in the soil profile suggest these compounds have migrated to deeper soil depths (up to 9 m below the surface). Quantifiable concentrations of PFOA and PFOS were found in the soil and underlying groundwater located approximately 17 m below the surface, with measured groundwater concentrations being 1 to 2 orders of magnitude less than soil concentrations. In addition, PFAS were also detectable in drainage ditches surrounding the field, suggesting potential for surface runoff and leaching.

A recent statewide spatiotemporal assessment<sup>70</sup> of PFAS in Iowa streams across a region of intense agricultural activity has reported at least one PFAS detected at ppt levels in 19 of the 60 streams sampled (32%), with 10 different PFAS detected statewide. The number of PFAS detected in the stream samples ranged from one to nine. The presence of PFAS in agricultural land potentially poses a risk of contamination to the food supply. Uptake of PFAS by different plant species (e.g., wheat, strawberry, carrot, lettuce) has been reported.<sup>71-73</sup>

A PFAS study included 32 surface soil samples collected from locations lacking direct human activity in North America (26 samples were from 18 states in the U.S., but none were from Virginia). Quantifiable levels of perfluoroalkyl carboxylates (PFCAs: perfluorohexanoic acid [PFHxA] and perfluorotetradecanoic acid [PFTeDA]) were found in all samples; total concentrations of PFCAs ranged from 29 ppt to 14.3 ppb (dw). Furthermore, quantifiable perfluoroalkane sulfonates (PFSAs: perfluorohexane sulfonic acid [PFHxS], PFOS, and perfluorodecane sulfonic acid [PFDS]) were found in all but one sample, and their concentrations ranged from below the limit of quantification (LOQ) to 3.27 ppb (dw).<sup>74</sup> This study reported that PFOA and PFOS were the most commonly detected analytes at concentrations up to 2.67 ppb for PFOA and 3.1 ppb for PFOS. It was suggested that atmospheric long-range transport of neutral PFAS followed by their oxidation and deposition provided a significant source of PFCAs and PFSAs to soils.

The atmosphere provides a medium for long-range transport and deposition of PFAS.<sup>75-77</sup> A recently published model<sup>78</sup> predicted that only 5% by mass of total emitted PFAS and 2.5% of total emitted GenX from a fluoropolymer manufacturing facility were deposited within ~150 km of the facility, with the remainder transported longer distances. The model predicted that PFAS with acid functionality have higher deposition due to enhanced water solubility and pH-driven partitioning to aqueous media. Once in the atmosphere, certain PFAS precursors can be oxidized into PFAS. For example, fluorinated telomer alcohols (FTOHs) and perfluorooctane sulfamido alcohols are present as residuals in some fluoropolymer products, and they can be released into

air because they are volatile.<sup>79</sup> Once in the air, FTOHs and fluorosulfamido alcohols can be atmospherically oxidized to form PFOA and PFOS, respectively.<sup>80, 81</sup> These substances can be deposited elsewhere later through rainfall.<sup>82-84</sup> Research suggests PFAS atmospheric deposition can be a major contributor to their presence in soil and surface waters.<sup>85-87</sup> Furthermore, some long-chain PFAS concentrations in street runoff equaled or exceeded their concentrations in wastewater influents.<sup>88</sup> Such findings suggest that stormwater runoff can be a significant contributor of PFAS in surface water.<sup>89-92</sup>

### **2.3. Environmental and human health impacts**

Of the long list of PFAS (Figure 3), the following have attracted worldwide regulatory attention since the 2000s owing to their persistence and their human and environmental health concerns:

- perfluoroalkyl carboxylic acids (PFCAs) with seven or more perfluorinated carbons;
- perfluoroalkane sulfonic acids (PFSAs) with six or more perfluorinated carbons; and
- individual compounds of PFCAs and PFSAs, in particular perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS).<sup>4, 93-96</sup>

Production of most long-chain PFAS has been phased out in the U.S., but long-chain PFAS are still produced and used elsewhere. In the U.S., the production of shorter-chain PFAS and GenX chemicals have replaced, in general, long-chain PFAS. These replacement chemicals include HFPO-DA (to replace PFOA) and its ammonium salt and perfluorobutane sulfonic acid (PFBS, a replacement for PFOS). However, there are also health concerns related to these replacement chemicals.<sup>97</sup>

Due to having both hydrophobic and lipophobic qualities as well as chemical and thermal stabilities, PFAS are stable and widely distributed in various environmental conditions. Because of their stability, bioaccumulation of PFAS can be significantly magnified up the trophic food chain of aquatic organisms (Table A1 of the Appendix).<sup>98-100</sup> There is substantial bioaccumulation potential for PFAS that varies among individual compounds, organisms, and species. For example, a recent comprehensive review paper<sup>100</sup> found that fish whole-body bioaccumulation factors (BAFs) for PFOS varied from 10 L/kg to 100,000 L/kg with a median value of 3,548 L/kg ( $n = 84$ ), and BAFs for PFOA ranged from 1 L/kg to 10,000 L/kg with a median value of 145 L/kg ( $n = 48$ ). This study also stated that in comparison with freshwater species, data are limited for marine species, and further research is needed. Distribution of PFAS also varies among different tissues of the same organism, and this distribution can be different depending on if the mode of PFAS intake is dietary or aqueous.<sup>99, 100</sup> Biodistribution in fish tissue follows the order of liver > blood > kidney when diet is the route of PFAS exposure to fish; however, this order is blood > kidney > liver when fish are exposed to PFAS-contaminated water. There is evidence that both phospholipids and proteins are important for tissue partitioning and accumulation of PFAS.<sup>101</sup> Bioaccumulation potential of PFAS depends both on the active transport mechanisms of PFAS in an organism and on the physicochemical properties of the particular PFAS compound.<sup>102</sup> For example, those PFAS with high  $K_{ow}$  values are highly bioaccumulative in the environment.<sup>62</sup> Exposure assessment for PFAS is complicated by the presence of PFAS precursors and their transformation products, which can occur both in the environment and within organisms.<sup>103</sup>

Detailed information on environmental exposure and health impacts can be found in a number of review papers.<sup>99, 101, 104-106</sup> Numerous investigations have reported high concentrations of PFAS in invertebrates, fish, reptiles, aquatic birds, and marine mammals worldwide. Predominant PFAS detected include PFOS (mean concentrations up to 1,900 ppb wet weight [ww]) and long-chain perfluoroalkyl carboxylates (PFCAs; sum of PFCAs up to 400 ppb ww).<sup>107</sup> A recent review<sup>99</sup> describes various impacts of PFAS on aquatic organisms and summarizes the ecotoxicity of several common PFAS for algae, invertebrates, fishes, and amphibians. Consumption of aquatic organisms contaminated with PFAS by humans and wildlife would move the substances further up the food chain.

The most recent comprehensive information on human exposure to PFAS and health impacts of PFAS is provided by a number of review papers<sup>101, 108-110</sup> and summarized by the ITRC,<sup>5</sup> the EPA,<sup>111</sup> and other federal agencies.<sup>112, 113</sup> Diet and drinking water have been suggested to be the major sources of human exposure to PFAS.<sup>101, 114</sup> Almost all residents of the U.S. and other industrialized nations have accumulated PFAS in their blood at low ppb levels.<sup>115-121</sup> The EPA stated the following with regards to human exposure to PFAS:

*Most people in the United States have been exposed to some PFAS. Most known exposures are relatively low, but some can be high, particularly when people are exposed to a concentrated source over long periods of time. Some PFAS chemicals can accumulate in the body over time. Current research has shown that people can be exposed to PFAS by: 1) Working in occupations such as firefighting or chemicals manufacturing and processing; 2) Drinking water contaminated with PFAS; 3) Eating certain foods that may contain PFAS, including fish; 4) Swallowing contaminated soil or dust; 5) Breathing air containing PFAS; and 5) Using products made with PFAS or that are packaged in materials containing PFAS.*<sup>111</sup>

Regarding the human health impacts of PFAS, the EPA stated the following:

*Exposure to certain levels of PFAS may lead to: 1) Reproductive effects such as decreased fertility or increased high blood pressure in pregnant women; 2) Developmental effects or delays in children, including low birth weight, accelerated puberty, bone variations, or behavioral changes; 3) Increased risk of some cancers, including prostate, kidney, and testicular cancers; 4) Reduced ability of the body's immune system to fight infections, including reduced vaccine response; 5) Interference with the body's natural hormones; and 6) Increased cholesterol levels and/or risk of obesity.*<sup>111</sup>

#### **2.4. Current and recommended regulations and thresholds**

Regulations on PFAS and evidence of their adverse human and environmental health impacts are rapidly evolving.<sup>29, 95, 122, 123</sup> Comprehensive background information on PFAS and ongoing research by EPA, the Centers for Disease Control and Prevention (CDC), and Agency for Toxic Substances and Disease Register (ATSDR) is available.<sup>7, 124, 125</sup> A summary of actions taken by EPA pertaining to PFAS since 2016 includes the following:

- 2016 – Listed PFOA and PFOS in fourth Contaminant Candidate List (CCL 4) for public drinking water systems.<sup>126</sup>
- 2016 – Established a lifetime health advisory level in drinking water of 70 ppt for PFOA and PFOS, individually, or in combination.<sup>127, 128</sup>
- 2019 – Set an interim screening level for groundwater at sites contaminated with PFOA and PFOS at 40 ppt.<sup>129</sup>
- 2019 – Published a PFAS action plan that includes development of maximum contaminant levels (MCL) for PFOA and PFOS and offers to assist states, tribes, and communities in addressing PFAS.<sup>130</sup>
- 2019 – Released draft toxicity assessments for GenX chemicals (HFPO-DA and its ammonium salt)<sup>131</sup> and PFBS.<sup>132</sup>
- 2021 – Listed multiple additional PFAS in fifth CCL (CCL 5) for drinking water systems.<sup>133</sup>
- 2021 – Included 29 PFAS in the fifth Unregulated Contaminant Monitoring Rule (UCMR 5) to be monitored by public water systems.<sup>134</sup>
- 2021 – Published regulatory determinations for contaminants on CCL 4, which includes a final determination to regulate PFOA and PFOS in drinking water.<sup>135</sup>
- 2022 – Proposing National Primary Drinking Water Regulations for PFOA and PFOS (expect final regulation in Fall 2023).<sup>136</sup>
- 2022 – Evaluating additional PFAS and considering regulatory actions to address groups of PFAS.<sup>136</sup>

