National Exposure Research Laboratory
Research Triangle Park, NC

Quality Assurance Project Plan: Non-Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) for New Hampshire Department of Environmental Services (NHDES)

October 2, 2017

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Note: This QAPP was conditionally approved upon receipt on October 2, 2017. Signatures were collected after clarifications to the QAPP were completed.

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A3. Distribution List

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A4. Project Organization

Table 1 below describes project personnel and their respective role and responsibility for this project.

Table 1. Project personnel roles and responsibilities.

Project Personnel	Role	Responsibility
Mark Strynar	Principal Investigator	Sample Analysis (water) and data reporting
John Washington	Principal Investigator	Sample Analysis (dispersion, soil, char) and data reporting
Andrew Lindstrom	Principal Investigator	Overall project development
Matthew Henderson	Principal Investigator	Non-targeted analysis of polymeric suspensions
Thom Jenkins	Laboratory technician	Extractions of soil and char samples
Myriam Medina-Vera	EPA project supervision	EPA Project oversight and approval
Sania W. Tong Argao	EMMD QA Manager	Advises on QA requirements, reviews and approves project QAPP and associated SOPs
Timothy Buckley	EMMD Coordinator	Coordinate project discussions between EMMD, R1 and NHDES
Megan F. Cassidy	Regional supervision	Assist with overall project coordination and to help lead efforts to communicate project results to NHDES and R1 constituents
Brandon Kernen	NHDES Project Coordinator	Assist with overall project coordination and communication, oversee sample collection and delivery, assist with interpretation of data and preparation of manuscripts
Clark B. Freise	NHDES supervision	Oversee and coordinate overall NHDES efforts, serve as key NHDES contact for R1 and ORD, direct communication of results within NH

A5. Problem Definition and Background

The New Hampshire Department of Environmental Services (NHDES) through EPA Region 1 and the National Exposure Research Laboratory (NERL) lab director requested the assistance of NERL's Exposure Methods and Measurements Division (EMMD) for the analyses of long and short-chain poly and perfluoroalkyl substances (PFAS) by high resolution mass spectrometry with a comprehensive assessment of the spectral data using library searches. The samples include water, soil, dispersion and char and would be obtained from two sites historically associated with releasing PFAS into the environment. NERL's expertise is needed to overcome the technical barriers encountered by NH including: 1) commercial laboratory analytical limitations for handling more complex sample matrices; 2) unknown nature of the compounds because they are proprietary, manufacturing byproducts or degradation compounds contained in raw materials;

and 3) lack of expertise and experience associated with advanced fluorochemistry and fate and transport properties.

Drs. Mark Strynar, John Washington and Andrew Lindstrom are considered experts in the area of polyfluoroalkyl substances (PFAS) including perfluoroalkyl ether carboxylic acids (PFECAs). They have authored about 28 publications on the topic. Most recently, the North Carolina Department of Environmental Quality (NCDEQ) contacted Dr. Mark Strynar due to his expertise and publication on "Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina," published on November 2016 (Environ. Sci. Technol. Lett. 2016, 3, 415−419: http://pubs.acs.org/doi/abs/10.1021/acs.estlett.6b00398). This particular publication investigated whether PFAS can be removed from impacted water sources through waste water treatment and triggered the interest of some states in seeking assistance from the US EPA. Matt Henderson is an expert in GC/GC/MS, an analytical technique that is expected to be useful for analysis of selected samples from this project.

The NHDES would like to use the data provided to: 1) understand the multimedia environmental distribution of fluorinated compounds generated when emitting PFAS to the air; 2) ensure drinking water treatment systems and remediation systems being designed to remove perfluorooctanoic acid (PFOA) and perfluorooctane Sulfonate (PFOS) are able to remove other PFAS compounds and associated degradates; 3) differentiate sources of contamination when and where there is the potential for multiple sources of contamination by identifying a signature of distribution of compounds for different sources of PFAS; 4) assess if conditions warrant the installation of treatment systems for air emissions to proactively prevent the contamination of the environment and drinking water with the newer alternative chemicals or precursor compounds; and 5) prioritize what contaminant(s) need a risk assessment based on what is actually being measured in the environment, including drinking water.

