DEPARTMENT OF ECOLOGY
State of Washington

Quality Assurance Project Plan

Poly- and Perfluoroalkyl Substances in Consumer Goods in Washington State

February 2015

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Publication Information

Washington State Department of Ecology policy requires an approved Quality Assurance Project Plan for all agency-sponsored sampling events. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post a report of the study to the Internet.

The plan for the study is available on the Department of Ecology's website at: https://fortress.wa.gov/ecy/publications/SummaryPages/1504009.html

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Quality Assurance Project Plan

Poly- and Perfluoroalkyl Substances in Consumer Goods in Washington State

February 5, 2015

Approved by:

Staff	Signature	Date
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Signatures are not available on the Internet version.

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Abstract

The Washington Department of Ecology's Hazardous Waste and Toxics Reduction (HWTR) and Waste 2 Resources (W2R) programs are conducting a study to evaluate the presence of per- and poly-fluoroalkyl substances (PFAS) in consumer goods. PFAS is listed as a persistent organic pollutant detected in the environment, wildlife, and humans. It can accumulate in a living organism and create a risk for animal and human health. For example, perfluorooctane sulfonate (PFOS), a perfluorinated compound, is a known persistent, bioaccumulative, and toxic (PBT) substance and shown to possess developmental and reproductive toxicity. (Olsen et al, 1999; Wang et al., 2009; Melzer, 2010)

This study focuses on the determination of PFASs in consumer goods and compliance with the Children's Safe Product Act and Executive Order 04-01. Executive Order 04-01 restricts state purchasing to products that do not contain persistent, bioaccumulative, and toxic (PBT) compounds identified in Washington's PBT List (WAC 173-333). Consumer products and products purchased via Washington State's Department of Enterprise Services (DES) contracts will be tested for total fluorine. The screening method does not differentiate between organic and inorganic compounds containing fluorine but provides an indication of total elemental fluorine content.

Prioritized products found to contain the highest levels of elemental fluorine will be tested for 70 individual PFAS. Samples will be screened using Particle Induced Gamma-ray Emission (PIGE) spectroscopy to identify those that contain more than ten parts per million (ppm) total fluorine. PIGE does not differentiate between organic or inorganic fluorine but can be used to prioritize samples based upon total fluorine concentration. Those samples with the highest total elemental fluorine potentially contain perfluorinated compounds. However, there is no guarantee that the samples containing the highest levels of total fluorine will contain either organic fluorine or any of the fluorinated compounds found in subsequent analyses.

The PIGE screening results will be evaluated and the samples containing the highest total fluorine concentrations will be prioritized for additional analysis. Samples identified for analysis will be analyzed using an LC/MS/MS method that analyzes for specific per- and poly-fluorinated alkyl substances (PFAS) classes including:

- 15 perfluoroalkyl carboxylates (e.g., PFOA).
- 7 perfluoroalkyl sulfonates (e.g., PFOS).
- 8 saturated and 4 unsaturated fluorotelomer carboxylates.
- 3 fluorotelomer sulfonates.
- 5 disubstituted perfluorophosphinic acids.
- 7 disubstituted polyfluorinated phosphate esters.
- 5 fluorotelomer mercaptoalkyl phosphate esters.
- N-ethyl perfluorooctanesulfonamidoethanol-based polyfluoroalkyl phosphate ester.

Chemicals identified in the analysis will be reported above the 1 ppm levels.

Background

Perfluorinated substances are organic substances in which all hydrogen-to-carbon bonds have been replaced with fluorine-to-carbon bonds. Polyfluorinated substances are similar substances in which some but not all of the hydrogen-to-carbon bonds have been replaced with fluorine-to-carbon bonds, producing compounds with a mixture of fluorine and hydrogen atoms connected to the carbon base. Perfluorinated substances of interest in the study and specifically perfluoroalkyl and poly-fluoroalkyl (PFASs) are subsets of the fluorinated substances.

