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Report on the Single-laboratory Validation of Clean Water Act Method 1621 for Adsorbable Organic Fluoride (AOF)

U.S. Environmental Protection Agency
Office of Water (4303T)
Office of Science and Technology
Engineering and Analysis Division
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Washington, DC 20460

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Disclaimer

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Questions or comments regarding this report should be addressed to:

S. Bekah Burket
Engineering and Analysis Division (4303T)
Office of Science and Technology
USEPA Office of Water
William Jefferson Clinton Building West
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460
Phone: 202-566-2569
E-mail: burket.sarah@epa.gov

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S. Bekah Burket	EPA OW/OST/EAD	Mike Martin	Hampton Roads Sanitation District
Adrian Hanley	EPA OW/OST/EAD	Louis Logan	Massachusetts Water Resources Authority
Brian D'Amico	EPA OW/OST/EAD	Steve Rhode	Massachusetts Water Resources Authority
Brian Pike	Pace Analytical® Services, LLC	Mahesh Pujari	Los Angeles City Sanitation
Nick Nigro	Pace Analytical® Services, LLC	Mirna Alpizar	General Dynamics Information Technology
Joel Kelly	Pace Analytical® Services, LLC	Harry McCarty	General Dynamics Information Technology
Jenifer Jones	EPA ORD/CESER	Brian Milewski	ASTM D19
Jody Shoemaker	EPA ORD/CESER	William Lipps	Shimadzu Scientific Instruments Inc. and member of ASTM D19
Thomas Speth	EPA ORD/CESER	Tom Patten	Pace Analytical® Services, LLC and member of ASTM D19
Ron MacGillivray	Delaware River Basin Commission	Takuro Kato	Mitsubishi Chemical and member of ASTM D19
Craig Forbes	Hampton Roads Sanitation District	Jayesh Gandhi	Metrohm and member of ASTM D19
Blaine Hoffman	Hampton Roads Sanitation District		

Executive Summary

The goal of this project was to complete a single-laboratory validation study of a screening method for determination of adsorbable organic fluorine (AOF) in aqueous samples. AOF is a "method-defined parameter" (MDP) meaning that the measurement result is defined solely by the method used to determine the analyte. In the case of AOF, this new screening method, Draft Method 1621, estimates an aggregate concentration of any organofluorine compounds in the sample that are retained on the granular activated carbon (GAC) sorbent and subsequently measured by combustion ion chromatography (CIC).

Currently, there are no methods for the detection of AOF in aqueous samples that are approved for use in Clean Water Act compliance monitoring. In response to this need, the US Environmental Protection Agency (EPA) convened a workgroup of EPA, laboratory, and utility staff, supported by contractors. The workgroup selected a draft ASTM International standard to be validated and reviewed all the products of this study.

The primary intended use of this method is for wastewater compliance monitoring and ten aqueous sample types, including wastewater effluents, influents, and surface water were tested in the single-laboratory validation study.

The single-laboratory validation study of this AOF method met all EPA's goals. The study generated initial precision and recovery data for aqueous matrices. Twenty-nine of thirty matrix spike samples analyzed during this study had spike recoveries between 50 and 150 percent. Only one result had a recovery above 150%. This level of performance is more than adequate for a screening method.

However, organofluorines are ubiquitous and the method is prone to contamination from various lines and valves in the adsorption unit, laboratory air, and background contamination from the capping material on the granular activated carbon (GAC) columns or from the carbon itself. Additionally, results may be biased based on the composition of organofluorines within a sample. This method still is useful as a screening-level tool to broadly assess organofluorine contamination in aqueous matrices. The method detection limit studies demonstrated that the method can be sensitive down to 2.4 µg F^-/L when using stringent instrument cleaning protocols and GAC columns containing low fluorine background. These points are emphasized in the method.

There also is a need for testing for organofluorines in biosolids, soils, sediments, and fish tissue, and portions of this draft method may form the basis for future studies, as technology advances and sample preparation techniques evolve.

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1. Introduction

The goal of this project was to complete a single-laboratory validation study of a procedure for adsorbable organic fluorine (AOF) which provides an estimated concentration of organic fluorine in aqueous environmental samples from per- and polyfluoroalkyl substances (PFAS), as well as from non-PFAS compounds such as pesticides and pharmaceuticals.

Background

The use of man-made organofluorine chemicals, including PFAS, fluorinated pharmaceuticals and fluorinated pesticides, is widespread. Of this group of chemicals, PFAS are of particular concern due to their persistence in the environment. PFAS comprise a group of thousands of man-made chemicals that have been in production since the 1940s and are found in a variety of consumer products such as cookware, food packaging, and water-repellent fabrics. Some of the most common legacy sources of PFAS were from the manufacture of non-stick materials and largely consisted of perfluorinated compounds such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

Voluntary efforts to phase out those compounds began in 2008, but they are persistent in the environment and resistant to typical environmental degradation processes. Since the phase out of PFOA and PFOS, a large variety of other polyfluorinated alkyl substances are now in common use as alternatives to PFOS and PFOA. PFAS are soluble in water and many are highly mobile. As a result, they are extensively distributed across all trophic levels and are found in soil, air, and groundwater at sites across the United States. Most PFAS do not breakdown readily in the environment and many are known to bioaccumulate in aquatic and terrestrial biota, with some compounds bioaccumulating more than others.

Various organizations and regulatory authorities at state, federal, and international levels are taking action to address the release of PFAS to the environment. However, developing analytical methods for each individual PFAS compound is impractical, if not impossible. Therefore, this project pursued a screening-level approach to evaluate PFAS and other organofluorine substances in aqueous matrices with an aggregate measure known as AOF.

Fluorine is the thirteenth most abundant element in the earth's crust; however, it is mostly found in inorganic forms such as fluorine salts and hydrogen fluorine. Although there are over 3000 naturally occurring organohalogens, only a handful of those compounds contain fluorine. Naturally occurring organofluorines have been documented to be produced abiogenically from volcanic and hydrothermal emissions, in the form of fluoroalkanes, as well as biogenically, on a much smaller scale, by some plants and bacteria, mainly as fluorinated carboxylic acids. Although this screening method cannot distinguish between naturally occurring and man-made organofluorine compounds, the natural sources account for only small quantities of organofluorines when compared to the known man-made compounds.

In addition to PFAS, fluorine is broadly used in the pharmaceutical and pesticide industries. Because of the stability of the carbon-fluorine bond, fluorine is used in pharmaceuticals to delay drug metabolism. Adding fluorine to organic compounds increases their lipophilicity because the carbon-fluorine bond is more hydrophobic than the carbon-hydrogen bond. This increases the bioavailability of the drug, allowing it to penetrate the cell membrane more easily. Fluorine is commonly used in the manufacturing of blood pressure medications, inhaled anesthetic agents, and antidepressants. Fluorine is also widely used in the pesticide industry for products used on plants, as well as products commonly used around the home to control various types of insects. Some of the most commonly applied fluorinated pesticides include cryolite, sulfuryl fluorine, and fipronil. Cryolite has been used since 1957 and it is predominantly used today on grapes, potatoes, and citrus fruit. It is sprayed on crops either from the ground or by aircraft. Sulfuryl fluorine has been used as a post-harvest food fumigant since 2004 and it breaks down rapidly in the human body to fluorine. Fipronil is a broad use insecticide that belongs to the

phenylpyrazole chemical family and has been used to control ants, beetles, cockroaches, fleas, ticks, termites, thrips, rootworms, and other insects in the United States in 1996. Fipronil is used in a wide variety of pesticide products, including granular products for grass, gel baits, spot-on pet care products, liquid termite control products, and products for agriculture. There are more than 50 registered products that contain fipronil.

Given this variety of organofluorine compounds, the method was tested using a variety of man-made organofluorines, including PFAS and non-PFAS compounds.

EPA Workgroup

EPA assembled a workgroup led by the Engineering and Analysis Division, which is part of the Office of Science and Technology within the Office of Water (OW/OST/EAD).

Due to the sheer number of products and compounds that contain organofluorine, the workgroup determined to test the chosen method on a few representatives from various groups of chemicals. The method tested reagent water aliquots spiked with PFAS compounds listed in Table 1-1, as well as with fluoxetine (an antidepressant) and fipronil (a pesticide).

Table 1-1 PFAS Compounds Tested

Analyte Name	Abbreviation
Perfluorobutanoic acid	PFBA
Perfluoropentanoic acid	PFPeA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorooctanoic acid	PFOA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnA
Perfluorododecanoic acid	PFDoA
Perfluorotridecanoic acid	PFTrDA
Perfluorotetradecanoic acid	PFTeDA
Perfluorobutanesulfonic acid	PFBS
Perfluoropentanesulfonic acid	PFPeS
Perfluorohexanesulfonic acid	PFHxS
Perfluoroheptanesulfonic acid	PFHpS
Perfluorooctane sulfonate	PFOS
Perfluorononanesulfonic acid	PFNS
Perfluorodecanesulfonic acid	PFDS
1*H*,1*H*,2*H*,2*H*-Perfluorohexane sulfonic acid	4:2FTS
1*H*,1*H*,2*H*,2*H*-Perfluorooctane sulfonic acid	6:2FTS
1*H*,1*H*,2*H*,2*H*-Perfluorodecane sulfonic acid	8:2FTS
Perfluorobutane sulfonamide	FBSA
Perfluorohexanesulfonamide	FHxSA
Perfluorooctanesulfonamide	PFOSA
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA
Hexafluoropropylene oxide dimer acid	HFPO-DA
4,8-Dioxa-3*H*-perfluorononanoic acid	ADONA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS
11-Chloroeicosafluoro-2-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS

During the initial phase of the study, PFHxS demonstrated the best and most consistent recoveries; therefore, this compound was chosen as the spike compound for the quality control samples and the real-world matrices. Observed recoveries for the compounds tested for this study are further discussed in Section 4 of the study report.

The EPA Office of Research and Development (ORD) performed a separate method validation study, also using the chosen method, on a broader set of single PFAS compounds, non-PFAS fluorinated compounds, as well as mixed PFAS standards. The ORD study did not have the same design as the EPA EAD study. Therefore, the results of ORD's testing were not used as part of this study; however, the results are summarized in Appendix C of this report.

Method Selection

The workgroup identified a draft standard from ASTM International (Reference 1) as the best starting point for the method procedure. EAD, in conjunction with members of the ASTM D19 Committee, prepared a hybrid study plan/quality assurance project plan to develop and validate an EPA procedure in a single laboratory that would be based on the original ASTM draft standard.

Combustion Ion Chromatography (CIC) is a technique that merges combustion analysis with ion chromatography to provide the simultaneous determination of halides chromatographically.

Study Objectives

The main objective of this study was to develop and characterize the performance of a new method for adsorbable organofluorine compounds that:

- Provided an aggregate response for adsorbable organofluorine compounds using CIC
- Could measure AOF at levels useful as a screening tool
- Could be implemented in a typical environmental laboratory using commercially available materials and instrumentation

Quantification

The test quantifies organic fluorine which has been adsorbed on 80 mg of granular activated carbon, combusted at high temperature, analyzed by ion chromatography, and quantified with an external standard calibration using inorganic fluorine.

Results Contained in this Report

The single-laboratory validation was performed by Pace Analytical® Services, LLC, IDEA Laboratory (hereafter referred to as Pace), Minneapolis, MN, under a purchase order issued by General Dynamics Information Technology (GDIT). As noted above, a parallel study was conducted by EPA ORD (Reference 2). The draft method has not yet been validated in a multi-laboratory study; therefore, the method performance discussed in this report should not be considered typical. QC limits and criteria will be established after EPA completes a multi-laboratory validation study.

The data tables contained in the body of this report are summaries of the data, and the full list of results is available in the various appendices.

2. Study Sample Matrix Selection

The wastewater samples used in the study were selected to meet the specifications in EPA's new method protocol (Reference 3), namely, that at least one of the wastewater matrix types should have one of the characteristics below:

- Total suspended solids (TSS) greater than 40 mg/L
- Total dissolved solids (TDS) greater than 100 mg/L
- Oil and grease (O&G) greater than 20 mg/L
- Conductivity as NaCl, greater than 120 mg/L
- Hardness as $CaCO_3$, greater than 140 mg/L

EPA obtained large volumes of real-world wastewaters from four major wastewater treatment operations: Delaware River Basin Commission (DRBC), Hampton Roads Sanitation District (HRSD), Los Angeles Sanitation and Environment (LASAN), and Massachusetts Water Resources Authority (MWRA), including samples of wastewater effluents and influents, as well as samples of aqueous matrices from indirect dischargers to those systems. EPA's support contractor, GDIT, collected a surface water sample from a creek in northern Virginia. All of the bulk samples shipped directly to Pace for testing. Table 2-1 lists the samples provided.

Table 2-1 Study Sample Matrix Sources

Sample Identification	Industry Type	Sample Identification	Industry Type
Sample #1	POTW-1	Sample #6	Bus Washing Station
Sample #2	POTW-2	Sample #7	Unspecified Industry
Sample #3	Hospital Effluent	Sample #8	POTW-4
Sample #4	Metal Finisher	Sample #9	Chemical Manufacturer Effluent
Sample #5	POTW-3	Sample #10	Surface Water

POTW – Publicly Owned Treatment Works

The bulk samples used for the AOF analysis were collected in certified PFAS-free, 1-L high-density polyethylene (HDPE) bottles, while the samples used to determine the water quality parameters were collected and preserved following the guidelines in 40 CFR Part 136, Table II.

Pace performed the analyses of water quality parameters for each study sample. At least one of the sample characteristic criteria was met by each of the bulk samples, and EPA deemed the samples suitable for use in the study. A summary of the sample characteristics is provided in Table 2-2. The values in **bold font** in Table 2-2 indicate that the sample met the requirements for that parameter.

Table 2-2 Water Quality Characteristics of the Study Samples (mg/L)

Sample #	TSS	TDS	O&G	Conductivity, as NaCl	Hardness
1	ND	**512**	ND	**572**	66.3
2	11.2	**405**	ND	**517**	115
3	**202**	**533**	8.9	**610**	28.2
4	ND	**115**	ND	**146**	60.7
5	**170**	**728**	**24.3**	**1082**	132
6	29.0	**3440**	13.5	**4461**	61.0
7	ND	**480**	ND	**534**	46.1
8	26.9	**863**	ND	**1094**	**272**
9	ND	98.0	ND	**140**	11.4
10	ND	**254**	ND	**315**	**595**

ND = Not detected

3. Approaches to Calibration and Quantification

The draft ASTM procedure calibrates the ion chromatograph (IC) using an inorganic fluorine standard. In order to normalize the results from any possible loss of analyte that may be caused by sample combustion, the instrument was calibrated by combustion, instead of using direct injection; however, the calibration standards did not go through carbon adsorption. The calibration curve is based on the concentration of fluorine ion in the standard (i.e., µg F^-/L) and not based on the mass or concentration of a specific compound.

Initial Calibration

The IC instrument was calibrated using a series of eight calibration standards designated as CS-1 to CS-8. The first calibration standard (CS-1) was a blank. The calibration fit was compared between a simple linear regression fit and a quadratic fit (1/x weighing), both of which were not forced through zero, and using a valley-to-valley peak integration approach. Table 3-1 summarizes the results of three separate initial calibrations performed between September 23 and September 28, 2021. For each calibration curve, the relative standard error (RSE) was calculated to assess the model fit, using Equation 1 below:

Equation 1. Relative Standard Error

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \frac{\left[\frac{x_i' - x_i}{x_i}\right]^2}{n-p}}$$

where:
x_i = Nominal concentration (true value) of each calibration standard
x'_i = Measured concentration of each calibration standard
n = Number of standard levels in the curve
p = Type of curve (1 = average, 2 = linear, 3 = quadratic)

Table 3-1 Initial Calibration Linearity and Stability

Calibration Point	Nominal Value (µg F^-/L)	Linear Fit				Quadratic Fit			
		% Recovery			RSD (%)	% Recovery			RSD (%)
		Cal 1	Cal 2	Cal 3		Cal 1	Cal 2	Cal 3	
CS-1	0	NA	NA	NA	--	NA	NA	NA	--
CS-2	0.5	89.2	72.0	84.4	10.8	80.2	85.8	100.2	11.6
CS-3	1.0	90.7	82.4	88.8	5.0	87.7	87.2	94.1	4.3
CS-4	2.0	95.9	96.7	94.2	1.4	95.9	96.7	94.3	1.3
CS-5	6.0	97.1	105.2	101.2	4.0	98.4	103.1	98.7	2.7
CS-6	10.0	103.4	103.1	104.8	0.86	104.3	101.6	102.9	1.4
CS-7	14.0	102.7	101.9	102.6	0.43	103.1	101.3	101.9	0.88
CS-8	20.0	98.2	97.9	97.5	0.34	97.7	98.7	98.5	0.53
RSE (7 Cal Pts)		7.1	15.2	9.4		12.2	9.9	4.6	
Correlative Coefficient		0.9994	0.9993	0.9991		0.9992	0.9998	0.9997	

NA = Not Applicable

A t-test was performed to compare the linear vs. quadratic fits. The test was performed for each calibration level, as well as for the combined set of recoveries. Based on the t statistics, there were no statistical differences between the means of both curve fits. The same approach was performed using the

F-test. Based on the F-test results, there were no differences between the variances of the linear and quadratic fits, either at the population level or at the individual calibration levels.
The quadratic fit gave slightly better recoveries at the lower concentration end of the curve, thus providing better sensitivity. Additionally, the mean RSE was slightly lower (8.9 for the quadratic fit versus 10.5 for the linear fit). Therefore, EPA decided to use a quadratic fit for the study.

During the study, the instrument was calibrated twice more after maintenance. All five calibrations were compared via ANOVA. Based on those test results, there was no statistical difference between the five calibrations. Results for the last two calibrations are summarized below.

Table 3-2 Calibration Linearity and Stability

Calibration Point	Nominal Value (µg F^-/L)	% Recovery	
		Cal 4	Cal 5
CS-1	0	NA	NA
CS-2	0.50	106.0	88.2
CS-3	1.0	94.1	94.7
CS-4	2.0	98.5	98.4
CS-5	6.0	101.1	100.6
CS-6	10.0	100.4	101.2
CS-7	14.0	99.7	101.3
CS-8	20.0	100.0	99.0
RSE (7 Cal Pts)		4.32	6.60
Correlative Coefficient		0.9999	0.9999

NA = Not Applicable

Calibration Extension

Based on the initial reconnaissance analyses of unspiked samples and the anticipated organofluorine concentrations for the spiked samples in the study, a calibration extension study was subsequently performed to increase the range of calibration from 20 µg F^-/L to 50 µg F^-/L. Three additional extended calibrations were completed and the model fit was assessed using RSE. Based on results from blanks and background level assessments during early method validation, the calibration levels were adjusted to reflect the method sensitivity. Also, using a zero point assumes that the analyte is not present in reagent water at any concentration, which is not the case for this method. Because of these two issues, the first two points, CS-1 and CS-2, of the original calibration range were dropped. Results for the new calibrations are summarized on Table 3-3 below. The new calibration range in Table 3-3 was used for the Nittoseiko-Mandel (hereafter referred to as "Mandel") GAC sorption studies and to analyze sample #9.

Table 3-3 Calibration Extension Linearity and Stability

New Calibration Point	Nominal Value (µg F^-/L)	Quadratic Fit			
		% Recovery			RSD (%)
		Cal 1	Cal 2	Cal 3	
CS-1	1.0	88	102	99	7.67
CS-2	2.0	111	102	104	4.39
CS-3	5.0	99	94	96	2.58
CS-4	10.0	104	101	99	2.87
CS-5	25.0	97	101	102	2.84
CS-6	50.0	101	100	100	0.62
RSE (6 Cal Pts)		9.84	3.86	3.54	
Correlative Coefficient		0.9997	0.9999	0.9999	

4. Characterization of Adsorption Media

There are a variety of sources for granular activated carbon (GAC) columns on the market. The amount of *in situ* fluorine contained in the carbon, as well as in the capping material, will determine the achievable detection limit at each laboratory using this method.

Prior to procuring the columns for the study, Pace conducted a small-scale investigation of the fluorine background levels in columns from five GAC vendors. For each vendor, 100-mL aliquots of deionized water were adsorbed onto six columns, and the columns were then washed with 25 mL of potassium nitrate wash solution. Because some column capping material may contain high levels of fluorine, the laboratory determined the background level of fluorine in the capping material versus the carbon, by individually evaluating just the carbon from a set of three columns, and then both the carbon with the capping material from three additional columns. The results of this comparison have been summarized in Table 4-1 below. The negative results shown in Table 4-1 are a function of not forcing the calibration through zero.

Table 4-1 Granular Activated Carbon Column Vendor Comparison

Vendor	Capping Material	Replicate 1	Replicate 2	Replicate 3	Mean	Std Dev
GAC + Capping Material (µg F^-/L)						
Nittoseiko-Mandel	Glass wool	0.245	0.145	0.371	0.254	0.113
CPI	Glass wool	0.035	0.184	0.060	0.093	0.080
UCT Enviro-Clean	Glass wool	0.180	0.224	0.360	0.255	0.094
Analytik-Jena (AOX/TOX)	Glass wool	8.51	9.27	11.02	9.60	1.29
Analytik-Jena (Low Fluorine)	Cellulose acetate	0.201	0.165	0.465	0.277	0.164
Sigma-Aldrich	Cellulose acetate	0.289	-0.148	-0.154	-0.004	0.254
GAC Only (µg F^-/L)						
Nittoseiko-Mandel		0.361	0.401	0.242	0.335	0.083
CPI		-0.018	-0.017	-0.042	-0.026	0.014
UCT Enviro-Clean		-0.029	0.096	-0.027	0.013	0.072
Analytik-Jena (AOX/TOX)		0.770	0.822	0.740	0.777	0.041
Analytik-Jena (Low Fluorine)		0.088	-0.003	-0.021	0.021	0.058
Sigma-Aldrich		0.095	0.132	0.088	0.105	0.024

The results exhibited varying degrees of background contamination across all the vendors. For example, the glass wool used in the generic Analytik-Jena (AOX/TOX) columns was responsible for over 90% of the fluorine background contamination. The initial instrument calibration range listed in Table 3-1 (Section 3) was used for this part of the study. For this vendor, the carbon by itself had fluorine levels above 0.70 µg F^-/L, which was above the lowest calibration point. The fluorine levels added by the capping material resulted in a mean background level over 9 µg F^- /L, which fell around the midpoint of the calibration curve. Based on the high background levels found in these columns, EPA made the decision not to include Analytik-Jena (AOX/TOX) as part of this study.

The Mandel columns were unique, in that the capping material did not seem to add any significant amount of fluorine to the carbon background level, while the capping materials used in the UCT, CPI, and Analytik-Jena (Low Fluorine) columns added over 90% of the fluorine background to the columns. The fluorine levels for the carbon plus the capping material for these four manufacturers fell below the first point of the calibration curve; however, these levels may still be above the calculated method detection limit (MDL) for individual laboratories. The percent contribution of background fluorine from the capping material for the Mandel, CPI, UCT, and the Analytik-Jena (Low Fluorine) GAC columns are

shown in Table 4-2. The negative results shown in Table 4-2 are a function of not forcing the calibration through zero.

Table 4-2 Background Fluorine Contribution by Column Capping Material

Vendor	Average µg F^-/L			% F^- Added by Capping Material
	GAC	GAC + Capping	Capping Material	
Nittoseiko-Mandel	0.335	0.254	-0.081	0
CPI	-0.026	0.093	0.093	100.0
UCT Enviro-Clean	0.013	0.255	0.242	94.9
Analytik Jena (Low Fluorine)	0.021	0.277	0.256	92.4

Sigma-Aldrich recently developed a new GAC column containing synthetic carbon. The manufacturer provided a sample of their new product to the laboratory for testing; however, the carbon presented an analytical challenge as it did not seem to fully combust, and it was consistently pulled into the instrument by the gas flow. For this reason, the Sigma-Aldrich columns were not used as part of this study. The manufacturer was informed of the issue, and they are currently working on a resolution.