A 2021 paper<sup>137</sup> provided a comprehensive review on approaches used by many state and federal environmental and health agencies to develop criteria to characterize and assess the risk from exposures to PFAS. However, criteria developed by different U.S. federal and state agencies varied widely and are evolving rapidly. For example, drinking water criteria developed for PFOA varied among different states from 2 ppt to 667 ppt. This wide range of selected criteria can be attributed to numerous factors, including:

- differences and variability in the data and information used,
- study/endpoint selection,
- assumptions and magnitude of uncertainty factors used in absence of and extrapolation of critical effect data,
- differences in underlying approaches to addressing exposure within criteria development, and/or
- policy decisions on levels of acceptable risk.<sup>137</sup>

The ITRC has provided a current list and status of state and federal standards and guidance values for PFAS in groundwater, drinking water, and surface water/effluent (wastewater) and in residential soil.<sup>7</sup> Currently, EPA, 29 U.S. states (but not Virginia), the European Union (EU), and nine countries have established advisory standards for PFAS in drinking water, groundwater, and/or surface water. Some of the state advisory standards are stricter (as low as 2 ppt) compared to the EPA advisory levels (70 ppt for PFOA and PFOS, individually, or in combination) and include other PFAS in addition to PFOA and PFOS (up to 24 compounds, including GenX). Some state advisory limits are less strict (up to 300 ppt) compared to the EPA advisory and are focused only on PFOA and PFOS.<sup>7</sup> Although Virginia does not currently have drinking water standards for PFAS, Chapter 1097 of the 2020 Acts of Assembly directs the Board of Health to adopt regulations establishing MCLs for PFOA, PFOS, and other PFAS as deemed necessary (HB 1257).<sup>138</sup>

Thirteen states have established soil screening levels and/or standards for groundwater and surface water protection (0.0006–10 ppm for PFOA and 0.00024–0.4 ppm for PFOS), and 21 states have established human health soil screening levels (0.00066–35 ppm for PFOA and 0.00088–3.2 ppm for PFOS).<sup>7</sup> At the international level, five countries have established soil-related standards. Levels to protect human health have also been recommended by the Environmental Quality Standards in the EU<sup>139</sup> and by the Great Lake Consortium for PFOS in fish, including fish consumption advisories.<sup>140</sup> The Great Lake Consortium used an uncertainty factor of 30 and the 2016 EPA reference dose (RfD) of  $2 \times 10^{-5}$  mg/kg/day to derive their 50 µg/kg for “one-meal-per-week” advice and 200 µg/kg for triggering “don’t-eat” advice.<sup>140</sup>

### **3. Occurrence of PFAS in Virginia’s Aquatic Environment**

A literature review<sup>62</sup> summarizing PFAS-related publications between 2009 and 2017 has identified 455 PFAS compounds, of which approximately 45% are anionic (negatively charged), 29% are zwitterionic (containing separate positively and negatively charged groups), 17% are cationic (positively charged), and 8% are neutral compounds. Some of the identified PFAS are potential precursor compounds of PFOA and PFOS. Throughout the world, various PFAS have been detected in drinking water,<sup>16</sup> natural waters,<sup>141, 142</sup> aquatic organisms,<sup>143-145</sup> sediments,<sup>63, 142</sup> wastewater,<sup>24</sup> biosolids,<sup>25-27</sup> and soils.<sup>74</sup> However, there is limited information on their occurrence in Virginia’s aquatic environment.

#### **3.1. Surface water and sediment**

Published concentrations of PFAS in surface water and sediment samples vary widely, ranging over more than seven orders of magnitude. Reported median levels of PFAS in aquatic systems worldwide are up to several hundred ppt (ng/kg, dw) in sediments, whereas their levels rarely exceed one hundred ppt (ng/L) in surface water; this finding suggests an overall tendency to accumulate in sediments.<sup>146</sup> Compared to reported levels of PFAS in aquatic systems elsewhere in the world, aquatic systems in the U.S. have the highest average levels of PFAS.<sup>146</sup> Information is lacking on the occurrence of PFAS in Virginia’s surface waters and sediment.

Variability in  $K_{ow}$  values among PFAS would likely lead to a higher occurrence of certain isomers within different phases. For example, more linear and longer-chain isomers, which have higher  $K_{ow}$  compared to those with more branched and shorter-chain isomers, are likely to occur

more frequently in organic matter fractions of sediment. Shorter-chain, branched congeners are more likely to occur in the aqueous phase.<sup>147</sup>

In 2019, discrete samples from 178 Pennsylvania water quality network stations were analyzed for 33 PFAS chemicals and 19 total oxidizable precursors (TOP). Passive samplers were deployed at 18 sites across Pennsylvania and analyzed for the same 33 PFAS chemicals.<sup>148</sup> Samples came from stream, river, and Lake Erie sites. This investigation found up to 10 PFAS in discrete samples from several sites and 18 PFAS in two passive samples. The highest total PFAS concentrations and all PFOS + PFOA results from discrete samples were below the EPA's drinking water lifetime health advisory level of 70 ng/L. The highest PFOS + PFOA time-weighted average (TWA) concentration from the passive samples was 212 ng/L at one site. Similar investigation is needed in Virginia's waters.

### **3.2. *Aquatic organisms, including fish tissue***

Recent assessments show widespread detection of PFAS in various aquatic organisms, including PFAS with a wide range of chain lengths and configurations and their precursors. The predominant PFAS found in all species, tissues, and locations analyzed worldwide is PFOS (mean concentrations up to 1.9 ppm [ww]), followed by long-chain PFCAs ( $\Sigma$ PFCAs up to 400 ppb [ww]).<sup>107</sup> The only record<sup>149</sup> of detection of PFAS in Virginia aquatic organisms was published in 2004. This study sampled osprey eggs from the Elizabeth River and the Middle Potomac River and reported detection of PFOA, PFOS, PFDA, and PFDS at up to several hundred ppb (ww) (Table A2 of the Appendix).

### **3.3. *Groundwater***

As shown in Table A2 in the Appendix, a 2016 Navy investigation reported detection of PFOA and PFOS above the EPA lifetime health advisory level in monitoring wells and on-base drinking-water supply wells at the Naval Auxiliary Landing Field Fentress (Chesapeake, Va.) and in some private wells located off site. Similar monitoring results (Table A2 of the Appendix) were reported for the on-site monitoring wells at the Naval Air Station Oceana (Virginia Beach, Va.) that is 12 miles north of the Naval Auxiliary Landing Field Fentress. The source of the PFAS at both sites is AFFF used for firefighting training activities conducted at the sites. The U.S. Navy is continuing to monitor the levels of PFAS in the groundwater and drinking water at those sites. The temporal and spatial changes of the levels of PFAS in the groundwater at the two sites are currently unknown.

### **3.4. *Public water supply and distribution systems***

Although PFAS are used in a variety of products that are potential sources for human exposure,<sup>150, 151</sup> one of the major sources for human exposure to PFAS is likely PFAS-contaminated drinking water.<sup>152</sup> It has been estimated that drinking water supplies for 6 million U.S. residents exceed EPA's lifetime health advisory for PFOA and PFOS (70 ppt, individually or combined).<sup>16</sup>

A 2016 publication<sup>16</sup> that summarizes publicly available concentration data from the UCMR 3<sup>127</sup> reported detection of PFOA and PFOS in drinking water samples collected from water utilities in central and eastern Virginia. Concentrations in these samples were reported at 20–70 ppt for PFOA and at 40–200 ppt for PFOS. However, a close inspection of the original

UCMR 3 data showed levels in all tested Virginia drinking water samples below the minimum reporting level (MRL) of 20 ppt for PFOA and 40 ppt for PFOS. Levels of other tested PFAS were also below the MRL, e.g., MRLs for other tested PFAS: perfluorononanoic acid (PFNA) = 20 ppt, perfluoroheptanoic acid (PFHpA) = 10 ppt, PFHxS = 30 ppt, and PFBS = 90 ppt.

Chapter 611 of the Virginia 2020 Acts of Assembly (HB 586) required the Commissioner of Health to convene a work group to study the occurrence of PFOA, PFOS, perfluorobutanoic acid (PFBA), PFHpA, PFHxS, PFNA, and other PFAS, as deemed necessary, in the Commonwealth's public drinking water.<sup>153</sup> Forty-five waterworks (forty with surface water sources; five with groundwater sources) participated in the study,<sup>154</sup> resulting in a total of 63 water samples collected from one or more locations. Results from the study found PFAS in quantities above the practical quantitation level (PQL) of 3.5 ppt at 15 of 63 sample locations. Samples from 48 collection sites did not contain any PFAS or, if PFAS were present, they were below the PQL. Specifically, the results indicate that PFAS are present above the PQL in drinking water produced from the Potomac River and Occoquan Reservoir, two major sources of water for waterworks in Northern Virginia. Ten samples from waterworks in the Northern Virginia region had at least one PFAS present in a quantity above the PQL, but none were above the EPA lifetime health advisory level of 70 ppt for PFOA and PFOS (individually or combined), and none exceeded any MCL established by other states. A GenX chemical, HFPO-DA, was detected in only two tested samples, one at 57 ppt in a sample from the Western Virginia Water Authority's Spring Hollow water treatment plant and the other at 4.0 ppt in a sample from the Town of Altavista. No other PFAS were detected above the PQL at the two locations with GenX detections. All other PFAS detections were 14 ppt or less. This study also pointed out that with more than 1,050 community waterworks in Virginia, the majority of which are classified as "small" (i.e., serving fewer than 3,300 consumers), the extent and level of PFAS contamination in drinking water from waterworks is still largely unknown.

