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 7th 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 August 2017 request asking for laboratory assistance analyzing per- and polyfluoroalkyl substances (PFAS) in various environmental media near an industrial site. The enclosed Report #7 provides non-targeted analysis laboratory results that tentatively identify various PFAS found in surface and groundwater 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 analytical 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, final 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

Timothy H. Watkins
Director

CC:

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# PFAS Environmental Contamination Associated with Manufacturing Sites in New Hampshire

## Laboratory Data Report #7: Non-targeted Analysis of PFAS in Water 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, and 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 7th report includes non-targeted analysis (NTA) results for 25 water samples and a trip blank collected from surface and ground water near an industrial site in New Hampshire. Samples were collected September 27, 2017 by NHDES. EPA/ORD Report #3[1] provided concentrations for 11 PFAS for the same samples using targeted analysis based on standards for the quantitation of the PFAS present in the samples. In contrast, this report presents NTA for the samples in which the presence or absence of a PFAS is identified and relative abundances (i.e., semiquantitative) of the PFAS are presented.

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 project Quality Assurance

[1] EPA/ORD NH Report #3. Technical support to New Hampshire—Targeted PFAS Measurements in Water. October 4, 2018.

Project Plan (QAPP)[2], our laboratory QAPP[3], and McCord *et al*. 2019.[4] In brief, water samples (500 mL) were filtered and then extracted using a WAX solid phase extraction cartridge. PFAS was removed from the cartridge in methanol and reduced to a volume of 1 mL under a gentle stream of nitrogen. An aliquot of the 1 mL concentrated sample was injected into an Agilent 1100 high performance liquid chromatograph (HPLC) coupled to an Agilent 6210 Time-of-Flight mass spectrometer (TOFMS). PFAS were analyzed using our non-targeted analysis (NTA) workflow.

NTA provides two important measurements. The first is a tentative identification of PFAS detected in the sample. PFAS are tentatively identified based on a combination of highly-resolved mass (Daltons to 4 decimal places) of the chemical along with patterns of fragmentation compared to on-line and in-house mass-spectral libraries. PFAS chemical identification is determined to various levels of confidence depending on the strength of evidence from automated and manual examination fragmentation spectra and/or comparison with mass spectral libraries.

The second measurement is an indication of the relative abundances of the PFAS present in the sample. The mass spectrometer detector provides integrated peak areas for the chromatogram of the compound mass (+/- 5ppm) at the specified retention time. The peak area counts are proportional to the mass of PFAS in the sample. Since the sample and injection volumes 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 NTA differ from those produced with routine laboratory target analysis. Without a standard curve to calibrate the relationship between peak area and a true 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 ~ 100 ppt) not accounting for any dilutions during sample preparation. Peak area counts are expected to have much greater sampling and analytical variability. For example, it is possible for field duplicates to differ by

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[2] 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), D-EMMD-PHCB-015-QAPP-01, October 2, 2017.

[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.

[4] 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, doi:10.3791/59142 (2019). https://www.jove.com/video/59142/identifying-per-polyfluorinated-chemical-species-with-combined

two or three-fold or more. Any application of NTA results should consider this inherently greater uncertainty.

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

**Summary of Results**

Compound Identification. Across all the water samples, the 24 PFAS listed in Table 2 we detected and tentatively identified by chemical formula, name, CAS registry number (CASRN), monoisotopic mass and retention time. Within the table, we have ordered PFAS by homologous series:

1) carboxylic acids (#1-10);
2) sulfonic acids (#11-14); and
3) the remainder ordered by monoisotopic mass (#15-24).

A larger number of chemical features likely to be PFAS (or breakdown products) were present, but we report these 24 based on criteria of abundance (or peak area) and high confidence in tentative identification. PFAS with CASRN 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)[5].

Abundance of Compounds. In Table 3, we provide results for the 24 PFAS identified in Table 2 for 25 water samples and a trip blank (TB). 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 >50,000 (yellow, orange and red tones) have the highest confidence that a compound is present in relatively greater abundance.

None of the PFAS compounds were detected at levels greater than the reporting limit in the field blanks. There are few QA/QC performance criteria available for NTA. The relative percent difference (RPD) of the field duplicate pairs is a measure of reproducibility in the samples. The RPD of analytes greater than RL averaged 25% for the sample pair EPAORD004/EPAORD005,

[5] U.S. EPA CompTox Chemicals Dashboard https://comptox.epa.gov/dashboard

and 43% for the sample pair EPAORD012/EPAORD013. Both met the project goal of RPD <50%.