An ANOVA statistical analysis demonstrated that there was no statistical difference between the Mandel, CPI, UCT, and Analytik-Jena (Low Fluorine) AOF background levels. To help further narrow the GAC selections, Pace also performed a small PFBS recovery study on GAC columns from the four vendors listed in Table 4-2. For this evaluation, five columns from each of the four vendors were selected. One column was analyzed as a background sample, using 100-mL aliquots of reagent water. The other four columns were analyzed using 100-mL aliquots of reagent water spiked with 600 ng of PFBS. All the columns were washed with nitrate and then combusted. Background-subtracted percent recoveries are listed in Table 4-3. During this side study, the laboratory noticed carbon migration out of the columns during sample sorption and elution (see Figure 1 below) for the CPI, UCT, and Mandel columns. This carbon migration was also observed by the EPA ORD laboratory during their method validation effort using the Mandel columns and the same adsorption unit model. Based on the carbon stability issues observed during the small-scale fluorine background study and PFBS recovery study, as well as the available supply from the manufacturers to cover the entire project, the Analytik-Jena (Low Fluorine) GAC columns were selected as the primary sorption columns. The Mandel columns were still tested to evaluate the prevalence and interference of carbon migration with the adsorption of organofluorine; however, these results were not used as part of the study report but are instead included as Appendix B. Two separate lot numbers from each of the two vendors were procured. Fluorine background levels, as well as adsorption capacities for individual PFAS compounds, mixed PFAS, fluoxetine, and fipronil were characterized using GAC from both vendors. The Analytik-Jena (Low Fluorine) columns were used to test for interferences caused by different concentrations of inorganic fluorine and chloride.

Table 4-3 Adsorption of PFBS at 600 ng per GAC Vendor

GAC Vendors	Percent Recoveries					RSD (%)
	Rep 1	Rep 2	Rep 3	Rep 4	Mean	
Nittoseiko-Mandel*	67.7	82.1	88.7	91.3	82.5	12.8
CPI*	118.6	70.7	74.7	81.2	86.3	7.7
UCT Enviro-Clean*	64.7	73.1	77.4	173.1	97.1	52.5
Analytik-Jena (Low Fluorine)	82.9	93.2	91.4	100.1	91.9	7.7

*Issues with capping material during elution

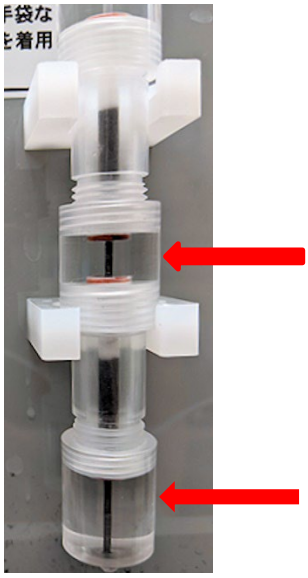

Figure 1 Carbon Migration from GAC Columns

A. GAC Background

The background levels of inorganic fluorine for the GAC columns were determined by analyzing five aliquots of unspiked reagent water, using two GAC columns in series for each aliquot, and taking all the aliquots through the procedure without washing the columns with nitrate. Two forms of nitrate washes were tested, potassium nitrate and sodium nitrate. Potassium nitrate is suggested as the wash solution by the combustion unit manufacturer to reduce the devitrification of the pyrolysis tube. However, the draft ASTM standard uses sodium nitrate. The laboratory analyzed five aliquots of unspiked reagent water, followed by column washes with 20 mL of 8.4 g/L potassium nitrate, and five aliquots of unspiked reagent water containing 0.5 mL 2M sodium nitrate, followed by a column wash with 25 mL of 0.01 M sodium nitrate. A total of 15 data points were produced from the background analysis.

Table 4-4 provides the information of the fluorine background level for each lot number.

Table 4-4 Fluorine Background Level per Lot Number (2 Columns)

	Inorganic Fluorine (µg F^-/L)				
	No Wash		$NaNO_3$ Wash		KNO_3 Wash
Sample	Lot #1	Lot #2	Lot #1	Lot #2	Lot #1
Replicate 1	1.928	0.079	0.147	0.769	0.361
Replicate 2	0.369	1.939	0.095	1.496	0.310
Replicate 3	2.674	-0.126	0.237	0.752	0.548
Replicate 4	0.766	0.282	0.543	0.984	0.485
Replicate 5	0.404	0.525	1.504	1.151	0.618

The maximum blank value allowed in the draft ASTM standard is 5 µg F^-/L. Both lot numbers of GAC columns met the maximum limit. There were no statistical differences between the means and the variances between the two lot numbers, based on a t-test and an F-test. There was however a statistical difference between the variances for Lot #1 washed with sodium nitrate versus those washed with potassium nitrate. Sodium nitrate was selected as the wash solution for this study and is the wash solution listed in the draft ASTM standard. However, additional method validation work at ORD confirmed that potassium nitrate is also a suitable wash solution (see Appendix C).

B. GAC Sorption Capacity

The sorption capacity of GAC was determined for 22 individual PFAS, a mixed PFAS standard containing 33 compounds, and for 2 non-PFAS fluorinated compounds. The actual results for all the adsorption recoveries are provided in Appendix D.

Prior to determining the adsorption capacity for PFAS and non-PFAS compounds on the GAC, the laboratory performed direct combustion, without carbon adsorption, of several individual standards covering a range of carbon chains from C_4 to C_{17} as well as for the mixed PFAS standard and the non-PFAS fluorinated compounds to provide baseline data on recoveries from combustion only. Only two compounds, PFBA and NMeFOSA, had recoveries below 50%, which might be due to analyte loss during combustion. Recoveries for each individual compound are listed in Table 4-5.

Table 4-5 Compound Recoveries by Direct Combustion

Compound	Formula	MW	Mass (ng F^-)	% Recovery
PFAS				
PFBA*	$C_4HF_7O_2$	214.04	621.4	**48.6**
4:2FTS	$C_6H_4F_9SO_3Na$	350.13	488.4	103.1
HFPO-DA*	$C_6HF_{11}O_3$	330.05	1266.5	81.3
PFHxS*	$C_6H_2F_{13}NO_2S$	399.13	618.8	87.1
ADONA*	$C_7H_5F_{12}O_4NO_4$	400.05	569.9	96.2
6:2FTS*	$C_8H_4F_{13}NaO_3S$	450.15	548.7	108.1
6:2PAP	$C_8H_4F_{13}O_4PNa$	488.05	506.1	92.9
PFOA*	$C_8HF_{15}O_2$	414.07	688.3	88.4
PFOS*	$C_8F_{17}SO_3K$	538.22	600.1	108.8
PFOSA*	$C_8H_2F_{17}NO_2S$	499.15	647.1	94.9
NMeFOSA	$C_9H_4F_{17}NO_2S$	513.17	629.4	**47.5**
8:2FTS	$C_{10}H_4F_{17}SO_3Na$	550.16	587.1	106.4
NEtFOSA	$C_{10}H_6F_{17}NO_2S$	527.2	612.7	82.0
NMeFOSE	$C_{11}H_8F_{17}NO_3S$	557.22	579.7	95.7
NMeFOSAA	$C_{11}H_6F_{17}NO_4S$	571.21	565.5	110.9
NEtFOSAA	$C_{12}H_8F_{17}NO_4S$	585.23	551.9	109.3
NEtFOSE	$C_{12}H_{10}F_{17}NO_3S$	571.25	565.4	96.6
10:2FTS	$C_{12}H_4F_{21}SO_3Na$	650.18	613.7	96.8
PFDoS	$C_{12}F_{25}SO_3Na$	722.14	657.8	103.6
6:6PFPi	$C_{12}F_{26}O_2PNa$	724.05	682.3	107.4
6:2diPAP	$C_{16}H_8F_{26}O_4PNa$	812.15	608.3	107.9
8:8PFPi	$C_{16}F_{34}O_2PNa$	924.08	699.1	103.4
Non-PFAS				
Fipronil*	$C_{12}H_4Cl_2F_6N_4OS$	437.15	751.4	96.1
Fluoxetine*	$C_{17}H_{18}F_3NO$-HCl	345.8	1391	84.4
Mixed PFAS				
30 PAR*	33 PFAS compounds	various	760.3	92.3

*These compounds were used for the subsequent individual carbon adsorption study.

Individual PFAS Compounds

One lot number of Analytik-Jena (Low Fluorine) columns was selected for testing of the adsorption capacity for the following individual PFAS compounds: PFBA, HFPO-DA, PFHxS, ADONA, 6:2FTS, PFOA, PFOS, and PFOSA. This subset of eight individual PFAS was selected after extensive method validation at ORD that included 35 individual PFAS, two fluorinated pharmaceuticals and two fluorinated herbicides (see Appendix C). The compounds selected had carbon chain lengths ranging from C_4 to C_8. Each analysis was performed in triplicate using 100-mL aliquots of reagent water spiked at approximately 6.0 and 19.0 µg F^-/L. The original approach included a spike at around the lowest point of the calibration curve (0.6 µg F^-/L); however, because the fluorine background on the GAC can be as high as 5 µg F^-/L, this lower spiking level did not produce usable results and therefore it was dropped from the project. The percent recoveries and RSD for both spiking levels (6.0 µg F^-/L and 19.0 µg F^-/L) for the individual PFAS compounds are summarized in Table 4-6. The recoveries are comparable to what was seen in the ORD study (see Appendix C).

Table 4-6 GAC Adsorption of Individual PFAS Compounds

	Spike Level 1 (~6 µg F^-/L)				Spike Level 2 (~19 µg F^-/L)			
	% Recovery			RSD (%)	% Recovery			RSD (%)
Compound	Rep 1	Rep 2	Rep 3		Rep 1	Rep 2	Rep 3	
PFBA	44.0	57.6	81.5	31.1	74.1	83.1	98.1	14.2
HFPO-DA	77.4	90.4	74.2	10.6	94.6	92.6	95.7	1.7
PFHxS	121.2	118.4	147.6	12.5	106.9	110.0	123.8	7.9
ADONA	234.4	270.6	272.2	8.3	159.6	160.9	155.4	1.8
ADONA*	90.8	88.4	92.8	2.4	127.0	113.9	117.9	5.6
6:2FTS	74.2	72.0	99.4	18.6	129.9	122.1	127.6	3.2
PFOA	167.3	157.1	193.7	10.9	149.2	144.3	139.8	3.3
PFOA*	132.3	143.3	174.8	14.7	125.1	134.8	120.1	5.9
PFOS	66.3	95.9	92.3	19.0	85.7	62.5	78.5	15.7
PFOSA	70.7	51.0	58.9	16.5	49.6	52.9	47.9	5.1

*Reprepared and analyzed in a separate analytical batch. Not blank corrected.

The percent recoveries for individual PFAS compounds selected for this study ranged from 44% (PFBA) to 272% (ADONA). However, the average recovery across all compounds and spike levels was 113%. Most results fell within 50 – 150%. Of the 60 results, three were below 50% recovery and ten results above 150% recovery. Results for PFBA at the lower spike level, which had an RSD >20% and one data outlier, were inconsistent. Shorter-chain PFAS, like PFBA, may be prone to lower recoveries, either due to combustion losses or breakthrough during the carbon adsorption procedure. PFBA had a 48.6% recovery during the direct combustion study (Table 4-5), however during the adsorption study, PFBA recoveries ranged from 44 % to 98.1% (Table 4-6). The higher recoveries observed during the adsorption study for PFBA might be due to contamination on the adsorption unit. Although the blanks that were run at the beginning of the batch did not show any contamination, the samples adsorbed after the PFBA samples, which were spiked with ADONA, showed high recoveries ranging from 155.4% to 272.2% (Table 4-6). Additionally, we observed a pattern of increasing concentrations during the sample batch, which indicated potential instrument carryover contamination.

Due to the high recoveries (>150%) observed for ADONA and PFOA during the adsorption study, a repeat analysis was performed in a separate analytical batch with reprepared samples. Initially, all results in Table 4-6 were adjusted by subtracting the first matrix blank that was analyzed with each batch. However, blanks analyzed during the repeat analysis for ADONA and PFOA were contaminated, with the opening blank showing contamination at 8.97 µg F^-/L and the closing blank at 5.7 µg F^-/L. The potential source of contamination for the method blanks was traced back to paper products that were used during transfer of the carbon and capping material to the combustion boat. In response, the laboratory analyzed a

1 cm x 2 cm section of each of the two paper products (paper towel and task wipe) via direct combustion. Fluorine was detected in the paper towel section (86 ng F^-), however, the concentration was not high enough to fully account for the level of blank contamination. The source of the blank contamination could not be confirmed. As a result, the results provided for the repeat analysis of ADONA and PFOA (designated with asterisks in Table 4-6) were not blank corrected because the blank values were higher than the spike levels.

A t-test was performed to check for statistical differences between the mean recoveries for the spike levels. The statistical analysis showed that there was a difference between the means for ADONA and 6:2FTS. A t-test analysis of the second set of results for ADONA did not show a statistical difference between the means for the spike levels. An F-test was also performed to check for statistical differences between the variances of the spike levels recoveries for each compound. There was a statistical difference in the variances for HFPO-DA and ADONA. The F-test for the second set of results for ADONA showed no statistical difference of the variances.

Figure 2 shows the average percent recoveries for single-compounds GAC adsorption for each spike level. The compounds are in order of increasing carbon chain length.

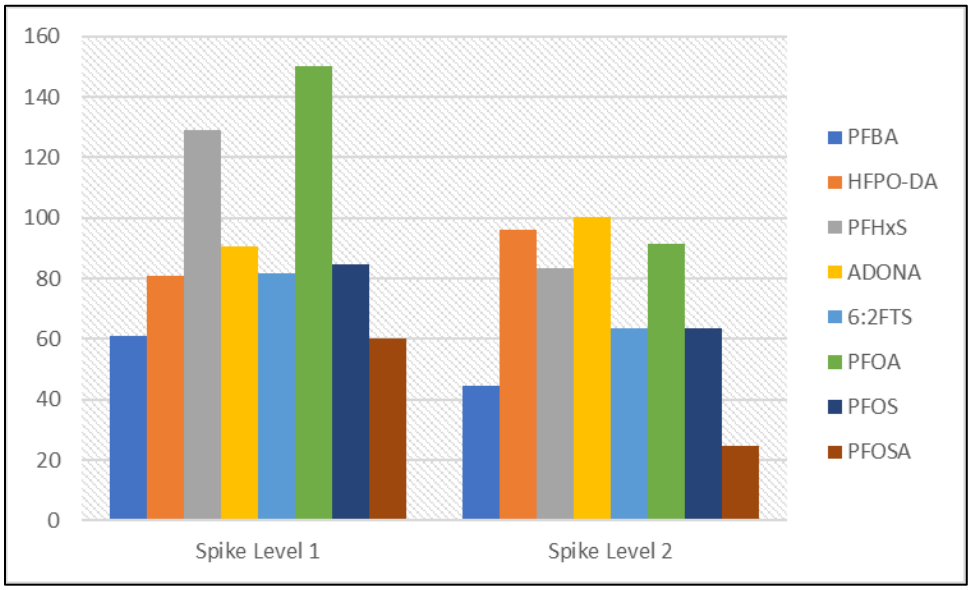

Figure 2 Average Percent Recoveries for Single-Compounds at Two Spike Levels (~6 and ~19 µg F^-/L)

For all analyses performed during this study, two GAC columns were used, in series, and the percent breakthrough (% B) was calculated using Equation 2 below.

Equation 2. Percent Breakthrough

$$\%\ Breakthrough = \frac{(M_2 - B_2) \times 100}{[(M_1 - B_1) + (M_2 - B_2)]}$$

where,
M_1 = Mass ng F^- for the first column
M_2 = Mass ng F^- for the second column
B_1 = Mass measured for first column of the initial MB, µg F^-
B_2 = Mass measured for second column of the initial MB, µg F^-

The percent breakthrough between the top and bottom columns was calculated using Equation 2 for each replicate. The maximum observed breakthrough during the entire study was 51.9%, which was observed

in only one replicate for PFBA spiked at 6 µg F^-/L. The percent breakthrough varied across the different individual PFAS and non-PFAS compounds, but breakthrough was generally below 40%. For this method, AOF concentrations are reported as the total from the top GAC, bottom GAC, and any quartz wool which might have been used to prefilter the sample, as explained in Section 10.

As discussed above, although most of the recovery results fell within 50 – 150%, the statistical analysis showed that there were differences in the adsorption of the compounds between the types of PFAS compounds. Extensive method validation work at ORD indicated that AOF recoveries may also differ based on adsorption unit (see Appendix C). The recovery of compounds was also dependent on fluorine background levels on the column, the cleanliness of the adsorption unit, and the stability of the carbon inside the column. Because this method requires blank correction, high levels in the blanks may over-correct the samples, biasing the results low. The particular adsorption unit used for this study contains tubing and valves which are difficult to clean and therefore some fluorine may remain behind and accumulate as more samples are adsorbed in the unit. Moving forward, the laboratory employed additional cleaning of lines and valves between samples with PFAS-free water and methanol to mitigate carryover contamination.

Mixed PFAS Standard

The adsorption capability of the carbon for a mixture of PFAS compounds was also tested. The mixed PFAS solution was purchased from Wellington Laboratories, Cat# PFAC30PAR. The mix contained 33 PFAS compounds: eleven (11) perfluoroalkylcarboxylic acids (C_4-C_{14}), seven (7) perfluoroalkyl sulfonates (linear and branched, C_4-C_{10}), three (3) telomer sulfonates, two (2) ether sulfonic acids, two (2) perfluorooctanesulfonamido acetic acids, three (3) perfluoroalkylsulfonamides, and GenX. The concentration of fluorine for each compound in the mixed standard was determined using Equation 3 below and then the total concentration of fluorine for the standard was used to calculate the spike levels. The laboratory analyzed three aliquots at 6.65 µg F^-/L (Level 1) and three aliquots spiked at 19.01 µg F^-/L (Level 2). Table 4-7 shows the recoveries of AOF at the different concentrations.

Equation 3. Fluorine Ion Mass

$$CM_{F_{PFAS}} = \frac{n_F \times A_F}{MW_{PFAS} \times M_{PFAS}}$$

where:

M_{PFAS} = Mass of the PFAS compound (or non-PFAS compound) in ng
MW_{PFAS} = Molecular weight of the PFAS compound (or non-PFAS compound) in $g \cdot mol^{-1}$
n_F = Number of fluorine atoms in the compound
A_F = Atomic weight of fluorine (18.998)

Table 4-7 GAC Adsorption of Mixed PFAS Compounds

	Spike Level 1 (6.65 µg F^-/L)				Spike Level 2 (19.01 µg F^-/L)			
	% Recovery			RSD	% Recovery			RSD
Compound	Rep 1	Rep 2	Rep 3	(%)	Rep 1	Rep 2	Rep 3	(%)
Mixed PFAS	175.9	215.7	209.7	10.7	115.4	115.2	106.9	4.3
Mixed PFAS*	120.1	128.6	95.3	15.1	88.5	87.0	87.6	0.9

*Reprepared and analyzed in a different analytical batch. Not blank corrected.

Adsorption of the mixed PFAS standard was evaluated in two different analyses. During the first batch, the Level 1 spiked samples were biased high because the spiking level was close to the fluorine background level. Due to the high recoveries, the mixed standard analysis was repeated with reprepared samples in a separate batch as part of the repeat analysis for ADONA and PFOA. As described above,

the method blanks analyzed in the reprepared batch showed contamination at 8.97 µg F^-/L, for the first blank and 5.7 µg F^-/L for the closing blank. The results provided for this batch in Table 4-7 (designated with an asterisk) are not blank corrected. For both analyses, there is a statistical difference between the means and the variances based on a t-test and an F-test. Percent breakthrough between the GAC columns for the mixed PFAS was below 50%.

Non-PFAS Compounds

The adsorption capability of the carbon for non-PFAS fluorinated compounds was tested by analyzing sets of aliquots of reagent water spiked with fluoxetine and fipronil. Both sets were analyzed in triplicate and spiked at approximately 6 µg F^-/L and 18 µg F^-/L. Table 4-8 shows the recoveries for both fipronil and fluoxetine.

Table 4-8 GAC Adsorption of Non- PFAS Fluorinated Compounds

	Spike Level 1 (~ 6.0 µg F^-/L)				Spike Level 2 (~18.0 µg F^-/L)			
	% Recovery			RSD (%)	% Recovery			RSD (%)
Compound	Rep 1	Rep 2	Rep 3		Rep 1	Rep 2	Rep 3	
First Method Blank Subtracted								
Fipronil	33.4	30.2	46.0	22.9	91.5*	68.7	66.8	18.2
Fluoxetine	42.9	76.4	68.8	28.0	67.9	69.4	68.4	1.2
Second Method Blank Subtracted								
Fipronil	93.2	90.0	105.6	8.6	91.5*	89.2	87.3	2.3
Fluoxetine	99.7	133.2	125.6	14.7	88.5	90.0	89.0	0.9

*Sample reprepared in separate batch

The analytical batch had one blank with a result of 4.14 µg F^-/L and a second blank had a result of 0.438 µg F^-/L. Unless there is obvious evidence of contamination in the adsorption unit, the first blank analyzed in the batch is subtracted from the sample results for the entire batch. Because the first blank in this batch was 10-fold higher than the second, the recoveries for fipronil were low. However, when utilizing the second blank for blank subtraction, the recoveries were within a 90 – 110% range. Replicate #1 for the fipronil spike level 2 was reprepared and analyzed in a separate analytical batch for confirmation, because the recovery observed in the original batch was ~180%. Regardless of the blank used for the subtraction, an F-test showed statistical differences between the variances of the two spike levels for fluoxetine. The column breakthrough for all replicates remained below 50%.

Non-PFAS fluorinated analytes were also included in validation work at ORD. For the four non-PFAS fluorinated chemicals included in the adsorption study, recoveries ranged from 41% to 104% across two different adsorption units (see Appendix C). Although varying degrees of adsorption were observed, results indicated that GAC columns have the capacity to adsorb both PFAS and non-PFAS fluorinated compounds.

C. Analytical Interferences

In ion chromatography, large concentrations of anions in samples can interfere with the peak resolution of the adjacent anions. In the case of fluoride, one such interference comes from chloride. Also, high concentrations of inorganic fluorine may be retained in the activated carbon which may not be fully removed by washing with sodium nitrate resulting in biased high values. The actual results for the interference analyses are provided in Appendix E.

Inorganic Fluorine

Fluorine, either organic or inorganic, is readily adsorbed into granular carbon. The volume of nitrate wash solution used in the method can remove inorganic fluorine up to a certain concentration. The volume of the wash solution may be increased; however, this may cause elution of the target analytes. Therefore, if the inorganic fluorine is not fully removed from the carbon with the nitrate wash, it will bias the AOF results high because the instrument cannot distinguish between the types of fluorine. To test the inorganic fluorine interference, the laboratory analyzed reagent water spiked with PFHxS and inorganic fluorine. The first set of three reagent water aliquots was spiked with PFHxS at 6.19 µg F^-/L and inorganic fluorine (from sodium fluorine) at 4 mg F^-/L, which is the maximum contaminant level allowed in drinking water. The second set of three reagent water aliquots was spiked with PFHxS at 6.19 µg F^-/L and 8 mg F^-/L of inorganic fluorine. PFHxS recoveries for this study are summarized in Table 4-9.

