



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

OFFICE OF
RESEARCH AND DEVELOPMENT

August 29, 2022

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

Dear Mr. Scott:

I am pleased to provide the enclosed report from the collaborative technical support to NHDES assisting with concerns over Perfluoropropionic acid (PFPrA) in drinking water in the Merrimack and Portsmouth areas. This report is in response to your December 2021 request asking for laboratory assistance analyzing PFPrA in water samples collected by NHDES. The limited samples were collected near locations where PFPrA was detected previously by a commercial laboratory. The enclosed report provides targeted analysis laboratory results for PFPrA in the samples provided.

It is our understanding that this information was requested by NHDES to help in the understanding of the analytical method and provide some comparison to data previously collected. This request relates to our research capabilities and interests applying targeted analysis methods for discovery of the nature and extent of PFAS environmental occurrence that may be potentially associated with industrial releases.

In this report, we provide PFPrA analytical results and compare to those provided to the commercial laboratory. 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 PFPrA. The data provided in the attached report indicates the lack of detectable PFPrA in the water samples collected. 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 several Agency efforts that continue EPA's commitment to advance the collective understanding of PFAS.

If you have any questions or concerns, do not hesitate to contact me at (513) 569-7852 or via email at Gilliland.Alice@epa.gov or alternate point of contact, Kevin Oshima at (513)569-7476 or via email at Oshima.Kevin@epa.gov. I look forward to our continued work together.

Sincerely,

Alice Gilliland
CEMM Director (Acting)

CC:

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PFPrA in Water Samples Collected in Select New Hampshire Sites

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 in Perfluoropropionic acid (PFPrA) in water samples collected from select sites. NHDES assumed responsibility for the collection of samples and their shipment to the ORD laboratory. ORD was responsible for sample extraction, methods development, 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 Investigator	Mark Strynar
Laboratory chemistry	Mark Strynar
Quality Assurance Review	Margie Vazquez
Management coordination and review	Myriam Medina-Vera, Kevin Oshima
Report preparation	Myriam Medina-Vera, Mark Strynar

This report includes targeted analysis results for 14 water samples (including a surface water sample, two duplicate samples, and two field blanks for quality assurance) collected from various water sources in southern New Hampshire. The samples were collected on March 1st and 2nd, 2022. To the extent possible, sample locations mirrored those collected in the 2021 Natural Resources Defense Council (NRDC) study.

The current data report provides a simple representation and summary of the analytical results. Therefore, the description of methods and quality assurance are brief and high-level. More detailed description of methods, quality assurance procedures, and data interpretation is available as a briefing. As study partners/collaborators, we anticipate that NHDES and Region 1 will assist in the coordination of official briefings as needed.

Methods in Brief. Sample collection was performed by NHDES. In preparation for sample collection, on February 9th, 2022, EPA/ORD shipped out some QC samples to the NHDES team consisting of a trip blank (to remain unopened) consisting of lab Deionized (DI) water in a HDPE bottle, a field blank (lab DI water to be opened in field and transferred to another sample bottle) and a blank bottle of DI water spiked at 50 ng/L PFPrA. The blank samples were to control for blank contamination from processing and collection and the spiked samples to account for analyte recovery. No matrix spike recovery in real samples was conducted. Samples collected (see Table 1) were stored at 4 °C upon receipt until analysis.

On March 1st and 2nd, 2022, NH DES collected ten water samples in southern NH (Table 1). To the extent possible, sample locations mirrored those collected in the 2021 NRDC study, and also included a surface water sample, two duplicate samples, and two field blanks for quality assurance. Samples were split and delivered to USEPA and the Eurofins lab on March 7th and 8th, 2022, respectively. NHDES contracted Eurofins to perform the analyses and the USEPA lab was requested to verify the results as there is no approved analytical method.

Sample ID	Sample Description
1951010_501	Bellamy Reservoir - treated
1951010_501	Bellamy Reservoir - treated - DUPLICATE
1951010_503	Portsmouth well - treated
1951010_DPW	Portsmouth DPW office tap
1531010_509	MVD 4/5 - treated
1531010_011/005	MVD 4/5 - untreated
1531010_511	Pennichuck WW interconnection with MVD - treated
1531010_16FRNCH	Allen residence - MVD water - pre home-treatment
1531010_16FRNCH	Allen residence - MVD water - pre home-treatment - DUPLICATE
MTBE_8278	Thomas residence - private well - untreated
MTBE_8178	Dunn residence - private well - untreated
08-SKB	Surface water - Highland Lake outlet - Sucker Brook
Field Blank	FIELD BLANK (Bellamy Reservoir - treated)
Field Blank	FIELD BLANK (Allen residence - MVD water - pre home-treatment)

Table 1. Samples collected in this study

ORD engaged in analytical method development in late 2021 into early 2022, since PFPrA was not an analyte regularly measured for in water samples by the ORD lab. Note that in-depth method development for this compound has not been conducted, therefore the method detection limit is not established. The limit of quantitation was conservatively established at 10 ng/L based on previous experience with other PFAS analytes and methods. In summary, PFPrA is a short chained perfluorinated carboxylic acid (PFCA) that is capable of capture by weak anion exchange (WAX) solid phase extraction for isolation and concentration. The sample preparation procedure is 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 extracted using a WAX solid phase extraction cartridge. PFPrA 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 1290 UPLC coupled to an Agilent 6546 Quadrupole Time-of-Flight (QTOF) mass spectrometer.

