



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CENTER FOR ENVIRONMENTAL MEASUREMENT AND MODELING
RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF
RESEARCH AND DEVELOPMENT

January 30, 2020

Mr. Clark Freise, Assistant Commissioner
New Hampshire Department of Environmental Services (NHDES)
29 Hazen Drive
P.O. Box 95
Concord, New Hampshire 03301

Dear Mr. Freise:

I am pleased to provide the enclosed 8th report from our ongoing collaborative technical support to NHDES assisting with concerns over per- and polyfluorinated alkyl substances (PFAS) environmental contamination associated with manufacturing sites. This report is in response to your October 2017 request asking for laboratory assistance analyzing per- and polyfluoroalkyl substances (PFAS) in various environmental media near an industrial site. The enclosed Report #8 provides non-targeted analysis laboratory results that tentatively identify various PFAS found in monitoring well samples.

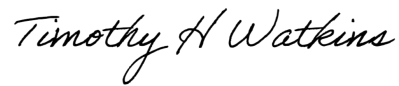
It is our understanding that this information was requested by NHDES to help in their ongoing investigation into the presence of PFAS in the environment near manufacturing facilities of interest. This request relates to our research capabilities and interests applying targeted and non-targeted analysis methods for discovery of the nature and extent of PFAS environmental occurrence that may be potentially associated with industrial releases. EPA continues to develop analytical methods for many PFAS compounds in various media including some of those included in this report. We are providing the results of our analysis as they become available.

In this report, we provide PFAS tentative identification and non-quantitative analytical results. We do not interpret exposure or risk from these values. EPA does not currently have health-based standards, toxicity factors, or associated risk levels for PFAS, other than perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorobutanesulfonic acid (PFBS). While the data provided in the attached reports indicate the presence (or lack) of PFAS in the water samples, we do not have sufficient information to offer interpretations related to human or environmental exposure and risk.

Thank you for inviting us to be part of this effort that helps to further both EPA's and New Hampshire's understanding of an important issue in the state. This is one of a number of Agency efforts that continue EPA's commitment to cooperative federalism.

If you have any questions or concerns, do not hesitate to contact me at (919) 541-2107 or via email at Watkins.tim@epa.gov or Brian Schumacher at (702) 798-2242 or via email at Schumacher.brian@epa.gov. I look forward to our continued work together.

Sincerely,



Timothy H. Watkins
Director

CC:

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PFAS Environmental Contamination Associated with Manufacturing Sites in New Hampshire

Laboratory Data Report #8: Non-targeted Analysis of PFAS in Monitoring Well Samples

Background. The New Hampshire Department of Environmental Services (NHDES), in coordination with EPA Region 1, requested the Office of Research and Development's (ORD's) technical support in analyzing per- and polyfluoroalkyl substances (PFAS) in manufacturing facilities and surrounding environmental media. NHDES assumed responsibility for the collection of samples and their shipment to the ORD laboratory. ORD was responsible for sample extraction and analysis. ORD's analysis and report team that contributed to this effort are listed in Table 1.

Table 1. EPA Office of Research and Development Lab Analysis and Report Team.

Responsibility	Personnel
ORD Principal Investigators	Andy Lindstrom, Mark Strynar, John Washington
Laboratory chemistry	Mark Strynar, James McCord
Quality Assurance Review	Christine Alvarez, Sania Tong-Argao
Management coordination and review	Myriam Medina-Vera, Tim Buckley, Kate Sullivan
Report preparation	Kate Sullivan

This 8th report includes non-targeted analysis (NTA) results for 4 water samples collected from monitoring wells near an industrial site in New Hampshire. Samples were collected May 30, 2018 by NHDES.

The current data report provides a simple representation and summary of NTA results. Therefore, the description of methods and quality assurance are brief and high-level. Additional reports and/or publications may be developed that will include a more detailed description of methods, quality assurance procedures, and statistical interpretation of the data. As study partners/collaborators, we anticipate that NHDES and Region 1 will assist in these reports and publications.