Table 4-9 Inorganic Fluorine Interference on GAC Adsorption

	4 mg F^-/L				8 mg F^-/L			
	% Recovery			RSD (%)	% Recovery			RSD (%)
Compound	Rep 1	Rep 2	Rep 3		Rep 1	Rep 2	Rep 3	
PFHxS	99.4	93.7	101.6	4.1	117.9	139.6	131.5	8.5

When PFHxS was spiked into reagent water at 6.19 µg F^-/L without any interfering inorganic fluorine present, the average recovery of the three replicates was 129.1% (Table 4-6). When the spiked sample had 4 mg F^-/L of inorganic fluorine added, the average recovery of the three replicates was 98.2%. The average recovery of the three replicates with 8 mg F^-/L of inorganic fluorine added was 129.7%. Based on the results, 25 mL of 0.01M sodium nitrate wash solution can completely remove up to 4 mg F^-/L of inorganic fluorine without causing any bias on the AOF results. When the concentration of inorganic fluorine increased to 8 mg F^-/L, AOF results were higher; however, the individual recoveries were not statistically different from the average of samples analyzed without inorganic fluorine. Therefore, for this method, field samples may contain up to 8 mg F^-/L of inorganic fluorine before the AOF results are artificially biased high by adsorbed inorganic fluorine that is not removed by the nitrate wash. Higher inorganic fluorine levels are not expected to be found in typical wastewaters and environmental samples and were not tested.

Inorganic Chloride

Chloride elutes closely with fluoride in ion chromatography, which may cause an interference when it is present at high concentrations in the sample. To test chloride interference, the laboratory analyzed a set of three aliquots of reagent water spiked with PFHxS at 6.19 µg F^-/L. The replicates were also spiked with sodium chloride at increasing concentrations of 100 mg Cl^-/L, 500 mg Cl^-/L, and 1000 mg Cl^-/L. PFHxS recoveries ranged from 75.2% to 124.2%, with the lowest observed recovery in the sample spiked with 1000 mg Cl^-/L (Table 4-10). Results indicated that field samples may contain up to 500 mg Cl^-/L without interfering with the peak integration for low levels of organic fluorine. At higher concentrations of chloride, the chloride peak interferes with fluorine peak integration, leading to biased results.

Table 4-10 Chloride Interference Test Results

	% Recovery of AOF		
Compound	100 mg Cl^-/L	500 mg Cl^-/L	1000 mg Cl^-/L
PFHxS	124.2	94.5	75.2

5. Method Detection Limit

As part of the method development effort, EPA required that the laboratory determine the method detection limit (MDL). For the purpose of the study, the MDL was determined using the revised MDL procedure *Definition and Procedure for the Determination of the Method Detection Limit*, Revision 2, December 2016, EPA 821-R-16-006, and also included at 40 CFR Part 136, Appendix B.

The revised procedure defines the MDL as:

> *"… the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results."*

The procedure consists of two parts: determination of the MDL based on method blanks (MDL_b), and determination of the MDL based on spiked samples (MDL_s). Both MDL_b and MDL_s are determined in a reference matrix, using at least seven replicates prepared and analyzed on three non-consecutive days.

The MDL_b is calculated as:

$$MDL_b = \overline{X} + t_{(n-1,1-\alpha=0.99)}S_b$$

where:

$\bar{X}$ = mean of the method blank results (use zero in place of the mean if the mean is negative)

$t_{(n\text{-}1,\ 1\text{-}\alpha\ =\ 0.99)}$ = the Student's *t*-value appropriate for the single-tailed 99th percentile *t* statistic and a standard deviation estimate with n-1 degrees of freedom.

S_b = sample standard deviation of the replicate method blank sample analyses.

Note: The equation above is used when all the method blanks for an individual analyte give numerical results. If some (but not all) of the method blank results give numerical results, then the MDL_b is set to be equal to the highest method blank result.

The MDL_s is calculated as:

$$MDL_s = t_{(n-1,\ 1-\alpha=0.99)}S_s$$

where:

$t_{(n\text{-}1,\ 1\text{-}\alpha\ =\ 0.99)}$ = the Student's *t*-value appropriate for a single-tailed 99th percentile *t* statistic and a standard deviation estimate with n-1 degrees of freedom.

S_s = sample standard deviation of the replicate spiked sample analyses.

For MDL determinations in this study, the reference matrix used was reagent water. After both an MDL_b and MDL_s have been determined, the initial MDL is set at the greater of the MDL_b and MDL_s value.

MDL Determination

This method tests for the aggregate concentration of organic fluorine which has been adsorbed onto the granular activated carbon. Since there are numerous PFAS and non-PFAS organofluorine compounds found in the environment, it would be impossible to determine an MDL that would include every compound. Therefore, PFHxS was selected as the compound to spike for MDL determination because individual compound spike recovery studies showed consistent recoveries ranging from 107 to 148%.

The laboratory performed two separate MDL studies using one lot number for the GAC selected for the study (see Section 4 of this report). The laboratory prepared and analyzed seven replicate method blanks and two sets of seven replicates of spiked samples. This approach yielded seven results for blanks and 14 results for spiked samples. The limitations of the instrument, more specifically the limitation presented by the observed GAC background, were kept in mind when estimating the initial MDL. The estimated initial MDL was set as three times the standard deviation of the initial background observed for the GAC columns. The spike levels were then established to be approximately between 2 and 10 times the estimated MDL, at 4.95 µg F^-/L (Study #1) and at 8.04 µg F^-/L (Study #2). The laboratory also estimated MDL_b and MDL_s for the second vendor (Mandel). However, due to poor GAC column performance, including carbon seeping out of the column and clogging the instrument, results from the Mandel columns are not discussed here, but are presented in Appendix B.

The laboratory provided all results to GDIT. After subjecting the results to a formal data review process, GDIT independently performed calculations of MDL_b and MDL_s, which are summarized in Table 5-1 below.

Table 5-1 MDL_b and MDL_s Calculations (µg F^-/L)

Method Blanks									
MB-1	**MB-2**	**MB-3**	**MB-4**	**MB-5**	**MB-6**	**MB-7**	**Mean**	**SD**	**MDL_b**
0.61	0.31	1.44	0.09	0.06	0.43	0.25	0.46	0.473	1.94
Spiked Matrix Study #1 (4.95 µg F^-/L)									
SP-1	**SP-2**	**SP-3**	**SP-4**	**SP-5**	**SP-6**	**SP-7**	**Mean**	**SD**	**MDL_s**
4.45	4.74	5.31	4.66	4.69	6.23	3.72	4.83	0.777	2.44
Spiked Matrix Study #2 (8.04 µg F^-/L)									
SP-1	**SP-2**	**SP-3**	**SP-4**	**SP-5**	**SP-6**	**SP-7**	**Mean**	**SD**	**MDL_s**
7.85	8.84	7.28	6.32	7.18	6.61	6.97	7.29	0.841	2.64

Because MDL Spiked Matrix Study #1 and #2 were spiked at different levels, the means were different and therefore a t-test was not a useful statistical tool with which to compare the observed results for the studies. However, a t-test was performed on the percent recoveries of the spiked MDL samples. Based on the two-tailed t-test, there was no statistical difference between the average percent recoveries between the MDL studies. Based on the results of an F-test, the variances between the two studies were not statistically different.

6. Initial Precision and Recovery

As part of the method development effort, EPA required that the laboratory perform three initial precision and recovery (IPR) studies. Each study consisted of a set of four reagent water aliquots, spiked at approximately 15 µg F^-/L. The first IPR study was spiked with the mixed 30 PFAS standard solution, the second with just PFHxS, and the third with just Fipronil. Percent recovery results for all three IPR studies are summarized in Table 6-1. The actual IPR study concentrations are provided in Appendix F.

Table 6-1 IPR Studies Recoveries

	% Recovery					RSD
Compound	**Rep 1**	**Rep 2**	**Rep 3**	**Rep 4**	**Mean**	**(%)**
Mixed PFAS	73.4	92.9	71.7	77.5	78.9	12.2
PFHxS	110.0	94.1	100.2	94.2	99.6	7.5
Fipronil	105.7	104.5	100.0	99.6	102.5	3.0

The individual and mean recoveries in all three studies fell well within 70 – 130%, with the lowest recoveries seen in the mixed PFAS standard. The recoveries for the mixed PFAS standard and Fipronil differed from the recoveries observed during the GAC adsorption testing (Section 4). However, results for PFHxS were consistent throughout all study phases. Recoveries for mixed standards may vary based on their composition, compound solubilities, and because surface adsorption can be irreproducible. Additional attention should be taken to ensure adequate instrument cleaning between sample batches.

7. Ongoing Precision and Recovery

As part of the quality control activities for the project and the draft procedure, ongoing precision and recovery (OPR) samples were analyzed with each study sample preparation batch. The study samples were analyzed in four batches, with one OPR per batch. The OPRs were spiked with PFHxS at 9.9 µg F^-/L. The observed recoveries were 88.2%, 84.5%, 92.6%, and 104.6%, well within the likely acceptance criteria for the final method. The average recovery was 92.4% and the standard deviation was 8.7%, thus demonstrating good accuracy and precision across those four batches.

8. Method Blanks

Two method blanks were analyzed with each analytical batch throughout the project. During the analysis of the inorganic fluorine and chloride interference testing (Section 4), one method blank returned a concentration of 18.62 µg F-/L. The high blank GAC column recoveries were traced back to earlier contamination on the adsorption unit within that sample batch. Therefore, any samples that had been eluted in the same contaminated adsorption port were prepared and analyzed again using fresh aliquots.

Because that high method blank was due to obvious contamination, the result was considered an outlier and not used for the statistical analysis of the results from all the method blanks. The 39 other method blank results used for this study are summarized in Table 8-1 below. The actual results for all 39 method blanks associated with each analytical activity are provided in Appendices D through G.

Table 8-1 Method Blank Summary (µg F^-/L)

# Blanks Analyzed	Minimum	Maximum	Mean	Std Dev	Median	# Above 3 µg/L	# Above 5 µg/L
39	0	8.97	1.30	1.92	0.48	5	3

9. Continuing Calibration Verification

A calibration verification (CV) standard was analyzed at the beginning and at the end of each analytical batch. As with the ICAL, the CV standards were combusted; however, they were not adsorbed onto the carbon columns. Verification was performed at three concentrations during the study, 2 µg F^-/L, 6 µg F^-/L, and 10 µg F^-/L (200 ng, 600 ng, and 1000 ng). A total of 59 calibration verification standards were analyzed during the study. The recoveries ranged from 85.6% to 102.8%, with an average recovery of 98%.

10. Matrix Spike Analyses

As part of the method development effort, EPA required that the laboratory analyze at least three (3) matrix spike (MS) aliquots of each of the 10 real-world environmental matrices. As described in Section 2 of this report, the laboratory was provided with nine (9) wastewaters and one (1) surface water for this purpose. The samples were stored in a refrigerator at 0 - 6 °C from receipt until the time of analysis. Although freezing the samples can prevent bacterial growth, which may cause degradation of certain PFAS compounds into other organofluorine compounds, this method broadly quantifies adsorbable organofluorine instead of individual compounds; therefore, refrigerated storage is allowed for up to 90 days. However, the final method will advise the user that aqueous samples should be analyzed as quickly as practical because bacterial and algal growth in the sample can cause clogging of the GAC column and interfere with sample adsorption.

At low pH levels, inorganic fluorine in the sample can cause high bias for AOF results, while organic carbon may lead to negative interferences and thus low bias by inhibiting quantitative adsorption of halogen bound organic substances to the activated carbon. Previous studies have recommended that the sample pH should be above 5 for proper carbon adsorption; however, at the moment, there is no established range for allowable levels of organic carbon in a sample. Therefore, in addition to the water quality parameters listed in Section 2, pH and total organic carbon (TOC) levels were determined for each of the study samples and results are summarized in Table 10-1 below. (Note that TOC was measured in these samples, rather dissolved organic carbon, because filtering the large numbers of samples required for the study in the field was considered impractical, especially given that the samples were collected by volunteers. In addition, because the samples were likely to be stored for at least several weeks before they were utilized, there was concern that the dissolved organic carbon content could change in storage and that the total organic carbon content, which includes the dissolved fraction, was less likely to change.)

Table 10-1 TOC and pH Results

Sample #	TOC (mg/L)	pH
#1	8.5	7.4
#2	13.3	7.3
#3	143	8.4
#4	5.8	6.6
#5	46.0	7.0
#6	96.5	6.5
#7	32.5	10.1
#8	22.4	6.9
#9	ND	3.6
#10	7.7	6.7

ND = Not Detected

Eight out of ten samples had pH values between 6.5 and 8.4, with one sample having a pH of 3.6 and another 10.1. Because Sample #9 had a pH of less than 5, fluorine-free potassium hydroxide (0.5 M) was used to adjust sample pH to 7, prior to analysis.

Study Sample Results

AOF background levels were determined for each of the study samples prior to preparing the spiked study samples. Although Sample #5 did not contain the highest total suspended solids, the GAC column and adsorption unit clogged when the unspiked sample was analyzed. Therefore, an empty column holder was fitted with quartz wool to pre-filter the sample and prevent clogging on the GAC. The quartz wool was placed in series, immediately before the top GAC column. A new aliquot of Sample #5 was analyzed

with the quartz wool pre-filter in place. The quartz wool was combusted in a separate combustion boat and the results from the quartz wool and both GAC columns were combined. A method blank was analyzed with the same technique, to ascertain the background of fluorine in the quartz wool. The results for the blank quartz wool and the two blank GAC columns were combined and used in the blank correction for Sample #5. For consistency, the spiked triplicate aliquots for Sample #5 were analyzed with the quartz wool, even though the sample was diluted 5x prior to spiking.

After a thorough review of the AOF background data, EPA and GDIT worked with the laboratory to determine three spiking levels (low, mid, and high) covering a range from 6 µg F^-/L to 15 µg F^-/L. Multiple aliquots of each sample were spiked with PFHxS at the sample-specific levels and analyzed in triplicate. Samples #3, #4, #5, #6, and #9 were diluted prior to spiking due to their high AOF background to keep the results within the calibration range. The pH of Sample #9 was adjusted to a pH of 7 using 0.5M potassium hydroxide solution prior to analysis of the aliquots for the AOF background levels, as well as prior to adding the spiking solution to the matrix spike aliquots.

The background AOF results, spike results, mean recoveries, and relative standard deviations (RSDs) of all matrix spike samples across all aqueous matrices are summarized below in Table 10-2. The spike recoveries were calculated by subtracting the AOF background results. The dilution factors for Samples #3, #4, #5, #6, and #9 were taken into account when calculating the percent recoveries.

Table 10-2 Study Samples Results

Sample #	Nominal Spike Conc. µg F^-/L	Background AOF (µg/ F^-L)	Recovery (%)				RSD (%)
			Replicate 1	Replicate 2	Replicate 3	Mean	
# 1	9.9	3.57	92.5	89.7	87.7	90.0	2.7
# 2	6.19	2.42	101.4	96.2	99.8	99.1	2.7
# 3[1]	15.47	18.8	119.1	128.3	132.4	126.6	5.4
# 4[1]	15.47	14.7	89.1	100.1	108.9	99.4	10.0
# 5[1]	9.9	10.5	109.6	164.2	105.2	126.3	26.0
# 6[1]	15.47	22.1	101.4	105.5	112.8	106.6	5.4
# 7	6.19	1.10	108.7	144.6	102.5	118.6	19.2
# 8	6.19	3.48	87.9	89.7	104.4	94.0	9.6
# 9[1,2]	15.47	22.0	107.9	102.9	106.4	105.8	2.4
#10	9.9	2.51	89.4	129.6	89.9	103.0	22.4

[1]Sample diluted 5x prior to spiking.
[2]Analyzed using the extended calibration curve. Sample pH adjusted prior to spiking and analysis.

Regardless of the observed variation across the sample sources, all the mean recoveries were between 90% and 130%. The lowest observed individual recovery was 87.9% while the highest was 164.2%. When considering a recovery range of 70 – 130%, a total of twenty-seven (90%) results fall within that range. If the range is widened to 50 – 150%, then a total of twenty-nine (96.7%) results fall within that range.

The average percent breakthrough between the columns for the study samples was 22.6%, with the maximum value at 41.7%.

Organic carbon in aqueous samples may yield a low bias for AOF results by competing for sites on the GAC, resulting in poor AOF adsorption. Therefore, the concentrations of TOC in each sample were compared to the mean recoveries of the spiked AOF and are presented in Figure 3. The TOC concentrations for the study samples ranged from 5.8 to 143 mg/L, with Sample #3 having the highest TOC. For Sample #3, a peak interference that required manual integration was observed next to the fluorine peak on the chromatogram for the bottom GAC column in all three sample replicates. This interference may be due to the high level of TOC; however, confirmation was not possible during the

study. The peak interference was not observed in any of the other study samples. Therefore, the presence of TOC levels of up to 143 mg/L did not seem to interfere with the adsorption of organofluorine.

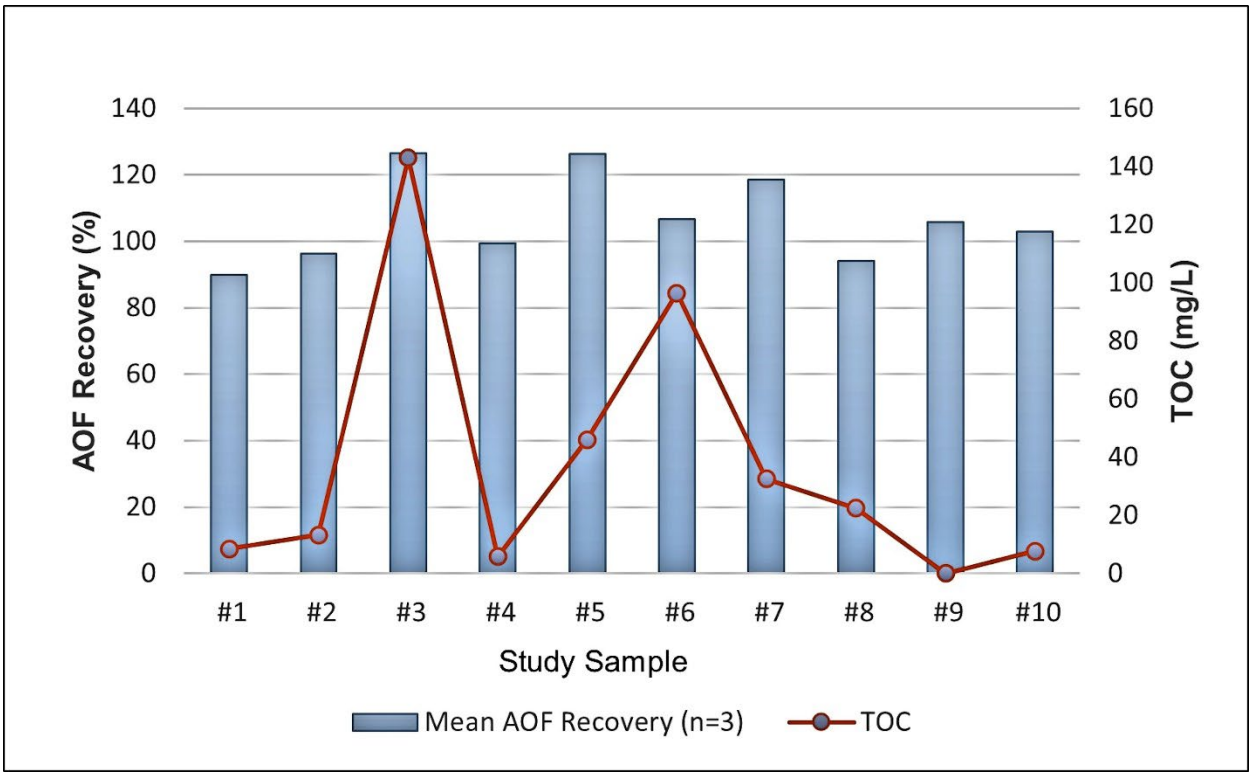

Figure 3 AOF Recovery vs. TOC Concentration

11. Data Review and Validation

Results for all analyses in this study were submitted as electronic data deliverables (EDDs) in Excel format and supported by raw data and reporting forms provided in PDF format equivalent to a hardcopy data package. Separate data submissions were provided for each technical directive (e.g., each task) in the study. Both the EDDs and the supporting raw data were reviewed for completeness and for data quality. Data were evaluated based on the preliminary method performance criteria described in the draft method. However, formal method performance criteria will be established through an upcoming multi-laboratory validation study. The data review process was patterned after that used for various other Office of Water studies.

Data qualifiers and comments were added to the EDD, and the file was saved with a new file name that indicated data had been reviewed. This approach preserves the original laboratory submission. While some data were qualified as part of this review process, the results were not rejected based on the laboratory's preliminary criteria, and the qualifiers applied by GDIT are intended to make the data user aware of potential data quality issues. The exception to this is in cases where the result did not meet qualitative identification criteria (e.g., retention time outside the window).

MDL, IPR, reconnaissance (unspiked real-world samples), MS, OPR and method blank results were evaluated in both the EDD and PDF raw data, while initial calibration and calibration verification results were not provided in the EDD and therefore only the PDF raw data were evaluated. Table 11-1 describes the type and number of analyses (including samples, calibration standards, and QC samples) that were reviewed.

Table 11-1 Type and Number of Analyses Reviewed

Sample Type	Description	# Analyses
Initial Calibration	NA	8
Calibration Verification	NA	59
Backgrounds	Reagent Water	40
Sorption	Single-compound Adsorption	96
Sorption	Mixed Compound Adsorption	12
Sorption	Non-PFAS Compound Adsorption	24
Interference	Inorganic Fluorine	6
Interference	Inorganic Chloride	3
MDL_b	Reagent Water	14
MDL_s	Spiked Reagent Water	28
IPR	Spiked Reagent Water	12
Reconnaissance	Unspiked Study Samples	9
MS	Spiked Study Samples	30
OPR	Spiked Reagent Water	4
Method Blanks	Reagent Water	50
	Total	**395**

Completeness check – The data report narratives in the data package were reviewed and any quality control or performance related issues were noted. The data were verified to be consistent with the narrative and appropriate validation qualifiers were applied. Electronic data deliverable (EDD) elements and results were checked for completeness and consistency with the raw data. Elements checked included EPA sample identifier, analysis date and time, laboratory qualifiers, found concentrations, sample sizes (volume), dilution factors, spiked amounts, percent recoveries, preparation date, and concentration units. Hardcopy and EDD data were checked to ensure that no data were missing or inconsistent for all samples and blanks. Hardcopy data were checked to ensure that all chromatograms and quantitation reports were

available for all analyses and that all samples were reported on the sample pretreatment and sample preparation worksheet records.

Sample Receipt Conditions – The sample receipt date was compared to the preparation date to ensure that the 90-day holding time for PFAS in water had been met. The temperature conditions upon receipt were checked to ensure that samples were received at a temperature of 0 – 6 °C. The storage temperature conditions after receipt were evaluated to ensure that the samples were stored at a temperature of 0 - 6 °C. Any samples not in compliance with these conditions were noted in the reviewed EDD. However, given the nature of the study and the use of bulk samples to prepare test samples, the temperature on receipt had no effect on EPA's ability to use the study results.

Sample Dilutions – Results were checked to ensure they were within the range of the calibration curve. One sample analyzed during the study sample reconnaissance to determine the background AOF concentration was slightly above the calibration range of 20 µg F^-/L. The result for this sample was flagged "ACR, J" as above calibration range and was considered an estimated value. Therefore, spiked samples were prepared using a 5x dilution for samples with high AOF backgrounds.

Initial Calibration – The initial calibrations were checked to ensure that at least 5 calibration standards were analyzed and that they covered the concentration range of 50 – 2000 ng F^- (0.5 – 20 µg F^-/L). The model fit (RSE) for the initial calibration standards was checked to ensure that it was ≤ 20%. The RSE calculations were independently performed by GDIT to ensure that they were within 1% of the reported values. (This 1% allowance accounts for rounding differences between the data available on the instrument and the values with fewer decimal places that are typically reported in the hard copy.)