A6. Project/Task Description

The New Hampshire Department of Environmental Services (NHDES) will sample multiple matrices and sites and send the samples to the appropriate US EPA facility (either Athens, GA or Research Triangle Park, NC). The samples include PFAS based dispersion products, char/carbon material, groundwater/wells, soil, and surface water. The dispersion, soil, and char samples will be sent to the NERL laboratory in Athens, GA for analysis by John Washington and Matt Henderson. John Washington will perform targeted analysis on all samples received in Athens and non-targeted analysis on soils and char samples. Matt Henderson will be performing non-targeted analysis on dispersion samples. The groundwater/wells and surface water samples will be sent to NERL's Research Triangle Park (RTP), NC laboratory for analysis by Mark Strynar and his analyst. The NERL, EPA R1 and NHDES will meet weekly to discuss logistics and any adjustments needed. Each NERL location will send an e-mail when samples have been received and report progress on the weekly meetings. The estimated number of samples are 12 raw dispersions, 3 char materials, 4 soil samples, 5 surface water samples and 17

groundwater/well samples. The specific sampling procedures are documented on NHDES' "Master Quality Assurance Project Plan of the
Hazardous Waste Remediation Bureau (HWRB), Waste Management Division (WMD), New Hampshire Department of Environmental Services (NHDES)" (November 2012, EQA FRA#13027) starting on page 246. NERL will follow their own protocols and QA plans as outlined in this QA project plan.

For this study, NHDES sent samples to EPA NERL starting August 17, 2017 during ongoing discussions between the organizations for this information gathering project. Preliminary analyses were conducted by Dr. Washington with some samples to better understand the matrices received. Analysis of some water samples received by Dr. Strynar was conducted using established methods. After decisions had been finalized regarding specific project plans, EPA was able to submit a QAPP for formal approval on October 2, 2017. The project timeline is shown in Table 2.

Table 2. Project timeline

Activity/Task	FY17	FY18				FY19	
	Q4	Q1	Q2	Q3	Q4	Q1	Q2
Field Sample Collection	X						
Exploratory sample analysis and method refinement	X	X					
Develop and Finalize QAPP	X	X					
Targeted sample analysis	X	X					
Targeted data analysis and reporting	X	X	X				
Non-targeted sample analysis		X	X	X	X	X	
Non-targeted data analysis and reporting		X	X	X	X	X	X

A7. Quality Objectives and Criteria for Measurement Data

The quality objectives of this project plan are to analyze 100% of the water, dispersion, char and soil samples received from the NHDES sampling events and report back the PFAS concentrations to NHDES. The estimation of additional PFAS that are not able to be quantitated due to lack of commercially available standards are to be semi-quantitatively estimated by best effort using available information.

For water samples, replicate analysis precision should be within +/- 20%. Percent accuracy of any spiked trip QA samples should be within 20% of the theoretical concentrations. Also, back prediction of calibration curve points should be within +/- 30% for the lowest calibration curve point and +/- 20% for all other calibration curve points. Finally, blank samples (trip blanks, method blanks and solvent blank) should be free of analytes to demonstrate control of field or laboratory contamination that may exist.

For char, soil, and dispersion samples, replicate analysis precision should be within +/- 30%. Back prediction of calibration curve points should be within +/- 30% for concentrations >15 pg/g and +/- 5 pg/g for concentrations <15 pg/g, with the least-squares calibration line maintaining central tendency. Finally, straight solvent blank samples should be free of analytes to

demonstrate control of laboratory contamination. Solids extractions involve numerous blow-down steps with aggressive solvents, and process blanks routinely have low detectable concentrations. These process-blank detections are handled and corrected for statistically as described below in Section B5.

A8. Special Training/Certifications

No specific training is required for this project, but the analysts shall have completed all site specific health and safety training requirements that are applicable and be competent in the operations of the analytical instrumentation being used. Records of this training are maintained by the SHEM office or by individual researchers, respectively. This document assumes laboratory personnel will have a thorough working knowledge of basic laboratory skills, reagents, and instrumentation. Any standard operating procedures (SOPs) utilized are designed to guide a competent laboratory worker in the analysis of per- and polyfluorinated compounds and it is not intended to instruct individuals on the basic aspects of analytical chemistry.

A9. Documents and Records

Planning Documents

This QAPP is the planning document for this study. Additional documentation will be maintained in laboratory record notebooks, chain of custody (CoC) forms, and the study file.

Tracking Documents

Drs. Mark Strynar (RTP) and John Washington (Athens) will retain copies of the sampling data logs, the field sample tracking forms, and the laboratory records describing the preparation and deployment of field quality control (QC) samples.