Methods in Brief. Water samples were analyzed with ultra-performance liquid chromatography mass spectrometry (UPLC-MS) using methods described within our Quality Assurance Project Plan (QAPP)¹ and McCord et al. 2019.² In brief, water samples (500 mL) were filtered and then

¹ National Exposure Research Laboratory, Quality Assurance Project Plan: Non-Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) for New Hampshire Department of Environmental Services (NHDES), October 2, 2017.

² McCord, J., Strynar, M. Identifying Per- and Polyfluorinated Chemical Species with a Combined Targeted and Non-Targeted-Screening High-Resolution Mass Spectrometry Workflow. *J. Vis. Exp.* (146), e59142,

extracted using a WAX solid phase extraction cartridge. PFAS was removed from the cartridge in methanol and the methanol blown down to a volume of 1 mL. An aliquot of the 1 mL concentrated sample was injected into an Agilent 1100 UPLC coupled to an Agilent 6210 Time-of-Flight mass spectrometer (TOF). PFAS were analyzed using our NTA workflow³. PFAS were analyzed using non-targeted analysis (NTA) methods.

NTA provides two important measurements. The first is a tentative identification of PFAS compounds detected in the sample. PFAS are tentatively identified based on a combination of mass spectral data along with patterns of fragmentation compared to on-line and in-house mass-spectral libraries. Analytes in each sample and process blank were identified to various levels of confidence depending on how much combined evidence from manual examination of MS/MS fragmentation spectra and/or comparison with mass spectral libraries.

The second measurement is an indication of the relative abundance of the PFAS is present in the sample. The mass spectrometer detector provides integrated peak areas for the chromatogram of the compound mass (+/- 5 ppm) at the specified retention time. The peak area counts are proportional to the mass of PFAS in the sample. Since the sample and injection volume are held constant, the peak area counts are also proportional to concentration, although the relationship varies based on compound.

It is important to understand how results of non-targeted analysis differ from those produced during routine laboratory analysis. Without a standard curve to calibrate the relationship between peak area and a mass or concentration value, the peak area counts alone should be considered a semi-quantitative indicator of relative abundance. Analyte peak areas can be compared between samples in a sample set to obtain relative concentrations but cannot be directly compared between analytes. Our experience indicates that measured abundances for PFAS are four to six orders of magnitude higher than the ppt concentration (e.g. $1e7 \sim 100$ ppt) not accounting for dilutions during sample preparation. Peak area counts are expected to have much greater inherent sampling and analytical variability, which may become evident in reproducibility assessments. For example, it is possible for field duplicates to differ by two or three-fold or more, and laboratory replicates to have greater variability than typically observed in routine laboratory analysis. Any application of NTA results should consider this inherently greater uncertainty.

The non-targeted analytical data generated by LC/MS were considered as a “detect” when acceptable chromatographic peaks and spectra were evident. Samples without a detectable peak are reported as “ND”. Samples with detected analytes were further screened to determine the reporting limit (RL) that accounts for contamination that may have occurred during sampling and analysis including field, laboratory, and instrument blanks. The RL was established for each compound by statistical analysis of the combined laboratory and field blanks, where $RL = AVE$

doi:10.3791/59142 (2019). <https://www.jove.com/video/59142/identifying-per-polyfluorinated-chemical-species-with-combined>

³ National Exposure Research Laboratory, Quality Assurance Project Plan: Non-Targeted Analyses of Per and Polyfluoroalkyl substances (PFAS) in Liquid Samples J-WECD-0031919-QP-1-0, September 18, 2019.

[blanks] + 3x STD [blanks]. Sample values less than this statistically defined threshold are reported as “<RL”.