Due to the chemical properties of fluorine, the fluorine-to-carbon bonds in PFAS are very strong and difficult to break. This high-bond strength causes PFAS to have unique properties, such as very high persistence and anti-stain and non-stick properties. These unique properties cause PFAS substances to be used widely in consumer products and particularly as surfactants and polymers, which contain a perfluoroalkyl moiety. Polymer applications include textile stain and soil repellents and food contact paper for its anti-grease and stain proof characteristics. Surfactant applications include fluoropolymer manufacture, and coatings and foams used to extinguish fires involving highly flammable liquids. (Buck, 2011) Perfluorooctanoic acid (PFOA), for example, was used extensively as an anti-stain agent under the tradename Scotchguard. Other widely used fluorinated compounds include Teflon and Gore-Tex.

Exposure to fluorinated compounds is widespread in the United States.

- The U.S. Centers for Disease Control and Prevention '… *found PFOA in the serum of nearly all the people tested, indicating that PFOA exposure is widespread in the U.S. population*.' (CDC, 2009)
- Calafat et al. (2007) reported that '…*PFOS, PFOA, PFHxS, and PFNA serum concentrations were measurable in each demographic population group studied*.'
- Many PFAS are expected to be widespread and '*Due to the strong C-F binding in the PFAS molecule, most of these compounds are extremely persistent, virtually indestructible and are, thus, expected to prevail in the environment.*' (Kallenborn, 2005)

Concerns are increasing on the possible impact of PFAS upon human health and the environment.

- Steenland et al. (2010) reported '…*animal data indicate that [PFOA] can cause several types of tumors and neonatal death and may have toxic effects on the immune, liver, and endocrine systems.*'
- Melzer et al (2010) reported '*Higher concentrations of serum PFOA and PFOS are associated with current thyroid disease in the U.S. general adult population.*'

- Impacts of most PFAS upon human health and the environment have been poorly studied although EPA noted that '*Given the long half of these chemicals in humans (years), it can reasonably be anticipated that continued exposure could increase body burdens to levels that would result in adverse outcomes*' (EPA, 2009).

Project Description

Consumer goods will be obtained from Washington Department of Enterprise (DES) clients or purchased in stores in Washington State from November 2014 to March 2015. Each product will be separated into a minimum of two samples, one for screening and, if selected, a second for more detailed analysis. Samples of each product will first be sent to Hope College in Holland, Michigan to screen for total fluorine. Results from the screening analyses will be used to prioritize samples for further analysis. Those samples containing a range of fluorine levels will be sent to Oregon State University for more detailed analysis.

Oregon State University will measure the PFAS concentrations in prioritized samples and specific random samples with no detectable fluorine concentration as a control. The objective of the study will be to:

1. Compare the screening method for total fluorine and liquid chromatography tandem mass spectrometry (LC-MS/MS) that quantify several PFAS levels in consumer products.
2. Quantify PFAS levels in a range of consumer products.

Comparison between the screening method and analytical results will depend on the presence of any of the 70 PFASs identified by LC-MS/MS in those samples identified by the screening methodology to contain high levels of total elemental fluorine.

Sampling Process Design (Experimental Design)

Consumer goods will be purchased from stores in Washington State or obtained from DES clients. Products will be selected based on the following criteria:

1. Detection of PFAS compounds has been reported in similar products.
2. Material Safety Data Sheets and related databases indicating the presence of PFASs.
3. Other data indicating the possible presence of PFAS compounds.

Each article to be sampled will be entered into an online database at the Department of Ecology and a chain-of-custody initiated for transfer to Hope College or Oregon State University. The chain-of-custody will be maintained throughout the sample analysis.

For packaged goods, items will be separated from their packaging and individual samples created for both the sample and sample packaging. Both samples will be screened for total elemental fluorine. Sufficient sample mass will be sent to Hope College to allow three replicate samples of each consumer product or its packaging to be screened for total elemental fluorine. Those samples that have detectable total elemental fluorine concentrations will then be marked for potential extraction followed by LC-MS/MS analysis. Representatives from Ecology, Hope College, and Oregon State University will meet to prioritize the screening results and decide which samples will be analyzed further. One out of every ten samples will be selected from those products that found no detectable levels of elemental fluorine during the screening analysis.

