



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
RESEARCH TRIANGLE PARK, NC 27711

July 24, 2018

Mr. Clark Freise, Assistant Commissioner
New Hampshire Department of Environmental Services
29 Hazen Drive
PO Box 95
Concord, New Hampshire 03301

Dr. Mr. Freise,

I am pleased to provide you with the attached report which presents additional results of analyses of per- and polyfluoroalkyl substances (PFAS) concentrations in char and soil samples collected by the New Hampshire Department of Environmental Services (NH DES) staff. This report provides results of non-targeted analyses of the same three soil and three char samples that were previously analyzed for C4-C18 "legacy" perfluorocarboxylates using targeted methods and delivered to the NH DES in our April 4, 2018 report. The current report is significant in identifying the presence of two PFAS series that to our knowledge has not been previously reported as an environmental contaminant.

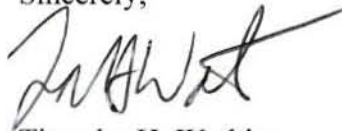
It is our understanding that this information was requested by the NH DES to help in their ongoing investigation into the presence of PFAS in the environment near manufacturing facilities of interest. This request relates to our research capabilities and interests applying targeted and non-targeted analysis methods for discovery of the nature and extent of PFAS environmental occurrence.

The U.S. Environmental Protection Agency continues to develop analytical methods for many PFAS compounds in various media including some of those included in this report. The data enclosed provides information related to the concentration of certain PFAS in the media sampled. In this report we do not interpret exposure or risk from these values. The 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). Therefore, while the data presented indicate the presence of two novel PFAS series, no conclusions can be made related to human or environmental exposure and risk.

Thank you for inviting us to be part of this effort that helps to further both the EPA's and New Hampshire's understanding of an important issue in the state. Providing this type of support to the NH DES aligns well with our research capabilities and interests in applying targeted and non-targeted analysis methods. It also demonstrates our commitment to, and the relevance of our research in support of, cooperative federalism to address pressing environmental health concerns of New Hampshire residents.

If you have any questions or concerns, do not hesitate to contact me at (919) 541-2106 or via email at watkins.tim@epa.gov or Tim Buckley at (919) 541-2454 or via email at buckley.timothy@epa.gov. I look forward to our continued work together.

Sincerely,

A handwritten signature in black ink, appearing to read 'Tim Watkins', with a long horizontal stroke extending to the right.

Timothy H. Watkins
Director

Attachment

cc: Meghan Cassidy, USEPA, Region 1
Deb Szaro, USEPA, Region 1
Jeff Morris, USEPA OPPT
Betsy Behl, USEPA, OW
Peter Grevatt, USEPA, OW
Andy Gillespie, USEPA, ORD
Timothy Buckley, USEPA, ORD

Technical Report #2: ORD Technical Support to New Hampshire: Non-Targeted PFAS Measurements in Char and Soil

Date: July 24, 2018

Report Team

- **Laboratory Chemists:** Drs. John Washington, Mark Strynar, Andy Lindstrom, Seth Newton, Thomas Jenkins, and James McCord
- **Quality Assurance Review:** Sania Tong-Argao and Brittany Stuart
- **Management Coordination and Review:** Drs. Myriam Medina-Vera, Jack Jones, Adam Biales, and Brian Schumacher
- **Report Preparation:** Dr. Tim Buckley

Summary of Methods and Results

New Hampshire Department of Environmental Services (NH DES), in coordination with Region 1, requested ORD's technical support in analyzing PFAS in environmental samples potentially impacted by industrial sites within the state. NH DES assumed responsibility for the collection of samples and their shipment to our laboratories. ORD was responsible for sample extraction and analysis. We are providing the results of our analysis as they become available. Our first report dated April 4, 2018 provided targeted analysis results for C4-C18 "legacy" perfluorocarboxylates in 3 soil and 3 char samples.

This is our second report and it includes non-targeted analysis results conducted by Dr. John Washington of the same soil and char samples previously reported (Report No. 1). The non-targeted analysis differs from the targeted in that chemical identification and quantification does not have the benefit of being based on a known standard. Accordingly, there is more uncertainty both in terms of identification and concentration estimation.