¹ 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.

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

PFPrA was analyzed using a modified method that has been employed in a series of targeted and Non-targeted (NTA) applications for several studies and years (McCord and Strynar 2019³; McCord et al., 2018⁴). No stable isotope labeled PFPrA currently exists for isotope dilution quantitation. Thus, the closest available PFCA in molecular weight was chosen to act as a surrogate. The select compound was 13C4-PFBA which is one carbon larger than PFPrA to serve this role. The contract lab doing parallel analysis chose the same isotope label as well. A 6-point extracted calibration curve consisting of PFPrA added into lab derived DI water from 1 to 50 ng/L was constructed on the day of extraction and analysis (See Figure 1, Table 2).

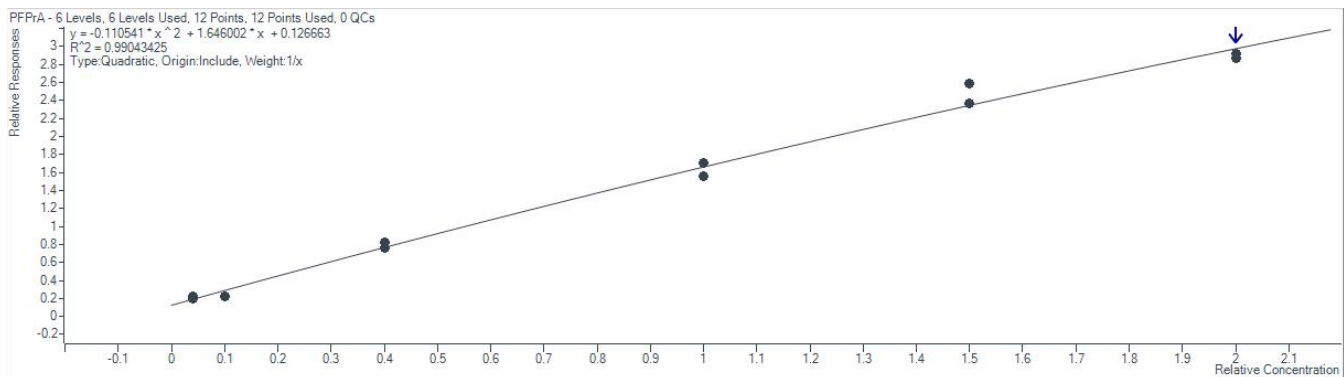


Figure 1-Six Point Calibration Curve

Calibration Curve	average value (ng/L)	Avg % Accuracy	Target QA %Accuracy
1 ng/L	1.3	133	70-130
2.5 ng/L	1.5	62	80-120
10 ng/L	10.4	104	80-120
25 ng/L	24.5	98	80-120
37.5 ng/L	40.0	107	80-120
50 ng/L	48.3	97	80-120
QC spike sample	Value ng/L	% Accuracy	Target QA %Accuracy
QC 50ng/L spike	43.4	86.8	80-120

Table 2-Calibration Curve-concentration range and Quality Control Spike concentration

³ James McCord and Mark Strynar. Identification of Per- and Polyfluoroalkyl Substances in the Cape Fear River by High Resolution Mass Spectrometry and Nontargeted Screening. Environmental Science & Technology 2019 53 (9), 4717-4727 DOI: 10.1021/acs.est.8b06017

⁴ James McCord, Seth Newton, Mark Strynar. Validation of quantitative measurements and semi-quantitative estimates of emerging perfluoroethercarboxylic acids (PFECAs) and hexfluoropropylene oxide acids (HFPOAs). Journal of Chromatography A. Volume 1551. 2018, Pages 52-58, ISSN 0021-9673, <https://doi.org/10.1016/j.chroma.2018.03.047>.

The analytical data generated by LC/MS were considered as a “detect” when acceptable chromatographic peaks and spectra were evident. Samples under the limit of quantitation (LOQ) of the analytical method were reported as “ND”.