Product Selection

Products will be obtained either directly from retailers in Washington State or through clients of Washington's DES. Products submitted for analysis will be selected based on one of two priorities:

1. Products either reported or believed through readily available data sources to contain the chemical of high concern to children, perfluorooctane sulfonic acid (PFOS) and its salts (Chemical Abstract Services Number 1763-23-1, among others (see Table 1)).
2. Products purchased by DES clients that are either known or suspected through readily available data sources to contain PFOS and related PFAS compounds.

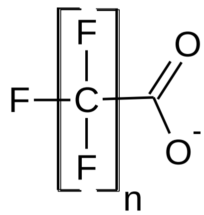
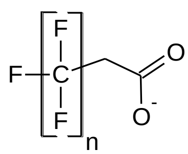
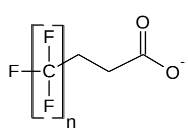
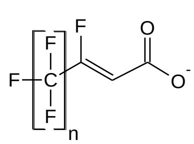
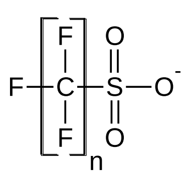
DES will establish contracts through which state agencies and related organizations purchase products at reduced and standardized costs. Ecology will work directly with DES staff responsible to obtain the names of clients purchasing products of interest from DES contracts. The clients will be contacted and asked to participate in the project by providing new products for analysis.

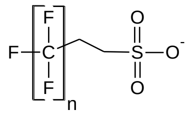
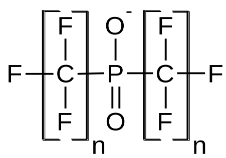
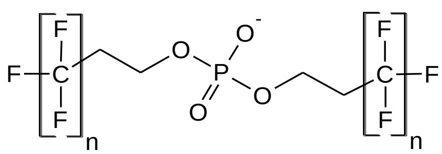
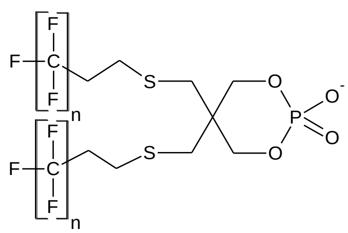
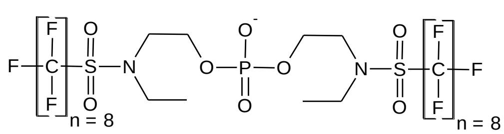
In addition to DES products, children's products will be purchased that may contain PFOS and other PFASs. Under the Washington Children's Safe Product Act, manufacturers are required to report to Ecology if any of their products contain one of the chemicals of high concern to children including PFOS. This reporting information is available via the internet and can be reviewed to determine if any products reported the presence of PFOS. If no product reports are available, all available data sources will be reviewed to determine children's products that may contain PFASs.

Target Chemicals

Table 1 identifies a list of targeted, individual PFAS known or suspected to be in consumer goods. The number of individual PFAS within various classes include fifteen perfluoroalkyl-carboxylates, four n:2 fluorotelomer (saturated) carboxylates, four n:3 fluorotelomer (saturated) carboxylates, four n:2 fluorotelomer (unsaturated) carboxylates, seven perfluoroalkyl sulfonates, three fluorotelomer sulfonates, five disubstituted perfluorophosphinic acids, seven disubstituted polyfluorinated phosphate esters, five fluorotelomer mercaptoalkyl phosphate esters, and one N-ethyl perfluorooctanesulfonamidoethanol-based polyfluoroalkyl phosphate ester.

Table 1. Family name, number of carbons in perfluorinated chain, acronym, and Chemical Abstracts Number (CAS) for PFAS analyzed for this study.