CoC forms will accompany the samples shipped to the respective PFAS analysis laboratory by NHDES, and these forms will be retained by EPA after analysis. This information will be maintained in a dedicated bound EPA laboratory notebook specific for this project. The PFAS analyst will maintain sample preparation records, and LC-MS/MS analysis logs. The study file will also contain the records of QA issues, amendments to plans and SOPs, audit reports, and corrective action reports. QA records, such as audit reports, corrective action reports, etc., will be maintained by the EPA PIs. Finally, Mark Strynar (RTP) and John Washington and Matthew Henderson (Athens) will maintain the study file documentation together with all associated final reports. All records will be maintained as per EPA specifications.

The Laboratory Research Notebooks (LRBs) is the place where records of the extraction and preparation of samples for analysis, the preparation of sampling containers (when appropriate), and the preparation of standard solutions for spiking and calibration are documented. Methods and reagents used are recorded and appropriate SOPs used for analysis are also cited.

The Sample Analyses records are the instrument logs that document the analyses of samples, and contain records of specific instrument conditions, and date and time of sample data acquisition.

B. DATA GENERATION AND ACQUISITION

B1. Experimental Design

NHDES has designed a set of samples to be collected to investigate the occurrence of PFAS in various sample types that are important to their study. The NERL PFAS researchers were not involved in the experimental design. However, constant discussions on needed QA elements were held by NHDES and the EPA research team and considered when finalizing the study design.

B2. Sampling Methods

The NHDES developed the sampling protocol used to collect the samples. NHDES' Quality Assurance Project Plan (QAPP) includes the procedures for sampling for PFAS starting on page 246 (*Master Quality Assurance Project Plan of the Hazardous Waste Remediation Bureau, Waste Management Division, New Hampshire Department of Environmental Services, November 2012, EQA RFA#13027*).

The following samples will be collected by NHDES using the procedures cited in the NHDES QAPP:

1) Samples of raw dispersion products consisting of PFAS compounds will be collected at two textile coating facilities - Five products will be sampled in the Stain-Gobain Performance Plastics at Merrimack, NH. Seven products will be sampled at the Textile Coating International facility in Manchester, NH. The total of twelve dispersions are expected to represent all the raw dispersions currently in use at the two facilities.
2) Sample Char/Carbon Material Taken from Air Emission Towers at Saint-Gobain. Three samples of solid materials that coat the interior of air emission towers will be collected as follows:

    - One sample from the "MA Tower" at Saint-Gobain. The "MA Tower" has been in operation at Saint-Gobain since 1994.
    - One sample from the "MS Tower" at Saint-Gobain. The "MS Tower" has been in operation at Saint-Gobain since 2002.
    - One sample from the "QX Tower" at Saint-Gobain. The "QX Tower" has been in operation at Saint-Gobain since 1989.

3) Sample Highly Contaminated Groundwater and Soil Immediately Downgradient of the Saint-Gobain Facility - A water sample will be collected from a shallow groundwater monitoring well immediately adjacent to and downgradient of the Saint-Gobain property.

A soil boring will be advanced 6-8 feet deep and approximately four soil profile samples will be collected.

4) Surface Water Sampling - One water sample will be collected from the stormwater outfall that discharges stormwater from the Saint-Gobain facility to the Merrimack River. Two samples of surface water will be collected from the Merrimack River up gradient and downgradient of the facility. Two water samples will be collected from Dumpling Brook which flows into the Merrimack River near the Saint-Gobain property.
5) Groundwater Sampling - Wells with Groundwater Exceeding 200 Parts-Per-Trillion PFOA will be collected from four private wells near Saint-Gobain.
6) Groundwater Sampling - Groundwater samples will be collected from four private wells located within three miles of the Saint-Gobain facility that exhibit PFOA concentrations between 50-100 ppt.
7) Groundwater Sampling - Groundwater with elevated PFOA and PFOS concentrations and located near additional sources of PFAS contamination will be collected from six private wells that exhibit a combined concentration of PFOA and PFOS above 70 ppt and are located in areas that are: 1) Likely impacted by PFAS releases to air associated with Saint-Gobain; and 2) Alleged to be potentially impacted by additional potential sources of PFAS.
8) Groundwater Sampling - Merrimack Village District Wells 4 and 5 - A groundwater sample will be collected from both Merrimack Village District (MVD) Well 4 and MVD Well 5.
9) Soil Sampling - Three soil samples will be collected from the area.