The PFAS reported here were identified and quantified using non-targeted analysis methods described within an approved Quality Assurance Project Plan (QAPP)¹. These methods are also generally described in Rankin et al., 2015.² In brief, each sample was divided into three ~1 g aliquots and extracted and analyzed in triplicate. Extracts were analyzed by liquid chromatography / mass spectrometry using a Waters Acquity UPLC coupled to a Waters Xevo G2-XS QTOF for non-targeted identification followed by a Waters Acquity UPLC coupled to a Waters Quattro Premier XE tandem for quantitation. The non-targeted PFAS are identified based on a combination of high-resolution mass spectral data along with patterns of fragmentation. Without the benefit of a standard, we quantify based on the fully fluorinated homologue for which we do have a standard. In effect, our quantification of the non-targeted analyte, in this

¹ Strynar, M.; Washington, J.; Lindstrom, A.; Henderson, W. 2017. Quality Assurance Project Plan: Non-Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) for New Hampshire Department of Environmental Services (NHDES). D-EMMD-PHCB-015-QAPP-01.

² K. Rankin, S. A. Mabury, T. M. Jenkins, J. W. Washington, A North American and global survey of perfluoroalkyl substances in surface Soil: Distribution patterns and mode of occurrence. *Chemosphere* 161, 333-341 (2015).

case the hydrogenated carboxylic acid, assumes that the mass spectrometer responds to the fully fluorinated species as it does the hydrogenated, i.e. yielding identical chromatographic peak areas. A calibration curve is used for quantification, however, the curve is developed for chemicals for which we have a standard and that are similar to our non-targeted analyte. In most cases, the standard is the fully fluorinated version of the PFAS we are quantifying as noted in Table 3. Our experience with these chemicals has shown that this means of estimation often is within an order of magnitude uncertainty. Some of the sample extracts required dilution so that concentrations were within the acceptable range of the calibration curve. The reported results have been adjusted for each dilution factor and flagged accordingly. These analyses were performed on samples and process blanks using internal-calibration curves for quantitation. The mean value of the triplicate analysis is reported.

Measurement precision was estimated by the relative standard deviation (RSD) from triplicate analysis of each sample. For char samples, the median RSD across all of the compounds was 4.4% and ranged from 0.7% to 31%. We observed greater variability in soil where concentrations were much lower. The median RSD for soil was 66% and ranged from 8.4% to 170%. Field blanks were not provided so limits of detection (LOD) and quantification (LOQ) were determined from process blanks at $p \leq 0.05$ and $p \leq 0.001$, respectively. Reported concentrations were corrected for any low detections in process blanks.

The non-targeted analysis identified two PFAS series not previously reported to our knowledge as an environmental contaminant. The first is a PFAS carboxylic acid series that ranges from C6 to C20 where there is a single hydrogen substitution for fluorine. Our identification of the chemicals in this series is provided in Table 1. We are confident in chemical identities based on mass-spectral data including high resolution mass and fragmentation data. However, at present we cannot determine the exact location of the hydrogen substitution, and therefore we have not specified a CAS number. The generic hydrogenated polyfluorinated carboxylic acid (HPFCA) structure is given in Figure 1 with the hydrogen arbitrarily placed in the terminal position.

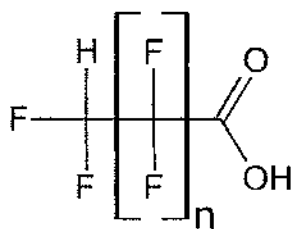


Figure 1. Generic structure of hydrogenated polyfluorinated carboxylic acid (HPFCA). At present, the exact position of the hydrogen is undetermined.

Table 1. PFAS Single Hydrogen Substituted Carboxylic Acid Series Identified Using Non-Targeted Analyses that are the Subject of this Report.

