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

OFFICE OF
RESEARCH AND DEVELOPMENT

April 23, 2020

Ken Kloo, Director
NJ Department of Environmental Protection
Division of Remediation Management
Mail Code 401-05M
401 East State Street
P.O. Box 420
Trenton, NJ 08625-0420

Subject: NJ DEP Data Report #4: Branching Characteristics in Soil Samples

Dear Mr. Kloo:

I am pleased to provide you with the attached laboratory report that includes additional targeted analysis results for per- and polyfluoroalkyl substances (PFAS) in soil samples. This is the 4th in a series of reports prepared as a part of EPA Office of Research and Development's (ORD) collaboration with the New Jersey Department of Environmental Protection (NJ DEP) and EPA Region 2 on the study, "Detection, Evaluation, and Assignment of Multiple Poly- and Perfluoroalkyl Substances (PFAS) in Environmental Media from an Industrialized Area of New Jersey." This report provides estimates of structural branching for Perfluorooctanoic Acid (PFOA) and Perfluorononanoic Acid (PFNA) in soil samples for which concentrations based on targeted analysis were previously reported in NJ DEP Report #1.

It is our understanding that this study was designed to help NJ DEP in their ongoing investigation into the presence of PFAS in the environment near manufacturing facilities of interest. This study 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 do not interpret exposure or risk from any reported values. EPA does not currently have final 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 report indicate the presence of PFAS in the soil samples, we do not have sufficient information to offer interpretations related to human or environmental exposure and risk.

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Thank you for inviting us to be part of this effort that helps to further both EPA's and New Jersey's understanding of an important issue in the state. This is just one of many Agency efforts that demonstrates 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. I look forward to our continued work together.

Sincerely,

Timothy H Watkins

Timothy H. Watkins
Director

Enclosure

CC:

Erica Bergman, NJDEP
Peter Lopez, USEPA Region 2
Matt Laurita, USEPA, Region 2
Nidal Azzam, USEPA, Region 2
Ariel Iglesias, USEPA, Region 2
Daniel D'Agostino, USEPA, Region 2
Kathleen Salyer, USEPA, OLEM
Jim Woolford, USEPA, OLEM
Tala Henry, USEPA, OCSPP
Mike Koerber, USEPA, OAR
Charlotte Bertrand, USEPA, OW
Jennifer Mclain, USEPA, OW
Jennifer Orme-Zavaleta, USEPA, ORD
Alice Gilliland, USEPA, ORD
Andy Gillespie, USEPA, ORD
Kevin Oshima, USEPA, ORD
Brian Schumacher, USEPA, ORD

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Detection, Evaluation, and Assignment of PFAS in Environmental Media from an Industrialized Area of New Jersey

Laboratory Data Report #4: Branching Characteristics in Soil Samples

Background. This report stems from a collaborative study with EPA ORD, EPA Region 2, and NJ DEP entitled "Detection, Evaluation, and Assignment of Multiple Poly- and Perfluoroalkyl Substances (PFAS) in Environmental Media from an Industrialized Area of New Jersey." NJ DEP assumed responsibility for the collection of samples and their shipment to the ORD laboratory. ORD was responsible for sample extraction and analysis of PFAS. Preparation of this report involved many from ORD assuming various roles and responsibilities provided below 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	John Washington, Brad Acrey
Quality Assurance Review	Brittany Stuart
Management coordination and review	Brian Schumacher, Tim Buckley
Report preparation	Kate Sullivan

This 4th report includes estimates of isomer branching in 24 soil samples and 2 field duplicates labeled PFSS that were collected by NJ DEP between November 8 and10, 2017. The samples were sent to and analyzed for PFAS under the direction of Dr. John Washington at ORD's laboratory in Athens, GA. Samples were received on November 14, 2017.

Methods in Brief. Samples were analyzed for PFAS with Ultra-Performance Liquid Chromatography Mass Spectrometry (UPLC-MS) using targeted analysis methods described within our Quality Assurance Project Plan (QAPP)[1] and that have been generally described in Rankin *et al.*, 2015[2]. Each sample was divided into three ~1 g aliquots and analyzed independently. Each aliquot was extracted with 90%/10% acetonitrile water followed by a liquid/liquid cleanup. Samples were analyzed using a Waters Acquity UPLC coupled to a Waters Quattro Premier XE tandem mass spectrometer. Concentrations of Perfluorooctanoic Acid (PFOA) and Perfluorononanoic Acid (PFNA) were determined with authentic standards. The

[1] National Exposure Research Laboratory, Quality Assurance Project Plan: Detection, Evaluation and Assignment of Multiple Poly and Per-fluoroalkyl Substances (PFAS) in environmental media from an industrialized area of New Jersey. Prepared for New Jersey Department of Environmental Protection (NJ DEP), D-EMMD-IEIB-010-QAPP-01, September 14, 2017.