Calibration Verification (CV) – All samples and blanks were checked to ensure they were bracketed by a CV every 10 samples. The observed recoveries for the CV were within 80 – 110%. The reported concentration calculations were independently performed by GDIT to ensure they were within 1% of the reported values.

OPR Recovery – The percent recoveries for the OPR were checked to ensure they were within preliminary control limits (i.e., 70 – 130%). Percent recovery calculations were independently performed to ensure they were within 1% of the reported values.

Matrix Spike Recovery – Spiked real-world matrices were used to prepare matrix spike samples and recoveries were checked to ensure they were within the preliminary control limits (i.e., 70 – 130%). Percent recoveries for a few samples were recalculated to ensure they were within 1% of the reported values. If recoveries were outside the limits, then results for the associated unspiked sample were qualified with "HMSR" for high recoveries. Out of 30 total results, 3 sample results were qualified with "HMSR." Because three matrix spike samples were prepared in each wastewater sample, rather than the traditional two, the RSD of the recoveries was calculated to evaluate precision of the three results.

Quantification Check - Concentration result calculations in each sample were independently performed by GDIT using equations provided in the draft to ensure they were within 1% percent of the reported values.

Table 11-2 List of Validation Flags Used

Validation Flag	Comments	Implications
ACR, J	Above Calibration Range, Estimated	The result for the sample was above the calibration range. The result is considered an estimated value.
HMSR	High Matrix Spike Recovery	High matrix spike (MS) recovery indicated a positive interference or a high bias. Isolated instances of high recovery are not uncommon, and patterns across multiple MS samples are more of a concern.

12. Conclusions

The single-laboratory validation study of the AOF method met EPA's outlined criteria:

1. *The method provides an aggregate response for adsorbable organofluorine from single compounds with chain lengths between C_4 and C_8 as well as non-PFAS fluorinated compounds using combustion ion chromatography.*

The study generated initial precision and recovery data for aqueous matrices. IPR recoveries between 80 – 120% were achieved in most of the 30 aqueous matrix spike samples analyzed during this study (25 out of 30 results, or 83%). The single-laboratory validation matrix spike results demonstrate that this method is capable of quantifying AOF from various environmental aqueous sources. However, this method is classified as a screening method in recognition of the low bias for certain organofluorines, particularly long-chain PFAS.

2. *The method is sensitive enough to be used as a screening method.*

The method validation study demonstrated that there were no negative effects on the adsorption of organofluorine onto carbon when the sample contains TOC at concentrations up to 140 mg/L. The nitrate wash employed in the method could remove up to 8 mg F^-/L of inorganic fluorine that may have been adsorbed in conjunction with organofluorines, reducing the positive bias from inorganic fluoride. The method is capable of adsorbing AOF in samples with chloride concentrations up to 500 mg Cl^-/L without causing peak interference in the chromatogram. When initial testing of these interfering constituents indicates that they exceed these limits, the sample will need to be diluted to mitigate the interferences. Due to the ubiquitous occurrence of PFAS, almost all method blanks contained some level of organofluorine. Blank results in this study suggest that AOF contamination can originate from the capping material used in the adsorption columns that could not be removed by washing the column with the nitrate solution and from contamination of the adsorption unit during routine use. Due to these factors, high blank levels were observed in certain cases. Thus, the single-laboratory validation data demonstrated that this method is sensitive; however, unless strict cleaning protocols are followed, the method can be subject to significant blank contamination. Nonetheless, the method can reliably screen for organofluorines at low part-per-billion levels.

3. *Can be implemented at a typical mid-sized full-service environmental laboratory.*

Not all laboratories own an adsorption unit or a combustion ion chromatography unit; therefore, the ease of implementation is unknown, but there is little doubt that a typical full-service laboratory could implement this procedure. The procedure has many similarities to other EPA halogen methods (e.g., Methods 1650 and 9020B). All the standards for the method are commercially available from one or more vendors. Also, two laboratories performed similar single-laboratory validation studies, the Pace IDEA laboratory, as detailed in the body of this report, and EPA's ORD Laboratory in Cincinnati, OH, as summarized in Appendix C. Both laboratories achieved similar method performance and results. This indicates that the method can likely be implemented in a typical mid-sized full-service environmental laboratory.

EPA's next step will be to initiate a multi-laboratory validation study of this method to demonstrate that it can be applied by a broader community of laboratories and to generate data for statistically derived method detection limits, minimum levels, and quality control limits that define method performance.

13. References

1. ASTM, WK68866, *New Test Method for Determination of Adsorbable Organic Fluorine in Waters and Wastewaters by Adsorption on Activated Carbon Followed by Combustion Ion Chromatography*, (no date), www.astm.org

2. Jones, Jenifer L. and Shoemaker, Jody A., 2022, *Development of a standardized adsorbable organofluorine screening method for wastewaters with detection by combustion ion chromatography*, in prep.

3. USEPA, 2018, *Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program,* EPA 821-B-16-001, Office of Water, Office of Science and Technology, Engineering and Analysis, Washington, DC, February 2018.

Appendix A
Study Plan

(This appendix attempts to preserve the pagination and numbering of the original document)

Study Plan/QAPP for Developing an Adsorbable Organic Fluorine Method

Prepared for

Adrian Hanley
U.S. Environmental Protection Agency
Office of Water
Office of Science and Technology
Engineering and Analysis Division (4303T)
1200 Pennsylvania Avenue, NW
Washington, DC 20460

Prepared by

CSRA LLC, a General Dynamics Information Technology company
6361 Walker Lane
Suite 300
Alexandria, VA 22310

Prepared under

EPA Scientific and Technical Support Contract EP-C-17-024

May 17, 2021

Approvals

ADRIAN HANLEY Digitally signed by ADRIAN HANLEY Date: 2021.06.29 14:35:54 -04'00'
Brian D'Amico, EPA EAD TASB Chief — Date

Adrian Hanley is acting for Brian D'Amico June 28 - July 2, 2021

ADRIAN HANLEY Digitally signed by ADRIAN HANLEY Date: 2021.06.29 14:34:12 -04'00'
Adrian Hanley, EPA WACOR — Date

Burket, Sarah Digitally signed by Burket, Sarah Date: 2021.05.28 09:55:38 -04'00'
Bekah Burket, EPA Project Manager — Date

LEMUEL WALKER Digitally signed by LEMUEL WALKER Date: 2021.06.17 10:39:43 -04'00'
Lemuel Walker, EPA QA Coordinator — Date

Lynn Walters Digitally signed by Lynn Walters Date: 2021.05.19 17:12:39 -04'00'
Lynn Walters, CSRA Program Manager — Date

Mirna Alpizar Digitally signed by Mirna Alpizar Date: 2021.05.19 15:29:35 -04'00'
Mirna Alpizar, CSRA Study Manager — Date

Marguerite E. Jones Digitally signed by Marguerite E. Jones Date: 2021.05.24 14:38:39 -04'00'
Marguerite Jones, CSRA QA Manager — Date

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DISCLAIMER

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Sarah (Bekah) Burket, EPA EAD
Lemuel Walker, EPA EAD
Lynn Walters, CSRA
Harry McCarty, CSRA
Mirna Alpizar, CSRA
Marguerite Jones, CSRA
ASTM D19 working group
EPA AOF working group

Study Plan for Developing an Adsorbable Organic Fluorine Method

SECTION 1. BACKGROUND

Various organizations and regulatory authorities at state, federal, and international levels are taking action to address the release of per- and polyfluoroalkyl substances (PFAS) to the environment. Some of the most common legacy sources of PFAS were from the manufacture of non-stick materials and were largely consisted of perfluorinated compounds such as perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonic acid (PFOA). Voluntary efforts to phase out those compounds began in 2008, but a large variety of other polyfluorinated alkyl substances are now in common use as alternatives to PFOS and PFOA. In addition, there are other significant sources of PFAS, including aqueous film-forming foams (AFFF) used in firefighting, that contain many more fluorine-containing compounds. Some estimates place the number of PFAS in current use at over 4,000; therefore, developing analytical methods for each individual PFAS compound is impractical, if not impossible.

EPA's Office of Water is investigating the use of an aggregate measure of PFAS and other organofluorine substances in wastewater, which has been termed "total organic fluorine" (TOF) by some, but is more appropriately called "adsorbable organic fluorine" (AOF). There is regulatory precedent at EPA for this aggregate measure approach, with the closest example being the use of adsorbable organic halogens (AOX) in regulation of the pulp and paper industry in the 1990s, through promulgation of EPA Method 1650C, Adsorbable Organic Halides by Adsorption and Coulometric Titration (Ref. 8.1). Other examples of regulatory precedent for the use of aggregate pollutant measures include, but are not limited to, oil and grease, biochemical oxygen demand, and whole effluent toxicity.

Most PFAS are adsorbed to some degree by the activated carbon used in Method 1650C; unfortunately, the response of the coulometric detector system in that method to fluorine is poor compared to that of chloride and the heavier halogens, leading to high detection and quantitation limits. In addition, coulometry is not specific to the individual halogens, but rather, detects them all as a group. This means, even if coulometry were able to detect fluorine, a method would not be able to distinguish between organofluorine (PFAS) or the more common organochlorine compounds. A potential solution described in the literature and available commercially from at least one or more instrument manufacturers is to use combustion followed by ion chromatography (CIC) as the detector for determining the organic fluorine adsorbed on the activated carbon column used in Method 1650C. Although EPA's alternate test procedure (ATP) under the Clean Water Act provides a mechanism for modifying approved methods, it does not allow for changes to detection systems. Therefore, the use of CIC or any other detector change for determining AOF would be considered a new method for monitoring compliance with Clean Water Act requirements. At the time of this writing, ASTM International Committee D19 on Water is developing a draft method for Absorbable Organic Fluorine by CIC. In accordance with the National Technology Transfer and Advancement Act (NTTAA), ASTM has agreed to share their draft method with EPA and work collaboratively in further development and validation of the method. EPA will use the data generated from this study to develop an EPA method, and ASTM will use the data to develop an ASTM standard. If EPA proposes its method for inclusion into 40 CFR Part 136, EPA will also propose the ASTM standard within the same rule (assuming the two methods have comparable QC requirements). The end goal is two methods, one EPA and one ASTM, intended for proposal at 40 CFR Part 136.

This document is a hybrid study plan and quality assurance project plan (QAPP) for the development of an EPA procedure, based on the original ASTM draft, for AOF that can be optimized and validated in a single laboratory. The format and content of the document are consistent with the EPA Office of Water's Hybrid Quality Assurance/Study Plan Format for Method Development and Method Validation Studies, Revision 1, July 2020. As such, it should be considered a "living document" that is intended to be updated as decisions are made by EAD and the study progresses. The study will be conducted in the following seven phases, as described in Sections 4.1 through 4.7 below.

- Phase 1: Identify an appropriate laboratory and provision the necessary analytical instrumentation
- Phase 2: Establish the calibration range and linearity of response
- Phase 3: Test adsorption media, all other reagents and materials, and potential sources of interference, including adsorption, combustion, or analytical interferences
- Phase 4: Establish the method detection limit
- Phase 5: Establish precision and recovery in a reference matrix, using common organofluorine compounds
- Phase 6: Evaluate method with real-world wastewater samples
- Phase 7: Test method with solid matrices

SECTION 2. STUDY OBJECTIVES

The main objective of this study is to develop and characterize the performance of a new method for adsorbable organofluorine compounds that:

- Provides an aggregate response for adsorbable organofluorine compounds using CIC
- Can measure AOF at levels useful for a screening tool
- Can be implemented in a typical environmental laboratory using commercially available materials and instrumentation

In addition to the overall objective described above, EAD has two general quality objectives for this study:

1. Except where otherwise directed, all validation data must be generated according to the analytical and quality assurance/quality control (QA/QC) procedures specified in this study plan and the QA/QC strategies in typical EPA-approved analytical methods for use in CWA programs (e.g., incorporate the twelve QC elements, where applicable, listed at 40 CFR Part 136.7).
2. All data produced must be capable of being verified for accuracy and inconsistencies by an independent reviewer of the analytical data package.

To meet these quality objectives, EPA and CSRA will employ the following QA/QC strategies:

- All project activities will be performed in accordance with this study plan
- The laboratory responsible for preparing and analyzing study samples must have demonstrated experience in performing work of a similar nature, preferably with experience in AOX in water samples and ion chromatography (IC), and must have a comprehensive QA program in place and operating throughout their study operations. The laboratory will be required to follow all QC procedures defined in Section 5 of this Study Plan. (These requirements will be included in the laboratory statement of work or memorandum of understanding.)
- This plan recognizes that during the development and optimization process, the QC practices normally applied to the running of samples or used in the validation phase may not be applicable. However, the developing laboratory is expected to maintain good lab and research practices; all experiments must be meticulously documented.
- Known QA/QC approaches are included in each study phase description hereafter (Section 4), however as method development is an iterative process, a supplemental QAPP (SQAPP) may be developed if additional QA measures are required. The SQAPP must be reviewed and approved by EPA before work on subsequent phase(s) of the project begins.

Cumulatively, these requirements are intended to ensure that the data produced in this study are of appropriate and documented quality.

SECTION 3. STUDY MANAGEMENT

The study will be managed by Bekah Burket, the EAD Project Manager, under the supervision of Adrian Hanley, the EPA Work Assignment Contracting Officer's Representative (WACOR), who will provide technical direction to CSRA. Lemuel Walker, the Quality Assurance Coordinator for EAD, will provide QA oversight for EPA.

Day-to-day management and coordination of study activities will be performed by CSRA Study Manager, Mirna Alpizar, under the supervision of the CSRA Work Assignment Manager, Harry McCarty, and the CSRA Program Manager, Lynn Walters, and in accordance with EAD guidance. Marguerite Jones, the Quality Assurance Manager for CSRA, will provide QA oversight for CSRA. The organization chart in Figure 1 below illustrates the relationship of these parties.

Note: The responsibilities illustrated in Figure 1 assume that CSRA will procure the services of the laboratory. If EPA is successful in recruiting a volunteer laboratory, the chart will be revised accordingly.

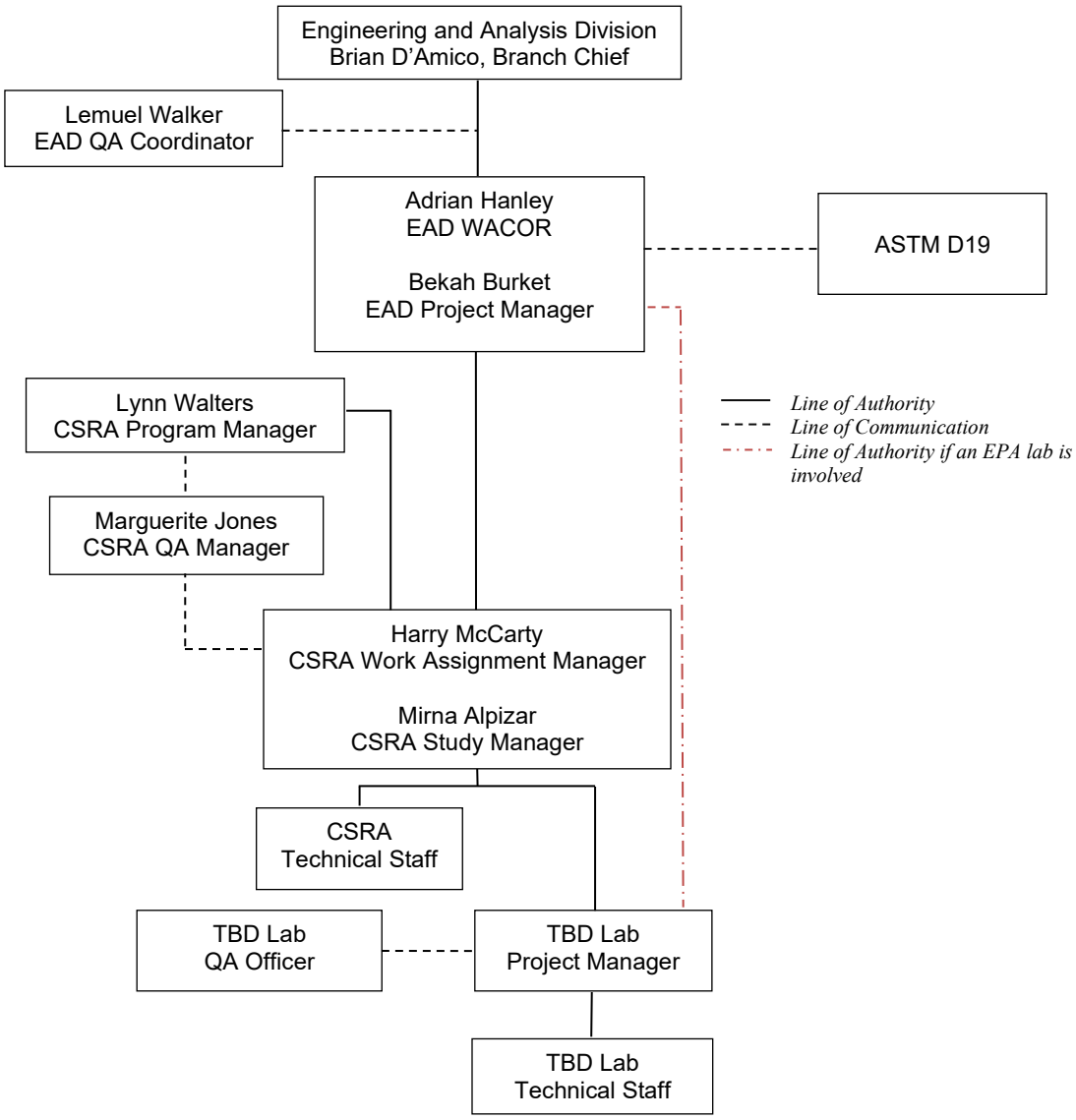

Figure 1. Organization Chart

The laboratory performing the study will be identified in the first phase. For the purposes of this version of this study plan, the laboratory will be referred to as "TBD Lab." The EAD Project Manager will be responsible for laboratory oversight if an EPA laboratory is used (see Section 4.1), and CSRA will provide assistance in monitoring laboratory progress. Alternatively, EPA will task CSRA with procuring the services of a commercial environmental laboratory and providing oversight of the laboratory.

For this study, TBD Lab will be expected to own and be familiar with the operation of an AOF CIC system. In the event that TBD Lab does not own an AOF CIC system, then the laboratory will be required to obtain an AOF CIC system and will be responsible for ensuring proper operation of their system and training of their analysts prior to participating in this study. TBD lab will, with oversight from CSRA, perform various studies needed to develop and optimize the method. Once the initial tests are complete and findings reviewed and approved by CSRA and EAD, the TBD Lab will prepare and analyze real-world and synthetic wastewater matrices for use in this study, obtained with assistance from EAD and CSRA as needed.

TBD Lab will submit their analytical results to CSRA. CSRA, under EPA direction, will review and evaluate all analytical data and assist EAD in drawing conclusions from the results. Depending on the

availability of resources, CSRA will either prepare a draft method document and a draft study report that summarizes these results and conclusions for EAD review, or will provide data and technical assistance to EAD staff to aid them in preparing such a report. Throughout each phase listed in Section 4, CSRA and EPA will also share all data generated during the study with ASTM.

SECTION 4. TECHNICAL APPROACH

The study will be performed in seven phases. Phase 1 (Section 4.1) involves identification of an appropriate laboratory with the necessary analytical instrumentation. Phase 2 (Section 4.2) will establish the calibration range and linearity of response. Phase 3 (Section 4.3) consists of testing adsorption media and all other reagents and materials, as well as testing potential interferences from inorganic fluorine. Phase 4 (Section 4.4) will establish a method detection limit (MDL) for aqueous matrices. Phase 5 (Section 4.5) involves determining precision and recovery in a reference matrix, using common organofluorine compounds. Phase 6 (Section 4.6) involves the evaluation of method performance in real-world wastewater samples. Phase 7 (Section 4.7) is focused on testing the potential applicability of the method to solid matrices.

Beginning with Phase 3 of the study, each parameter to be tested will be performed using a set of two granular activated carbon (GAC) columns, placed in tandem on the absorption module. The carbon from each column must be combusted individually and the percentage breakthrough calculated using Equation 1 below:

$$\%\, Breakthrough = \frac{(C_2 - B_2) \times 100}{[(C_1 - B_1) + (C_2 - B_2)]} \qquad \text{Eq 1}$$

where:
C_1 = Measured µg F^- on the first column
C_2 = Measured µg F^- on the second column
B_1 = µg F^- for first column from reagent water blank
B_2 = µg F^- for second column from reagent water blank

4.1 Phase 1 - Identify an Appropriate Laboratory and Provision the Necessary Analytical Instrumentation

The focus of Phase 1 is to identify an appropriate laboratory in which to perform the single-laboratory testing. EAD is considering using in-house resources, including one of EPA's Regional laboratories or the Office of Research and Development (ORD) laboratories. The advantage of using in-house laboratory resources is largely financial, in that EPA can avoid the costs associated with contracting an outside laboratory.

The EAD Project Manager, Bekah Burket, will be responsible for contacting ORD and the Regions to ascertain their capabilities, interest, and availability. Ideally, one of the laboratories will:

- Possess a CIC instrument and the necessary sample processing equipment
- Have experience running the sample preparation process for EPA Method 1650 (AOX) or similar sorption procedures
- Have staff available who are experienced in method development and evaluation
- Have management support for the project
- Have a comprehensive QA program in place and operating throughout their study operations
- Follow all QC procedures defined in Section 5 of this Study Plan

In the event that in-house resources are not available, EAD will task CSRA with obtaining the services of a commercial environmental laboratory using the approach used by CSRA for previous method

development projects; this approach includes an assessment of laboratory competency prior to selection and ensuring that the selected laboratory meets the criteria listed above.

Once a laboratory is identified through either process, EAD and CSRA will work with them to formalize the process and schedule for completing the study as outlined in this plan or revising the plan where necessary. The requirements of the study plan will be incorporated into a memorandum of understanding (MOU) for an in-house laboratory, or a contractual statement of work (SOW) for a commercial laboratory contracted by CSRA.

4.2 Phase 2 - Establish the Calibration Range and Linearity of Response

Phase 2 of the project will involve performing initial calibrations and assessing the linearity of the instrument response. The laboratory will perform at least three initial calibrations to demonstrate the applicable range of the procedure. Each calibration should contain at least 5 calibration levels and fall within the applicable range specified by the instrument manufacturer. The choice of the standard will be discussed by EAD, CSRA, and the laboratory during the early portion of the study, based on instrument vendor recommendations and other information.

The calibration model to be used will be external standard calibration, because any possible internal standard would be combusted and converted to fluorine during sample processing and analysis. A simple linear regression model will be used, not forced through the origin, and an initial acceptance limit will be a correlative coefficient of ≥ 0.995. However, relative standard error (RSE) will also be employed to assess model fit.

Before proceeding with later phases of the effort, EAD, CSRA, and the laboratory will discuss the results from Phase 2.

4.3 Phase 3 - Test Adsorption Media, Other Reagents and Materials, and Potential Interferences

After the laboratory is chosen in Phase 1, EAD and CSRA will work with that laboratory to identify potential sample sorbents for AOF. Based on previous literature search efforts, there are two main types of sorbents that have been used by researchers. Those are granular activated carbon (GAC) and weak anion exchange (WAX) media. GAC is the sorption media used in Method 1650 for AOX, and it has a well-established history for organochlorine compounds. WAX media have been used in many procedures for specific organofluorine components, including specific PFAS analytes, as well as a sorbent in some literature reports of extractable organic fluorine. However, we will examine WAX media only if results from GAC are deemed unsatisfactory.