Carbon No.	Compound Name	Acronym	Anion Formula
HC6	Hydro-polyfluorohexanoic acid	HPFH _x A	HC ₆ F ₁₀ O ₂
HC7	Hydro-polyfluoroheptanoic acid	HPFH _p A	HC ₇ F ₁₂ O ₂
HC8	Hydro-polyfluorooctanoic acid	HPFOA	HC ₈ F ₁₄ O ₂
HC9	Hydro-polyfluorononanoic acid	HPFNA	HC ₉ F ₁₆ O ₂
HC10	Hydro-polyfluorodecanoic acid	HPFDA	HC ₁₀ F ₁₈ O ₂
HC11	Hydro-polyfluoroundecanoic acid	HPFUA	HC ₁₁ F ₂₀ O ₂
HC12	Hydro-polyfluorododecanoic acid	HPFDoA	HC ₁₂ F ₂₂ O ₂
HC13	Hydro-polyfluorotridecanoic acid	HPFTrA	HC ₁₃ F ₂₄ O ₂
HC14	Hydro-polyfluorotetradecanoic acid	HPFTeA	HC ₁₄ F ₂₆ O ₂
HC15	Hydro-polyfluoropentadecanoic acid	HPFPDA	HC ₁₅ F ₂₈ O ₂
HC16	Hydro-polyfluorohexadecanoic acid	HPFH _x DA	HC ₁₆ F ₃₀ O ₂
HC17	Hydro-polyfluoroheptadecanoic acid	HPFH _p DA	HC ₁₇ F ₃₂ O ₂
HC18	Hydro-polyfluorooctadecanoic acid	HPFODA	HC ₁₈ F ₃₄ O ₂
HC19	Hydro-polyfluorononadecanoic acid	HPFNDA	HC ₁₉ F ₃₆ O ₂
HC20	Hydro-polyfluoroicosanoic acid	HPFIA	HC ₂₀ F ₃₈ O ₂

The second series discovered is a polyfluorinated sulfonic acid series, again with a single hydrogen substitution (Table 2). The generic hydrogenated polyfluorinated sulfonic acid (HPFSA) structure is given in Figure 2 with the hydrogen arbitrarily placed in the terminal position.

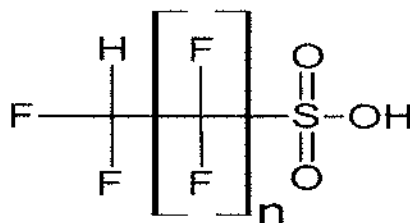


Figure 2. The generic structure of hydrogenated polyfluorinated sulfonic acid (HPFSA). At present, the exact position of the hydrogen is undetermined.

Table 2. PFAS Single Hydrogen Substituted Sulfonic Acid Series Identified Using Non-Targeted Analyses that are the Subject of this Report.

Carbon No.	Compound Name	Acronym	Anion Formula
HSC4	Hydro-polyfluorobutanesulfonate	HPFBS	HC ₄ F ₈ SO ₃
HSC5	Hydro-polyfluoropentanesulfonate	HPFPS	HC ₅ F ₁₀ SO ₃
HSC6	Hydro-polyfluorohexanesulfonate	HPFH _x S	HC ₆ F ₁₂ SO ₃
HSC7	Hydro-polyfluoroheptanesulfonate	HPFH _p S	HC ₇ F ₁₄ SO ₃
HSC8	Hydro-polyfluorooctanesulfonate	HPFOS	HC ₈ F ₁₆ SO ₃
HSC9	Hydro-polyfluorononanesulfonate	HPFNS	HC ₉ F ₁₈ SO ₃
HSC10	Hydro-polyfluorodecanesulfonate	HPFDS	HC ₁₀ F ₂₀ SO ₃
HSC11	Hydro-polyfluoroundecanesulfonate	HPFUS	HC ₁₁ F ₂₂ SO ₃
HSC12	Hydro-polyfluorododecanesulfonate	HPFD ₀ S	HC ₁₂ F ₂₄ SO ₃
HSC13	Hydro-polyfluorotridecanesulfonate	HPFTrS	HC ₁₃ F ₂₆ SO ₃
HSC14	Hydro-polyfluorotetradecanesulfonate	HPFTeS	HC ₁₄ F ₂₈ SO ₃
HSC15	Hydro-polyfluoropentadecanesulfonate	HPFPDS	HC ₁₅ F ₃₀ SO ₃
HSC16	Hydro-polyfluorohexadecanesulfonate	HPFH _x DS	HC ₁₆ F ₃₂ SO ₃
HSC17	Hydro-polyfluoroheptadecanesulfonate	HPFH _p DS	HC ₁₇ F ₃₄ SO ₃
HSC18	Hydro-polyfluorooctadecanesulfonate	HPFODS	HC ₁₈ F ₃₆ SO ₃

As was observed for perfluorocarboxylates in our first report, the hydrogen substituted analogues tended to occur at higher concentrations in char relative to soil samples. The stack char concentrations of HPFCA ranged from <LOD (limit of detection) to 140 µg/g (HC10). (Note, the upper range is uncertain because some values are only specified as exceeding the calibration range.) Among the char samples, “NHCharMA” levels generally exceeding levels observed for char from “MS” or “QX” stack samples.