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

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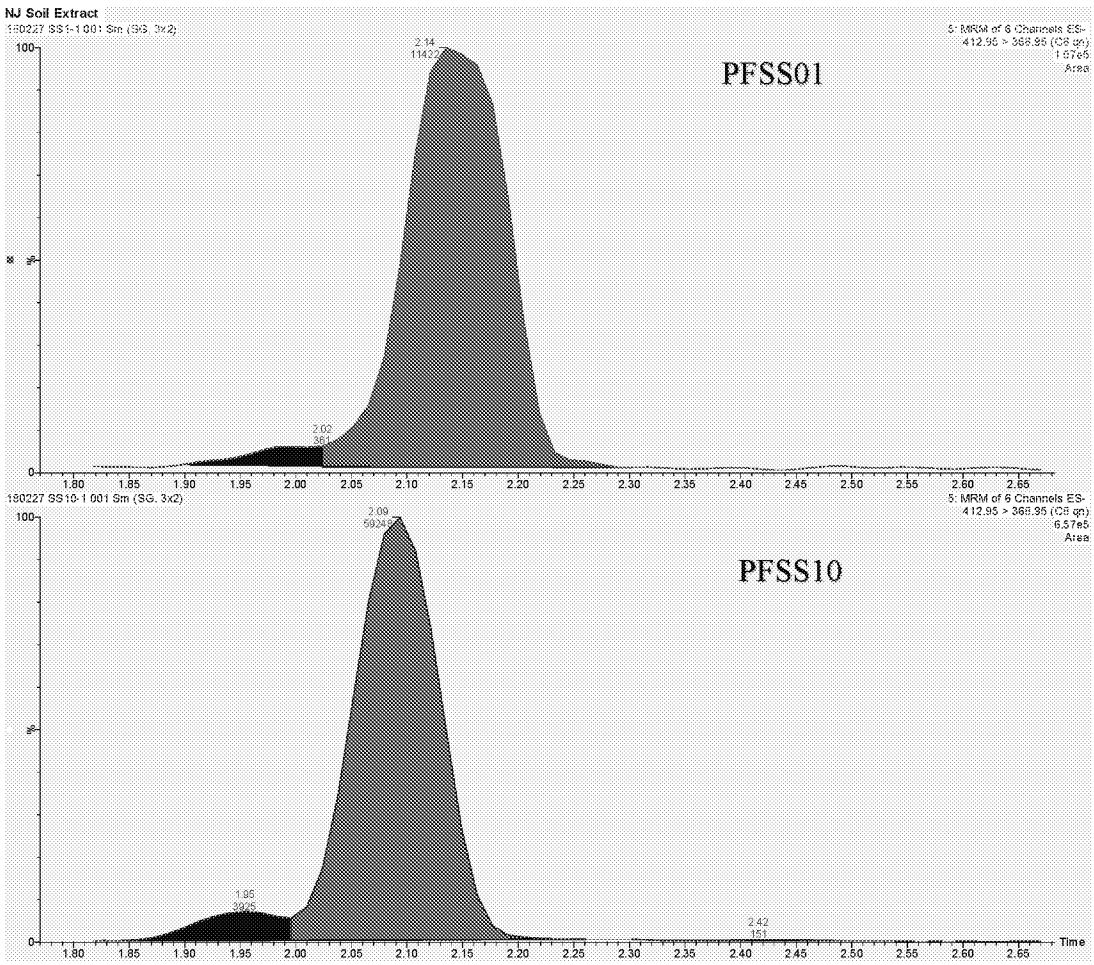
quantitated concentration results for 26 soil samples were previously reported in NJ DEP Report #1[3].