## **4. Ambient Water Monitoring of PFAS**

### **4.1. Frequently monitored PFAS**

Historically, PFOA and PFOS have been the focus of many ambient water investigations.<sup>124-128</sup> With time, more and more PFAS, including GenX chemicals, have been added in the target analyte list for testing environmental samples.<sup>129-132</sup> Currently, there are four major EPA analytical methods for testing PFAS in environmental samples. The EPA Methods 533<sup>155</sup> and 537.1<sup>156</sup> are designed for drinking water and test for 25 and 18 PFAS, respectively. Using both methods, a total of 29 unique PFAS can be effectively measured in drinking water. The EPA Method 8327<sup>157</sup> has been tested for 24 PFAS in surface water, groundwater, and wastewater matrices. The EPA draft Method 1633<sup>158</sup> is a single-laboratory validated method to test for 40 PFAS compounds in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue. Draft Method 1633 is the only EPA method that addresses ambient water monitoring samples. This draft method can be used in various applications, including National Pollutant Discharge Elimination System (NPDES) permits. Comparison of all four EPA methods and grouping of the PFAS can be found in Table A3 of the Appendix. Additional methods developed by other agencies are summarized by the ITRC.<sup>7</sup>



## 4.2. Sampling, handling, processing, and analytical methods

Detailed sampling, handling, and processing methods for surface water, sediment, and fish tissue are outlined in EPA draft Method 1633<sup>158</sup> and in guidance documents developed by the PFAS Action Response Team of the Michigan Department of Environment, Great Lakes, and Energy (EGLE) Water Resources Division (Table A4 of Appendix). Additionally, the *National Field Manual for the Collection of Water-Quality Data* by the U.S. Geological Survey (USGS) should be consulted when finalizing the protocols for sample collection, handling, and processing.<sup>159</sup>

The following sections summarize key points stated in both the EPA draft Method 1633 and the Michigan PFAS monitoring methods. Because analytical methods for PFAS compounds are at the ppt level and PFAS are in many products, including personal care products, clothing, and containers, precautions must be taken diligently to prevent false positives due to cross-contamination during sampling, handling, processing, and analysis.<sup>160</sup> Both methods recommend to verify that any items or materials used during any part of the process, even those that will not come into direct contact with the sample, be PFAS-free; this verification is recommended even when PFAS are not listed as the active or inactive ingredients. Reagent water free of PFAS should be used for all QA/QC samples, which are pre-defined in the pre-sampling and objective-specific Quality Assurance Project Plan (QAPP).<sup>160</sup>

Commonly used PFAS analytical methods are the EPA Methods 533,<sup>155</sup> 537.1,<sup>156</sup> 8327,<sup>157</sup> and 1633<sup>158</sup> (draft). The Department of Defense (DOD) methods, DOD QSM 5.3<sup>161</sup> and 5.4<sup>162</sup> have also been used by some commercial laboratories. The EPA draft Method 1633 is recommended for the proposed ambient water PFAS monitoring in Virginia because this method is designed for testing of PFAS in wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue.

### 4.2.1. Surface water

Michigan's "Surface Water PFAS Sampling Guidance"<sup>163</sup> states the following: "A preferred sampling sequence should be established prior to any sampling event to reduce the risk of cross contamination. In general, the sampling sequence should begin in areas expected or known to be least contaminated, proceeding to anticipated areas or identified to be most contaminated." The decision on sampling sequence can be determined based on 1) past testing results; and 2) site information on possible PFAS uses and potential PFAS migration patterns. Table 1 provides a summary of key recommendations from the Michigan guidance on preventing PFAS cross contaminations.<sup>163</sup> Field sampling equipment that is in direct contact with samples and used at multiple sites or sampling locations should be decontaminated using the materials listed in Table 1. The guidance further advises, "When boats are used on rivers, samples should always be collected on the upgradient side of the boat."

**Table 1. Recommendation for surface water monitoring program to prevent PFAS cross contamination<sup>163</sup>**

Materials of tubing, equipment, containers, and supplies	Materials for decontamination	Sample collection, preservation, treatment, and storage	Other suggestions
<ul style="list-style-type: none"> <li>• High-density polyethylene (HDPE)</li> <li>• Low-density polyethylene (LDPE) tubing</li> <li>• Polypropylene</li> <li>• Silicone</li> <li>• Stainless-steel</li> <li>• Any items used to secure sampling bottles made from: natural rubber; nylon (cable ties), uncoated metal springs; and polyethylene</li> </ul>	<ul style="list-style-type: none"> <li>• Alconox<sup>®</sup>, Liquinox<sup>®</sup>, or Citranox<sup>®</sup></li> <li>• Triple rinse with PFAS-free deionized water</li> <li>• Cotton cloth or untreated paper towel</li> <li>• Polyethylene or polyvinyl chloride (PVC) brush to remove particulates</li> <li>• Commercially available deionized water in an HDPE container if the water is verified to be PFAS-free</li> <li>• Municipal drinking water if it is known to be PFAS-free</li> </ul>	<ul style="list-style-type: none"> <li>• Wash hands and wear a fresh pair of powderless nitrile gloves</li> <li>• Collect samples on the upgradient side of a boat</li> <li>• Use preprinted labels</li> <li>• HDPE or polypropylene sample bottles with Teflon<sup>®</sup>-free caps (linerless HDPE or polypropylene caps)</li> <li>• Set the cap on a clean surface (cotton sheeting, HDPE sheeting, triple rinsed cooler lid, etc.)</li> <li>• Bottles should be opened immediately prior to sampling and capped immediately after collecting the sample</li> <li>• Double bag a sample bottle using resealable LDPE storage bags (i.e., Ziploc<sup>®</sup>)</li> <li>• Use regular wet ice in cooler for temporary sample storage and shipment</li> <li>• Must not exceed 50 °F (10 °C)</li> </ul>	<p><b><i>Allowable:</i></b></p> <ul style="list-style-type: none"> <li>• Loose paper (non-waterproof, non-recycled)</li> <li>• Rite in the Rain<sup>®</sup> notebooks</li> <li>• Aluminum, polypropylene, or masonite field clipboards</li> <li>• Ballpoint pens, pencils, and fine or ultra-fine point Sharpie<sup>®</sup> markers</li> <li>• List of allowable sunscreens, and insect repellents (applied in the staging area, away from sampling bottles and equipment followed by thoroughly washing hands) can be found in reference 163</li> </ul> <p><b><i>Need to be screened to ensure PFAS free before use:</i></b></p> <ul style="list-style-type: none"> <li>• Plastic clipboards, binders, or spiral hard cover notebooks</li> <li>• All markers not listed as allowable</li> <li>• Post-It<sup>®</sup> Notes or other adhesive paper products</li> </ul>

		<p>during the first 48 hours after collection</p> <ul style="list-style-type: none"> <li>• Ship by overnight courier</li> <li>• Glass filters are recommended to be used for filtering samples or use of a centrifuge in the laboratory to replace filtering</li> </ul>	<ul style="list-style-type: none"> <li>• Waterproof field books</li> <li>• Municipal water</li> <li>• Recycled paper towels or chemically treated paper towels</li> <li>• Latex gloves</li> <li>• Water and/or dirt resistant leather gloves</li> <li>• Any special gloves required by a Health and Safety Plan (HASP)</li> <li>• Tyvek<sup>®</sup> suits, clothing that contains Tyvek<sup>®</sup> or coated Tyvek<sup>®</sup></li> <li>• Aluminum foil</li> <li>• Chemical or blue ice</li> <li>• Plastic storage bags other than those listed as allowable</li> <li>• LDPE bottles</li> </ul> <p><b><i>Precautions:</i></b></p> <ul style="list-style-type: none"> <li>• Wear PFAS-free clothing, personal protective equipment, and personal care products<sup>163</sup></li> <li>• Brought and consumed food only outside the vicinity of the sampling area</li> <li>• Bottled water</li> <li>• Hydration drinks (i.e., Gatorade<sup>®</sup>, Powerade<sup>®</sup>)</li> </ul>
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Depending on sampling depths, different surface water sampling methods are listed in Michigan's "Surface Water PFAS Sampling Guidance"<sup>163</sup> (Table 2). The guidance<sup>163</sup> recommends that: *"Unless specifically required by the project objectives, surface water samples should not be taken at the top layer of the water body or of surface scums. PFAS are expected to accumulate at the surface water air interface or be present in the surface runoff, so samples taken at the surface are likely to result in high biased results that are not representative of the bulk surface water."*

<b>Table 2. Most frequently used surface water sampling methods<sup>163</sup></b>		
<b>Depth to Surface Water</b>	<b>Sample Locations</b>	<b>Sampling Method</b>
0–5 feet	Streams, rivers, creeks, tributaries, lakes, lagoons, ponds, and impoundments	Direct method, swing, telescoping, and Van Dorn, depth integrating samplers
>5 feet	Large streams, rivers, tributaries, lakes, lagoons, ponds, and impoundments	Peristaltic pump, swing, telescoping, Van Dorn, Kemmerer, and depth integrating samplers

Polar organic chemical integrative samplers (POCIS) were used by the USGS and Pennsylvania Department of Environmental Protection (PDEP) to monitor the presence of PFAS in surface water at 18 sites across Pennsylvania.<sup>148</sup> The passive samplers provided time-weighted average concentrations from one-month deployments. The POCIS are comprised of microporous polyethersulfone membranes with a solid phase sorbent (Oasis HLB) that samples hydrophilic contaminants.

The EPA draft Method 1633<sup>158</sup> recommends the following: Aqueous samples should be analyzed as soon as possible; however, samples may be held in the laboratory for up to 90 days from collection before extraction when stored at  $\leq -20^{\circ}\text{C}$  and protected from light. When stored at  $0\text{--}6^{\circ}\text{C}$  and protected from light, aqueous samples may be held for up to 28 days before extraction, with the caveat that samples do not have perfluorooctane sulfonamide ethanols and perfluorooctane sulfonamidoacetic acids (Table A3). When these chemicals are present, samples need to be extracted within 7 days because their transformation in the samples may result in elevated concentrations of other PFAS compounds.