EPA will analyze samples received through the chain of custody according to established protocols and procedures.

B3. Sample Handling and Chain of Custody

The water samples collected by NHDES for EPA/NERL analysis will contain a 5 mL spike of 35% nitric acid to preserve the sample. The NHDES will provide their chain of custody (CoC) form when shipping samples to EPA. The EPA researcher will sign the chain of custody and keep a copy for record. Chain of custody forms will be shipped with samples and include information such as collected by name/date, shipped by name/date, and received by name/date plus any additional sampling information necessary to document sampling location and special comments (e.g., sample leak).

Soil, char, and dispersions are stored at room temperature prior to extraction. Extracts are stored in a refrigerator and no holding times are applicable to the samples.

The sample IDs are defined by the field collectors. Both RTP and Athens lab staff uses these assigned sample IDs and do not assign new ones.

B4. Analytical Methods

B4.1 Analysis of Water Samples (RTP, NC)

The analytical procedures used for this project in RTP are detailed in the following SOPs:

- D-EMMD-PHCB-062-SOP-01: *Method for Extraction and Analysis of Perfluoroethercarboxylic acids (PFECAs) from Surface Water, Well Water and Waste Water by Ultra-High Performance Liquid Chromatography (UPLC)-Tandem Mass Spectrometry (MS/MS)*

- D-EMMD-PHCB-043-SOP-03: *Improved Method for Extraction and Analysis of Perfluorinated Compounds (PFCs) from Surface Waters and Well Water by Ultra-High Performance Liquid Chromatography (UPLC)-Tandem Mass Spectrometry (MS/MS)*

- D-EMMD-PHCB-034-SOP-01: *Analytical method for non-targeted and suspect screening in environmental and biological samples using Time of Flight Mass Spectrometry (TOFMS)*

B4.2 Analysis of soil, char and dispersion samples (Athens, GA)

The analytical procedures used for this project in Athens are detailed in the following SOPs:

- D-EMMD-ECB-010-SOP-01: *Exhaustive Extraction of Charged Per- and Polyfluorinated Alkyl Substances (PFASs) from Contaminated Soil & Sediment Samples with Ion-Pairing Cleanup*
- D-EMMD-ECB-011-SOP-01: *Exhaustive Extraction of Soil-Fluorotelomer Polymer Microcosms for Fluorotelomer and Perfluorinated Monomer Compounds*
- Rankin et al. (2016)*: A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence.*
- For non-targeted extraction and GC-MS analysis of the dispersion samples, existing methods as outlined in peer-reviewed journal articles will be used as a basis from which to start. Established methods are being developed, and the resulting methods used to extract and analyze the dispersion samples will be documented in a research notebook.

Non-targeted GC/MS analysis will be conducted on either an Agilent, Leco, or Waters gas chromatograph coupled to their respective mass spectrometers. All GC-MS spectrometers will be tuned and calibrated using perfluorotributylamine (PFTBA), according to the manufacturer's instructions, before each sample set. Sample extracts will be analyzed under full-scan (*m/z* 50-850), electron ionization-MS conditions. Instrument parameters that are analyte-specific will be recorded in the instrument log book and laboratory notebook of PI (or approved user). Exploratory extraction methodology utilizing both headspace and solid phase microextraction (SPME) will be conducted based on published protocols (i.e. peer reviewed journal articles) and refined as necessary. Method development and methods deemed appropriate for non-targeted analysis will be recorded in the laboratory notebook of the

PI. Preliminary identification of compounds will be completed by recording the m/z values of peaks of interest, compared to in house, putative identification databases and confirmed by LC/MS.

B5. Quality Control

QC field spikes were added to the protocol in an effort to assess performance of the analytical methods. A high and a low QC spike sample (e.g., 100 and 500 ng/L) containing analytes of interest shall be prepared in the lab and shipped out with any set of sample bottles. Actual concentrations used will be documented in laboratory research notebooks. In addition to control for lab/process contamination, a laboratory prepared blank should be prepared and shipped to NHDES as well.

The limit of quantitation (LOQ) of the RTP method is the lowest point on the calibration curve (e.g., 10.0 ng/L (10 ppt)). However, lower LOQs are achievable with this method through modification of the concentration step which will be documented if necessary. The verified calibration range of the method used is 10-1000 ng/L. Results will be reported with the appropriate flags when the original sample concentration is beyond the method calibration range.