Soil concentrations were orders of magnitude lower than char samples. As a result, we report soil levels in pg/g instead of µg/g. The observed variation ranges from <LOD to 157 pg/g. As was observed for PFCA in our first report, concentrations of the hydrogenated substituted PFCA tended to be much higher in soil sample “S1” relative to “S2” or “S3.” Having identified these novel PFAS in char and soil, we will also be looking for these same novel PFAS in water and air samples to be included in later reports.

At this time we provide concentration estimates for only HPFCA because we observed higher concentrations of the HPFCA series relative to HPFSA. Based on a comparison of peak areas between the carbon equivalents in the two series, HPFCA levels in char exceeded HPFSA by a factor of 2 to 50 except for C6 and C8 where HPFSA was greater by a factor of 10 and 1.2, respectively (results not provided). We would not expect to find HPFSA in soil at appreciable

levels because char PFAS concentrations generally exceed soil, and levels of HPFSA were generally low in char. As mentioned above, the concentrations reported below in Table 3 are considered semi-quantitative, likely within an order of magnitude of the actual value.

Table 3. Concentration Estimates of Single Hydrogen Substituted PFAS Carboxylic Acids from Non-Targeted Analysis.

Carbon No.*	Sample ID	Matrix	Conc.	Unit	Flag(s)**
HC6	NHCharMS	Char	2.98	µg/g	D1
HC7	NHCharMS	Char	0.631	µg/g	D1
HC8	NHCharMS	Char	4.79	µg/g	D1
HC9	NHCharMS	Char	10.6	µg/g	D1
HC10	NHCharMS	Char	9.32	µg/g	D1
HC11	NHCharMS	Char	2.64	µg/g	D1
HC12	NHCharMS	Char	7.95	µg/g	D1
HC13	NHCharMS	Char	2.99	µg/g	D1
HC14	NHCharMS	Char	10.8	µg/g	D1
HC15 as C14	NHCharMS	Char	5.75	µg/g	D1
HC16	NHCharMS	Char	16.1	µg/g	D1
HC17 as C16	NHCharMS	Char	4.02	µg/g	D1
HC18	NHCharMS	Char	6.30	µg/g	D1
HC19 as C18	NHCharMS	Char	1.24	µg/g	D1, <LOQ
HC20 as C20	NHCharMS	Char	0.392	µg/g	D1, <LOQ
HC6	NHCharQX	Char	--	µg/g	D1, <LOD
HC7	NHCharQX	Char	0.142	µg/g	D1, <LOQ
HC8	NHCharQX	Char	--	µg/g	D1, <LOD
HC9	NHCharQX	Char	1.71	µg/g	D1, <LOQ
HC10	NHCharQX	Char	--	µg/g	D1, <LOD
HC11	NHCharQX	Char	0.620	µg/g	D1
HC12	NHCharQX	Char	--	µg/g	D1, <LOD
HC13	NHCharQX	Char	0.547	µg/g	D1, <LOQ
HC14	NHCharQX	Char	0.592	µg/g	D1, <LOQ
HC15 as C14	NHCharQX	Char	0.885	µg/g	D1
HC16	NHCharQX	Char	0.379	µg/g	D1, <LOQ
HC17 as C16	NHCharQX	Char	0.220	µg/g	D1, <LOQ
HC18	NHCharQX	Char	0.213	µg/g	D1, E1
HC19 as C18	NHCharQX	Char	--	µg/g	D1, <LOD
HC20 as C18	NHCharQX	Char	--	µg/g	D1, <LOD
HC6	NHCharMA	Char	36.4	µg/g	D1
HC7	NHCharMA	Char	8.66	µg/g	D1
HC8	NHCharMA	Char	67.7	µg/g	D1
HC9	NHCharMA	Char	101	µg/g	D1
HC10	NHCharMA	Char	140	µg/g	D1
HC11	NHCharMA	Char	26.6	µg/g	D1
HC12	NHCharMA	Char	> 43.3	µg/g	D1, E2
HC13	NHCharMA	Char	22.5	µg/g	D1
HC14	NHCharMA	Char	> 43.3	µg/g	D1, E2
HC15	NHCharMA	Char	42.9	µg/g	D1