The highest peak areas were generally observed for the carboxylic acids and sulfonic acid compounds (Chem. Ref. #1-14) for which concentrations determined with authentic standards were previously reported in ORD NH Report #3[6]. Other PFAS (Chem. Ref. #15-24) were found at various abundances within the samples. For compounds evaluated in both targeted analysis and NTA, results are qualitatively similar in that the same compounds were generally more abundant in the same samples. However, NTA often did not detect compounds quantitated at low concentrations with targeted analysis.

[6] ORD NH Report #3: Technical Support to New Hampshire DEP-Targeted PFAS Measurements in Waters. October 4, 2018.

**Table 2. PFAS Tentatively Identified in Water Samples by Non-Targeted Analysis.**

| Chem Ref. # | Tentatively Identified Compound Name | CAS Number | Formula | Monoisotopic Mass (Daltons) | Retention Time |
|---|---|---|---|---|---|
| 1 | Perfluorobutanoic acid (PFBA) | 375-22-4 | C4 H F7 O2 | 213.9866 | 1.52 |
| 2 | Perfluoropentanoic acid (PFPeA) | 2706-90-3 | C5 H F9 O2 | 263.9830 | 3.68 |
| 3 | Perfluorohexanoate (PFHxA) | 92612-52-7 | C6 H F11 O2 | 313.9798 | 5.07 |
| 4 | Perfluoroheptanoic acid (PFHpA) | 375-85-9 | C7 H F13 O2 | 363.9765 | 5.82 |
| 5 | (PFHpA-CO2 fragment) | | C6 H F13 | 319.9867 | 5.81 |
| 6 | Perfluorooctanoic acid (PFOA) | 335-67-1 | C8 H F15 O2 | 413.9733 | 6.33 |
| 7 | (PFOA-CO2 fragment) | | C7 H F15 | 369.9834 | 6.33 |
| 8 | Perfluorononanoic acid (PFNA) | 375-95-1 | C9 H F17 O2 | 463.9697 | 6.76 |
| 9 | (PFNA-CO2 fragment) | | C8 H F17 | 419.9799 | 6.76 |
| 10 | Perfluorodecanoic acid (PFDA) | 335-76-2 | C10 H F19 O2 | 513.9658 | 7.17 |
| 11 | Perfluorobutanesulfonate (PFBS) | 375-73-5 | C4 H F9 O3 S | 299.9497 | 4.22 |
| 12 | Perfluoropentanesulfonate (PFPeS) | 2706-91-4 | C5 H F11 O3 S | 349.9470 | 5.25 |
| 13 | Perfluorohexane Sulfonate (PFHxS) | 355-46-4 | C6 H F13 O3 S | 399.9434 | 5.88 |
| 14 | Perfluorooctanesulfonate (PFOS) | 1763-23-1 | C8 H F17 O3 S | 499.9362 | 6.75 |
| 15 | 3:2 Fluorotelomer alcohol | 755-40-8 | C5 H5 F7 O | 214.0224 | 1.24 |
| 16 | Perfluoro-3-(1H-perfluoroethoxy)propane | 3330-15-2 | C5 H F11 O | 285.9851 | 5.33 |
| 17 | Tridecafluoroheptaneperoxoic acid | 139702-34-4 | C7 H F13 O3 | 379.9712 | 5.98 |
| 18 | Undecafluorocyclohexanemethanol dihydrogen phosphate | 32582-74-4 | C7 H4 F11 O4 P | 391.9713 | 6.04 |
| 19 | Perfluorohexanesulfonamide | 41997-13-1 | C6 H2 F13 N O2 S | 398.9571 | 5.07 |
| 20 | 6:2 Fluorotelomer sulfonic acid (6:2FtS) | 27619-97-2 | C8 H5 F13 O3 S | 427.9745 | 6.30 |
| 21 | Perfluoropentane sulfonamido amine | 68555-78-2 | C10 H13 F11 N2 O2 S | 434.0563 | 4.12 |
| 22 | Perfluorooctanesulfonamide (PFOSA) | 754-91-6 | C8 H2 F17 N O2 S | 498.9501 | 6.33 |
| 23 | 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluorononyl methacrylate | 1841-46-9 | C13 H8 F16 O2 | 500.0217 | 6.75 |
| 24 | POLYFLGSID_880958 | 72494-14-5 | C33 H42 F8 N2 O4 | 682.3026 | 12.88 |