The focus of Phase 3 testing will be to establish the following characteristics of potential sorbents:

- Commercial availability
- Compatibility with the existing sorption equipment
- Sorptive capacity for AOF constituents (e.g., how much mass can they sorb from a typical size aqueous sample, and potential breakthrough or carryover)
- Sorptive capacity for inorganic fluorine
- Background level of fluorine on the sorbent that cannot be removed by conditioning the sorbent

The sorptive capacity will be evaluated for both individual PFAS and mixtures of PFAS constituents spiked into reagent water. PFAS constituents will span several known classes and chain lengths of PFAS compounds. Additionally, selected non-PFAS fluorinated compounds (e.g., a pesticide and a pharmaceutical) will be evaluated. The specific constituents will be discussed by EAD, CSRA, and the laboratory early in the project, but may include PFOS, which has been the focus of much of the health-

related news about PFAS. Other potential PFAS constituents are those included in EPA methods for drinking water, such as Method 537.1 (Ref. 8.2), because pure standards of those constituents are commercially available.

A suitable sorbent will not contain any detectable AOF. Each potential sorbent will be used to prepare multiple method blanks that are carried through the entire analytical procedure. The results from the method blanks will be used to compare the potential sorbents. If available, multiple lots and manufacturers of each sorbent will be tested to evaluate lot-to-lot variation. During evaluation of method blanks, the laboratory will also identify and attempt to reduce any potential sources of PFAS contamination, as well as determine if carryover contamination is likely from high levels of fluorine in a previous sample.

The laboratory also will assess the background level of inorganic fluorine in each potential sorbent. Washing the sorbent with 25 mL aqueous sodium nitrate may reduce positive interference from inorganic fluorine. To test background levels of inorganic fluorine on the sorbent, results from washed and unwashed process blanks will be compared. For all testing from Phase 3 on, pH of washing solutions and samples should be between 6 and 8.

Inorganic fluorine is present in environmental samples from a variety of sources and most notably, it is added to drinking water to prevent tooth decay. Therefore, it is expected to be present in effluents derived from domestic sewage, as well as industrial effluents from facilities that use potable water in their processes. To test for the sorptive capacity of each sorbent for inorganic fluorine, the laboratory will analyze a set of reagent water aliquots spiked with known PFAS constituents and a second set of aliquots spiked with the same known PFAS constituents plus an inorganic fluorine salt, such as sodium fluorine or stannous fluorine. All analyses will be performed using two GAC columns for each aliquot. The percent breakthrough between the first and second columns will be calculated for each spiked compound using Equation 1. The initial tests will use 4 mg/L of inorganic fluorine, which is the maximum contaminant limit (MCL) for fluorine in drinking water, and depending on the results, additional sets of samples with increasing concentrations of the inorganic fluorine may be tested.

Other potential interferents, such as high levels of chloride ion and dissolved organic carbon (DOC), will be tested in a similar manner. For example, to test the possible interference of chloride, recoveries of known PFAS constituents will be determined in a set of reagent water samples that have also been spiked with increasing concentrations of chloride (for example, NaCl).

Before proceeding with later phases of the effort, EAD, CSRA, and the laboratory will discuss the results from Phase 3. Determining the capacities of the various sorbents will allow EAD to balance the characteristics of the specific sorbents, the sensitivity of the CIC instrumentation, and different sample sizes to develop the most practical method parameters for the AOF procedure.

4.4 Phase 4 - Establish the Method Detection Limit

Following successful demonstration of the calibration range and linearity, the laboratory will determine the MDL using the revised MDL procedure published in 2017 at Code of Federal Regulations (CFR), Title 40, Part 136, Appendix B (Ref. 8.3). The laboratory will prepare and analyze at least seven replicate reagent water samples spiked with a known PFAS component and an equal number of unspiked reagent water samples over three non-consecutive days and determine the MDL_s (the MDL based on spiked samples) and MDL_b (the MDL based on method blanks), respectively. Depending on the results of Phases 2 and 3, the spiking compound may be the same one used to perform the calibration, and the spiking level will be based on the guidance in the revised MDL procedure, the results for the initial calibration in Phase 2, and other information, such as recovery data.

Given the prevalence of low levels of PFAS components in sampling equipment and instrumentation, the MDL for the procedure may be based on the MDL_b, rather than the MDL_s. Several iterations of the MDL study may be required. EAD, CSRA, and the laboratory will discuss the results from Phase 4 before proceeding with later phases of this effort.

4.5 Phase 5 - Establish Precision and Recovery

The laboratory will perform at least three separate initial precision and recovery (IPR) studies to provide sufficient data for development of draft performance specifications. Each of the three IPR studies will be performed using spiked reagent water as the reference matrix.

The IPR consists of four replicate samples of reagent water spiked with the same known PFAS components used for the MDL study and carried through the entire analytical process (sample preparation and analysis). During this phase, the laboratory will evaluate recoveries for some individual PFAS compounds, at least one PFAS mixture, and some non-PFAS constituents. Exact spike concentrations will be determined by EAD, CSRA and the laboratory, based on the results of Phases 2 and 4, but ideally, there should be three spiking levels, one at about 3 to 5 times the MDL, one around the midpoint of the calibration range, and the other at the expected maximum of the calibration curve, or at the maximum concentration to prevent breakthrough. The laboratory will calculate the percent (%) recovery (%R) using Equation 2:

$$\%\,Recovery = \%R = \frac{C_s}{C_n} \times 100 \qquad \text{Eq. 2}$$

where:
C_s = Measured concentration of the spiked sample aliquot
C_n = Nominal (theoretical) concentration of the spiked aliquot

The laboratory will calculate the relative standard deviation (RSD) from the results of the four replicates using Equation 3:

$$RSD = \frac{SD}{C_{avg}} \times 100 \qquad \text{Eq. 3}$$

where:
SD = Standard deviation of C_s for the four replicates
C_{avg} = Average measured concentration for the four replicates

The CSRA Study Manager will review the IPR data and work with the EPA Project Manager to establish draft performance criteria for % Recovery and RSD of the IPR based on the single-laboratory study results.

4.6 Phase 6 - Evaluate Method with Real-world Wastewater Samples

Following a brief review of the Phase 5 results by EPA and CSRA to ensure that study goals for this phase were met, CSRA will direct the laboratory to proceed with the sixth phase of the study. The focus of Phase 6 is to evaluate the AOF procedure in various wastewater matrices. The laboratory will analyze at least nine different wastewater matrices, covering matrix categories analogous to those specified for ATPs. Wastewater may consist of effluents from a publicly owned treatment works (POTW) or a substitute wastewater as specified in ASTM D 5905 - 98 (Reapproved 2018), Standard Specification for Substitute Wastewater (Ref. 8.4). At least one of the wastewater matrices should have at least one of the following characteristics such that each criterion below is represented by at least one wastewater:

- Total suspended solids (TSS) greater than 40 mg/L
- Total dissolved solids (TDS) greater than 100 mg/L
- Oil and grease greater than 20 mg/L
- NaCl greater than 120 mg/L
- Hardness as $CaCO_3$ greater than 140 mg/L

The laboratory will be responsible for determining the five parameters listed above in each of the wastewater matrix types, using methods approved at 40 CFR Part 136, such that the individual sample characteristics are known. EAD, CSRA, and the laboratory will discuss adding any interferences identified during Phase 3 to these wastewater samples.

EAD and CSRA will assist the laboratory in obtaining sufficient volumes of real-world wastewater matrices from various sources.

Note: EAD may utilize excess sample volume archived from another method development study, if practical. Although those samples have been stored in glass bottles with PTFE lid liners that in theory could contribute PFAS to the samples, for the purpose of testing an AOF procedure in this study, such potential contamination is not a major concern because the source of the AOF in the samples is not at issue, just the ability of the procedure to detect AOF in real-world samples.

Four replicate samples of each wastewater matrix will be evaluated as spiked and unspiked samples. In summary, wastewater samples will be spiked with the PFAS compound used to perform the IPR and MDL studies. Unspiked samples should be analyzed first to determine the background levels which may affect the spike amounts of PFAS to be added to the spiked samples. The spike amounts will be determined at a later date by the EPA Project Manager and CSRA Study Manager after consulting with the laboratory on the results of the background levels.

The laboratory will determine the recovery of AOF in each spiked sample using Equation 2 above. Duplicate precision for the MS/MSD pairs will be determined using Equation 4 below.

$$RPD = \frac{C_2 - C_1}{(C_1 + C_2)/2} \qquad \text{Eq. 4}$$

where:
C_1 = Concentration for MS
C_2 = Concentration for MSD

4.7 Phase 7 – Testing Method with Solid Matrices

After successful completion of Phases 1 through 6 for aqueous samples, the laboratory will investigate the potential applicability of the CIC method to solid matrices, including biosolids, sediment, and fish tissue. Limited published data indicate that total and extractable organic fluorine can be determined in solid samples via CIC (Ref. 8.5). Initially, a solid sample will be spiked with a known PFAS constituent and then the sample will be subjected to a liquid extraction with analytical-grade solvents. The solvent extract will then be processed like the aqueous sample, by sorption and CIC analysis. If initial testing is successful, the laboratory will repeat Phases 4 and 5 for the relevant solid matrices. The remainder of Phase 7 will consist of replicate analyses of solid matrices, similar to that described in Phase 6 for aqueous samples. However, because analysis of solids is a secondary method priority, fewer matrix types will be evaluated.

SECTION 5. QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

The AOF procedure will incorporate many of the traditional QA/QC procedures found in EPA methods for the analysis of organic contaminants, including, but not limited to:

- Initial precision and recovery (IPR)
- Initial calibration (ICAL), 5-point minimum
- Calibration verification (VER)
- Method blank carried through the entire procedure
- Laboratory control sample (LCS)
- Carryover check (can be calculated from LCS)
- Matrix spike/ Matrix spike duplicate (MS/MSD)

The QC data from this study will be used to evaluate the performance of the draft procedure, and to develop single-laboratory performance data. Known QA/QC approaches are included within each study phase description. As method development is an iterative process, any additional QA measures may be included in an SQAPP as needed.

It is the laboratory's responsibility to maintain their instrumentation and to ensure that all study samples are analyzed on a properly calibrated instrument. If the calibration linearity is outside the nominal criteria, the laboratory will take standard measures to attempt to correct the problem before any study samples are analyzed. The laboratory is also responsible for inspecting all study samples and standards to ensure they meet all study requirements. If typical measures do not correct the problem or if study schedules will be impacted due to necessary repairs or replacement of study samples or standards, the laboratory will notify the CSRA Study Manager to indicate the impact on study schedules, the laboratory's plans to resolve the problem(s), and if any study samples will need to be reanalyzed.

The laboratory will report the results from the QC operations, either in electronic format, or if necessary, in hard copy. CSRA will compile the QC results in a database specific to this project (See Section 6).

SECTION 6. DATA REPORTING AND MANAGEMENT

The laboratory will be required to (1) report summary-level electronic data and supporting raw data, and (2) maintain their raw data for a period of seven (7) years and provide them upon request. Raw data will include all certificates of analysis, calibration data, quantitation reports (including peak areas or heights), bench sheets, and laboratory notebooks showing weights, volumes, manual calculations, and other data that will allow verification of the calculations performed and will allow the final results reported to be traced back to the raw data.

The laboratory will adhere to the following rules when reporting data:

- All reports and documentation, including instrument print-outs and other raw data, must be sequentially paginated, clearly labeled with the laboratory name, and labeled to provide sufficient identification for method blanks, calibration, etc., necessary to link the raw data with associated summary reports.
- Results from all analyses, including failed experiments, must be reported, including calibration data and any dilutions or reanalyses performed
- Results of all measurements must be reported to three significant figures in the appropriate reporting units (e.g., µg/L for water samples) to facilitate review and evaluation
- The terms "zero" and "trace" are not to be used; the term "not detected" (ND) is to be used for each measurement for which no signal is produced or if method-specified qualitative identification criteria are not met.
- Every value must be reported, even if the value is negative. If the value is below the lowest calibration standard, a "J" flag must be applied to this value.
- Results must be reported for all study samples, including QC samples.

In addition, the laboratory will be required to submit a written "narrative report" with each data package. The narrative report will contain detailed descriptions of any difficulties encountered in the generation of

the analytical results and QC data and any attempts to resolve the difficulties. It also will contain a detailed description of any necessary modifications to the draft AOF procedure.

The laboratory must have a comprehensive data management plan in place that is consistent with the principles set forth in the Good Automated Laboratory Practices, EPA 2185, August 1995 Edition, or with commonly employed data management procedures approved by The NELAC Institute (TNI). This data management plan must be in place and in use at all times during the performance of this study.

CSRA will store all study records and submitted data (hard copy and electronic) in an organized fashion on a secure local area network that is backed up nightly and as needed in hardcopy files in their secure office facility, throughout the duration of their contract.

SECTION 7. EVALUATION OF METHOD PERFORMANCE

As noted earlier, EPA and CSRA will perform brief examinations of the results of each phase of the study before authorizing the laboratory to proceed with the next study phase. Those examinations will mainly focus on completeness of the data submitted (e.g., were all required samples analyzed and results reported?) and on cursory assessments of the QC results (e.g., is there evidence of gross contamination in the blanks and do the QC results indicate that the laboratory is capable of analyzing samples at the levels of interest?). If incompleteness or performance issues are identified as a result of the reviews by EPA and/or CSRA, then the EPA Project Manager and the CSRA Study Manager will document those findings and work with the laboratory to resolve the issues. However, individual QC failures will not necessarily negate the results of a particular analysis. Rather, they will be used as indicators of performance issues that may be related to the concentrations of specific interferences and conditions being tested.

EPA and CSRA will use the results of the study and other information from the laboratory to determine if the procedure supports the ability to detect AOF at concentrations of interest to EPA, and if the procedure is found to be capable, EPA and CSRA will develop a formal EPA method for AOF. The method will be prepared in EPA's standard format for 1600-Series methods and subjected to internal reviews at EPA.

EPA's overall goal is to develop method performance data for the draft AOF procedure. The results of all analyses will be provided to ASTM for their own method review and evaluation. EPA and CSRA will evaluate all results for the analyses performed in the seven phases using common statistical procedures (Refs. 8.6 - 8.8) such as:

- *t*-tests, to determine if the mean results for an analyte differs between "treatments" (e.g., spiking levels or background levels of potential interferences)
- F-tests, to determine if the variance (standard deviation squared) for an analyte differs between "treatments"
- Analysis of variance (ANOVA), to determine how the differences between the components and the treatments affect overall variability

EPA and CSRA will use the results from the replicate samples to develop draft acceptance QC criteria for initial precision and recovery (IPR) tests, ongoing precision and recovery (OPR) tests, MS/MSD recovery limits, relative percent difference (RPD) limits, etc.

EPA and CSRA will develop tables of method performance data, including precision and accuracy, as a function of analyte concentration that will provide an indication of expected performance of the procedures under typical conditions. Such tables can be included in the revised procedure as further evidence of its overall capabilities or limitations.

Because this is a method development effort, there are no *a priori* quality control acceptance criteria, and data from the study will not be excluded from consideration simply because they appear to fail some pre-

conceived performance expectations. All study results will be subjected to statistical evaluations, and suspected outliers will be examined in detail by CSRA and the laboratory before they are excluded from use in developing method performance summaries.

Finally, EPA and CSRA will compile a report on the single-laboratory study that documents the effort and includes summaries of the results, which will be shared with ASTM D19.

SECTION 8. REFERENCES

8.1 EPA Method 1650, Revision C, Adsorbable Organic Halides by Adsorption and Coulometric Titration, August 1997, USEPA, Office of Water, Engineering and Analysis Division, https://www.epa.gov/sites/production/files/2015-10/documents/method_1650c_1997.pdf

8.2 Method 537.1, Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Version 2.0, March 2020, EPA/600/R-20/006, USEPA, Office of Research and Development, Cincinnati, Ohio.

8.3 *Federal Register* Volume 82, Number 165. August 28, 2017). Final Rule. pp. 40836 - 40941, Federal Register Online via the Government Printing Office. http://www.gpo.gov

8.4 ASTM D5905-98 (2018), Standard Practice for the Preparation of Substitute Wastewater, ASTM International, West Conshohocken, Pennsylvania, 2018. http://www.astm.org

8.5 Yeung, L.W.Y.; Miyake, Y.; Wang, Y.; Taniyasu, S.; Yamashita, N.; Lam, P.K.S. 2009. Total fluorine, extractable organic fluorine, perfluorooctane sulfonate and other related fluorochemicals in liver of Indo-Pacific humpback dolphins (*Sousa chinensis*) and finless porpoises (*Neophocaena phocaenoides*) from South China. *Environmental Pollution* (157): 17-23.

8.6 ASTM D2777-13 (2013), Standard Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water, ASTM International, West Conshohocken, Pennsylvania, 2013. www.astm.org

8.7 SAS Institute Inc. 1994. SAS/STAT User's Guide, Volume 2, GLM-VARCOMP. Version 6, 4th Edition, June 1994.

8.8 Berry, D. A.; Lindgren, B. W. 1990. Statistics: Theory and Methods. pp. 286-290, 600-618. Brooks/Cole Publishing Company. Pacific Grove, California.

Appendix B
Results for Mandel Granular Activated Carbon (GAC) Columns

Results for Mandel Granular Activated Carbon (GAC) Columns

At the beginning of method validation study, the laboratory observed that the carbon in the CPI, UCT, and Mandel columns tended to move out of the columns during sample sorption and elution. Given that this phenomenon was observed for columns from these three suppliers, and the fact that the Mandel columns were more readily available, only the Mandel columns tested to see how this migration of carbon interfered with the adsorption of organofluorine. The results of this testing are discussed below.

GAC Background

The background levels of inorganic fluorine for two lot numbers of the Mandel GAC columns were determined by analyzing five aliquots of unspiked reagent water, using two GAC columns in tandem for each aliquot, and taking all the aliquots through the procedure without washing the columns with nitrate. The laboratory also analyzed five aliquots of unspiked reagent water followed by a column wash with 20 mL of 8.4 g/L potassium nitrate, and five aliquots of unspiked reagent water containing 0.5 mL 2M sodium nitrate followed by a column wash with 25 mL of 0.01 M sodium nitrate.

Table B-1 Inorganic Fluorine Background Level (µg F^-/L)

Sample	No Wash		$NaNO_3$ Wash		KNO_3 Wash
	Lot #1	Lot #2	Lot #1	Lot #2	Lot #1
Replicate 1	6.527	1.075	2.239	2.943	2.446
Replicate 2	11.295	1.579	14.253	3.185	9.507
Replicate 3	10.587	9.045	2.303	2.218	2.139
Replicate 4	18.942	7.763	3.545	3.028	5.608
Replicate 5	16.991	2.473	7.261	4.174	16.122

The levels of inorganic fluorine in the Mandel columns were high and highly variable. Based on an F-test, there were statistical differences between variances of the lots, as well as the variances between Lot #1 washed with $NaNO_3$ and Lot #1 washed with KNO_3. A t-test showed no statistical differences between the means.

Single PFAS Compound Adsorption

One lot number was tested for the adsorption capacity for the following individual PFAS compounds: PFBA, HFPO-DA, PFHxS, ADONA, 6:2FTS, PFOA, PFOS, and PFOSA. Each analysis was performed in triplicate using 100-mL aliquots of reagent water spiked at approximately 6.0 and 19.0 µg F^-/L. The results are summarized in Table B-2 and Table B-3.

Table B-2 Adsorption of Individual PFAS Compounds

	Spike Level 1 (~6 µg F^-/L)				Spike Level 2 (~19 µg F^-/L)			
	% Recovery			RSD	% Recovery			RSD
Compound	Rep 1	Rep 2	Rep 3	(%)	Rep 1	Rep 2	Rep 3	(%)
PFBA	28.3	31.2	39.3	17.3	53.1	56.8	57.5	4.2
HFPO-DA	89.7	104.2	100.6	7.7	86.4	93.4	101.0	7.8
PFHxS	65.3	85.2	121.7	31.5	75.2	78.1	75.5	2.1
ADONA	89.7	107.4	85.8	12.2	113.4	100.9	103.7	6.2
6:2FTS	22.6	27.6	29.9	14.0	89.3	98.2	112.7	11.8
PFOA	70.3	84.0	103.6	19.5	101.9	95.4	94.5	4.2
PFOS	38.2	34.5	41.2	8.9	72.6	70.7	124.6	34.3
PFOSA	18.7	14.5	16.9	12.6	31.9	34.9	30.9	6.4

Table B-3 Blank Values for Sorption Batches

Analytical Batch	Matrix Blanks (µg F^-/L)	
	Opening Blank	Closing Blank
PFOA	0.865	0.091
PFOS and PFOSA	2.032	0.880
PFHxS and 6:2FTS	4.472	14.419
PFBA and HFPO-DA	-0.578	2.570
ADONA and Mixed Std	0.667	0.843

PFBA showed recoveries that were comparable to recoveries observed in the direct combustion experiments discussed in Section 4 of the study report as well as in various other published studies. The recoveries for 6:2FTS were low, due to both poor adsorption of this compound onto the carbon as well as high blank values for the batch. The opening blank had contamination of 4.472 µg F^-/L and the closing blank of 14.419 µg F^-/L. PFHxS was also tested in the same batch as 6:2FTS; however, because this compound is better adsorbed onto the carbon, the recoveries were less affected by the high blank correction. Both PFOS and PFOSA were analyzed in the same batch. The opening blank had a value of 2.032 µg F^-/L, and the closing blank showed a value of 0.880 µg F^-/L. The recoveries observed for PFOSA using the Analytik-Jena (Low Fluorine) columns were low but not nearly as low as the recoveries on the Mandel columns.

For PFOS, the recoveries for spike level #1 were very low, but the recoveries for spike level #2 were similar to those observed during the Analytik-Jena (Low Fluorine) column testing. These recoveries demonstrated that the difference in adsorption for individual compounds, combined with the migration of carbon from the column and the variability of blank background levels, can greatly affect the recovery of PFAS compounds.

Mixed PFAS Standard Adsorption

The adsorption capacity of the carbon for a mixture of PFAS compounds was tested for both sources of GAC. The mixed PFAS solution was purchased from Wellington Laboratories, Cat# PFAC30PAR. The laboratory analyzed three aliquots spiked at 6.65 µg F^-/L and three aliquots spiked at 19.01 µg F^-/L.

Table B-4 Adsorption of Mixed PFAS Compounds

Compound	Spike Level 1 (6.65 µg F^-/L)				Spike Level 2 (19.01 µg F^-/L)			
	% Recovery			RSD (%)	% Recovery			RSD (%)
	Rep 1	Rep 2	Rep 3		Rep 1	Rep 2	Rep 3	
Mixed PFAS	56.8	61.1	64.1	6.0	83.5	77.9	79.4	6.0

All the recoveries for the mixed standards fell within 50 – 150%.

Non-PFAS Fluorinated Compound Adsorption

The adsorption capacity of the carbon for non-PFAS fluorinated compounds was tested by analyzing two sets of aliquots of reagent water spiked with fluoxetine and fipronil. Both sets were analyzed in triplicate and spiked at approximately 6 µg F^-/L and 18 µg F^-/L. As seen in Table B-5, there were very good recoveries for both non-PFAS fluorinated compounds that were tested.

Table B-5 Adsorption of Non- PFAS Fluorinated Compounds

Compound	Spike Level 1 (~ 6.0 µg F^-/L)				Spike Level 2 (~18.0 µg F^-/L)			
	% Recovery			RSD	% Recovery			RSD
	Rep 1	Rep 2	Rep 3	(%)	Rep 1	Rep 2	Rep 3	(%)
Fipronil	85.7	92.9	83.8	5.5	99.9	100.1	97.0	1.8
Fluoxetine	88.8	98.6	89.7	5.9	80.0	78.5	80.0	1.1

Method Detection Limit

The laboratory performed two separate MDL studies using one lot number of the Mandel GAC columns. The laboratory prepared and analyzed seven replicate method blanks and two sets of seven replicate spiked samples. This approach yielded seven results for blanks and 14 results for spiked samples. The estimated initial MDL was set as three times the standard deviation of the initial background observed for the GAC columns. The spike levels were then established to be approximately between 2 and 10 times the estimated MDL, at 4.95 µg F^-/L (Study #1) and at 8.04 µg F^-/L (Study #2).