As stated in EPA draft Method 1633:<sup>158</sup> 1) typical sample size is 500 mL; however, sample size may be up to 1,000 mL; 2) for aqueous samples that contain particles and solid samples, percent solids should be determined using a separate sample collected in a 250-mL or 125-mL container; 3) smaller sample volumes may be acceptable for samples containing solids greater than specified for this method, or when unavoidable due to high levels of PFAS; 4) a collected sample containing  $< 50$  mg suspended solids/sample should be used in its entirety without filtering before further extraction and cleanup of matrix background interferences; and 5) subsampling should be avoided whenever possible. Michigan's "Surface Water PFAS Sampling Guidance"<sup>163</sup> recommends using glass filters or a centrifuge for solids removal from water samples. Solid-phase extraction (SPE) and carbon cleanup are used to extract PFAS and remove interferences from the water sample for later analysis on an ultrahigh performance liquid

chromatography/tandem mass spectrometer (UPLC/MS/MS). The EPA draft Method 1633 recommends that sample SPE extracts can be stored in the dark at  $\leq 0-4^{\circ}\text{C}$  for up to 90 days until analyzed. However, they need to be analyzed on the UPLC/MS/MS/ within 28 days if samples contain ether sulfonates. Sample extracts may need to be analyzed as soon as possible if nonafluoro-3,6-dioxaheptanoic acid (NFDHA) is an important analyte.

The EPA draft Method 1633 provides quality control protocols in Section 9.0 and calibration and standardization methods in Section 10.0. Draft Method 1633 provides detailed information for sample preparation in Section 11.0. Sample extraction, carbon cleanup, and concentration are described in Section 12.0. The UPLC/MS/MS analytical procedures are given in Section 13.0 of EPA draft Method 1633.<sup>158</sup>

All field quality-control samples, including equipment rinse blanks (EB), field blanks (FB), and trip blanks (TB), should be prepared using PFAS-free reagent water,<sup>160</sup> and all laboratory QA/QC samples should be prepared using the protocol listed in the EPA draft Method 1633.<sup>158</sup>

#### *4.2.2.Streambed/Lakebed*

Michigan's "Sediment PFAS Sampling Guidance"<sup>164</sup> provides recommendations for preventing PFAS cross-contamination that are similar to those in its "Surface Water PFAS Sampling Guidance"<sup>163</sup> (Table 1). A preferred sampling sequence should be established before any sampling event to first collect samples in areas where it is expected or known to be least contaminated and last in areas anticipated or identified to be most contaminated. All equipment should be PFAS-free, including equipment that will directly come into contact with sediment samples and that which will not directly contact the sediment samples. Materials for sample collection, preservation, treatment, and storage are similar to those listed for surface water (Table 1).

Field sampling equipment that is in direct contact with samples and used at multiple sites or sampling locations should be decontaminated before and after sampling using materials listed in Table 1. The EPA draft Method 1633<sup>158</sup> recommends collecting sediment samples as grab samples using 500-mL wide-mouth HDPE containers with linerless HDPE or polypropylene caps and filling the container no more than  $\frac{3}{4}$  full with the sample. To use the core sediment sample method listed in Michigan's "Sediment PFAS Sampling Guidance,"<sup>164</sup> a clear acetate or other PFAS-free liner should be used inside the steel core barrel when collecting sediment cores. Once a sediment core is collected and the liner is removed, the core should be cut open to reveal a "clean" face for sampling for PFAS analyses.

The EPA draft Method 1633<sup>158</sup> recommends the following for preservation, treatment, and storage of sediment samples: 1) protect sediment samples stored in HDPE containers from light and keep them at  $0-6^{\circ}\text{C}$  from the time of collection until receipt at the laboratory; 2) once arrived in a laboratory, collected sediment samples must be stored at  $\leq -20^{\circ}\text{C}$  until sample preparation; 3) sediment samples may be held for up to 90 days before extraction if stored in the dark at  $\leq -20^{\circ}\text{C}$ , with the caveat that samples may need to be extracted as soon as possible if NFDHA is an analyte of interest.

The sample processing and extraction protocol listed in the EPA draft Method 1633<sup>158</sup> recommends the following: 1) use a stainless spoon to mix the sample in its original jar; 2) remove rocks, invertebrates, and foreign objects; 3) remove vegetation from the sample before homogenization or cut vegetation into small pieces and include in the sample, based on project requirements; 4) mix the sample thoroughly, stirring from the bottom to the top and in a circular motion along the sides of the jar, and break particles to less than 1 mm by pressing against the side of the container; 5) ensure the homogenized sample is even in color and has no separate layers; 6) store the homogenized material in its original container or in multiple smaller containers; 7) determine percent solids of the sediment samples; and 8) make sure each wet sediment sample provides 5 g dry weight, and extract samples using the method listed in Section 11.3 of the EPA draft Method 1633.<sup>158</sup> The samples are further SPE-extracted, cleaned, and concentrated using methods listed in Section 12.0 of the EPA draft Method 1633.<sup>158</sup> Final sample extracts can be stored in the dark at  $\leq 0-4$  °C for up to 90 days until analyzed on UPLC/MS/MS. However, they need to be analyzed within 28 days if samples contain ether sulfonates. Samples may need to be analyzed as soon as possible if NFDHA is an important analyte. The EPA draft Method 1633 details calibration and standardization protocols in Section 10.0 and UPLC/MS/MS analytical procedures in Section 13.0.<sup>158</sup> All field and laboratory QA/QC samples should be prepared using the protocol listed in Section 9.0 of the EPA draft Method 1633.<sup>158</sup>

#### 4.2.3. Fish tissue

Recommendations for preventing PFAS cross-contamination in Michigan's "Fish Tissue PFAS Sampling Guidance"<sup>165</sup> are similar to its "Sediment PFAS Sampling Guidance"<sup>164</sup> and "Surface Water PFAS Sampling Guidance"<sup>163</sup> (Table 1). A preferred sampling sequence should be established before any sampling event. First collect samples in areas where it is expected or known to be least contaminated, and collect samples last in areas anticipated or identified to be most contaminated. All equipment should be free of PFAS, including equipment that will directly come into contact with the fish samples and any item that will not directly contact the fish samples. Materials for sample collection, preservation, treatment, and storage are similar to those listed for surface water and sediment (Table 1). Field sampling equipment that is in direct contact with samples and used at multiple sites or sampling locations should be decontaminated before and after sampling using materials listed in Table 1.

Michigan's "Fish Tissue PFAS Sampling Guidance"<sup>165</sup> states: "*Several factors should be considered when selecting the fish species that will be targeted for collection:*

- *Species and sizes normally consumed by anglers should be selected if results are expected to be used by the Michigan Department of Health and Human Services (MDHHS) "Eat Safe Fish" Program.*
- *If ecological risk assessment is a project goal, then fish of a size and species likely to be eaten by piscivorous birds and mammals should be targeted.*
- *Consider targeting species to match samples from other Michigan waters that have been analyzed for PFAS. This allows spatial comparisons without the potential complications of inter species differences.*
- *Migratory patterns of a species should be considered when sampling in a river reach open to the Great Lakes if the results are to be used to evaluate water quality in the stream. A species that is highly mobile or exhibits seasonal migrations may not be sufficiently representative of conditions in the stream of capture."*

The Michigan guidance further recommends that: 1) the ideal sample size consists of a total of at least 10 fish and includes both sexes; 2) an ideal sample will include fish in a range of lengths; 3) if fish tissue results are used to develop consumption advisories, the fish sampled should be those that are likely to be eaten and not those with abnormal deformities, gross internal lesions, or other obvious health issues.

The EPA draft Method 1633<sup>158</sup> recommends that: 1) fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis; 2) if whole fish are collected, wrap the fish in aluminum foil or food-grade polyethylene tubing, and maintain at 0–6 °C from the time of collection until receipt at the laboratory, to a maximum time of 24 hours; 3) if a longer transport time is necessary, fish should be frozen upon collection (before shipping) and shipped to the laboratory on dry ice. Once received by the laboratory, the samples must be protected from light and stored at ≤ -20 °C until prepared. Store unused samples in HDPE containers or wrapped in aluminum foil and keep at ≤ -20 °C. Fish tissue samples may be held for up to 90 days if stored by the laboratory in the dark and at ≤ -20 °C, with the caveat that samples may need to be extracted as soon as possible if NFDHA is an important analyte.

The EPA draft Method 1633<sup>158</sup> states the following: 1) common requests for analysis of fish tissue include whole fish with the skin on, whole fish with the skin removed, edible fish fillets (filleted in the field or by the laboratory), specific organs, and other portions; 2) if the laboratory must dissect the whole fish to obtain the appropriate tissue for analysis, cover the benchtop with clean aluminum foil and use clean processing equipment (knives, scalpels, tweezers) to dissect each sample to prevent cross-contamination; 3) samples should be handled in a semi-thawed state for compositing and/or homogenization; 4) all tissue comprising a sample is collected in a stainless-steel bowl during grinding, then mixed using a stainless-steel spoon; 5) if using a grinder, after the entire sample has been processed, mix the ground tissue with a spoon, transfer back to the grinder, and repeat the grinding at least two more times until the homogenized tissue has a consistent texture and color; and 6) homogenized samples must be stored in clean HDPE containers and stored frozen for subsequent extraction and cleanup.