**Table 3. Non-Targeted Analysis Semi-Quantitation (Peak Area Counts) of PFAS in Water Samples.**

| Chem Ref. # | EPAORD 001 | EPAORD 002 | EPAORD 003 | EPAORD 004 | EPAORD 005 | EPAORD 006 | EPAORD 007 | EPAORD 008 | EPAORD 009 | EPAORD 010 | EPAORD 011 | EPAORD 012 | EPAORD 013 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 40,400 | 13,900 | 12,900 | 149,000 | 183,000 | 686,000 | 21,200 | 20,300 | 154,000 | 104,000 | 248,000 | 45,600 | 53,200 |
| 2 | 102,000 | 15,700 | 16,600 | 670,000 | 838,000 | 2,970,000 | 62,100 | 38,000 | 371,000 | 356,000 | 997,000 | 126,000 | 153,000 |
| 3 | 173,000 | 19,500 | 15,000 | 826,000 | 1,010,000 | 4,260,000 | 103,000 | 57,600 | 562,000 | 632,000 | 1,870,000 | 218,000 | 266,000 |
| 4 | 229,000 | <RL | <RL | 616,000 | 765,000 | 2,760,000 | 155,000 | 81,600 | 464,000 | 689,000 | 1,800,000 | 421,000 | 490,000 |
| 5 | 103,000 | 8,710 | 6,030 | 258,000 | 312,000 | 984,000 | 70,900 | 41,200 | 162,000 | 284,000 | 624,000 | 211,000 | 178,000 |
| 6 | 1,010,000 | 38,200 | 19,700 | 2,610,000 | 3,250,000 | 11,800,000 | 495,000 | 266,000 | 2,290,000 | 2,440,000 | 6,600,000 | 1,580,000 | 2,260,000 |
| 7 | 504,000 | 20,600 | 10,300 | 1,210,000 | 1,470,000 | 4,810,000 | 272,000 | 172,000 | 1,060,000 | 1,210,000 | 3,040,000 | 1,010,000 | 1,160,000 |
| 8 | 182,000 | 40,500 | 16,200 | 43,800 | 45,300 | 95,700 | 5,700 | ND | 15,500 | 11,000 | 6,300 | ND | ND |
| 9 | 85,700 | 19,500 | 7,740 | 23,600 | 26,600 | 55,600 | ND | ND | 13,000 | 6,030 | ND | ND | ND |
| 10 | 183,000 | 41,800 | 152,000 | 149,000 | 53,700 | 41,100 | ND | ND | ND | 6,380 | ND | ND | ND |
| 11 | 42,500 | 10,400 | 10,600 | 61,200 | 112,000 | 64,000 | 36,500 | 22,300 | 70,800 | 79,100 | 152,000 | 43,900 | 53,600 |
| 12 | 21,700 | ND | ND | 33,300 | 38,900 | 62,000 | 10,500 | 6,860 | 5,850 | 20,000 | 76,000 | 52,700 | 67,100 |
| 13 | 120,000 | 12,000 | 8,650 | 101,000 | 128,000 | 184,000 | 38,600 | 19,500 | 36,200 | 51,000 | 118,000 | 649,000 | 870,000 |
| 14 | 327,000 | 62,500 | 147,000 | 444,000 | 451,000 | 2,530,000 | 19,300 | 61,200 | 21,100 | 11,600 | 25,000 | 74,100 | 95,300 |
| 15 | 135,000 | 199,000 | 180,000 | 108,000 | 146,000 | 16,800 | ND | ND | 4,140 | 8,900 | 5,850 | 2,050 | ND |
| 16 | 8,260 | 6,920 | ND | 5,610 | ND | 8,000 | 5,750 | ND | ND | 5,600 | 7,030 | 4,130 | 6,680 |
| 17 | 35,200 | 12,100 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 18 | 9,270 | ND | ND | 18,100 | 22,000 | 64,800 | 8,110 | ND | 9,060 | 25,900 | 78,300 | ND | ND |
| 19 | 5,650 | ND | ND | 21,900 | 22,200 | 81,100 | ND | ND | 13,100 | 22,000 | 67,800 | 8,170 | 9,020 |
| 20 | ND | ND | ND | 26,100 | 33,400 | 646,000 | ND | ND | ND | ND | ND | ND | ND |
| 21 | 16,600 | ND | ND | 20,200 | 29,100 | 15,100 | 41,100 | 16,000 | 19,900 | ND | ND | 3,330 | ND |
| 22 | 53,700 | ND | ND | 117,000 | 118,000 | 233,000 | 33,200 | 21,300 | 89,600 | 128,000 | 306,000 | 113,000 | 121,000 |
| 23 | 15,900 | 4,380 | 1,780 | 8,910 | 14,300 | 156,000 | ND | 1,150 | ND | ND | ND | 3,150 | 8,740 |
| 24 | 172,000 | 154,000 | 153,000 | 556,000 | 649,000 | 622,000 | 584,000 | 538,000 | 626,000 | 528,000 | 303,000 | 258,000 | 454,000 |