Summary of Results

Compound Identification. Across the three well samples and duplicate, we detected and tentatively identified 12 different PFAS listed in Table 2 by chemical formula, name, CAS number, monoisotopic mass and retention time, where available. A larger number of chemical features likely to be breakdown products of the reported compounds were present, but we report these 12 based on criteria of abundance (or peak area) and high confidence in tentative identification. A CAS registry number is available for 10 of the 12 compounds. These same 10 PFAS are registered in EPA’s Chemistry dashboard (<https://comptox.epa.gov/dashboard>) where additional information about these chemicals can be found (U.S. EPA CompTox, 2019)⁴.

Abundance of Compounds. In Table 2, we provide results for the 14 PFAS identified in the monitoring well samples. Results are given as peak area counts superimposed on a heat map where gradations in color reflect seven classifications of peak area from low (non-detect) to high (>1,000,000). The heat map is useful in showing where PFAS “light-up” in terms of detection and high peak areas. Heatmap values >100,000 (yellow, orange and red tones) have the highest confidence that a compound is present in relatively higher abundance.

None of the PFAS compounds were detected at levels greater than the reporting limit in the trip blank. There are few QA/QC performance criteria available for NTA. We report the relative percent difference (RPD) of the field duplicate pair as a measure of reproducibility in the samples. The RPD of analytes greater than the RL averaged 12% for the sample pair MWGZ1A/MWGZ1B and met the project goal of RPD <50%.

⁴ U.S. EPA CompTox Chemicals Dashboard <https://comptox.epa.gov/dashboard>

Table 2. Non-Targeted Analysis Semi-Quantitation (Peak Area Counts) of PFAS in Water Samples.

Compound Name	Short Name	Monoisotopic Mass (Daltons)	Formula	CAS Number	Retention Time	MWGZ1A	MWGZ1B	MWGZ2	MWGZ3	TB
Perfluoropropanoic acid	PFPA	163.99	C3 H F5 O2	422-64-0	1.78	193,000	189,000	281,000	413,000	ND
Perfluorobutanoic acid	PFBA	213.9868	C4 H F7 O2	375-22-4	3.91	879,000	1,050,000	1,680,000	1,940,000	ND
Perfluorobutanesulfonic acid	PFBS	299.9504	C4 H F9 O3 S	375-73-5	6.06	148,000	175,000	120,000	79,800	ND
Perfluoropentanoic acid	PFPeA	263.9846	C5 H F9 O2	2706-90-3	5.82	3,090,000	3,540,000	3,590,000	4,170,000	ND
Perfluoropentanesulfonic acid	PFPeS	349.9477	C5 H F11 O3 S	2706-91-4	6.82	178,000	206,000	305,000	63,400	ND
Perfluorohexanoic acid	PFHxA	313.9797	C6 H F11 O2	92612-52-7	6.74	2,540,000	2,970,000	2,480,000	<RL	<RL
Perfluorohexanesulfonic acid	PFHxS	399.9433	C6 F13 H O3 S	355-46-4	7.35	330,000	359,000	775,000	658,000	<RL
Perfluoroheptanoic acid	PFHpA	363.9781	C7 H F13 O2	375-85-9	7.31	8,390,000	9,020,000	17,500,000	8,130,000	ND
Perfluorooctanoic acid	PFOA	413.9741	C8 H F15 O2	335-67-1	7.76	21,200,000	23,700,000	38,300,000	55,600,000	<RL
Perfluorooctanesulfonamide	PFOSA	498.9507	C8 H2 F17 N O2 S	754-91-6	7.83	419,000	449,000	542,000	577,000	ND
C8H F13 O3		391.9721	C8H F13 O3		7.53	197,000	227,000	362,000	154,000	ND
C7 H F13 O (decarboxylated C8 H F13 O3)		347.9825	C7 H F13 O		7.52	139,000	157,000	248,000	85,000	ND

LEGEND	
Color	Peak Area Category
ND	No peak area detected
<RL	Less than the Reporting Limit
	>RL - 50,000
	50,000 - 100,000
	100,000 - 200,000
	200,000 - 500,000
	500,000 - 1,000,000
	>1,000,000