Table B-6 MDL_b and MDL_s Calculations (µg F^-/L)

Matrix Blanks									
MB-1	MB-2	MB-3	MB-4	MB-5	MB-6	MB-7	Mean	SD	MDL_b
0.14	1.17	0.6	4.7	-0.42	-0.76	-0.30	0.733	1.87	4.7
Spiked Matrix Study #1 (4.95 µg F^-/L)									
SP-1	SP-2	SP-3	SP-4	SP-5	SP-6	SP-7	Mean	SD	MDL_s
4.45	4.66	5.90	5.20	4.32	3.49	4.01	4.58	0.79	2.48
Spiked Matrix Study #2 (8.04 µg F^-/L)									
SP-1	SP-2	SP-3	SP-4	SP-5	SP-6	SP-7	Mean	SD	MDL_s
7.61	10.95	4.48	3.97	6.48	6.67	6.67	6.69	2.28	7.18

Because the two MDL studies were spiked at different levels, the means were different and therefore a t-test was not a usable statistical tool to compare the observed concentration for the studies. However, a t-test was performed on the percent recoveries of the MDL spiked samples. Based on a two-tailed t-test, there was no statistical difference between the mean percent recoveries between the MDL studies.

Based on the results of an F-test, the variances were statistically different when comparing the observed concentrations; however, when comparing the recoveries, there was no statistical difference between the variances.

The MDL studies for the Analytik-Jena (Low Fluorine) columns were compared to the studies for the Mandel columns (e.g., Study #1 vs. Study #1). Even though the calculated MDL_s for Study #2 on the Mandel columns was much higher than the Analytik-Jena (Low Fluorine) columns, a two-tailed t-test showed no statistical difference between the means of the replicate spiked sample results; however, an F-test showed a statistical difference in the variances between the results for the columns from the two vendors.

Appendix C
Summary of the ORD Adsorbed Organic Fluorine Method Validation Effort

Summary of the ORD Adsorbed Organic Fluorine Method Validation Effort

The Environmental Protection Agency (EPA) Office of Research and Development (ORD) performed a method validation study for adsorbable organic fluorine (AOF) using the draft ASTM standard as a guide. The method was tested using single PFAS compounds and non-PFAS fluorinated compounds as well as a mixed PFAS standards in reagent water, surface water, and wastewater samples. Below is a summary of the results compiled from the ORD study.

I. Instrument Setup and Calibration

Each sample was adsorbed onto two granular activated carbon (GAC) columns. The carbon from each column was combusted in a Nittoseiko Analytech AQF-2100H combustion unit coupled with a Thermo Scientific Dionex™ HPIC system. Separation was done using a Dionex™ IonPac™ AS24, 7 µm, 2 x 250 mm IC column and a 2 x 50 mm guard column. The system used a combination of oxygen and argon gas for combustion and a potassium hydroxide eluent.

The IC was calibrated by direct injection, using seven calibration standards of sodium fluorine in the range of 2 µg/L to 500 µg/L. Fluorine was quantitated using a 1/x weighted quadratic calibration curve. The relative standard error (RSE) was calculated for each of the two curves, with identical concentrations, to check for linearity. The RSEs for both curves were well below 20%. The calibration curves were verified prior to each analytical batch using a 50 µg/L solution prepared from a secondary sodium fluorine source.

Table C-1 Calibration by IC Direct Injection

Calibration Point	Nominal Value (µg/L)	6/2/2021		8/8/2021	
		Measured (µg F^-/L)	% Rec	Measured (µg F^-/L)	% Rec
CAL-1	2	2.3	114	2.2	111
CAL-2	5	5.0	100	4.8	96
CAL-3	10	9.8	98	9.3	93
CAL-4	50	50.3	101	50.1	100
CAL-5	100	99.4	99	99.2	99
CAL-6	250	250.3	100	252.6	101
CAL-7	500	499.9	100	498.9	100
		RSE	6.94	**RSE**	6.96

II. GAC Background Levels

Prior to determining the method detection limits (MDL), the fluorine background levels for the GAC columns used for this project (Mandel NS-TXAPPC4) were determined. The adsorption was done using a Mitsubishi TXA-04 adsorption unit. Later in the study, a second adsorption unit was added, Analytik-Jena APU SIM, and the study was done in parallel using both units, for the MDL studies and the reagent water fortified samples. Table C-2 shows the baseline concentration of inorganic fluorine found in the dry GAC, as well as after the GAC was washed with 25 mL of 8.2 g/L potassium nitrate.

Table C-2 Baseline Contamination of Ceramic Boats, Dry GAC, and GAC Washed with KNO_3

Source	Measured AOF Concentration (µg F^-/L)						Mean (µg F^-/L)	RSD (%)
	1	2	3	4	5	6		
Ceramic Boats	0.041	0.031	0.030	0.029	0.030	0.033	0.032	14
Dry GAC	0.720	0.530	0.760	0.510	0.760	0.800	0.68	19
Washed GAC	0.510	0.510	1.040	0.440	0.750	0.770	0.67	34

III. Method Detection Limit

Two MDL studies were performed using the MDL procedure at 40 CFR Part 136, Appendix B. The MDL determination was performed using PFPeS as the spiked compound. An MDL study consisting of 9 replicates of each, blanks and spikes, was adsorbed using the Mitsubishi TXA-04 adsorption unit, while another 7 replicates of each, blanks and spikes, were adsorbed using the Analytik-Jena APU SIM adsorption unit. The MDL_b and MDL_s were calculated for each unit, as well as the combined MDL_b and MDL_s using all 16 replicates. The MDL from the Mitsubishi adsorption unit was higher than the one from the Analytik-Jena unit, likely due to the fact that this adsorption unit uses a lot of tubing for sample transfer, which gives more surface area for adsorption of fluorine and makes it harder to clean properly.

Table C-3 MDLs from Two Adsorption Units

Adsorption Unit	MDL_b	MDL_s (Not blank corrected)	MDL_s (Blank corrected)*	Final MDL
Analytik-Jena APU SIM (7 reps)	1.474	0.546	0.453	1.474
Mitsubishi TX-04 (9 reps)	1.761	2.164	2.238	2.238
Combined MDL (16 reps)	1.549	1.469	1.531	1.549

*Blank correction was done using the average of the MDL blanks performed for that day.

IV. Single-Compound Analysis

Several single compounds were tested in reagent water (100-mL aliquots) to check their adsorption capacity. Both PFAS compounds and non-PFAS fluorinated compounds were adsorbed on GAC columns using both adsorption units. The compounds were spiked at levels between 10 and 20 µg/L. From the 234 total results, 68% had recoveries in the range of 70 – 130%. When the limit was lowered to 50 – 130%, 81% of the data fell within the range.

It is important to note that PFAS compounds with longer carbon chains, generally C >10, usually had lower recoveries, due to their ability to stick more readily onto surfaces. The lower recoveries were more pronounced when the Mitsubishi unit was used. For PFBA, the low recovery may be due to the fact that this compound does not adsorb very well onto carbon, but once more, the recoveries for the Mitsubishi unit were much lower than for the Analytik-Jena unit. Interestingly, for the non-PFAS fluorinated compounds, even though all four compounds have very long carbon chains, fluconazole and atorvastatin had an average recovery of 94%, while trifluralin and oxyfluoren had average recoveries of 50%. Results are summarized on Table C-4 below.

Table C-4 Recoveries for Reagent Water Spiked with Individual Compounds

Compound	Molecular Formula	Percent Recoveries per Adsorption Unit						Combined % Rec			RSD (%)
		Analytik-Jena APU SIM			Mitsubishi TX-04			Mean	Min	Max	
PFAS Compounds											
PFBA	$C_4HF_7O_2$	62	62	68	47	48	48	56	47	68	16.9
PFMPA	$C_4HF_7O_3$	93	100	101	102	103	99	100	93	103	3.7
FBSA-I	$C_4H_2F_9NO_2S$	101	94	99	93	106	86	96	86	106	7.2
PFBS	$C_4HF_9O_3S$	92	79	127	120	127	101	108	79	127	18.8
PFEESA	$C_4HF_9O_4S$	93	88	91	89	91	89	90	88	93	2.0
PFPeA	$C_5HF_9O_2$	100	77	95	107	108	108	99	77	108	12.2
PFMBA	$C_5HF_9O_3$	100	99	92	111	109	110	103	92	111	7.5
NFDHA	$C_5HF_9O_4$	101	97	101	106	106	117	105	97	117	6.6
PFPeS	$C_5HF_{11}O_3S$	98	107	111	110	110	94	105	94	111	6.8
FBET (4:2FTOH)	$C_6H_5F_9O$	96	94	85	90	96	98	93	85	98	5.2
HFPO-DA	$C_6HF_{11}O_3$	97	95	103	92	96	94	96	92	103	3.9
4:2FTS	$C_6H_4F_9SO_3Na$	102	95	99	106	106	107	102	95	107	4.6
PFHxS	$C_6H_2F_{13}NO_2S$	104	106	106	99	102	104	103	99	106	2.5
PFHxPA	$C_{13}H_{11}F_{13}NO_3P$	90	90	93	81	102	91	91	81	102	7.7
FHUEA	$C_8H_2F_{12}O_2$	100	97	93	103	102	99	99	93	103	3.5
FHEA	$C_8H_3F_{13}O_2$	96	100	100	99	100	100	99	96	100	1.7
PFOA	$C_8HF_{15}O_2$	82	82	83	84	76	75	80	75	84	4.9
6:2PAP	$C_8H_4F_{13}O_4PNa$	82	83	88	87	90	67	83	67	90	10.2
PFOS	$C_8F_{17}SO_3K$	97	104	95	91	87	85	93	85	104	7.5
9Cl-PF3ONS	$C_8HClF_{16}O_4S$	91	82	92	96	89	82	88	82	96	6.3
PFDA	$C_{10}F_{19}O_2$	68	72	72	84	82	82	77	68	84	8.8
FOSAA	$C_{10}H_4F_{17}NO_4S$	82	85	84	79	87	82	83	79	87	3.0
PFDPA	$C_{10}H_2F_{21}O_3P$	83	81	64	94	107	96	88	64	107	17.0
11Cl-PF3OUdS	$C_{10}HClF_{20}O_4S$	47	75	69	39	58	41	55	39	75	**26.9**
N-AP-FHxSA	$C_{11}H_{13}F_{13}N_2O_2S$	83	83	86	55	41	43	65	41	86	**32.6**
NMeFOSE	$C_{11}H_8F_{17}NO_3S$	22	34	58	22	20	21	30	20	58	**49.4**
FDUEA	$C_{12}H_2F_{20}O_2$	66	61	61	41	55	49	56	41	66	16.3
NEtFOSE-M	$C_{12}H_{10}F_{17}NO_3S$	37	43	44	31	31	33	37	31	44	15.7
FDEA	$C_{12}H_3F_{21}O_2$	58	60	70	48	57	47	57	47	70	14.6
N-TamP-FHxSA	$C_{12}H_{15}F_{13}N_2O_2S$	74	79	82	55	61	76	71	55	82	14.9
10:2FTS	$C_{12}H_4F_{21}SO_3Na$	69	69	72	55	64	58	64	55	72	10.4
FDET (10:2FTOH)	$C_{12}H_5F_{21}O$	45	54	45	50	45	49	48	45	54	7.6
6:6PFPi	$C_{12}F_{26}O_2PNa$	79	75	74	47	31	31	56	31	79	**40.5**
PFTeDA	$C_{14}HF_{27}O_2$	45	46	45	30	25	30	37	25	46	**25.8**
6:2FTAB	$C_{15}H_{19}F_{13}N_2O_4S$	79	79	74	73	78	82	78	73	82	4.4
Non-PFAS Fluorinated Compounds											
Fluconazole	$C_{13}H_{12}F_2N_6O$	95	100	99	97	103	104	100	95	104	3.7
Trifluralin	$C_{13}H_{16}F_3N_3O_4$	47	53	49	51	48	49	50	47	53	4.4
Oxyfluorfen	$C_{15}H_{11}ClF_3NO_4$	48	56	49	41	55	46	49	41	56	11.4
Atorvastatin	$C_{33}H_{35}FN_2O_5$	90	88	84	87	90	86	87	84	90	2.5

V. Multi-compound Analysis

Since this is a screening method that detects the "total" adsorbable organic fluorine, sets of blank aliquots spiked with mixed standards used for EPA Method 533 and EPA Method 537.1 were tested to try and replicate the mixture of PFAS that may be encountered in real-world samples. Two sets of triplicates were adsorbed using the Mitsubishi TXA-04 and another two sets using the Analytik-Jena APU SIM. The recoveries were within 50 – 130%. Again, samples adsorbed using the Mitsubishi unit had lower recoveries, but mainly for the Method 537.1 mixed standard. This mix contains four compounds, NMeFOSAA, NEtFOSAA, PFTeDA, and PFTrDA, that are not present on the Method 533 mixed standard. These four compounds have longer carbon chains, which have been proven to readily adsorb to surfaces. Because the Mitsubishi unit has more tubing for sample transfer, more of these kind of "sticky" compounds are likely to be lost during sample preparation. One of these four compounds, PFTeDA, was analyzed during the single-compound testing. This compound had an average recovery of 45% on the Analytik-Jena unit, while it had an average recovery of 28% on the Mitsubishi unit. Table C-5 provides the observed percent recoveries for each unit.

Table C-5 Recoveries for Reagent Water Spiked with Mixed Compounds

Mixed Standard	Percent Recoveries per Adsorption Unit						Combined % Rec			RSD (%)
	Analytik-Jena APU SIM			Mitsubishi TX-04			Mean	Min	Max	
EPA 533	92.3	93.0	94.7	85.5	81.8	85.4	88.8	81.8	94.7	5.9
EPA 537.1	92.2	81.6	89.9	62.4	73.8	66.1	77.7	62.4	92.2	15.9

There was also an analysis done on the Analytik-Jena unit for PFPeS spiked at 40.2 µg F^-/L. The average recovery of the triplicate analysis for this compound was 99.5%.

VI. Real-world Sample Analysis

Two surface waters and 9 wastewaters were analyzed by ORD using this method. Aliquots from all 11 samples were spiked with PFPeS and a separate batch of aliquots was spiked with the mixed PFAS standard used for EPA Method 537.1. Because the pK_a of hydrogen fluorine is 3.19, preservation of the samples to pH < 2 can lead to high amounts of inorganic fluorine that may be adsorbed onto the GAC, which cannot be fully washed out with nitrate and may bias the results high; therefore, the lowest pH allowed for the sample was 5.0. The wastewaters had pH values ranging from 5.4 to 11.7. The wastewaters used were collected for a previous project and had been stored in a refrigerator for at least several years. However, because the purpose of the study was to check for adsorption capacity and matrix interferences, this was not thought to be an issue and no new samples were collected. Due to the long storage time, some of the wastewater samples had high levels of particulates, most likely caused by bacterial growth, and the samples needed to be pre-filtered using a plug of glass wool prior to carbon adsorption to prevent the columns from clogging. For these samples, the pre-filter material was combusted separately, and the result added to the combined results from both columns. The background of the pre-filter material was also determined and added to the blank result for subtraction.

Table C-6 Water Quality Parameters for the Wastewater Samples

Sample ID	Source	pH	TSS (mg/L)	TDS (mg/L)	O&G (mg/L)	NaCl, as Conductivity	Hardness, as $CaCO_3$
WW #2	Landfill Leachate	7.2	168	4564	0.6667	7163	330
WW #3	Metal Finisher	11.7	188	3681	1.07	4530	20.4
WW #4	POTW Effluent	7.2	244	403	10.9	838	23.5
WW #5	Hospital	5.4	5.51	384	0.967	777	93.6
WW #6	POTW Influent	6.8	72	772	3.93	1708	67.5
WW #7	Bus Washing Station	6.5	29	509	23	688	23.2

Table C-6 Water Quality Parameters for the Wastewater Samples

Sample ID	Source	pH	TSS (mg/L)	TDS (mg/L)	O&G (mg/L)	NaCl, as Conductivity	Hardness, as $CaCO_3$
WW #8	Power Plant	7.2	8.97	143	0.333	256	31.8
WW #9	Pulp and Paper Effluent	7.4	37	1992	187	2815	205
WW #10	POTW Effluent	6.9	9.69	893	0.0	1839	127

The samples spiked with PFPeS had mean recoveries in the range of 70 – 130%, with the exception of WW #2. That specific sample was a landfill leachate and caused a lot of interferences and issues in the adsorption unit. However, looking at the results for the individual samples, the recoveries ranged from 12% to 152%, with samples WW #3 and WW #6 having the highest deviation between the replicates, most likely due to the fact that these samples were pre-filtered before carbon adsorption.

Table C-7 Recoveries for Real-world Samples Spiked with PFPeS

Sample ID	Nominal Spike (µg F^-/L)	% Recovery				RSD (%)	Avg % Breakthrough
		Rep 1	Rep 2	Rep 3	Mean		
SW#1	10.1	123	122	115	120	3.3	14.8
SW#2	10.1	99	98	83	94	9.6	18.8
WW#2	19.9	37	40	39	39	4.4	44.8
WW#3*	19.9	96	64	130	97	**34.4**	20.3
WW#4	10.1	87	80	84	84	4.1	35.2
WW#5	10.1	90	94	96	94	3.0	20.8
WW#6*	10.1	103	12	142	86	**77.6**	13.3
WW#7	10.1	58	72	82	71	17.1	33.0
WW#8	10.1	92	91	89	91	1.8	6.6
WW#9*	10.1	123	152	102	126	20.1	17.9
WW#10	10.1	79	93	94	89	9.8	20.8
						Min	12.4
						Max	152.1

*Sample prefiltered. Recovery includes combustion of the prefilter.

For the samples that were spiked with the Method 537.1 mixed PFAS standard, the mean recoveries were between 50% and 130%, with the exception of sample WW #2. When looking at the for the individual samples, the recoveries ranged from 32% to 167%. Sample WW #6 had one replicate with high recovery, which may be an outlier due to the fact that this sample had to be pre-filtered.

Table C-8 Recoveries for Real-world Samples Spiked with Method 537.1 Mixed PFAS Standard

Sample ID	Nominal Spike (µg F^-/L)	% Recovery				RSD (%)	Avg % Breakthrough
		Rep 1	Rep 2	Rep 3	Mean		
SW#1	10.0	83	73	85	80	8.0	16.0
SW#2	10.0	69	88	78	78	12.5	21.2
WW#2	20.0	32	36	33	34	6.2	45.0
WW#3*	20.0	64	79	54	66	19.4	18.6
WW#4	10.0	51	51	56	52	5.9	37.7
WW#5	10.0	55	60	73	63	14.7	23.2
WW#6*	10.0	73	167	103	114	**42.1**	21.3
WW#7	10.0	144	102	112	119	18.5	33.2
WW#8	10.0	90	85	82	86	5.0	9.0
WW#9	10.0	65	58	80	67	16.9	31.5
WW#10	10.0	71	72	83	75	8.8	23.6
						Min	32.0
						Max	166.8

*Sample prefiltered. Recovery includes combustion of the prefilter.

Appendix D
Organofluorine Adsorption Results

Organofluorine Adsorption Results

Table D-1 Adsorption of PFOS – 01/17/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat blank	-6.2	-	-	-	-	-
CCV 600 ng F	573.1	-	-	-	-	95.5
Method Blank Rep 1 Top Col	30.5	0.305	0.673	-	-	-
Method Blank Rep 1 Bottom Col	36.8	0.368				
PFOS 60 ng Rep 1 Top Col	118	1.18	1.265	0.592	-47.8	98.7
PFOS 60 ng Rep 1 Bottom Col	8.5	0.085				
PFOS 60 ng Rep 2 Top Col	42.8	0.428	0.444	-0.229	153.7	-38.2
PFOS 60 ng Rep 2 Bottom Col	1.6	0.016				
PFOS 60 ng Rep 3 Top Col	46	0.46	0.41	-0.263	158.9	-43.8
PFOS 60 ng Rep 3 Bottom Col	-5	-0.05				
PFOS 600 ng Rep 1 Top Col	463.5	4.635	4.651	3.978	-8.8	66.3
PFOS 600 ng Rep 1 Bottom Col	1.6	0.016				
PFOS 600 ng Rep 2 Top Col	512.4	5.124	6.424	5.751	16.2	95.9
PFOS 600 ng Rep 2 Bottom Col	130	1.3				
PFOS 600 ng Rep 3 Top Col	572	5.72	6.209	5.536	2.2	92.3
PFOS 600 ng Rep 3 Bottom Col	48.9	0.489				
PFOS 1800 ng Rep 1 Top Col	1342.1	13.421	16.105	15.432	15.0	85.7
PFOS 1800 ng Rep 1 Bottom Col	268.4	2.684				
PFOS 1800 ng Rep 2 Top Col	1167.6	11.676	11.917	11.244	-1.1	62.5
PFOS 1800 ng Rep 2 Bottom Col	24.1	0.241				
PFOS 1800 ng Rep 3 Top Col	1452.3	14.523	14.811	14.138	-0.6	78.5
PFOS 1800 ng Rep 3 Bottom Col	28.8	0.288				
Method Blank Rep 2 Top Col	134.6	1.346	1.503	-	-	-
Method Blank Rep 2 Bottom Col	15.7	0.157				
CCV 600 ng F	597.5	-	-	-	-	99.6

Table D-2 Adsorption of PFOA – 01/18/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-18.7	-	-	-	-	-
CCV 200 ng F	171.2	-	-	-	-	85.6
Method Blank Rep 1 Top Col	53.2	0.532	0.532	-	-	-
Method Blank Rep 1 Bottom Col	-0.8	-0.008				
PFOA 69 ng Rep 1 Top Col	72.4	0.724	0.724	0.192	-12.9	27.8
PFOA 69 ng Rep 1 Bottom Col	-2.2	-0.022				
PFOA 69 ng Rep 2 Top Col	100.1	1.001	1.277	0.745	37.0	108.0
PFOA 69 ng Rep 2 Bottom Col	27.6	0.276				
PFOA 69 ng Rep 3 Top Col	159.8	1.598	3.039	2.507	57.5	363.3
PFOA 69 ng Rep 3 Bottom Col	144.1	1.441				
PFOA 688 ng Rep 1 Top Col	950.6	9.506	12.039	11.507	22.0	167.3
PFOA 688 ng Rep 1 Bottom Col	253.3	2.533				
Method Blank Rep 2 Top Col	194.4	1.944	3.458	-	-	-
Method Blank Rep 2 Bottom Col	151.4	1.514				
PFOA 688 ng Rep 2 Top Col	872.3	8.723	11.339	10.807	24.2	157.1
PFOA 688 ng Rep 2 Bottom Col	261.6	2.616				
PFOA 688 ng Rep 3 Top Col	999.1	9.991	13.856	13.324	29.0	193.7
PFOA 688 ng Rep 3 Bottom Col	386.5	3.865				
PFOA 1893 ng Rep 1 Top Col	2327.1	23.271	28.785	28.253	19.5	149.2
PFOA 1893 ng Rep 1 Bottom Col	551.4	5.514				
PFOA 1893 ng Rep 2 Top Col	2341.4	23.414	27.851	27.319	16.2	144.3
PFOA 1893 ng Rep 2 Bottom Col	443.7	4.437				
PFOA 1893 ng Rep 3 Top Col	2285.7	22.857	27.003	26.471	15.7	139.8
PFOA 1893 ng Rep 3 Bottom Col	414.6	4.146				
CCV 600 ng F	588.6	-	-	-	-	98.1