For extraction and cleanup, the EPA draft Method 1633<sup>158</sup> recommends weighing 2 g ww (1 g is allowed but > 2 g is not recommended) of homogenized tissue into a 15-mL polypropylene centrifuge tube. Reseal the container with the remaining homogenized portion of the sample and return it to frozen storage for use if reanalysis is needed. The procedure in Section 11.4 of the EPA draft Method 1633 should be followed for sample extraction before further SPE extraction, cleanup of matrix background interferences, and concentration (Section 12.0). The final sample extracts can be stored in the dark at ≤ 0–4 °C for up to 90 days until analyzed on UPLC/MS/MS. However, they need to be analyzed on UPLC/MS/MS/ within 28 days if samples contain ether sulfonates. Samples may need to be analyzed as soon as possible if NFDHA is an important analyte. The EPA draft Method 1633 provides detailed calibration and standardization protocol in Section 10.0 and UPLC/MS/MS analytical procedures in Section 13.0.<sup>158</sup> All field and laboratory QA/QC samples should be prepared using the protocol listed in Section 9.0 of the EPA draft Method 1633.<sup>158</sup>

### **4.3. Monitoring approaches utilized by other states (including any available cost information)**

Out of 29 states that have established standard/guidance values for drinking water and groundwater, only six states (Alaska, Colorado, Florida, Michigan, Minnesota, and Oregon) have additional standard/guidance values for surface water. Eight states (Five Great Lake States and Alaska, Connecticut, and New Jersey) have issued fish-consumption advisories for PFAS, particularly PFOS.<sup>7</sup> In general, site-specific selection is a commonly used approach for sampling. The EPA methods 533 and 537.1 and the EPA draft Method 1633 are frequently used as the recommended testing methods for PFAS. The overall sampling guidance for surface water, sediment, and aquatic biota, as well as analytical methods for PFAS can be found in a comprehensive document prepared by the ITRC.<sup>7</sup> Specifically, Michigan has established the most detailed documentation on site selection approaches, sampling guidance, and testing methods for its ambient water PFAS monitoring program (Table A4 of Appendix). Michigan's documents have been modeled by many other states for their PFAS monitoring programs. For example, a similar ambient water monitoring program was used by the New Jersey Department of Environmental Protection to assess the occurrence, magnitude, and distribution of 13 PFAS in surface water, sediment, and 12 fish species at 11 targeted New Jersey waterbodies known or suspected to be impacted by PFAS sources.<sup>166</sup> The fish species tested are common at each site and are typically sought after for consumption by recreational or subsistence anglers.

The EPA maintains a list of state-certified laboratories, many of which can conduct PFAS analyses in drinking water.<sup>167, 168</sup> Costs for PFAS analysis for drinking water samples may vary among commercial labs and is typically \$300 or more per sample (Table A5 of Appendix). Many certified commercial laboratories also provide PFAS analysis for surface water, sediment, and fish tissues at a higher cost, ranging from \$350 to \$600/sample (Table A5 of Appendix). Some uncertified-laboratories, including university research laboratories, charge as little as ~\$100/sample to test PFAS in environmental samples; however, the results are not admissible in court but can be used for preliminary screening tests.

### **4.4. Monitoring priority and schemes**

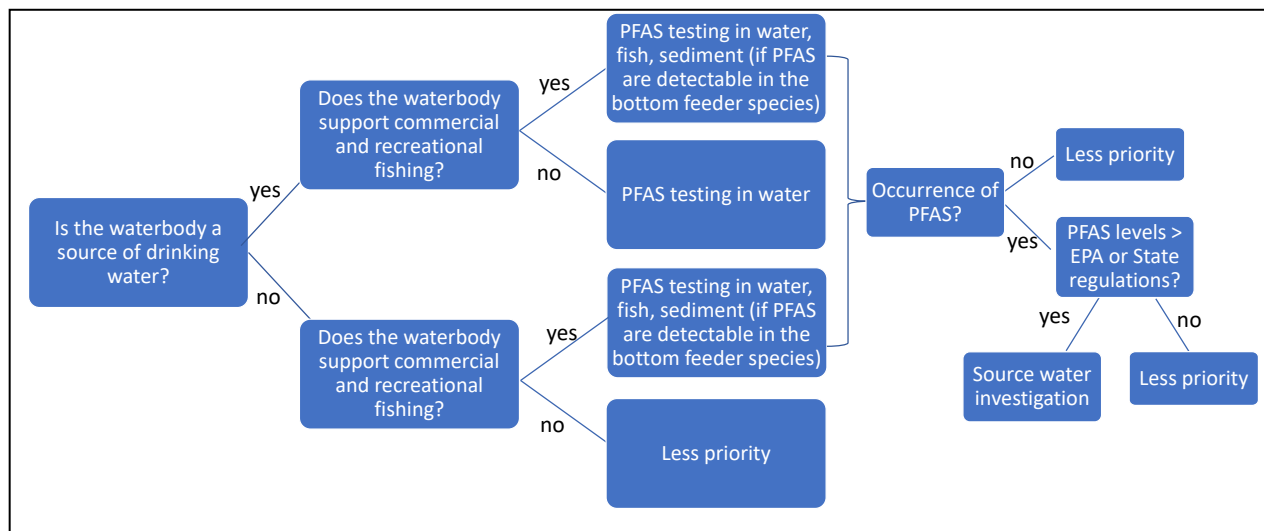
When time and financial resources are constraints, priority should be given to investigation of Virginia waterbodies that have been known or suspected to be near or impacted by an operation where PFAS have been used or generated. Among these waterbodies, priority should be given to surface waters that are used as drinking water sources and/or provide commercial and/or recreational fishing. Drinking water and consumption of fish have been suggested to be the major sources of exposure<sup>101, 114</sup> and accumulation<sup>115-121</sup> of PFAS in humans. Determination of priority and schemes for further investigation of PFAS in Virginia ambient waters should be based on the outcome of recently completed PFAS monitoring on 45 drinking waterworks (40 with surface water sources, five with groundwater sources) by the VDH<sup>154</sup> and two ongoing projects by the USGS and VDEQ: "Statewide Reconnaissance of PFAS in Rivers and Streams in Virginia" and the "Environmental Sampling of in the Middle Chickahominy River Watershed, Virginia."

#### **4.4.1. Priority waterbodies/media to monitor**

As shown in Figure 5, priority waterbodies for PFAS monitoring should include: 1) rivers/reservoirs that are sources for drinking water; and 2) waterbodies, especially in the Chesapeake Bay, that support commercial and recreational fishing. This strategy assumes that



fish consumption and drinking water are major sources of human exposure to PFAS.<sup>101, 114</sup> Once PFAS are detectable in the water of the targeted rivers/reservoirs, the occurrence of PFAS in the wadable streams flowing into the rivers/reservoirs should be further investigated. Water collection should be representative of flow conditions and the water column of the targeted waterbody. Appropriate methods specified in *National Field Manual for the Collection of Water Quality Data*<sup>159</sup> by the USGS should be used.

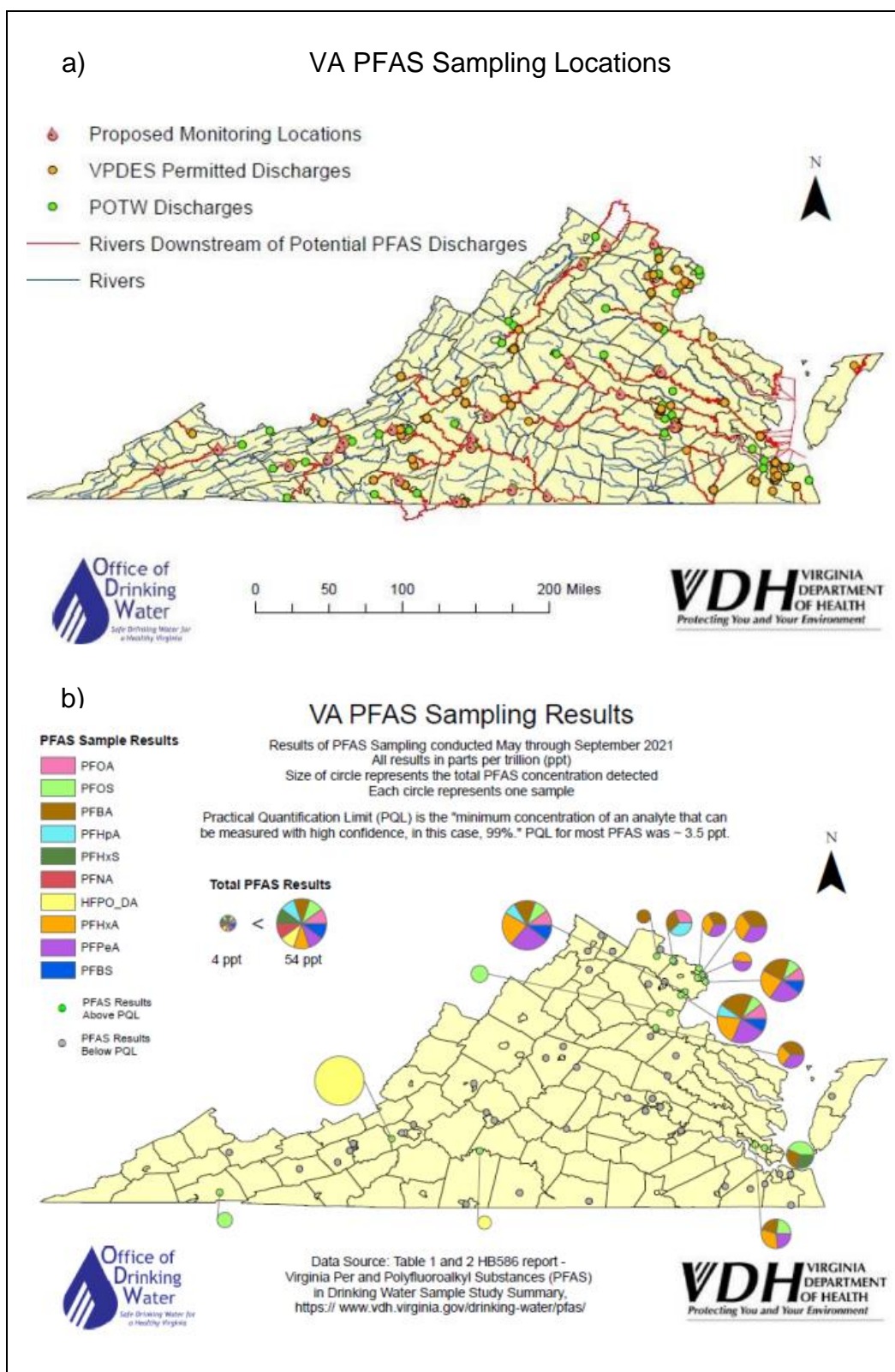


**Figure 5.** Suggested decision trees for determining priorities for PFAS monitoring in ambient waters.

If PFAS are detectable in a waterbody, fish species representing different trophic levels (top-level predator, mid-level predator, and bottom feeder) and those that are frequently consumed by humans should be collected and tested for PFAS in their edible portions. Prioritize fish sampling sites to those with high concentrations of PFAS in the water, particularly if PFOA and PFOS are present. Sediment should be tested only if PFAS are present in both water and bottom feeders (Figure 5).