NJ DEP is interested in the characteristics of structural PFOA and PFNA branching in the soil samples. Many PFAS in the past were made by the industrial process of electrochemical fluorination (ECF) which leads to branched and linear structures. A second method called telomerization is purported to lead only to linear PFAS structures. Branched and linear PFAS may be chromatographically separated if gradients are sufficient for resolution. If present in a sample, the branched and linear peaks for PFOA and PFNA were integrated separately by the analyst for estimation of percent branched isomers. An example of chromatographic separation of isomer structures in PFOA is provided for two samples in Figure 1. The portions of the sample that are branched and linear sum to 100% of the total peak area. Percent ratios of linear and branched isomers are conventionally described in peer-reviewed literature as qualitative[2].

Figure 1. Example of chromatograph separation PFOA (C8) branched and linear isomers in PFSS1 and PFSS10: fronting (dark blue color) is branched and large peak (teal color) is linear.



[3] NJ DEP Laboratory Data Report #1: Targeted analysis of PFCA in Soil. U.S. EPA/ORD, January 31, 2019.

Results. Table 2 provides the estimated branched percentage of each of the 26 soil samples labeled PFSS based on its proportion of total analyte peak area (branched + linear). Table 2 also provides the concentration of PFOA and PFNA for these soil samples as previously reported in NJ DEP Report #1. The compound concentrations and branching proportion are calculated as the average of aliquot triplicates. The linear portions of the PFOA and PFNA concentrations can be determined as 100-Branched %.

The average percent of the sample concentrations that was branched was 2.4% for PFOA and 1.7% for PFNA. The branched portion exceeded 5% of total in just one sample (PFSS002) for PFOA and in two samples (PFSS002 and PFSS023) for PFNA.

To characterize laboratory repeatability, at least 3 replicate measurements were performed on 30 of the 78 individual sample aliquots. The average coefficient of variation (CV) of the repeated measurements for the branched isomers was 21% for PFOA and 84% for PFNA. These CVs were relatively high because small differences between aliquots were amplified by the small branched proportion in the samples. The CVs for the linear proportion that made up most of the PFOA and PFNA concentrations were 0.7% and 3.6%, respectively. Similarly, the relative percent differences (RPDs) of the branched portions of both PFOA and PFNA in 2 sample/duplicate pairs ranged from 6 to 46% while the RPDs of the linear portions ranged from 0.2 to 0.6%.

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Table 2. Percent (%) Branching for PFOA and PFNA in soil samples based on peak area counts.

	Perfluorooctanoic Acid (PFOA)		Perfluorononanoic Acid (PFNA)	
	$C_8HF_{15}O_2$		$C_9HF_{17}O_2$	
Sample ID	Total PFOA[&] (pg/g)	% Branched[*]	Total PFNA[&] (pg/g)	% Branched[*]
PFSS001	398	4.1%	2,710	0.7%
PFSS002	196 (JD)	5.2%	91.2	8.5%
PFSS003	422	2.6%	770	1.2%
PFSS004	1,070 U)	2.5%	2,630 (JD)	0.5%
PFSS005	242 (U)	2.4%	691	0.8%
PFSS006	295 (U)	3.1%	766	0.8%
PFSS007	749	3.0%	1,220	1.1%
PFSS008	ND	NA	295	0.6%
PFSS009	162(U)	3.5%	522	0.8%
PFSS010	1,900	4.9%	286	1.6%
PFSS011	317	4.2%	784	0.5%
PFSS012	573	3.6%	445	0.8%
PFSS013	619	3.3%	1,150	0.6%
PFSS014	415 (JD)	1.2%	887 (JD)	0.4%
PFSS015	599 (JD)	1.3%	614 (JD)	0.4%
PFSS016	264	0.3%	651	0.0%
PFSS017	405	0.2%	711	0.3%
PFSS018	160 (U)	0.6%	356	0.3%
PFSS019	151 (U)	2.1%	337 (U)	3.5%
PFSS020	92.7 (U)	1.2%	475	0.6%
PFSS021	689	1.2%	626	2.7%
PFSS022	1,250	3.0%	658	2.5%
PFSS023	330 (U)	1.1%	446	7.5%
PFSS024	892	1.6%	731	3.2%
PFSSDUP1	804	0.7%	862	2.9%
PFSSDUP3	185 (U)	2.2%	846	1.1%

[&] Concentrations reported in NJ DEP Report #1.

* % branched is based on analyte peak area counts of three independently extracted replicates.

ND: Non-detect based on no integratable peak area.

NA: Sample concentration is ND, branching not determined.

U: Sample result is less than the limit of quantitation (<LOQ). The associated value is an estimate.

JD: Sample triplicates do not meet acceptance criteria for precision. The associated value is an estimate.