Summary of Results

Lacking a matched stable isotope labeled surrogate is less than ideal for quantitation in complex environmental samples like water. Until a match isotope labeled surrogate is possible the best available approach is a closely matching surrogate such as the ¹³C₄- Perfluorobutanoic acid (PFBA) which was chosen as a stand in. This approach however is not without the pitfalls of the inability to account for the ion enhancement or suppression in complex environmental samples. In addition, PFPrA is a small mobile perfluoroalkyl carboxylic acid (PFCA) that is poorly retained on reversed phase columns and likely is influenced by other matrix interferences that are also poorly retained. An alternative LC approach called HILIC was attempted in methods development stage but was ultimately not used for chromatographic separation for this analysis due to the need for further method development. Future method development efforts are intended to account for PFPrA and other short chained PFAS in environmental samples but have not yet been conducted.

The calibration curve was acceptable with $R^2 > 0.99$ for the range of the curve. The back prediction of the calibration curve showed some deviation from ideal (+/- 30% at LOQ and +/-20% for the remainder of the curve). The Level of Quantitation (LOQ) was set at 10 ng/L for a conservative estimate. The linearity of the curve suggests that with additional method's development, values of 1-2.5 ng/L may be measurable with some additional error associated with it. The recovery of the spiked sample at 50 ng/L PFPrA was 86.8% which is within the target range of +/-20%. All blank samples including non-injections, solvent blanks and prepared blanks (trip blank and method blank) did not have measurable PFPrA above the lowest calibration standard.

According to both analyses, USEPA and the contracting lab- Eurofins, concentrations of PFPrA were below the method level of quantitation across all samples. Results from Eurofins indicated that only one sample (1531010_011/005: untreated water from MVD wells 4/5) was above the reporting limit and had a concentration of 4.8 ng/L. Results from USEPA ORD indicated that concentrations of PFPrA in all samples were less than 10 ng/L (limit of quantitation set for the EPA method) and were likely less than 1 ng/L. Results in Table 3 show that both methods are in agreement reporting that all samples are below 10 ng/L. The validity of these results is inferred by reproducibility across duplicate samples and laboratory split samples. Measurement of PFPrA and other short-chain PFAS compounds continues to improve as standards become available and as labs develop more robust methods for quantifying these challenging analytes.

		2022					
		Eurofins				USEPA ORD	
Sample ID	Sample Description	Conc. (ng/L)	Qualifier *	MDL (ng/L)	RL (ng/L)	Conc. (ng/L)	LOQ (ng/L)**
1951010_501	Bellamy Reservoir - treated	2.1	J	1.7	4.3	ND	1 - 10
1951010_501	Bellamy Reservoir - treated - DUPLICATE	2.4	J	1.7	4.2	ND	1 - 10
1951010_503	Portsmouth well - treated	2.6	J	1.8	4.4	ND	1 - 10
1951010_DP W	Portsmouth DPW office tap	2.1	J	1.8	4.5	ND	1 - 10
1531010_509	MVD 4/5 - treated	3.8	J	1.8	4.5	ND	1 - 10
1531010_011/005	MVD 4/5 - untreated	4.8		1.7	4.3	ND	1 - 10
1531010_511	Pennichuck WW interconnection with MVD - treated	2.4	J	1.8	4.4	ND	1 - 10
1531010_16F RNCH	Allen residence - MVD water - pre home-treatment	3.3	J	1.7	4.3	ND	1 - 10
1531010_16F RNCH	Allen residence - MVD water - pre home-treatment - DUPLICATE	3.4	J	1.8	4.5	ND	1 - 10
MTBE 8278	Thomas residence - private well - untreated	3.5	J	1.7	4.3	ND	1 - 10
MTBE 8178	Dunn residence - private well - untreated	4.4	J	1.8	4.5	ND	1 - 10
08-SKB	Surface water - Highland Lake outlet - Sucker Brook	ND		1.7	4.3	ND	1 - 10
Field Blank	FIELD BLANK (Bellamy Reservoir - treated)	ND		1.8	4.6	ND	1 - 10
Field Blank	FIELD BLANK (Allen residence - MVD water - pre home-treatment)	ND		1.8	4.4	ND	1 - 10

Table 3-Comparison of analytical results from commercial lab and USEPA.

*J = Result is less than the reporting limit (RL) but greater than or equal to the method detection limit (MDL) and the concentration is an approximate value.

**Per Mark Strynar (USEPA ORD): Note that method development for this compound has not been conducted, therefore method detection limits are not established. The limit of quantitation (LOQ) could be set at 10 ng/L for a conservative estimate of the lower limit of quantitation.

However even with deviation beyond the ideal, linearity of the curve suggests values of 1-2.5 ng/L would be measurable with some additional error associated with that measurement. None of the collected sample had quantifiable levels of PFPrA above the limit of quantitation regardless of the establishment of 1, 2.5 or 10 ng/L as the lower limit of quantitation from ORD analysis.

Abbreviations: Conc. = concentration; ND = not detected