Family Name and Structure	n	Acronym	CAS #
Perfluoroalkyl carboxylates (n=15)	4	PFBA	45048-62-2
	5	PFPeA	45167-47-3
	6	PFHxA	92612-52-7
	7	PFHpA	120885-29-2
	8	PFOA	45285-51-6
	9	PFNA	72007-68-2
	10	PFDA	73829-36-4
	11	PFUnDA	196859-54-8
	12	PFDoDA	171978-95-3
	13	PFTriDA	862374-87-6
	14	PFTeDA	365971-87-5
	15	PFPeDA	1214264-29-5
	16	PFHxDA	1214264-30-8
	17	PFHpDA	57475-95-3
	18	PFOcDA	798556-82-8
n:2 Fluorotelomer (saturated) carboxylates (n=4)	4	4:2 FTCA	70887-89-7
	6	6:2 FTCA	53826-12-3
	8	8:2 FTCA	882489-13-6
	10	10:2 FTCA	912576-45-5
n:3 Fluorotelomer (saturated) carboxylates (n=4)	3	3:3 FTCA	1169706-83-5
	5	5:3 FTCA	914637-49-3
	7	7:3 FTCA	812-70-4
	9	9:3 FTCA	143260-97-3
n:2 Fluorotelomer (unsaturated) carboxylates (n=4)	4	4:2 FTUCA	1003193-94-9
	6	6:2 FTUCA	889944-75-6
	8	8:2 FTUCA	1003193-95-0
	10	10:2 FTUCA	1003193-96-1
Perfluoroalkyl sulfonates (n=7)	4	PFBS	45187-15-3
	5	PFPS	175905-36-9
	6	PFHxS	108427-53-8
	7	PFHpS	146689-46-5
	8	PFOS	45298-90-6
	9	PFNS	474511-07-4
	10	PFDS	126105-34-8

Family Name and Structure	n	Acronym	CAS #
Fluorotelomer sulfonates (n=3)	4	4:2 FTSA	414911-30-1
	6	6:2 FTSA	425670-75-3
	8	8:2 FTSA	481071-78-7
Disubstituted perfluorophosphinic acids (n=5)	**4**	**4:4 PFPi**	**613232-24-9**
	4	4:6 PFPi	not found
	6	6:6 PFPi	1411714-08-3
	6	6:8 PFPi	1411714-10-7
	8	8:8 PFPi	1411714-12-9
Disubstituted polyfluorinated phosphate esters (n=7)	4	4:2 diPAP	not found
	4/6[1]	4:2/6:2 diPAP	667465-18-1
	6	6:2 diPAP	not found
	6/8[1]	6:2/8:2 diPAP	1411713-89-7
	8	8:2 diPAP	1411713-91-1
	8/10[1]	8:2/10:2 diPAP	1411713-93-3
	10	10:2 diPAP	1411713-97-7
Fluorotelomer mercaptoalkyl phosphate esters (n=5)	6	6:2 FTMAP	1295524-36-5
	6/8[1]	6:2/8:2 FTMAP	not found
	8	8:2 FTMAP	138655-66-0
	8/10[1]	8:2/10:2 FTMAP	not found
	10	10:2 FTMAP	not found
N-ethyl perfluorooctanesulfonamidoethanol-based polyfluoroalkyl phosphate ester (n=1)	8	SAmPAP	1380245-78-2
			

Organization and Schedule

Table 2 lists the individuals involved in the project and Table 3 describes the project schedule.

Table 2. Organization of Project Staff and Responsibilities

Staff	Title	Responsibilities
Jennifer Field	Oregon State University Principal Investigator (PI)	Writes the QAPP. Oversees receipt of samples at Oregon State University; extraction and analysis of samples by LC-MS/MS; data reporting.
Graham Peaslee	Hope College, Michigan PI	Provides input on QAPP. Oversees sample receipt at Hope College; total fluorine analysis; data reporting.
Alex Stone	Project Manager, Washington Department of Ecology	Oversees field sample and transportation of sample to the laboratories at Oregon State and Hope College; conducts QA review of the draft QAPP; approves the final QAPP.
Ken Zarker	Management Sponsor, Washington Department of Ecology	Approves final QAPP and project.
Samuel Iwenofu	Quality Assurance Officer, Washington Department of Ecology	Reviews the draft QAPP; approves the final QAPP.