Table 3. Concentration Estimates of Single Hydrogen Substituted PFAS Carboxylic Acids from Non-Targeted Analysis.

Carbon No.*	Sample ID	Matrix	Conc.	Unit	Flag(s)**
HC16	NHCharMA	Char	> 21.8	µg/g	D1, E2
HC17	NHCharMA	Char	31.7	µg/g	D1
HC18	NHCharMA	Char	> 21.8	µg/g	D1, E2
HC19	NHCharMA	Char	1.37	µg/g	D1
HC20	NHCharMA	Char	0.356	µg/g	D1, <LOQ
HC6	NHEPAORD-S1	Soil	50.9	pg/g	UD, <LOQ
HC7	NHEPAORD-S1	Soil	3.11	pg/g	UD, <LOQ
HC8	NHEPAORD-S1	Soil	50.9	pg/g	UD
HC9	NHEPAORD-S1	Soil	113	pg/g	UD, <LOQ
HC10	NHEPAORD-S1	Soil	122	pg/g	UD
HC11	NHEPAORD-S1	Soil	28.3	pg/g	UD
HC12	NHEPAORD-S1	Soil	104	pg/g	UD
HC13	NHEPAORD-S1	Soil	23.8	pg/g	UD
HC14	NHEPAORD-S1	Soil	157	pg/g	UD
HC15 as C14	NHEPAORD-S1	Soil	33.9	pg/g	UD
HC16	NHEPAORD-S1	Soil	142	pg/g	UD
HC17 as C16	NHEPAORD-S1	Soil	8.95	pg/g	UD, <LOQ
HC18	NHEPAORD-S1	Soil	13.6	pg/g	UD, <LOQ
HC19 as C18	NHEPAORD-S1	Soil	--	pg/g	UD, <LOD
HC20 as C18	NHEPAORD-S1	Soil	--	pg/g	UD, <LOD
HC6	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC7	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC8	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC9	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC10	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC11	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC12	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC13	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC14	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC15 as C14	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC16	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC17 as C16	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC18	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC19 as C18	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC20 as C18	NHEPAORD-S2	Soil	--	pg/g	UD, <LOD
HC6	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD
HC7	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD
HC8	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD
HC9	NHEPAORD-S3	Soil	14.3	pg/g	UD, <LOQ
HC10	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD
HC11	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD
HC12	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD
HC13	NHEPAORD-S3	Soil	2.93	pg/g	UD, <LOQ
HC14	NHEPAORD-S3	Soil	11.2	pg/g	UD, <LOQ
HC15 as C14	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD

Table 3. Concentration Estimates of Single Hydrogen Substituted PFAS Carboxylic Acids from Non-Targeted Analysis.

Carbon No.*	Sample ID	Matrix	Conc.	Unit	Flag(s)**
HC16	NHEPAORD-S3	Soil	10.9	pg/g	UD, <LOQ
HC17 as C16	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD
HC18	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD
HC19 as C18	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD
HC20 as C18	NHEPAORD-S3	Soil	--	pg/g	UD, <LOD

*Unless specified otherwise, the hydrogen substituted PFAS was quantified based on the fully fluorinated analogue.

** Flags defined:

- UD = undiluted
- D1 = 10-fold dilution
- <LOQ = values are less than LOQ but exceed Limit of Detection (LOD) defined as exceeding process blanks at P<0.05 level of significance
- <LOD = Less than limit of detection and not significantly different than process blanks
- E1= sample/analyte exceeded established precision criteria of +/- 30%
- E2= the calibration range for the corresponding PFCA was exceeded so that the reported values are greater than the highest calibration standard. The calibration range varied by carbon length.