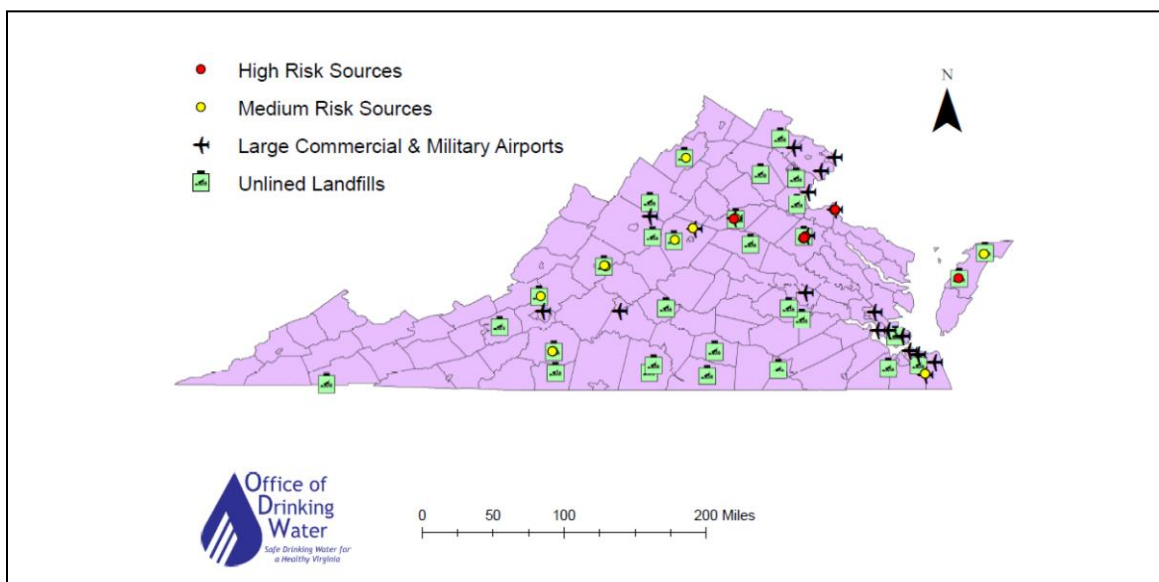
#### 4.4.2. Priority locations to sample

Selection of PFAS ambient water sampling locations should adhere to the following priority sequence: targeted stations near facilities generating, utilizing, or releasing PFAS > routine stations > randomly selected stations. The VDH's PFAS drinking water monitoring program identified major surface water supplies based on the potential sources of PFAS contamination that VDEQ identified from industrial classification codes and information in discharge permits. These potential sources include: 1) Publicly Owned Treatment Works (POTWs) with significant industrial users; and 2) Virginia Pollution Discharge Elimination System (VPDES) discharge permits (direct dischargers). Based on this information, VDH selected 22 major sources of water for their PFAS drinking water monitoring program (Figure 6a). Results of VDH's PFAS drinking water monitoring suggest that priority PFAS ambient water sampling locations should include locations where PFAS are detectable in the drinking water samples and at high levels as shown in Figure 6b. The surface water PFAS monitoring program should give high priority to the sites listed in Figure 6.



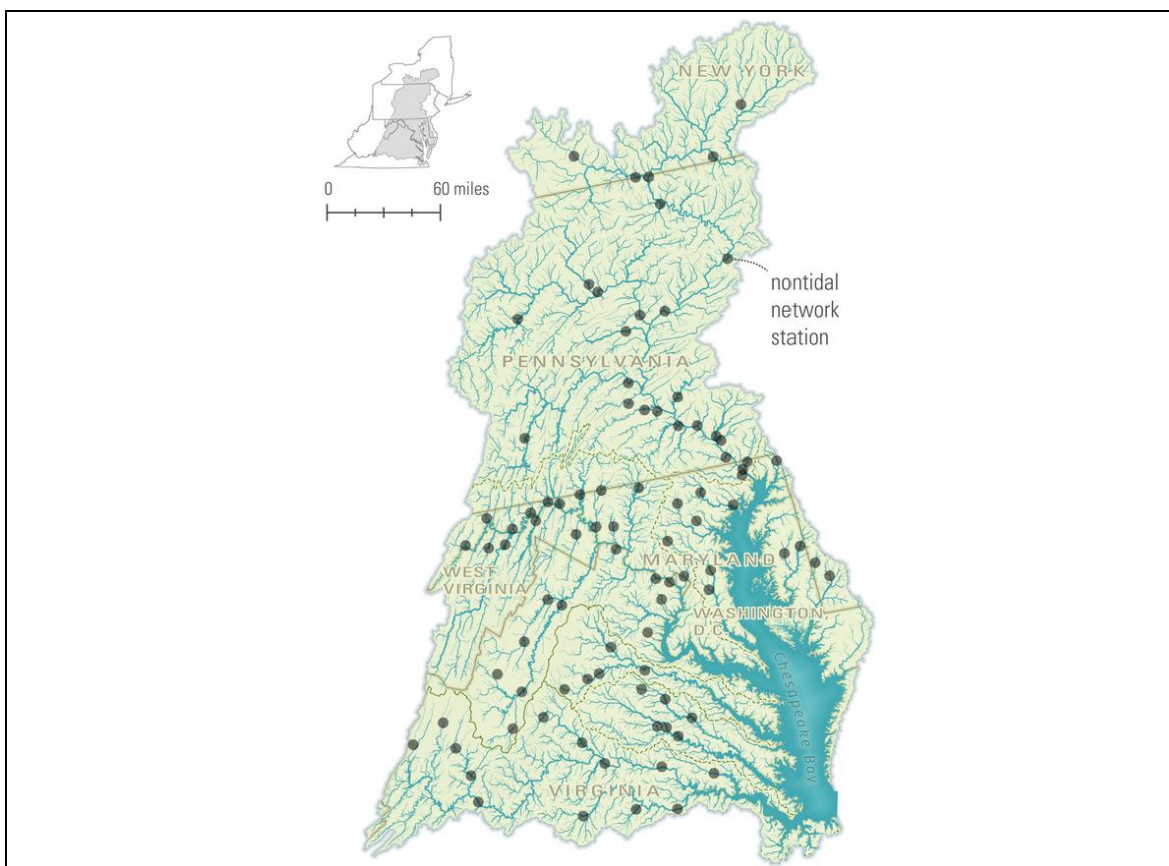
**Figure 6.** a) VDH's PFAS sampling locations of surface water sources that are potentially impacted by PFAS and associated surface water intake locations by drinking water treatment facilities; and b) Results of VDH's PFAS drinking water monitoring program.<sup>154</sup>

Additionally, surface water potentially affected by military or commercial airports, unlined landfills, and biosolids land application should also be included when identifying surface waterbodies that possibly receive PFAS input. Figure 7 shows the large military and commercial airports and unlined landfills identified by the VDH's PFAS drinking water monitoring program as potential PFAS sources affecting groundwater that are used as drinking water sources. A map detailing the locations receiving biosolids land application would be useful for further determination of additional ambient water sampling sites.



**Figure 7.** Large military and commercial airports and unlined landfills identified by the VDH's PFAS drinking water monitoring program as the potential PFAS sources affecting groundwater that are used as drinking water sources.<sup>154</sup>

Furthermore, priority should be given to the monitoring stations in the USGS Chesapeake Bay Watershed Nontidal Monitoring Program (Figure 8).<sup>169, 170</sup> Sampling at those sites allows VDEQ to leverage its partnership with USGS and to get loading estimates at these stations. Combining the USGS monitoring stations with the VDEQ's tidal stations would help characterize ecological and human health exposure to PFAS in the Chesapeake Bay. Sequence of sampling from these locations should be from the sites that are the closest to the Chesapeake Bay to the sites that are further from the Bay. This proposed sequence is based on the economic and natural resource value of the Chesapeake Bay and its streams and rivers. They are essential to a healthy and vibrant economy in Virginia, and the Bay's fisheries and seafood industry is vital to the local economy.<sup>171</sup> Additionally, further determination on site selection for PFAS fish and sediment testing would depend on the outcome of PFAS occurrence in surface water at the VDEQ's Probabilistic Monitoring (ProbMon) Network sites and other targeted monitoring sites that were included in the VDEQ's ongoing project of "Statewide Reconnaissance of PFAS in Rivers and Streams in Virginia."



**Figure 8.** The distribution of USGS nontidal network (NTN) stations in the Chesapeake Bay watershed as of 2018.<sup>169,170</sup>

#### 4.4.3. Monitoring frequency

Financial, personnel, and time resources are important factors determining PFAS monitoring frequency. At a minimum, surface water monitoring should include one base-flow collection followed by one storm-flow collection. For fish monitoring, the USGS conducts monthly sampling at a site during a one-year period because of temporal variation of PFAS in a waterbody. This frequency would be ideal, but given VDEQ's resource constraints, the agency could add PFAS analyses to its established fish contaminant monitoring program. Specifically, for Tier 1 sampling, the VDEQ's Water Quality Monitoring Strategy<sup>11</sup> suggests to collect, at each station, five to ten similar size individuals of the same species. A top-level predator (e.g., largemouth bass), a mid-level predator (e.g., bluegill), and a bottom feeder (e.g., catfish species) are usually targeted at Tier I sampling stations. Adult fish are collected because their potential for exposure to environmental contamination has occurred over a longer period, in comparison to juvenile fish. Tier II investigations typically involve laboratory analysis of five to ten individual filet samples or multiple composite samples of two or three top- or mid-level predators and one or two bottom feeders at each station to increase the statistical power of comparisons. Analysis of sediment samples may only be needed if PFAS are present in both water and bottom feeding fish. When sediment monitoring is needed, one sample collected during base flow should be the minimum.