Table 3. Proposed Schedule for Completing Field and Laboratory Work and Reports

Field and laboratory work	Due date	Lead staff
Field work completed	30 March 2015	Alex Stone
Laboratory analyses completed	30 June 2015	Graham Peaslee and Jennifer Field
Final reports		
Laboratory project managers	As data becomes available or prior to July 31, 2015	Jennifer Field and Graham Peaslee
Ecology project manager	Final project report prior to December 31, 2015	Alex Stone

Sample Collection and Preparation

Samples will be identified using applicable portions of the Ecology Product Sampling Standard Operating Procedure (Ecology, 2014). Samples will be shipped using standard chain-of-custody techniques to Hope College for screening or to Oregon State University for full analysis. Chain-of-custody will be maintained throughout the collection and transfer process.

Analytical Procedures

Total Fluorine Surface Analysis

Total elemental fluorine analysis from each replicate sample will be done using Particle Induced Gamma-ray Emission (PIGE) spectroscopy. (Carvahlho, 2001; Hoque, 2002; Lavielle, 2011; Olabanji, 1997; Roelandts, 1996; Roelandts, 1985; Roelandts, 1986; Samudralwar, 1993; Volfinger, 1994; Robertson, 1992; Calastrini, 1998) Using nitrile gloves, each replicate sample will be removed from its sample bag and dust will be gently removed with compressed air. The samples will then be mounted on a metal target frame **Error! Reference source not found.**(Figure 1) either with plastic adhesive tape or clips and irradiated with ~10 nA of 3.4 MeV (mega electron volts) protons for 60-180 seconds. The gamma-rays observed from each sample at 110 keV (kilo electron volts) and 197 keV will be measured at 45º to the incident beam with a cadmium telluride (CdTe) solid-state detector and recorded via multichannel analyzer.

From the recorded gamma-ray spectrum of each replicate sample (Figure 2), the number of total fluorine counts above background per microCoulomb of beam will be recorded. An average of three replicate samples will be performed and all products or packaging with total fluorine measured above threshold (~10-20 mg/kg) will be flagged as positive for fluorine. The average number of fluorine counts per microCoulomb of beam will be recorded together with a positive or negative total fluorine status.

Limit of detection (LOD) is defined as 10 mg/kg of material for papers and textile surfaces with current methods, and limit of quantification (LOQ) is defined as 25 mg/kg.