For the Athens laboratory, the limit of detection (LOD) and limit of quantification (LOQ) are defined using a two-mean Student's t-test having common, but unknown variance:

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{s^2_{pooled}\left(\frac{1}{n_1}+\frac{1}{n_2}\right)}}$$

where t is the test statistic used to define LOD and LOQ, $\overline{x_1}$ is the mean of each soil, $\overline{x_2}$ is the process-blank mean, s^2_{pooled} is the pooled sample variance, and numbers of observations are given by $n_1 = 3$ soil replicates and n_2 = the number of process-blanks. The pooled sample variance is defined as:

$$s^2_{pooled} = \frac{(n_1-1)\Sigma(x_1-\overline{x_1})^2+(n_2-1)\Sigma(x_2-\overline{x_2})^2}{n_1+n_2-2}$$

To define LOQ and LOD, calculated values of t are compared to critical t values ($t_{critical}$) for a one-tailed t-test, abbreviated $t_{\alpha(1),\upsilon}$ where α is the specified significance level, (1) signifies one-tailed, and υ is the degrees of freedom ($\upsilon = n_1 + n_2 - 2$). For three of each sample replicates and process blanks, the $t_{critical}$ values we chose were 7.1732 at $\alpha = 0.001$ and 2.1319 at $\alpha = 0.05$. So LOQ is defined as $t > t_{0.001(1),6}$ and LOD as $t > t_{0.05(1),6}$, meaning there is a respective 99.9% and 95% certainty the observed sample concentration statistically exceeds the process-blank levels. By using this standard statistical approach, detection limits are minimized, albeit at the cost of having unique limits for each sample arising from the sample-specific standard deviation among the three replicates. Sample values exceeding the LOQ are reported as blank corrected, i.e., reported sample concentrations are analytical concentrations minus mean process-blank values.

For non-targeted analysis in Athens and RTP, instrument blanks will be analyzed prior to the start of each sample set and periodically, as deemed necessary by the PI, during sample analysis. Due to the unknown nature of the compounds of interest, commercially available standards are currently unavailable and a surrogate mix of compounds (e.g., telomer alcohols and perfluorinated esters) will be analyzed in lieu of internal standards during analysis. For the Athens lab, a surrogate mix will be analyzed periodically as needed to monitor instrument response as well as chromatographic separation of analytes of interest.

Quality control criteria for water, soil, and sediment samples are discussed in further detail in the SOPs referenced in this document. Please refer to these specific procedures for additional details about QC for each procedure.

B6/B7. Instrument/Equipment Calibration, Testing, Inspection, Maintenance

The RTP MS analytical systems are tuned by the manufacturer annually during regularly scheduled preventive maintenance service, or more frequently if conditions warrant. The system is manually tuned by the service technician to ensure ion intensities, relative ion abundances, mass resolution, and ion peak shape are within manufacturer's specifications. Data on tune performance parameters is available in the instrument log file. The calibration of the LC-MS/MS response for individual compounds is based on the calibration curve solutions that are analyzed with each batch that is analyzed. In general, at a minimum, a 7-point calibration curve that spans the linear instrument detection range is analyzed at the beginning and end of each batch of samples analyzed. In this way, the calibration curve of standards reflects the condition of the instrument while samples are being analyzed. After the batch has been analyzed, the calibration curves are generated. The correlation coefficient should be > 0.98 for the calibration to be accepted. If the correlation coefficient is not > 0.98, the data will be flagged appropriately. Laboratory prepared QC spikes (high and low) will help to assess quantitative control. Curves with outlier points in the middle ranges suggest that the entire batch was out of control, invalidating this batch and making it necessary to rerun the entire batch from any raw material that remains from the original sample bottle that has been preserved in the lab. Certain outlier points at the low or high end may be excluded if adequate justification can be made (e.g., concentrations obviously below or above the linear response point of the instrument). Any samples with concentrations of an analyte more than 10% above the top calibration point require appropriate dilution of the primary sample (preserved in the lab) and complete reprocessing and reanalysis of that sample for that particular compound.