| 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 |

**Table 3. (continued). Non-Targeted Analysis Peak Area Counts of PFAS in Water Samples.**

| Chem Ref. # | EPAORD 014 | EPAORD 015 | EPAORD 016 | EPAORD 017 | EPAORD 018 | EPAORD 019 | EPAORD 020 | EPAORD 021 | EPAORD 022 | EPAORD 023 | EPAORD 024 | EPAORD 901 | TB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 8,710 | 29,700 | 29,500 | 35,500 | 15,000 | 37,100 | 23,000 | 23,400 | 60,400 | 89,400 | 30,900 | 21,100 | ND |
| 2 | 6,270 | 88,200 | 81,300 | 59,000 | 18,000 | 84,800 | 38,600 | 38,000 | 179,000 | 357,000 | 66,800 | 55,600 | ND |
| 3 | 5,610 | 96,200 | 151,000 | 110,000 | 26,900 | 108,000 | 48,400 | 51,900 | 219,000 | 481,000 | 76,700 | 155,000 | ND |
| 4 | <RL | 101,000 | 175,000 | 197,000 | 57,500 | 136,000 | 71,600 | 78,200 | 281,000 | 669,000 | 91,300 | 345,000 | ND |
| 5 | 4,120 | 44,400 | 81,000 | 67,300 | 24,400 | 55,300 | 33,600 | 30,200 | 125,000 | 248,000 | 45,700 | 141,000 | ND |
| 6 | 41,600 | 445,000 | 542,000 | 1,090,000 | 378,000 | 528,000 | 356,000 | 351,000 | 842,000 | 3,120,000 | 211,000 | 2,370,000 | ND |
| 7 | 23,200 | 237,000 | 300,000 | 525,000 | 206,000 | 265,000 | 185,000 | 186,000 | 439,000 | 1,450,000 | 126,000 | 1,060,000 | ND |
| 8 | ND | ND | 3,500 | 5,140 | ND | 6,540 | 6,240 | 5,850 | 7,310 | 8,530 | ND | 6,680 | ND |
| 9 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 10 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 11 | 8,770 | 65,200 | 82,800 | 258,000 | 38,700 | 428,000 | 24,900 | 11,500 | 118,000 | 14,100 | 14,500 | 13,400 | ND |
| 12 | ND | ND | 9,260 | 9,340 | 7,810 | 7,570 | 7,430 | ND | 11,900 | 6,900 | 7,030 | ND | ND |
| 13 | 5,610 | 22,100 | 19,500 | 38,700 | 30,100 | 27,900 | 29,600 | 24,000 | 42,800 | 42,100 | 30,400 | 29,200 | ND |
| 14 | ND | 17,800 | ND | 34,300 | 14,900 | 11,700 | 17,300 | 13,800 | 5,670 | 25,600 | 7,890 | 44,700 | ND |
| 15 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | 1,850 | ND | ND |
| 16 | 6,600 | 6,430 | 48,500 | 7,080 | 7,250 | 7,020 | 9,480 | 6,950 | 10,300 | 11,000 | 7,520 | 8,140 | ND |
| 17 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 18 | ND | ND | ND | ND | ND | ND | ND | ND | ND | 17,900 | ND | 9,230 | ND |
| 19 | ND | ND | 6,700 | ND | ND | ND | ND | ND | 6,130 | 10,800 | ND | ND | ND |
| 20 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 21 | ND | 7,580 | 6,840 | 36,400 | 155,000 | 9,610 | 11,400 | 15,500 | 11,700 | ND | 17,000 | 25,800 | ND |
| 22 | ND | 30,700 | 30,200 | 58,100 | 23,000 | 31,500 | 21,800 | 21,200 | 39,900 | 116,000 | 13,900 | 99,400 | ND |
| 23 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | 4,310 | ND |
| 24 | 410,000 | 332,000 | 360,000 | 306,000 | 525,000 | 224,000 | 318,000 | 283,000 | 331,000 | 257,000 | 219,000 | 225,000 | <RL |

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