Table D-3 Adsorption of PFOSA – 01/19/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	13.8	-	-	-	-	-
CCV 1000 ng F	1015.7	-	-	-	-	101.6
Method Blank Rep 1 Top Col	-20	-0.2	0	-	-	-
Method Blank Rep 1 Bottom Col	0	0				
PFOSA 65 ng Rep 1 Top Col	69.5	0.695	1.106	1.106	37.2	170.2
PFOSA 65 ng Rep 1 Bottom Col	41.1	0.411				
PFOSA 65 ng Rep 2 Top Col	102.7	1.027	1.917	1.917	46.4	294.9
PFOSA 65 ng Rep 2 Bottom Col	89	0.89				
PFOSA 65 ng Rep 3 Top Col	111.6	1.116	2.2	2.2	49.3	338.5
PFOSA 65 ng Rep 3 Bottom Col	108.4	1.084				
PFOSA 647 ng Rep 1 Top Col	385.8	3.858	4.574	4.574	15.7	70.7
PFOSA 647 ng Rep 1 Bottom Col	71.6	0.716				
PFOSA 647 ng Rep 2 Top Col	308	3.08	3.3	3.3	6.7	51.0
PFOSA 647 ng Rep 2 Bottom Col	22	0.22				
PFOSA 647 ng Rep 3 Top Col	273	2.73	3.809	3.809	28.3	58.9
PFOSA 647 ng Rep 3 Bottom Col	107.9	1.079				
PFOSA 1941 ng Rep 1 Top Col	857.9	8.579	9.631	9.631	10.9	49.6
PFOSA 1941 ng Rep 1 Bottom Col	105.2	1.052				
PFOSA 1941 ng Rep 2 Top Col	960.3	9.603	10.271	10.271	6.5	52.9
PFOSA 1941 ng Rep 2 Bottom Col	66.8	0.668				
PFOSA 1941 ng Rep 3 Top Col	835.1	8.351	9.295	9.295	10.2	47.9
PFOSA 1941 ng Rep 3 Bottom Col	94.4	0.944				
Method Blank Rep 2 Top Col	226.2	2.262	2.844	-	-	-
Method Blank Rep 2 Bottom Col	58.2	0.582				
CCV 200 ng F	186.8	-	-	-	-	93.4

Table D-4 Adsorption of PFHxS – 01/20/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-23.5	-	-	-	-	-
CCV 200 ng F	178	-	-	-	-	89.0
Method Blank Rep 1 Top Col	37.5	0.375	0.381	-	-	-
Method Blank Rep 1 Bottom Col	0.6	0.006				
Method Blank Rep 2 Top Col	112.1	1.121	1.196	-	-	-
Method Blank Rep 2 Bottom Col	7.5	0.075				
PFHxS 62 ng Rep 1 Top Col	331.1	3.311	4.145	3.764	22.0	607.1
PFHxS 62 ng Rep 1 Bottom Col	83.4	0.834				
PFHxS 62 ng Rep 2 Top Col	224.7	2.247	3.089	2.708	30.9	436.8
PFHxS 62 ng Rep 2 Bottom Col	84.2	0.842				
PFHxS 62 ng Rep 3 Top Col	175.5	1.755	2.849	2.468	44.1	398.1
PFHxS 62 ng Rep 3 Bottom Col	109.4	1.094				
PFHxS 619 ng Rep 1 Top Col	674	6.74	7.885	7.504	15.2	121.2
PFHxS 619 ng Rep 1 Bottom Col	114.5	1.145				
PFHxS 619 ng Rep 2 Top Col	650.3	6.503	7.712	7.331	16.4	118.4
PFHxS 619 ng Rep 2 Bottom Col	120.9	1.209				
PFHxS 619 ng Rep 3 Top Col	643.9	6.439	9.519	9.138	33.6	147.6
PFHxS 619 ng Rep 3 Bottom Col	308	3.08				
PFHxS 1857 ng Rep 1 Top Col	1831.7	18.317	20.236	19.855	9.6	106.9
PFHxS 1857 ng Rep 1 Bottom Col	191.9	1.919				
PFHxS 1857 ng Rep 2 Top Col	1898.9	18.989	20.801	20.42	8.8	110.0
PFHxS 1857 ng Rep 2 Bottom Col	181.2	1.812				
PFHxS 1857 ng Rep 3 Top Col	1930.3	19.303	23.379	22.998	17.7	123.8
PFHxS 1857 ng Rep 3 Bottom Col	407.6	4.076				
CCV 600 ng F	514.8	-	-	-	-	85.8

Table D-5 Adsorption of HFPO-DA – 01/26/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat blank	-6.6	-	-	-	-	-
CCV 600 ng F	598.1	-	-	-	-	99.7
Method Blank Rep 1 Top Col	8.2	0.082	1.212	-	-	-
Method Blank Rep 1 Bottom Col	113	1.13				
Method Blank Rep 2 Top Col	573.4	5.734	5.889	-	-	-
Method Blank Rep 2 Bottom Col	15.5	0.155				
HFPO-DA 127 ng Rep 1 Top Col	104.9	1.049	1.025	-0.187	617.1	-14.7
HFPO-DA 127 ng Rep 1 Bottom Col	-2.4	-0.024				
HFPO-DA 127 ng Rep 2 Top Col	104.2	1.042	3.098	1.886	49.1	148.5
HFPO-DA 127 ng Rep 2 Bottom Col	205.6	2.056				
HFPO-DA 127 ng Rep 3 Top Col	133.4	1.334	1.454	0.242	-417.4	19.1
HFPO-DA 127 ng Rep 3 Bottom Col	12	0.12				
HFPO-DA 633 ng Rep 1 Top Col	531	5.31	6.109	4.897	-6.8	77.4
HFPO-DA 633 ng Rep 1 Bottom Col	79.9	0.799				
HFPO-DA 633 ng Rep 2 Top Col*	1249.6	12.496	13.06	11.848	-4.8	187.2
HFPO-DA 633 ng Rep 2 Bottom Col*	56.4	0.564				
HFPO-DA 633 ng Rep 3 Top Col	531.1	5.311	5.906	4.694	-11.4	74.2
HFPO-DA 633 ng Rep 3 Bottom Col	59.5	0.595				
HFPO-DA 1900 ng Rep 1 Top Col	1673.3	16.733	19.194	17.982	7.4	94.6
HFPO-DA 1900 ng Rep 1 Bottom Col	246.1	2.461				
HFPO-DA 1900 ng Rep 2 Top Col	1638.5	16.385	18.807	17.595	7.3	92.6
HFPO-DA 1900 ng Rep 2 Bottom Col	242.2	2.422				
HFPO-DA 1900 ng Rep 3 Top Col	1842.2	18.422	19.401	18.189	-0.8	95.7
HFPO-DA 1900 ng Rep 3 Bottom Col	97.9	0.979				
CCV 600 ng F	597.3	-	-	-	-	99.6

*Redone on 02/11/2022

Table D-6 Adsorption of PFBA and ADONA – 02/03/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-15.9	-	-	-	-	-
CCV 1000 ng F	961.4	-	-	-	-	96.1
Method Blank Rep 1 Top Col	13.4	0.134	0.483	-	-	-
Method Blank Rep 1 Bottom Col	34.9	0.349				
Method Blank Rep 2 Top Col	0.3	0.003	0.064	-	-	-
Method Blank Rep 2 Bottom Col	6.1	0.061				
PFBA 621 ng Rep 1 Top Col	184.3	1.843	3.215	2.732	37.4	44.0
PFBA 621 ng Rep 1 Bottom Col	137.2	1.372				
PFBA 621 ng Rep 2 Top Col	239.8	2.398	4.062	3.579	36.7	57.6
PFBA 621 ng Rep 2 Bottom Col	166.4	1.664				
PFBA 621 ng Rep 3 Top Col	256.9	2.569	5.545	5.062	51.9	81.5
PFBA 621 ng Rep 3 Bottom Col	297.6	2.976				
PFBA 1864 ng Rep 1 Top Col	816.9	8.169	14.298	13.815	41.8	74.1
PFBA 1864 ng Rep 1 Bottom Col	612.9	6.129				
PFBA 1864 ng Rep 2 Top Col	990	9.9	15.965	15.482	36.9	83.1
PFBA 1864 ng Rep 2 Bottom Col	606.5	6.065				
PFBA 1864 ng Rep 3 Top Col	1170.8	11.708	18.773	18.29	36.7	98.1
PFBA 1864 ng Rep 3 Bottom Col	706.5	7.065				
ADONA 570 ng Rep 1 Top Col	962.6	9.626	13.844	13.361	29.0	234.4
ADONA 570 ng Rep 1 Bottom Col	421.8	4.218				
ADONA 570 ng Rep 2 Top Col	1072	10.72	15.906	15.423	31.4	270.6
ADONA 570 ng Rep 2 Bottom Col	518.6	5.186				
ADONA 570 ng Rep 3 Top Col	1096.5	10.965	15.996	15.513	30.2	272.2
ADONA 570 ng Rep 3 Bottom Col	503.1	5.031				
ADONA 1710 ng Rep 1 Top Col	2243.2	22.432	27.777	27.294	18.3	159.6
ADONA 1710 ng Rep 1 Bottom Col	534.5	5.345				
ADONA 1710 ng Rep 2 Top Col	2206	22.06	27.999	27.516	20.3	160.9
ADONA 1710 ng Rep 2 Bottom Col	593.9	5.939				
ADONA 1710 ng Rep 3 Top Col	2231.7	22.317	27.058	26.575	16.5	155.4
ADONA 1710 ng Rep 3 Bottom Col	474.1	4.741				
CCV 1000 ng F	1019.7	-	-	-	-	102.0

Table D-7 Adsorption of 6:2FTS and Mixed PFAS Standard – 02/07/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-13.8	-	-	-	-	-
CCV 1000 ng F	993.8	-	-	-	-	99.4
Method Blank Rep 1 Top Col	94.7	0.947	0.981	-	-	-
Method Blank Rep 1 Bottom Col	3.4	0.034				
Method Blank Rep 2 Top Col	-2.8	-0.028	0.042	-	-	-
Method Blank Rep 2 Bottom Col	4.2	0.042				
6:2 FTS 658 ng Rep 1 Top Col	566.7	5.667	5.862	4.881	3.3	74.2
6:2 FTS 658 ng Rep 1 Bottom Col	19.5	0.195				
6:2 FTS 658 ng Rep 2 Top Col	498.8	4.988	5.719	4.738	14.7	72.0
6:2 FTS 658 ng Rep 2 Bottom Col	73.1	0.731				
6:2 FTS 658 ng Rep 3 Top Col	588.5	5.885	7.522	6.541	24.5	99.4
6:2 FTS 658 ng Rep 3 Bottom Col	163.7	1.637				
6:2 FTS 1920 ng Rep 1 Top Col	2222.7	22.227	25.919	24.938	14.7	129.9
6:2 FTS 1920 ng Rep 1 Bottom Col	369.2	3.692				
6:2 FTS 1920 ng Rep 2 Top Col	2129.6	21.296	24.421	23.44	13.2	122.1
6:2 FTS 1920 ng Rep 2 Bottom Col	312.5	3.125				
6:2 FTS 1920 ng Rep 3 Top Col	2148.1	21.481	25.476	24.495	16.2	127.6
6:2 FTS 1920 ng Rep 3 Bottom Col	399.5	3.995				
30PAR 665 ng Rep 1 Top Col	869	8.69	12.681	11.7	33.8	175.9
30PAR 665 ng Rep 1 Bottom Col	399.1	3.991				
30PAR 665 ng Rep 2 Top Col	848.6	8.486	15.326	14.345	47.4	215.7
30PAR 665 ng Rep 2 Bottom Col	684	6.84				
30PAR 665 ng Rep 3 Top Col	1077.7	10.777	14.924	13.943	29.5	209.7
30PAR 665 ng Rep 3 Bottom Col	414.7	4.147				
30PAR 1901 ng Rep 1 Top Col	1853	18.53	22.926	21.945	19.9	115.4
30PAR 1901 ng Rep 1 Bottom Col	439.6	4.396				
30PAR 1901 ng Rep 2 Top Col	1854.8	18.548	22.871	21.89	19.6	115.1
30PAR 1901 ng Rep 2 Bottom Col	432.3	4.323				
30PAR 1901 ng Rep 3 Top Col	1779	17.79	21.302	20.321	17.1	106.9
30PAR 1901 ng Rep 3 Bottom Col	351.2	3.512				
CCV 1000 ng F	1012.2	-	-	-	-	101.2

Table D-8 Adsorption of Fipronil and Fluoxetine – 02/08/2022

Identification	ng	µg/L	Total (µg/L)	First Blank		Second Blank		% Brk
				Blk Corrected	% Rec	Blk Corrected	% Rec	
Boat Blank	-18.4	-	-	-	-	-	-	-
CCV 1000 ng	1012.2	-	-	-	101.22	-	-	-
Method Blank Rep 1 Top Col	359.3	3.593	4.18	-	-	-	-	-
Method Blank Rep 1 Bottom Col	58.7	0.587						
Method Blank Rep 2 Top Col	4.1	0.041	0.438	-	-	-	-	-
Method Blank Rep 2 Bottom Col	39.7	0.397						
Fipronil 626 ng Rep 1 Top Col	621.8	6.218	6.273	2.093	33.43	5.8	93.2	-
Fipronil 626 ng Rep 1 Bottom Col	5.5	0.055						25.4
Fipronil 626 ng Rep 2 Top Col	605.6	6.056	6.072	1.892	30.22	5.6	90.0	-
Fipronil 626 ng Rep 2 Bottom Col	1.6	0.016						30.2
Fipronil 626 ng Rep 3 Top Col	601.2	6.012	7.059	2.879	45.99	6.6	105.8	16.0
Fipronil 626 ng Rep 3 Bottom Col	104.7	1.047						
Fipronil 1825 ng Rep 1 Top Col*	3609.2	36.092	36.87	32.69	179.12	36.4	199.6	0.6
Fipronil 1825 ng Rep 1 Bottom Col*	77.8	0.778						
Fipronil 1825 ng Rep 2 Top Col	1596.9	15.969	16.716	12.536	68.69	16.3	89.2	1.3
Fipronil 1825 ng Rep 2 Bottom Col	74.7	0.747						
Fipronil 1825 ng Rep 3 Top Col	1576.8	15.768	16.372	12.192	66.81	15.9	87.3	0.1
Fipronil 1825 ng Rep 3 Bottom Col	60.4	0.604						
Fluoxetine 659 ng Rep 1 Top Col	609.6	6.096	7.008	2.828	42.91	6.6	99.7	11.5
Fluoxetine 659 ng Rep 1 Bottom Col	91.2	0.912						
Fluoxetine 659 ng Rep 2 Top Col	612.7	6.127	9.213	5.033	76.37	8.8	133.2	49.7
Fluoxetine 659 ng Rep 2 Bottom Col	308.6	3.086						
Fluoxetine 659 ng Rep 3 Top Col	711.4	7.114	8.714	4.534	68.80	8.3	125.6	22.3
Fluoxetine 659 ng Rep 3 Bottom Col	160	1.6						
Fluoxetine 1813 ng Rep 1 Top Col	1526.4	15.264	16.483	12.303	67.86	16.0	88.5	5.1
Fluoxetine 1813 ng Rep 1 Bottom Col	121.9	1.219						
Fluoxetine 1813 ng Rep 2 Top Col	1579.1	15.791	16.763	12.583	69.40	16.3	90.0	3.1
Fluoxetine 1813 ng Rep 2 Bottom Col	97.2	0.972						
Fluoxetine 1813 ng Rep 3 Top Col	1565.1	15.651	16.571	12.391	68.35	16.1	89.0	2.7
Fluoxetine 1813 ng Rep 3 Bottom Col	92	0.92						
CCV 1000 ng F	984.2	-	-	-	98.42	-	-	-

*Redone on 02/11/2022

Table D-9 Reanalysis for Adsorption of Fipronil and FHFPO-DA – 02/11/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-14.3	-	-	-	-	-
CCV 1000 ng F	985.6	-	-	-	-	98.6
Method Blank 021122 Rep 1 Top Col	9.0	0.09	0.09	-	-	-
Method Blank 021122 Rep 1 Bottom Col	-2.3	-0.023				
Method Blank 021122 Rep 2 Top Col	0.6	0.006	0.062	-	-	-
Method Blank 021122 Rep 2 Bottom Col	5.6	0.056				
Fipronil 1825 ng Rep 1 Top Col	1599.6	15.996	16.785	16.695	4.7	91.5
Fipronil 1825 ng Rep 1 Bottom Col	78.9	0.789				
HFPO-DA 633 ng Rep 2 Top Col	555.6	5.556	5.81	5.72	4.4	90.4
HFPO-DA 633 ng Rep 2 Bottom Col	25.4	0.254				
CCV 1000 ng F	1001.1	-	-	-	-	100.1

Table D-10 Adsorption of ADONA, PFOA, and Mixed PFAS Standard – 03/29/2022 Reanalysis

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-57.8	-	-	-	-	-
CCV 200 ng F	194.2	-	-	-	-	97.1
Method Blank 032922 Rep 1 Top Col	-20.6	-0.206	8.966	-	-	-
Method Blank 032922 Rep 1 Bottom Col	896.6	8.966				
ADONA 570 ng Rep 1 Top Col	517.8	5.178	5.178	5.178	0	90.8
ADONA 570 ng Rep 1 Bottom Col	-13.3	-0.133				
ADONA 570 ng Rep 2 Top Col	504	5.04	5.04	5.04	0	88.4
ADONA 570 ng Rep 2 Bottom Col	-19.7	-0.197				
ADONA 570 ng Rep 3 Top Col	522.1	5.221	5.287	5.287	1.2	92.8
ADONA 570 ng Rep 3 Bottom Col	6.6	0.066				
ADONA 1852 ng Rep 1 Top Col	1989.5	19.895	23.528	23.528	15.4	127.0
ADONA 1852 ng Rep 1 Bottom Col	363.3	3.633				
ADONA 1852 ng Rep 2 Top Col	1980.4	19.804	21.102	21.102	6.2	113.9
ADONA 1852 ng Rep 2 Bottom Col	129.8	1.298				
ADONA 1852 ng Rep 3 Top Col	2056.6	20.566	21.83	21.83	5.8	117.9
ADONA 1852 ng Rep 3 Bottom Col	126.4	1.264				
PFOA 688 ng Rep 1 Top Col	747.6	7.476	9.1	9.1	17.8	132.3
PFOA 688 ng Rep 1 Bottom Col	162.4	1.624				
PFOA 688 ng Rep 2 Top Col	811.1	8.111	9.86	9.86	17.7	143.3
PFOA 688 ng Rep 2 Bottom Col	174.9	1.749				
PFOA 688 ng Rep 3 Top Col	806.6	8.066	12.027	12.027	32.9	174.8
PFOA 688 ng Rep 3 Bottom Col	396.1	3.961				
PFOA 1893 ng Rep 1 Top Col	2343.5	23.435	25.345	25.345	7.5	133.9
PFOA 1893 ng Rep 1 Bottom Col	191	1.91				
PFOA 1893 ng Rep 2 Top Col	2169	21.69	23.688	23.688	8.4	125.1
PFOA 1893 ng Rep 2 Bottom Col	199.8	1.998				
PFOA 1893 ng Rep 3 Top Col	2333.5	23.335	25.519	25.519	8.6	134.8
PFOA 1893 ng Rep 3 Bottom Col	218.4	2.184				
30PAR 665 ng Rep 1 Top Col	683.6	6.836	7.985	7.985	14.4	120.1
30PAR 665 ng Rep 1 Bottom Col	114.9	1.149				
30PAR 665 ng Rep 2 Top Col	668.5	6.685	8.55	8.55	21.8	128.6
30PAR 665 ng Rep 2 Bottom Col	186.5	1.865				
30PAR 665 ng Rep 3 Top Col	529	5.29	6.335	6.335	16.5	95.3
30PAR 665 ng Rep 3 Bottom Col	104.5	1.045				
30PAR 1901 ng Rep 1 Top Col	1550.4	15.504	16.823	16.823	7.8	88.5
30PAR 1901 ng Rep 1 Bottom Col	131.9	1.319				
30PAR 1901 ng Rep 2 Top Col	1523.5	15.235	16.533	16.533	7.9	87.0
30PAR 1901 ng Rep 2 Bottom Col	129.8	1.298				
30PAR 1901 ng Rep 3 Top Col	1518.6	15.186	16.659	16.659	8.8	87.6
30PAR 1901 ng Rep 3 Bottom Col	147.3	1.473				
Method Blank 032922 Rep 2 Top Col	45.2	0.452	5.721	5.721	-	-
Method Blank 032922 Rep 2 Bottom Col	526.9	5.269				
CCV 1000 ng F	1003.8	-	-	-	-	100.4

Appendix E
Interferences with Adsorption of PFAS Results

Interferences with Adsorption of PFAS Results

Table E-1 Interference of Inorganic Fluorine and Chloride – 02/09/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	15.4	-	-	-	-	-
CCV 1000 ng F	1026.3	-	-	-	-	102.6
Method Blank Rep 1 Top Col*	1826.4	18.264	18.62	Contamination of Elution Station Spot #1		
Method Blank Rep 1 Bottom Col*	35.6	0.356				
Method Blank Rep 2 Top Col	20.5	0.205	0.32	-	-	-
Method Blank Rep 2 Bottom Col	11.5	0.115				
619 ng PFHxS 4 mg/L F Rep 1 Top Col	604.9	6.049	6.475	6.155	-0.6	99.4
619 ng PFHxS 4 mg/L F Rep 1 Bottom Col	42.6	0.426				
619 ng PFHxS 4 mg/L F Rep 2 Top Col	595.2	5.952	6.123	5.803	1.5	93.7
619 ng PFHxS 4 mg/L F Rep 2 Bottom Col	17.1	0.171				
619 ng PFHxS 4 mg/L F Rep 3 Top Col	541.1	5.411	6.61	6.29	-7.0	101.6
619 ng PFHxS 4 mg/L F Rep 3 Bottom Col	119.9	1.199				
619 ng PFHxS 8 mg/L F Rep 1 Top Col*	1426.6	14.266	19.925	19.605	406.4	316.7
619 ng PFHxS 8 mg/L F Rep 1 Bottom Col*	565.9	5.659				
619 ng PFHxS 8 mg/L F Rep 2 Top Col	701.8	7.018	8.959	8.639	-16.4	139.6
619 ng PFHxS 8 mg/L F Rep 2 Bottom Col	194.1	1.941				
619 ng PFHxS 8 mg/L F Rep 3 Top Col	696.2	6.962	8.457	8.137	-11.2	131.5
619 ng PFHxS 8 mg/L F Rep 3 Bottom Col	149.5	1.495				
619 ng PFHxS 100 mg/L Cl Top Col	640.5	6.405	8.011	7.691	-11.8	124.2
619 ng PFHxS 100 mg/L Cl Bottom Col	160.6	1.606				
619 ng PFHxS 500 mg/L Cl Top Col	710	7.1	Incomplete combustion			
619 ng PFHxS 500 mg/L Cl Bottom Col	-11.7	-0.117				
619 ng PFHxS 1000 mg/L Cl Top Col*	765.3	7.653	10.884	10.564	-37.2	170.7
619 ng PFHxS 1000 mg/L Cl Bottom Col*	323.1	3.231				
CCV 1000 ng F	984.2	-	-	-	-	98.4

*Contamination on elution station spot #1 affected MB Rep 1, 8 mg/L F Rep 1 (redone 2/11/2022), and 1000 mg/L Cl (redone 2/15/2022).