The Athens LC-MS/MS is tuned by the researcher. The calibration of the LC-MS/MS response for individual compounds is based on the calibration curve solutions run for each project. For any batch of samples, if check standards fall out of acceptable range (defined above), a new calibration curve is generated. All calibrations are carried out with mass-labeled matrix internal standards. In general, at a minimum, a 7-point calibration curve is analyzed. Calibration is carried out with 1/x weighting and resulting correlation coefficient should be > 0.98. For some very long-chain PFCAs (e.g., C16, C18) quadratic calibrations might be necessary. In these cases, effort will be expended to minimize the range of calibration. For linear calibrations, any samples with concentrations of an analyte more than 10% above the top calibration point require

appropriate dilution of the primary sample (preserved in the lab) and complete reprocessing and reanalysis of that sample for that particular compound. For quadratic calibrations, all samples must fall completely within the range of the calibration standards.

B8. Inspection/Acceptance of Supplies and Consumables

All supplies and consumable materials, such as solvents, reagents, labware, extraction cartridges, and other materials used in this analysis have been subjected to continuous testing as part of the RTP laboratory's research for the past 5 years. Only materials that have been found to be reliably free from PFAS contamination will be used. To ensure that these materials remain free of potential contaminants, solvent blanks, matrix blanks, and field blanks will be analyzed with every analytical batch run in this evaluation. Results from these analyses must show that all analytes are <LOQ. If any of these analyses yield target analyte concentrations that are >LOQ, the results of the entire batch will be flagged and a systematic evaluation of the materials used in the entire process will be conducted until the source of the contamination is found. Once the contaminated material has been identified, it will be replaced with a new batch or lot that has been tested to be free from contamination and the entire batch will be rerun.

For the Athens laboratory, materials will be used that are as free from contamination to the extent feasible; however, the harsh extraction method required for soil, char, and dispersion samples, may result in residual analyte. This will be monitored through the preparation and analysis of process blanks as described in Section B5. The LOD and LOQ will be determined with pooled analysis of these blanks. Sample values are reported as blank corrected.

B9. Non-direct Measurements

No secondary/existing data will be used for this project so this section is not applicable.

B10. Data Management

The data files are the electronic versions of these data. The electronic version of data is calculated by the instrument software and then exported to Excel. The file path(s) for where electronic data is stored will be documented in a laboratory notebook. Raw data (including electronic data on individual PC hard drives and group shared drives) will be backed up to a network or external hard drive. All data generated will be maintained Drs. Mark J. Strynar, Matthew Henderson, and John Washington until completion of the project. Upon completion, data will be stored in accordance with EPA's record management policy. All instrument data will be backed up to network drives routinely and will be archived along with other supporting data and relative correspondence at the completion of the study. Printed data will be referenced, signed and dated in accordance with the Office of Research & Development's Policy and Procedure Manual Section 13.02 on Paper Laboratory Records. The laboratory notebook will be the record for any procedure conducted in the laboratory and will provide the objective, procedure details, data references and discussion for project development. These entries will give a full and complete statement of the situation being examined, a specific hypothesis relating

to the situation, and a brief experimental protocol designed to answer the questions posed in the hypothesis. Data will be recorded from these experiments and a discussion of the results will be presented with conclusions drawn. Any standard, solution, or sample made during these investigations will be marked with a reference number, traceable to a specific entry in the lab notebook. The laboratory notebooks are the property of the EPA and will be stored in accordance with EPA's record management policy.

When shipping samples from NHDES to the RTP or Athens PFAS laboratory, NHDES will include the CoC sheets for each sample contained within the shipment.

Upon receipt at the laboratory, the sample custodian will check the contents of each shipping container for sample container breakage, and will verify that contents match the shipping lists. After logging in each sample, and signing CoC forms, the samples will be transferred to the proper storage facility.

In the laboratory, the data will be verified and checked at several levels. The instrument operator will generate the calibration curves, apply the curves to detected analytes, and complete a first pass assessment of accuracy of identification of analytes in samples. This will be done on-screen using an automated procedure where the system pages through the data for identification of each analyte in each sample. If adjustments are needed in the integration area, baseline, or peak identification, this will be done manually by the analyst. Electronic output will include a copy of the method, a copy of each calibration curve with equation and fit printed, run list, and a summary of the quantitation for each analyte. As noted above, the electronic files will be stored on the instrument computer and backed up routinely.

The technical reviewer will review data for accuracy in identification and quantification. This reviewer will monitor retention time, mass transition, and qualifier ion ratios.