#### 4.5. Recommendations

Because more than 4,000 PFAS<sup>3, 4</sup> have been produced and used on the global market in a wide range of industrial and consumer products, they are frequently detected in various environmental matrixes and are found to be persistent in the environment. Many PFAS have various adverse human health impacts.<sup>111</sup> Diet and drinking water have been suggested to be the major sources of human exposure to PFAS.<sup>101, 114</sup> Many states (29 states) have established PFAS monitoring programs and health advisory standards for PFAS in drinking water, and a few states (8 states) have established fish consumption advisories for PFAS. Although VDH has recently conducted a preliminary PFAS investigation of drinking water, there is a need to further assess the occurrence and distribution of PFAS in ambient waters in Virginia.

Financial resources, personnel, and time are key factors determining the size of the proposed PFAS ambient water monitoring program. Consequently, a tiered approach for PFAS monitoring is proposed. Monitoring priority should be given to surface waters that are used as drinking water sources and/or provide commercial and/or recreational fishing. Selection of PFAS ambient water sampling locations should observe the following priority sequence: targeted stations near facilities generating, utilizing, or releasing PFAS > routine stations > randomly selected stations. Surface waters known and expected to be affected by military or commercial airports, unlined landfills, and biosolids land application should also be identified as potential monitoring targets. Top priority should be given to the Chesapeake Bay and its streams and rivers because they are essential to a healthy and vibrant economy in Virginia. The strategy for further investigation of PFAS in Virginia ambient waters should be based on the outcome of recently completed PFAS monitoring on 45 drinking waterworks (40 with surface water sources, five with groundwater sources) by the VDH<sup>154</sup> and two ongoing projects by the USGS and VDEQ: “Statewide Reconnaissance of PFAS in Rivers and Streams in Virginia” and “Environmental Sampling of in the Middle Chickahominy River Watershed, Virginia.”

The following publications should be followed for sample collection, processing, preservation, storage, and analysis:

- *National Field Manual for the Collection of Water Quality Data*<sup>159</sup> by USGS;
- PFAS sampling guidances for water,<sup>163</sup> sediment,<sup>164</sup> and fish tissue<sup>165</sup> by Michigan EGLE; and
- draft Method 1633<sup>158</sup> by the EPA.

These documents are also recommended for QA/QC protocols and methods for preventing PFAS cross-contamination.



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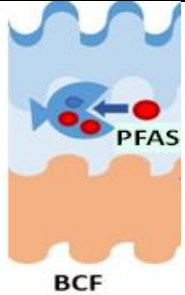
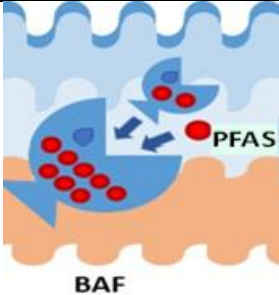
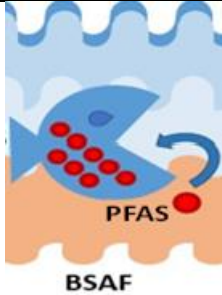

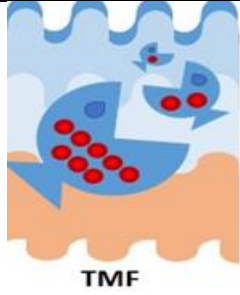


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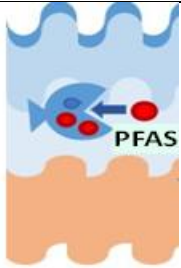
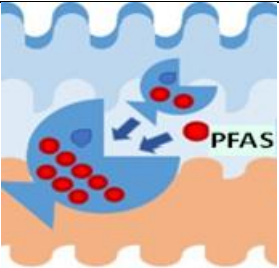
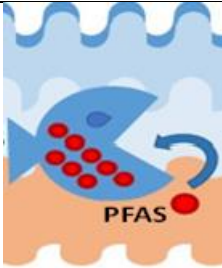
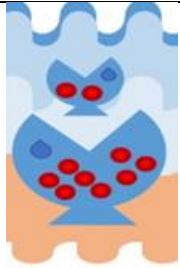
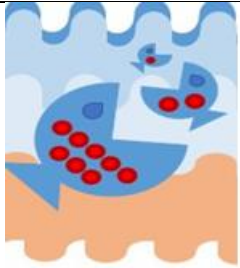
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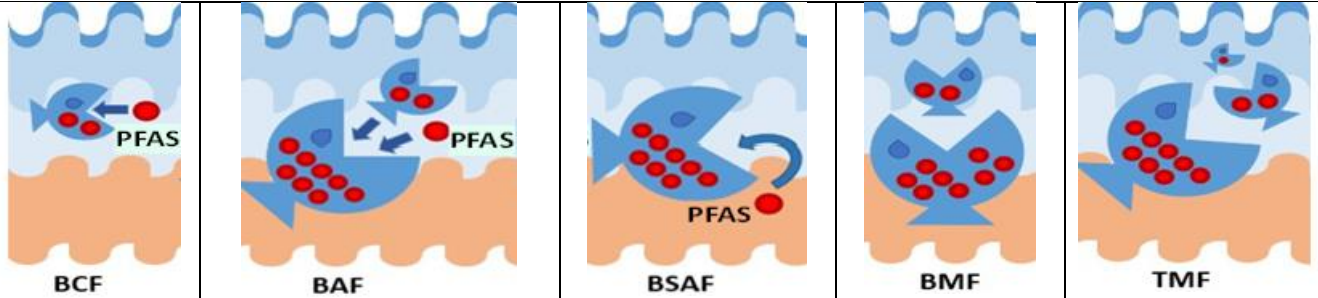
## Appendix

**Table A1. Reported values for PFAS bioaccumulation parameters\* for aquatic organisms.<sup>99</sup>**

PFAS	Organism						Water Sediment
PFOS	kelp algae	2,900–4,600					
PFOA	( <i>Thallus laminariae</i> )	6,700–14,300					
PFOS	different trophic levels of aquatic animals	3,300–8,000					
PFOA	(aquatic fauna)	6,400–9,700					
PFOS	floating plants in Lake Baiyangdian (China)		1,000–12,589				
PFOA			79–5,012				
PFNA			794–25,119				
PFDA			1,585–15,849				
OBS	wild crucian carp ( <i>Carassius carassius</i> )		1,148 (in muscle) 13,804 (in blood)				
PFAS	biota ( <i>Ruditapes philippinarum</i> )		339–20,893	20–316			
PFOS	benthic fish ( <i>Pseudogobius sp.</i> )				0.346		
PFOA					0.021		
<sup>14</sup> C-PFOA	zebrafish ( <i>Danio rerio</i> )	20–30					
PFOS	zebrafish larvae	113–193					
F-53B		125–358					
OBS		20–48					

PFAS	Organism						Water Sediment
		BCF	BAF	BSAF	BMF	TMF	
PFOS	amphibians ( <i>Rana pipiens</i> , <i>Anaxyrus americanus</i> , <i>Ambystoma tigrinum</i> )	47–259					
PFOA		0.46–2.5					
PFOS	tadpoles of <i>R. pipiens</i>	19.6–119.3					
PFBuA	<i>Holothuria tubulosa</i>		2.82 (in gonads); 12.89 (in intestine)				
PFOS			331,131 (in gonads); 346,737 (in intestine)	191 (in gonads); 7.4 (in intestine)			
PFOA				12.59 (in gonads); 3,631 (in intestine)			
PFOS	grass carp muscle from the Xiamen freshwater area (China)	6,430–7,960					
PFOA		8,160–9,680					
PFOS	saltwater, soft tissues of <i>Ocypode stimpsoni</i>	3,270–4,240					
PFOA		6,490–7,440					
PFOS	soft tissues of <i>Ostrea gigas</i>	4,180–6,430					
PFOA		6,410–9,680					

PFAS	Organism						Water Sediment
PFBA	Archaeogastropoda and Neogastropoda				0.7–3.3		
PFHpA							
PFHxS							
FOSA	Gironde Estuary (France)				>1		
PFCAs							
C9–C14 PFCA	urban river environment (Orge, France)					>1	
C7–C10 PFSA							
PFDoA	fish ( <i>Leuciscus cephalus</i> )		5,011,872 (in plasma); 501,187 (in liver & gills); 316,228 (in gonads); 100,000 (in muscle)				
all 19 types of PFAS	Jiaozhou Bay (China) soft tissues of saltwater clam ( <i>Ruditapes philippinarum</i> )		339–20,893				
PFUnDA	tilapia liver	142,764					
		22,953					
PFDA							
PFDoA		7,729					
PFOS		3,551					

PFAS	Organism					
		BCF	BAF	BSAF	BMF	TMF
PFUnDA	tilapia muscle	9,169				
PFNA	whole dusky sleeper ( <i>Eleotris fusca</i> )	1,627				
PFHxS	bivalves (soft tissues of golden freshwater clam)	2,781				
PFHpA	paddle crab ( <i>Ovalipes catharus</i> )	1,523				
PFHxS	gastropods (golden apple snail)	1,606				

\* *Bioconcentration factor (BCF)* (L/kg) =  $[\text{PFAS}]_{\text{Organism}} (\mu\text{g/kg}) / [\text{PFAS}]_{\text{Water}} (\mu\text{g/L})$

*Bioaccumulation factor (BAF)* (L/kg) =  $(k_{\text{Respiratory}} + k_{\text{Dietary}}) [\text{PFAS}]_{\text{Diet}} / ([\text{PFAS}]_{\text{Water}} / k_{\text{Elimination}})$

*Biota-sediment accumulation factor (BSAF)* =  $[\text{PFAS}]_{\text{Organism}} / [\text{PFAS}]_{\text{Sediment}}$

*Biomagnification factor (BMF)* =  $[\text{PFAS}]_{\text{Predator}} / [\text{PFAS}]_{\text{Prey}}$ , or  $\text{BMF} = \text{BAF}_{\text{Predator}} / \text{BAF}_{\text{Prey}}$ , or  $\text{BMF} = [\text{PFAS}]_{\text{Organism}} / [\text{PFAS}]_{\text{Diet}}$

*Trophic magnification factor (TMF)* =  $10^{((\log[\text{PFAS}]_{\text{Organism},n} - \log[\text{PFAS}]_{\text{Organism},1}) / (n - 1))}$ .