Table E-2 Interference of Inorganic Fluorine Reanalysis – 02/10/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-14.9	-	-	-	-	-
CCV 1000 ng F	1001.6	-	-	-	-	100.2
Method Blank Rep 2 Top Col	5.2	0.052	0.609	-	-	-
Method Blank Rep 2 Bottom Col	55.7	0.557				
619 ng PFHxS 500 mg/L Cl Top Col	609	6.09	6.457	5.848	-3.2	94.5
619 ng PFHxS 500 mg/L Cl Bottom Col	36.7	0.367				
Method Blank Rep 4 Top Col	32.5	0.325	1.439	-	-	-
Method Blank Rep 4 Bottom Col	111.4	1.114				
CCV 1000 ng F	1028.3	-	-	-	-	102.8

Table E-3 Interference of Inorganic Fluorine Reanalysis – 02/11/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-14.3	-	-	-	-	-
CCV 1000 ng F	985.6	-	-	-	-	98.56
Method Blank 021122 Rep 1 Top Col	9	0.09	0.09	-	-	-
Method Blank 021122 Rep 1 Bottom Col	-2.3	-0.023				
Method Blank 021122 Rep 2 Top Col	0.6	0.006	0.062	-	-	-
Method Blank 021122 Rep 2 Bottom Col	5.6	0.056				
619 ng PFHxS 8 mg/L F Rep 1 Top Col	501.1	5.011	7.386	7.296	32.6	117.9
619 ng PFHxS 8 mg/L F Rep 1 Bottom Col	237.5	2.375				
CCV 1000 ng F	1001.1	-	-	-	-	100.11

Table E-4 Interference of Chloride Reanalysis – 02/15/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	4.2	-	-	-	-	-
CCV 1000 ng F	993	-	-	-	-	99.3
Method Blank 021522 Rep 1 Top Col	24	0.24	0.261	-	-	-
Method Blank 021522 Rep 1 Bottom Col	2.1	0.021				
Method Blank 021522 Rep 2 Top Col	-3.6	-0.036	0.182	-	-	-
Method Blank 021522 Rep 2 Bottom Col	18.2	0.182				
619 ng PFHxS 1000 mg/L Cl Top Col	495.1	4.951	4.913	4.652	-1.3	75.2
619 ng PFHxS 1000 mg/L Cl Bottom Col	-3.8	-0.038				
CCV 1000 ng F	935.6	-	-	-	-	93.6

Appendix F
Results for the Initial Demonstration of Capability

Results for the Initial Demonstration of Capability

Table F-1 IDC Studies Day 1 – 02/10/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-14.9	-	-	-	-	-
CCV 1000 ng F	1001.6	10.016	-	-	-	100.2
Method Blank Rep 1 Top Col	226	2.26	Contaminated Elution Position #1*			
Method Blank Rep 1 Bottom Col	761.1	7.611				
Method Blank Rep 2 Top Col	5.2	0.052	0.609	-	-	-
Method Blank Rep 2 Bottom Col	55.7	0.557				
Method Blank Rep 3 Top Col	21.0	0.21	0.309	-	-	-
Method Blank Rep 3 Bottom Col	9.9	0.099				
MDL-1 PFHxS 495 ng Rep 1 Top Col	498.3	4.983	5.239	4.453	-6.5	90.0
MDL-1 PFHxS 495 ng Rep 1 Bottom Col	25.6	0.256				
MDL-2 PFHxS 495 ng Rep 2 Top Col	458.8	4.588	5.524	4.738	7.7	95.7
MDL-2 PFHxS 495 ng Rep 2 Bottom Col	93.6	0.936				
MDL-3 PFHxS 495 ng Rep 3 Top Col	885.4	8.854	Contaminated Elution Position #1**			
MDL-3 PFHxS 495 ng Rep 3 Bottom Col	214.7	2.147				
MDL-1 PFHxS 804 ng Rep 1 Top Col	812	8.12	8.631	7.845	-0.6	97.6
MDL-1 PFHxS 804 ng Rep 1 Bottom Col	51.1	0.511				
MDL-2 PFHxS 804 ng Rep 2 Top Col	919	9.19	9.63	8.844	-1.3	110.0
MDL-2 PFHxS 804 ng Rep 2 Bottom Col	44.0	0.44				
MDL-3 PFHxS 804 ng Rep 3 Top Col	776.9	7.769	8.069	7.283	-3.4	90.6
MDL-3 PFHxS 804 ng Rep 3 Bottom Col	30.0	0.3				
IPR-1 PFHxS 1547 ng Rep 1 Top Col	1647.8	16.478	17.624	17.015	3.5	110.0
IPR-1 PFHxS 1547 ng Rep 1 Bottom Col	114.6	1.146				
IPR-2 PFHxS 1547 ng Rep 2 Top Col	2499.2	24.992	Contaminated Elution Position #1**			
IPR-2 PFHxS 1547 ng Rep 2 Bottom Col	248	2.48				
IPR-3 PFHxS 1547 ng Rep 3 Top Col	1515	15.15	16.108	15.499	2.6	100.2
IPR-3 PFHxS 1547 ng Rep 3 Bottom Col	95.8	0.958				
IPR-4 PFHxS 1547 ng Rep 4 Top Col	1425.6	14.256	15.178	14.569	2.5	94.2
IPR-4 PFHxS 1547 ng Rep 4 Bottom Col	92.2	0.922				
Method Blank Rep 4 Top Col	32.5	0.325	1.439	-	-	-
Method Blank Rep 4 Bottom Col	111.4	1.114				
CCV 1000 ng F	1028.3	-	-	-	-	102.8

*Blank not used in the calculation of MDL_b due to gross contamination
**Samples redone on 02/12/2022

Table F-2 IDC Studies Day 2 – 02/12/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	-14.3	-	-	-	-	-
CCV 1000 ng F	985.6	-	-	-	-	98.56
Method Blank 021122 Rep 5 Top Col	9.0	0.09	0.09	-	-	-
Method Blank 021122 Rep 5 Bottom Col	-2.3	-0.023				
Method Blank 021122 Rep 6 Top Col	0.6	0.006	0.062	-	-	-
Method Blank 021122 Rep 6 Bottom Col	5.6	0.056				
MDL-3 PFHxS 495 ng Rep 1 Top Col	521	5.21	5.383	5.307	3.3	-
MDL-3 PFHxS 495 ng Rep 1 Bottom Col	17.3	0.173				
MDL-4 PFHxS 495 ng Rep 2 Top Col	480	4.8	4.732	4.656	-1.5	-
MDL-4 PFHxS 495 ng Rep 2 Bottom Col	-6.8	-0.068				
MDL-5 PFHxS 495 ng Rep 3 Top Col	398.2	3.982	4.769	4.693	16.8	-
MDL-5 PFHxS 495 ng Rep 3 Bottom Col	78.7	0.787				
MDL-4 PFHxS 804 ng Rep 1 Top Col	622.6	6.226	6.397	6.321	2.7	-
MDL-4 PFHxS 804 ng Rep 1 Bottom Col	17.1	0.171				
MDL-5 PFHxS 804 ng Rep 2 Top Col	680.9	6.809	7.256	7.18	6.2	-
MDL-5 PFHxS 804 ng Rep 2 Bottom Col	44.7	0.447				
IPR-2 PFHxS 1547 ng Rep 1 Top Col	1423.6	14.236	14.646	14.556	2.8	94.1
IPR-2 PFHxS 1547 ng Rep 1 Bottom Col	41.0	0.41				
IPR-1 30PAR 1530 ng Rep 1 Top Col	1087.5	10.875	11.327	11.237	4.0	73.4
IPR-1 30PAR 1530 ng Rep 1 Bottom Col	45.2	0.452				
IPR-2 30PAR 1530 ng Rep 2 Top Col	1098.2	10.982	14.311	14.221	23.4	92.9
IPR-2 30PAR 1530 ng Rep 2 Bottom Col	332.9	3.329				
IPR-3 30PAR 1530 ng Rep 3 Top Col	1039.6	10.396	11.064	10.974	6.1	71.7
IPR-3 30PAR 1530 ng Rep 3 Bottom Col	66.8	0.668				
IPR-4 30PAR 1530 ng Rep 4 Top Col	1110.2	11.102	11.947	11.857	7.1	77.5
IPR-4 30PAR 1530 ng Rep 4 Bottom Col	84.5	0.845				
CCV 1000 ng F	1001.1	-	-	-	-	100.11

Table F-3 IDC Studies Day 3 – 02/14/2022

Identification	ng F^-	µg/L	Total (µg/L)	Blk Corrected	% Brk	% Rec
Boat Blank	6.5	-	-	-	-	-
CCV 1000 ng F	1006	-	-	-	-	100.6
Method Blank 021422 Rep 7 Top Col	25.7	0.257	0.434	-	-	-
Method Blank 021422 Rep 7 Bottom Col	17.7	0.177				
Method Blank 021422 Rep 8 Top Col	9.5	0.095	0.248	-	-	-
Method Blank 021422 Rep 8 Bottom Col	15.3	0.153				
MDL-6 PFHxS 495 ng Rep 1 Top Col	649.4	6.494	6.570	6.229	-1.6	125.8
MDL-6 PFHxS 495 ng Rep 1 Bottom Col	7.6	0.076				
MDL-7 PFHxS 495 ng Rep 2 Top Col	411.4	4.114	4.059	3.718	-6.4	75.1
MDL-7 PFHxS 495 ng Rep 2 Bottom Col	-5.5	-0.055				
MDL-6 PFHxS 804 ng Rep 1 Top Col	681.4	6.814	6.952	6.611	-0.6	133.6
MDL-6 PFHxS 804 ng Rep 1 Bottom Col	13.8	0.138				
MDL-7 PFHxS 804 ng Rep 2 Top Col	723.4	7.234	7.308	6.967	-1.5	140.7
MDL-7 PFHxS 804 ng Rep 2 Bottom Col	7.4	0.074				
IPR-1 Fipronil 1565 ng Rep 1 Top Col	1654.8	16.548	16.971	16.537	1.5	105.7
IPR-1 Fipronil 1565 ng Rep 1 Bottom Col	42.3	0.423				
IPR-2 Fipronil 1565 ng Rep 2 Top Col	1643.4	16.434	16.783	16.349	1.1	104.5
IPR-2 Fipronil 1565 ng Rep 2 Bottom Col	34.9	0.349				
IPR-3 Fipronil 1565 ng Rep 3 Top Col	1589	15.89	16.091	15.657	0.2	100.0
IPR-3 Fipronil 1565 ng Rep 3 Bottom Col	20.1	0.201				
IPR-4 Fipronil 1565 ng Rep 4 Top Col	1531	15.31	16.024	15.59	3.4	99.6
IPR-4 Fipronil 1565 ng Rep 4 Bottom Col	71.4	0.714				
CCV 1000 ng F	967.7	-	-	-	-	96.8

Appendix G
Study Sample Results

Study Sample Results

Table G-1 Study Samples Background Reconnaissance Results – 02/28/2022

Identification	Mass Observed (ng)	Concentration Units µg/L			% Brk	% Rec	Validator Flag	Dilution	Sample Volume (mL)
		Column Conc	Total Conc	Blk Corrected					
Boat Blank	0.5	-	-	-	-	-	-	-	-
0 ng F	0	-	-	-	-	-	-	1	0.2
50 ng F	44.1	-	-	-	-	88.2	-	1	0.2
100 ng F	94.7	-	-	-	-	94.7	-	1	0.2
200 ng F	196.8	-	-	-	-	98.4	-	1	0.2
600 ng F	603.3	-	-	-	-	100.6	-	1	0.2
1000 ng F	1012.2	-	-	-	-	101.2	-	1	0.2
1400 ng F	1418.5	-	-	-	-	101.3	-	1	0.2
2000 ng F	1980.4	-	-	-	-	99.0	-	1	0.2
Method Blank 022822 Rep 1 Top Col	48.7	0.487	0.889	-	-	-	-	1	100
Method Blank 022822 Rep 1 Bot Col	40.2	0.402							
Method Blank 022822 Rep 2 Top Col	53	0.53	1.141	-	-	-	-	1	100
Method Blank 022822 Rep 2 Bot Col	61.1	0.611							
Sample 1 022822 Top Col	289.7	2.897	4.462	3.573	32.5	-	-	1	100
Sample 1 022822 Bottom Col	156.5	1.565							
Sample 2 022822 Top Col	206.8	2.068	3.304	2.415	34.5	-	-	1	100
Sample 2 022822 Bottom Col	123.6	1.236							
Sample 3 022822 Top Col	1374.7	13.747	19.676	18.787	29.4	-	-	1	100
Sample 3 022822 Bottom Col	592.9	5.929							
Sample 4 022822 Top Col	1257.9	12.579	15.563	14.674	17.6	-	-	1	100
Sample 4 022822 Bottom Col	298.4	2.984							
Sample 5 022822 Glass Wool	452.8	4.528	11.61	10.513	21.5	-	-	1	100
Sample 5 022822 Top Col	534.7	5.347							
Sample 5 022822 Bottom Col	173.5	1.735							
Sample 6 022822 Top Col	1769.8	17.698	22.971	22.082	22.1	-	ACR, J	1	100
Sample 6 022822 Bottom Col	527.3	5.273							
Sample 7 022822 Top Col	109.8	1.098	1.99	1.101	44.5	-	-	1	100
Sample 7 022822 Bottom Col	89.2	0.892							
Sample 8 022822 Top Col	264.6	2.646	4.372	3.483	38.0	-	-	1	100
Sample 8 022822 Bottom Col	172.6	1.726							
Sample 10 022822 Top Col	184.8	1.848	3.398	2.509	45.8	-	-	1	100
Sample 10 022822 Bottom Col	155	1.55							
Glass wool cleanliness check	20.8	0.208	0.208	-	-	-	-	-	-
MB Carbon Check	66.7	0.667	0.667	-	-	-	-	-	-
CCV 600 ng F	561.2	-	-	-	-	93.5	-	1	0.2

Table G-2 Study Samples 1, 4, and 7 Spike Results – 03/22/2022

Identification	Mass Observed (ng)	Concentration Units µg/L				% Brk	% Rec	Validator Flag	Dilution	Sample Volume (mL)
		Column Conc	Spiked Conc	Total Conc	Blk Corrected					
Boat Blank	-2.7	-0.027	-	-	-	-	-	-	-	-
CCV 200 ng F	190.5	-	-	-	-	-	95.3	-	1	0.2
Method Blank 030222 Rep 1 Col 1	27.2	0.272	-	0.415	-	-	-	-	1	100
Method Blank 030222 Rep 1 Col 2	14.3	0.143								
OPR 030222 Top Col	877.7	8.777	9.9	9.146	8.731	2.6	88.2	-	1	100
OPR 030222 Bottom Col	36.9	0.369								
Sample1 MS Rep 1 Top Col	859.1	8.591	9.9	13.144	12.729	34.6	-	-	1	100
Sample1 MS Rep 1 Bottom Col	455.3	4.553								
Sample1 MS Rep 2 Top Col	998.4	9.984	9.9	12.865	12.45	22.0	-	-	1	100
Sample1 MS Rep 2 Bottom Col	288.1	2.881								
Sample1 MS Rep 3 Top Col	831.8	8.318	9.9	12.675	12.26	34.4	-	-	1	100
Sample1 MS Rep 3 Bottom Col	435.7	4.357								
Sample4 MS Rep 1 Top Col	1575.2	15.752	15.47	17.14	16.725	7.4	-	-	1	100
Sample4 MS Rep 1 Bottom Col	138.8	1.388								
Sample4 MS Rep 2 Top Col	1761.2	17.612	15.47	18.838	18.423	5.9	-	-	1	100
Sample4 MS Rep 2 Bottom Col	122.6	1.226								
Sample4 MS Rep 3 Top Col	1830.7	18.307	15.47	20.202	19.787	8.9	-	-	1	100
Sample4 MS Rep 3 Bottom Col	189.5	1.895								
Sample7 MS Rep 1 Top Col	545.9	5.459	6.19	8.244	7.829	33.7	-	-	1	100
Sample7 MS Rep 1 Bottom Col	278.5	2.785								
Sample7 MS Rep 2 Top Col	613.6	6.136	6.19	10.469	10.054	41.7	-	HMSR	1	100
Sample7 MS Rep 2 Bottom Col	433.3	4.333								
Sample7 MS Rep 3 Top Col	544.3	5.443	6.19	7.858	7.443	30.5	-	-	1	100
Sample7 MS Rep 3 Bottom Col	241.5	2.415								
Method Blank 030222 Rep 2 Col 1	91.9	0.919	-	1.72	-	-	-	-	1	100
Method Blank 030222 Rep 2 Col 2	80.1	0.801								
CCV 1000 ng F	1000.2	-	-	-	-	-	100.0	-	1	0.2

Table G-3 Study Samples 2, 3, and 5 Spike Results – 03/03/2022

Identification	Mass Observed (ng)	Concentration Units µg/L				% Brk	% Rec	Validator Flag	Dilution	Sample Volume (mL)
		Column Conc	Spiked Conc	Total Conc	Blk Corrected					
Boat Blank	-1.1	-	-	-	-	-	-	-	-	-
CCV 200 ng F	184.9	-	-	-	-	-	92.5	-	1	0.2
Method Blank 030322 glass wool	4.1	0.041	-	0.383	-	-	-	-	1	100
Method Blank 030322 Rep 1 Top Col	22.3	0.223								
Method Blank 030322 Rep 1 Bot Col	16	0.16								
OPR 030322 Rep 1 Top Col	939.2	9.392	9.9	9.551	9.168	-0.01	92.6	-	1	100
OPR 030322 Rep 1 Bottom Col	15.9	0.159								
Sample2 MS Rep 1 Top Col	640.8	6.408	6.19	9.073	8.69	28.83	-	-	1	100
Sample2 MS Rep 1 Bottom Col	266.5	2.665								
Sample2 MS Rep 2 Top Col	645	6.45	6.19	8.75	8.367	25.58	-	-	1	100
Sample2 MS Rep 2 Bottom Col	230	2.3								
Sample2 MS Rep 3 Top Col	624.7	6.247	6.19	8.974	8.591	29.88	-	-	1	100
Sample2 MS Rep 3 Bottom Col	272.7	2.727								
Sample3 MS Rep 1 Top Col	1688.1	16.881	15.47	22.567	22.184	24.91	-	-	1	100
Sample3 MS Rep 1 Bottom Col	568.6	5.686								
Sample3 MS Rep 2 Top Col	1721.9	17.219	15.47	23.987	23.604	28.00	-	-	1	100
Sample3 MS Rep 2 Bottom Col	676.8	6.768								
Sample3 MS Rep 3 Top Col	1736.2	17.362	15.47	24.625	24.242	29.30	-	HMSR	1	100
Sample3 MS Rep 3 Bottom Col	726.3	7.263								
Sample5 MS Rep 1 glass wool	94.5	0.945	9.9	13.379	12.955	20.21	-	-	1	100
Sample5 MS Rep 1 Top Col	983.8	9.838								
Sample5 MS Rep 1 Bottom Col	259.6	2.596								
Sample5 MS Rep 2 glass wool	208.9	2.089	9.9	18.779	18.355	20.75	-	HMSR	1	100
Sample5 MS Rep 2 Top Col	1314.7	13.147								
Sample5 MS Rep 2 Bottom Col	354.3	3.543								
Sample5 MS Rep 3 glass wool	95.9	0.959	9.9	12.942	12.518	35.58	-	-	1	100
Sample5 MS Rep 3 Top Col	769.6	7.696								
Sample5 MS Rep 3 Bottom Col	428.7	4.287								
Method Blank Rep 2 Top Col	80	0.8	-	1.563	-	-	-	-	1	100
Method Blank Rep 2 Bot Col	76.3	0.763								
CCV 1000 ng F	991.7	-	-	-	-	-	99.2	-	-	0.2

Table G-4 Study Samples 6, 8, and 10 Spike Results – 03/05/2022

Identification	Mass Observed (ng)	Concentration Units µg/L				% Brk	% Rec	Validator Flag	Dilution	Sample Volume (mL)
		Column Conc	Spiked Conc	Total Conc	Blk Corrected Conc					
Boat Blank	-2.7	-0.027	-	-	-	-	-	-	-	-
CCV 200 ng F	179.7	-	-	-	-	-	89.9	-	1	0.2
Method Blank 030522 Rep 1 Top Col	12.9	0.129	-	0.255	-	-	-	-	1	100
Method Blank 030522 Rep 1 Bot Col	12.6	0.126								
OPR 030522 Rep 1 Top Col	839.2	8.392	9.9	8.625	8.37	1.3	84.5	-	1	100
OPR 030522 Rep 1 Bottom Col	23.3	0.233								
Sample6 MS Rep 1 Top Col	1689.9	16.899	15.47	20.363	20.108	16.6	-	-	1	100
Sample6 MS Rep 1 Bottom Col	346.4	3.464								
Sample6 MS Rep 2 Top Col	1543.9	15.439	15.47	20.987	20.732	26.2	-	-	1	100
Sample6 MS Rep 2 Bottom Col	554.8	5.548								
Sample6 MS Rep 3 Top Col	1817.6	18.176	15.47	22.116	21.861	17.4	-	-	1	100
Sample6 MS Rep 3 Bottom Col	394	3.94								
Sample8 MS Rep 1 Top Col	656.5	6.565	6.19	9.182	8.927	27.9	-	-	1	100
Sample8 MS Rep 1 Bottom Col	261.7	2.617								
Sample8 MS Rep 2 Top Col	715.2	7.152	6.19	9.293	9.038	22.3	-	-	1	100
Sample8 MS Rep 2 Bottom Col	214.1	2.141								
Sample8 MS Rep 3 Top Col	731.1	7.311	6.19	10.201	9.946	27.8	-	-	1	100
Sample8 MS Rep 3 Bottom Col	289	2.89								
Sample10 MS Rep 1 Top Col	1045.3	10.453	9.9	11.616	11.361	9.1	-	-	1	100
Sample10 MS Rep 1 Bottom Col	116.3	1.163								
Sample10 MS Rep 2 Top Col	1075.3	10.753	9.9	15.592	15.337	30.7	-	-	1	100
Sample10 MS Rep 2 Bottom Col	483.9	4.839								
Sample10 MS Rep 3 Top Col	960.7	9.607	9.9	11.667	11.412	16.9	-	-	1	100
Sample10 MS Rep 3 Bottom Col	206	2.06								
Method Blank 030522 Rep 2 Col 1	69.8	0.698	-	1.318	-	-	-	-	1	100
Method Blank 030522 Rep 2 Col 2	62	0.62								
CCV 1000 ng F	997.2	-	-	-	-	-	99.7	-	1	0.2

Table G-5 Study Sample 9 Reconnaissance and Spike Results – 03/16/2022

Identification	Mass Observed (ng)	Concentration Units µg/L				% Brk	% Rec	Validator Flag	Dilution	Sample Volume (mL)
		Column Conc	Spiked Conc	Total Conc	Blk Corrected Conc					
Boat Blank	-57.3	-	-	-	-	-	-	-	-	-
CCV 200 ng F	193.4	-	-	-	-	-	96.7	-	-	0.2
Method Blank 031622 Rep 1 Top Col	-26.3	-0.263	-	-0.519	-	-	-	-	1	100
Method Blank 031622 Rep 1 Bot Col	-25.6	-0.256								
OPR 031622 Top Col	1035.6	10.356	-	10.36	10.36	0	104.6	-	1	100
OPR 031622 Bottom Col	-0.3	-0.003								
Sample 9 Top Col	1747.4	17.474	-	22.04	22.04	20.7	-	-	1	100
Sample 9 Bottom Col	456.7	4.567								
Sample9 MS Rep 1 Top Col	1912	19.12	15.47	21.10	21.10	9.4	107.9	-	1	100
Sample9 MS Rep 1 Bottom Col	198.3	1.983								
Sample9 MS Rep 2 Top Col	1950.2	19.502	15.47	20.33	20.33	4.1	102.9	-	1	100
Sample9 MS Rep 2 Bottom Col	82.9	0.829								
Sample9 MS Rep 3 Top Col	1963.8	19.638	15.47	20.88	20.88	5.9	106.4	-	1	100
Sample9 MS Rep 3 Bottom Col	123.7	1.237								
Method Blank 031622 Rep 2 Top Col	39.5	0.395	-	0.395	-	-	-	-	1	100
Method Blank 031622 Rep 2 Bot Col	-2.7	-0.027								
CCV 1000 ng F	991.2	-	-	-	-	-	99.1	-	-	0.2