The LC-MS/MS analytical data for samples are preprocessed and initially reviewed using spreadsheet software; this is a three-step process and is described as follows:

1) The LC-MS/MS summary data are electronically transferred into an Excel spreadsheet or exported as a delimited text file that can be read in Excel. This consists of the analysis date, the sample identification number and classification (e.g., blank, QC, calibration, unknown), target analyte names, analyte and internal standard (IS) peak area counts, analyte/IS peak area ratios, quantitation ion/qualifier ion ratio, and concentration of analyte in ng/L. The first reviewer assures that this electronic transfer has been made accurately and completely.

2) The first reviewer hand-enters into the spreadsheet any ancillary analytical data required for the Excel spreadsheet to calculate final concentrations, e.g., dilution factors, calibration standard concentration adjustments. Any hand-entered data will be checked by a second analyst. The spreadsheet functions as a user friendly interface for data entry and also imposes uniformity on the reported data. For the RTP samples, the spreadsheet requests data values in specific units that have a uniform accuracy, i.e., number of significant digits. The straight-forward design of

the spreadsheet also permits all the data from any given analytical run to be reviewed by the task leaders without requiring them to invest time learning new software.

3) The final analyte concentrations are reported in ng/L for water and pg/g for solid matrices using validated equations that take into account dilution factors, standard purity and salt concentration if needed, and volume/mass of unknown sample used in the analysis.

The QA Manager or appropriate designee will review a subset of all laboratory data for accuracy in reporting, transcription, and calculations.

C. ASSESSMENTS AND OVERSIGHT

C1. Assessments and Response Actions

Data audits will be a random check of electronic and hand-entered data conducted by the EPA EMMD QA Manager or appropriate designee. These audits will focus on review of data transcription, calculation, and reporting. The EMMD QAM will report to the researcher any findings requiring corrective action. Any findings and corrective measures will be noted in the file and discussed in the final report.

Internal quality control measures described in this QAPP, implemented by the technical staff and monitored by the EPA PIs, will give information on data quality on a day-to-day basis. A secondary reviewer will be designated to QA audit the data quality prior to EMMD QAM data audit. The responsibility for interpreting the results of these checks and resolving any potential problems is shared between the technical staff and EPA PIs. In addition, the NHDES field and technical staff will report any problems that could potentially affect the data quality to the EPA PIs. The EPA staff will also be responsible for identifying problems that could affect data quality or the ability to use the data upon receipt of the samples and during the analyses. Any problems that are identified will be addressed by taking actions to control the problem, identify a solution to the problem, and ameliorate losses and correct data, where possible. All of the actions taken by the EPA PIs to correct issues will be documented in research notebooks as part of the project records.

Technical systems audits (TSAs) or surveillance audits may be conducted by the EMMD QAM or designee to assess implementation of this QAPP. Any findings will be reported to the respective EPA PIs and corrective actions will be implemented to address those findings. Ideally, the quality control measures regulating the operation of each work area will be sufficient to maintain acceptable performance and data quality. However, in the event that a study component is not operating within the limits of acceptability, as determined by a QA assessment, a formal account of the matter must be documented by the PI as part of the project records.

The report should contain the following information:

- Description and duration of problem
- Probable cause and resolution of problem
- Statement describing data affected by problem
- Feasibility of repeating work activity and/or generating new data.

No further work may be performed until the problem has been satisfactorily resolved, and the PIs, after consult with the QA Manager as needed, has acknowledged approval to continue work.

C2. Reports to Management

The NHDES, EPA R1 and EMMD staff will meet weekly, unless deemed unnecessary, to discuss the progress of the project. The EMMD Division Director will be responsible for transmitting data results thru EPA's R1 to the NHDES. These reports will be provided on a timeline agreed upon by all parties.

Results of any QA audits will be reported as part of the final report. This section will summarize any errors, deficiencies, or deviations from the QA documentation that may or may not have an effect on the data.

D. DATA VALIDATION AND USABILITY

D1/D2. Data Review, Verification, and Validation/Verification and Validation Methods

The data will undergo QA review by a secondary reviewer that would check for completeness, calculations, and transcription errors before delivering the data to NHDES. The data will be reported with appropriate data quality flags, as needed.

Field Sample Data Review

Not applicable as EPA staff will only be conducting sample analyses of field samples collected by NHDES. CoCs will be reviewed upon receipt of samples for any discrepancies as described in Section B3. Noted discrepancies will be documented either on the chain of custody or in the research notebook.