Table A2. Occurrence of PFAS in Virginia’s waters							
Type of compound*	Water (ppt)	Sediment (ppb dw)	Organisms (ppb ww)	Locations		Ref	
PFOA+PFOS	41/43 wells: 1.26–493,600			Columbia Aquifer groundwater	Naval Air Station Oceana, Virginia Beach, Virginia	21	
PFBS	28/43 wells: detectable–4,950						
PFHpA	31/47 wells: detectable–13,900						
PFHxS	37/47 wells: detectable–52,400						
PFNA	21/47 wells: detectable–2,660						
PFOA+PFOS	5/6 well: 1.01–639.3			Yorktown Aquifer groundwater			
PFBS	1/6 well: detectable						
PFHpA	2/6 well: detectable–22.4						
PFHxS	3/6 well: detectable–24						
PFNA	1/6 well: detectable						
PFOA	drinking water: 1,800			Naval Auxiliary Landing Field Fentress, Chesapeake, Virginia			
PFOS	drinking water: 1,000						
PFOS			110–227	Elizabeth River (osprey eggs)		149	
PFOA			NQ				
PFDS			NQ–41				
PFDA			NQ				
PFOS			255–317	Middle Potomac River (osprey eggs)			
PFOA			NQ–7.2				
PFDS			91–119				
PFDA			NQ–20.3				

\*See Figure 3 for compound classification and acronym.

dw = dry weight basis; ww = wet weight basis; NQ = not quantifiable

<b>Table A3. Comparison of EPA methods for PFAS analysis</b>						
<b>Analyte</b>	<b>Abbreviation</b>	<b>CAS#</b>	<b>Method 533*</b>	<b>Method 537.1*</b>	<b>Method 8327†</b>	<b>Method 1633††</b>
<b>Perfluoroalkyl carboxylic acids</b>						
Perfluorobutanoic acid	PFBA	375-22-4	X		X	X
Perfluoropentanoic acid	PFPeA	2706-90-3	X		X	X
Perfluorohexanoic acid	PFHxA	307-24-4	X	X	X	X
Perfluoroheptanoic acid	PFHpA	375-85-9	X	X	X	X
Perfluorooctanoic acid	PFOA	335-67-1	X	X	X	X
Perfluorononanoic acid	PFNA	375-95-1	X	X	X	X
Perfluorodecanoic acid	PFDA	335-76-2	X	X	X	X
Perfluoroundecanoic acid	PFUnDA	2058-94-8	X	X	X	X
Perfluorododecanoic acid	PFDODA	307-55-1	X	X	X	X
Perfluorotetradecanoic acid	PFTeDA	376-06-7		X	X	X
Perfluorotridecanoic acid	PFTrDA	72629-94-8		X	X	X
<b>Perfluoroalkyl sulfonic acids (acid form)</b>						
Perfluorobutanesulfonic acid	PFBS	375-73-5	X	X	X	X
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	X		X	X
Perfluorohexanesulfonic acid	PFHxS	355-46-4	X	X	X	X
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	X		X	X
Perfluorooctanesulfonic acid	PFOS	1763-23-1	X	X	X	X
Perfluoro-1-nonanesulfonic acid	PFNS	68259-12-1			X	X
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3			X	X
Perfluorododecanesulfonic acid	PFDoS	79780-39-5				X
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	X			
<b>Fluorotelomer sulfonic acids</b>						
1H,1H, 2H, 2H-Perfluorohexanesulfonic acid	4:2FTS	757124-72-4	X		X	X
1H,1H, 2H, 2H-Perfluorooctanesulfonic acid	6:2FTS	27619-97-2	X		X	X
1H,1H, 2H, 2H-Perfluorodecanesulfonic acid	8:2FTS	39108-34-4	X		X	X



Analyte	Abbreviation	CAS#	Method 533*	Method 537.1*	Method 8327†	Method 1633††
<b>Perfluorooctane sulfonamides</b>						
N-methylperfluorooctane sulfonamidoacetic acid	N-MeFOSAA	2355-31-9				X
N-ethylperfluorooctane sulfonamidoacetic acid	N-EtFOSAA	2991-50-6				X
Perfluoro-1-octanesulfonamide	PFOSA	754-91-6			X	X
<b>Perfluorooctane sulfonamidoacetic acids</b>						
N-ethylperfluorooctane sulfonamidoacetic acid	N-EtFOSAA	2991-50-6		X	X	X
N-methylperfluorooctane sulfonamidoacetic acid	N-MeFOSAA	2355-31-9		X	X	X
<b>Perfluorooctane sulfonamide ethanols</b>						
N-ethylperfluorooctane sulfonamide ethanol	NEtFOSE	1691-99-2				X
N-methylperfluorooctane sulfonamide ethanol	NMeFOSE	24448-09-7				X
<b>Per- and Polyfluoroether carboxylic acids</b>						
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	X	X		X
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	X	X		X
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	X			X
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	X			X
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	X			X
<b>Ether sulfonic acids</b>						
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	X	X		X
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	X	X		X
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7				X
<b>Fluorotelomer carboxylic acids</b>						
3-Perfluoropropyl propanoic acid	3:3FTCA	356-02-5				X
2H,2H,3H,3H-Perfluorooctanoic acid	5:3FTCA	914637-49-3				X
3-Perfluoroheptyl propanoic acid	7:3FTCA	812-70-4				X

\*Method 533 and Method 537.1 are for drinking water

†Method 8327 is for surface water, groundwater, and wastewater

††Method 1633 is for wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue

<b>Table A4. Michigan ambient water PFAS monitoring program</b>		
Agency	Michigan Department of Environment, Great Lakes, and Energy (EGLE) Water Resources Division ( <a href="https://www.michigan.gov/pfasresponse/">https://www.michigan.gov/pfasresponse/</a> )	
Approaches	<ul style="list-style-type: none"> <li>➤ Site-specific sampling <ul style="list-style-type: none"> <li>○ based on if PFAS was known or suspected to have been used at a site and other historical information</li> <li>○ to monitor rivers and lakes that are used as drinking water sources</li> </ul> </li> <li>➤ Routine monitoring of rivers and lakes. If a sample exceeds water quality standards, staff work upstream until they find the source(s) contributing to the PFAS</li> <li>➤ Watershed-scale monitoring</li> </ul>	
Samples tested (as of July 2020)	surface water	>1,000 samples from 298 water bodies
	fish	2,200 fish fillets from 86 water bodies
Sampling Guidance	surface water	<a href="https://www.michigan.gov/pfasresponse/0,9038,7-365-88059_91297---,00.html">https://www.michigan.gov/pfasresponse/0,9038,7-365-88059_91297---,00.html</a>
	sediment	
	fish	
Testing methods	surface water	EPA Method 8327
	sediment	EPA draft Method 1633 or ASTM Method D7979
	fish	

Table A5. Cost/sample examples for analysis of PFAS at certified laboratories*			
Company	Testing methods	Sample matrix	Cost/sample (\$)***
Anatek Labs ( <a href="https://www.anateklabs.com/pfas_testing">https://www.anateklabs.com/pfas_testing</a> )	EPA methods 533, 537.1	Drinking water	350
Pace Analytical® ( <a href="https://www.pacelabs.com/">https://www.pacelabs.com/</a> )	EPA methods 533, 537.1	Drinking water	350–450 varies on number of samples, delivery schedule, and estimated delivery date and other project requirements
	EPA Method 8327, EPA draft Method 1633, DOD QSM 5.3 and 5.4 (DOD method)	Surface water	
	EPA Method 8327, EPA draft Method 1633, DOD QSM 5.3 and 5.4 (DOD method), PFAS by Isotope Dilution (Pace® method), True-TOF® (Pace® method), Adsorbable Organoflourines (AOF) method (currently is validated by EPA), TOP Assay (published method)	Sediment	
	DOD QSM 5.3 and 5.4 (DOD method), EPA draft Method 1633, PFAS by Isotope Dilution (Pace® method)	Fish tissue	350–450, plus 30–150 per sample for prep of most small to average sized fish, varies based on fillet only versus whole fish grind versus compositing needed
RTI Laboratories ( <a href="https://rtilab.com/">https://rtilab.com/</a> )	EPA Method 537.1	Drinking water	300
	DOD QSM 5.3 Table B-15 (DOD method)	Sediment, fish	350
	EPA draft Method 1633		
SGS AXYS ( <a href="https://www.sgsaxys.com/">https://www.sgsaxys.com/</a> )	EPA draft Method 1633	Surface water	385–443
		Sediment	405–463
		Fish tissue	518–588
Wisconsin State Laboratory of Hygiene ( <a href="http://www.slh.wisc.edu/environmental/pfas/">http://www.slh.wisc.edu/environmental/pfas/</a> )	EPA Method 537.1	Drinking water	300–420
	33 compounds (includes all 18 compounds in EPA 537.1)		330–585

\*A complete list of accredited commercial and non-commercial laboratories provided by the Division of Consolidated Laboratory Services of Virginia Department of General Services can be found at the following weblink: <https://dgs.virginia.gov/division-of-consolidated-laboratory-services/certification-accreditation/find-a-lab/>.

\*\*\*All listed prices were estimations quoted in April-May 2022.