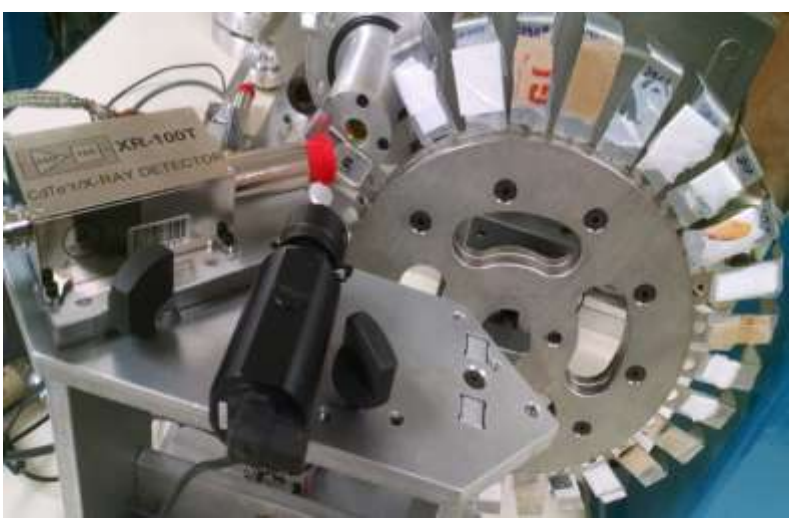


Figure 1*. PIGE target wheel with 30 target frames in place.*

LC-MS/MS Analysis

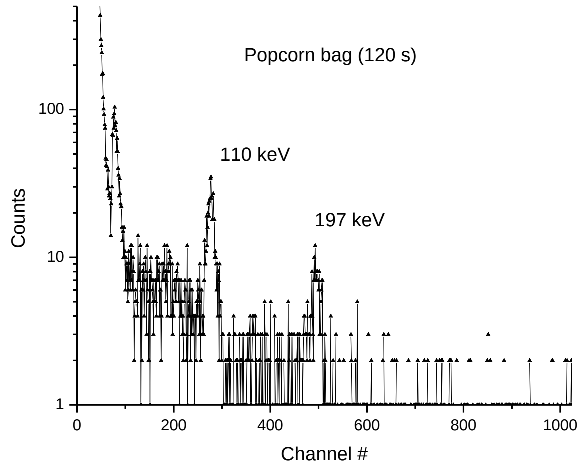


Figure 2: Typical total fluorine spectrum from a PFC-treated paper with fluorine peaks marked.

Products will be analyzed using an approach based on extraction with a method (Gebbink, 2013; Trier, 2011) developed for the analysis of paper and packaging. Samples of materials, such as paper, (1.7-2.2 g) will be ground and extracted three times with warm 60ºC methanol. The three extracts will be centrifuged for ten minutes and the liquid extracts combined and reduced to near dryness under a stream of dry nitrogen. The extract will be refrigerated overnight at 4ºC to allow for precipitate formation. The sample will then be warmed to room temperature and centrifuged for ten minutes. The supernatant will be transferred and the volume brought to 5 mL with methanol and spiked with stable-isotope labeled internal standards. The final extract will be diluted 1:100 prior to LC-MS/MS analysis.

The LODs and LOQs for PFAS on paper are currently being developed but will be in the ng/g (ppm) range. No LOQs exist for other consumer product matrices using this method.

Budget

Table 4 lists the project budget.

Table 4. Project Budget

Analysis	# of Samples	Cost per sample	Total
Screen for total fluorine (Hope)	605	$35.00	$21,175
Extraction and LC-MS/MS analysis (OSU)	64	$450.00	$28,800
Total			**$49,975**

Quality Objective

The quality objective for this project is to obtain high quality data so that the amount of PFAS in consumer products can be accurately determined to the extent practicable given the quantification of isomers in PFASs, matrix effects, and interferences. This objective will be achieved through careful attention to sampling, labeling, sample processing, storage, measurement, and quality control procedures, which are described in this plan.

Measurement Quality Objectives

For total fluorine, the average and the 95 percent Confidence Interval of three replicate samples will be recorded for all products or packaging for which total fluorine is measured above a threshold (~10-20 mg/kg). Measurement quality objectives (MQOs) for total fluorine analysis are outlined in Table 5.

Table 5. MQOs for Laboratory Analyses

Analysis	Laboratory control (recovery)	Matrix spikes (recovery)	Replicates (n=3)	Method Blanks
Total fluorine	NA	NA	± 20%	<LOQ
LC-MS/MS	70-130%	70-130%	± 20%	<LOQ

<LOQ = less than the limit of quantification; varies by PFAS analyte

Quality Control Procedures

Field

No field quality control procedures are anticipated for this project.

Laboratory

Table 6 shows laboratory QC samples planned for this project. Split duplicate samples will be used to assess the variability in the data due to sampling, transport, and storage.

Table 6. Quality Control Tests for Total Fluorine and LC-MS/MS.