Data Reduction

The instrument software reports results in peak area counts; the transition from area counts to ng/L or pg/g is done in the instrumentation software and is exported as Excel Spreadsheets. The Excel spreadsheets will contain all analytical data required to meet the QA objectives, including target analyte concentrations expressed as ng/L or pg/g, limits of quantitation (LOQ) or limits of

detection (LOD), comments, and field and laboratory QC results. All analytical data will be linked to the Sample ID number.

Data Verification

The goal of data verification is to ensure that complete and accurate analytical information is available for all samples analyzed by the laboratory. Data verification begins during and after the period of analysis, and data entry into the Excel spreadsheet. The key personnel of the analytical team will perform the first level of review, ensuring that all data have been validated. The mechanisms used for all data transcriptions and transmissions will be reviewed, and a random subset of all transcriptions checked. For data requiring calculation of results, a random subset (approx. 5%) of the raw data will be recalculated.

Once the chemical measurement data have been exported into Excel, the following QA/QC checks to validate the data will be carried out:

- Sample ID checks to verify that all Sample IDs with reported data are valid Sample IDs, i.e., they were logged in as received from NHDES,

- Missing data checks to verify that all Sample IDs received from the field either had a full set of analytical data reported or were disqualified, as documented in the CoC data,

- Duplicate data checks, to verify that the same analytical data were not imported into the Excel spreadsheet twice for a given sample,

- Out-of-range checks, to verify that all data for data fields limited to a code set did not violate that code set,

- Calculation verification; for any calculations performed within the Excel spreadsheet a random subset of the raw data are calculated using an independent calculation source (Excel spreadsheet) for validation.

Data quality flags will be assigned to each chemical measurement record as needed to identify the quality and usability of the record. Data quality flags will be assigned as documented in each report, if necessary.

Verification and Validation Methods

The verification of the data will be encompassed in the results of the QC samples in each shipment of water sample unknowns. Since these QC samples will be generated in the lab prior to shipment to the field, these samples will reflect all the sample preparation, shipping, storage, and handling of actual field samples. For laboratory and field blanks, if the background level for a given target analyte is unacceptably high, the target analyte results for all samples affected by this background will be flagged. The recoveries of analytes in these field samples will be an accurate reflection of recovery of analytes throughout the entire process. In addition, the recovery of the IS compounds will demonstrate the method performance on a sample by sample

basis. Since the ISs are the labeled version of the "average" analyte of each class, the IS recoveries can be used to effectively account for losses during analytical procedures on a sample by sample basis.

D3. Analysis and Reconciliation with User Requirements

The EPA RTP and Athens PFAS labs will summarize the chemical analyses of the samples in a final report for NHDES that will provide information to determine data quality and the range of target analyte levels found in the samples.

E. References

Mei Sun, Elisa Arevalo, Mark Strynar, Andrew Lindstrom, Michael Richardson, Ben Kearns, Adam Pickett, Chris Smith, and Detlef R. U. Knappe; "*Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina.*" Environmental Science & Technology Letters 2016 3 (12), 415-419 DOI: 10.1021/acs.estlett.6b00398

Mark Strynar, Sonia Dagnino, Rebecca McMahen, Shuang Liang, Andrew Lindstrom, Erik Andersen, Larry McMillan, Michael Thurman, Imma Ferrer, and Carol Ball; "*Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS).*" Environmental Science & Technology 2015 49 (19), 11622-11630 DOI: 10.1021/acs.est.5b01215

Lasier, P. J., J. W. Washington, S. M. Hassan and T. M. Jenkins (2011). "*Perfluorinated chemicals in surface waters and sediments from northwest Georgia, USA, and their bioaccumulation in Lumbriculus variegatus.*" Environmental Toxicology and Chemistry **30**(10): 2194-2201.

Rankin, K., S. A. Mabury, T. M. Jenkins and J. W. Washington (2015). "*A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence.*" Chemosphere **161**: 333-341.

Washington, J. W., J. J. Ellington, T. M. Jenkins and J. J. Evans (2007). "*Analysis of perfluorinated carboxylic acids in soils: Detection and quantitation issues at low concentrations.*" Journal of Chromatography A **1154**(1-2): 111-120.

Washington, J. W., W. M. Henderson, J. J. Ellington, T. M. Jenkins and J. J. Evans (2008). "*Analysis of perfluorinated carboxylic acids in soils II: Optimization of chromatography and extraction.*" Journal of Chromatography A **1181**(1-2): 21-32.