	Method blanks	Positive control (total fluorine)	Matrix overspike (LC-MS/MS)	Laboratory Replicates (n=3 of single sample)**
Total fluorine	NA	1/batch*	NA	each sample will be analyzed in triplicate
PFAS by LC-MS/MS	1/batch*	NA	1/batch*	1/batch*

NA = not applicable (no extraction required) **batch = no more than 10 samples*

***Results will be reported as an average of the three replicates*

For the screening method, a positive total fluorine control will be tested with each batch of samples. A positive control is an inorganic fluorine compound mixed with a non-fluorine containing substrate yielding a sample of known fluorine concentration. In each batch, a positive sample will be analyzed in triplicate to provide a % relative standard deviation that can be applied to estimate the uncertainty about reported concentrations for samples in that batch.

For the LC-MS/MS method, a Method Blank will be run with each batch. A Matrix Blank is a sample vial containing blank solvents, which is subjected to the extraction procedures. The extract from the Method Blank is spiked with internal standards and analyzed. In this manner, cross contamination during the extraction process is evaluated. A sample vial will be spiked with PFAS standards and the final extract will be spiked with internal standards creating a PFAS Matrix overspike. Surrogates for many PFAS are not available for this project but stable-isotope labeled internal standards are available for select PFAS.

Data Management Procedures

For the total fluorine screening analysis, each target wheel (30 samples) will be digitally photographed for reference, and each replicate PIGE measurement will generate a spectrum that will be digitally archived at Hope College. In addition, all PIGE analyses conducted will be summarized in a spreadsheet, showing both individual measurements, average of three replicate measurements and regular (1/batch) measurements of a fluorine standard. This spreadsheet will be shared online with Oregon State University.

Raw data from LC-MS/MS analyses will be archived with product identifier information. Data that has passed quality control will be summarized in data packages that will be sent to Ecology. Data packages containing data generated by Hope College and OSU will be created including any significant changes to the analytical methodology, an explanation of problems encountered, corrective actions taken, and explanation of data qualifiers.

Report

A final report detailing the data for the consumer products and the major findings of the study will be created. The final report will include:

- Consumer products analyzed.
- Concentrations of total fluorine screening results for all consumer products.
- Concentrations of individual PFAS chemicals in consumer products that tested positive for total fluorine in the screening analyses and select negative samples.
- Comparison of the total fluorine and LC-MS/MS analysis.
- Assessment on the occurrence of PFAS in consumer products

Data Verification and Validation

Laboratory project managers will verify that

- Methods and protocols specified in this project plan were followed.
- All calibrations, QC tests, and intermediate calculations were performed for all samples.
- Data are consistent, correct, and complete, with no errors or omissions.

Evaluation criteria will include the acceptability of procedural blanks, calibration, QC tests, and appropriateness of data qualifiers assigned.

Laboratory project managers will provide case narratives to the Ecology project manager, describing the quality of the laboratory data. Case narratives should include

- Any problems encountered with the analyses.
- Corrective actions taken.
- Changes to the referenced method.
- An explanation of data qualifiers.

Narratives will also address the condition of samples on receipt, sample preparation, methods of analysis, instrument calibration, and results of QC tests.

Data Quality (Usability) Assessment

The Ecology project manager will assess the quality of the data, based on case narratives and data packages, to determine whether MQOs were met for this study. The Ecology project manager will determine whether the data should be accepted, accepted with additional qualification, or rejected and re-analysis considered. If any issues arise, data quality and usability will be discussed in the final report.

Appendix

Acronyms and Abbreviations

The following are acronyms and abbreviations used in this report.

LC-MS/MS	Liquid Chromatography – tandem Mass Spectrometry
PFAS	Per- and Poly-Fluorinated Alkyl Sulfonates
PIGE	Particle Induced Gamma-ray Emission
QA	Quality Assurance
QC	Quality Control
PI	Principal Investigator

Units of Measurement

g	gram
keV	kilo (or thousand) electron volts
kg	kilogram
MeV	Mega (or million) electron volts
mg	milligram
ng	nanogram
ppm	parts per million

References

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