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

OFFICE OF RESEARCH AND DEVELOPMENT

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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 Report #5: Non-targeted Analysis Results of PFAS in Sediment

Dear Mr. Kloo:

I am pleased to provide you with the attached laboratory report that includes non-targeted analysis (NTA) results for per- and polyfluoroalkyl substance (PFAS) in sediment samples. This is the fifth 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." The enclosed Report #5 provides results of the occurrence of chloro-perfluoro-polyether-carboxylates (ClPFPECAs) in 24 sediment samples based on non-targeted analysis.

It is our understanding that this information was requested by NJ DEP 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 tentative identification and semi-quantitative analytical results for PFAS. We do not interpret exposure or risk from these 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 reports indicate the presence (or lack) of PFAS in the MM5 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 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

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

Laboratory Data Report #5: Non-targeted Analysis of PFAS in Sediments

Background. This report stems from a collaborative study with EPA ORD, 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. ORD's analysis and support team for this data report are listed in Table 1.

Table 1. EPA Office of Research and Development 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, John Washington

This 5th report includes results of non-targeted analysis of 20 sediment samples and 4 field quality assurance/quality control (QA/QC) samples including 2 field duplicates and 2 field blanks collected by NJ DEP between October 23 and November 1, 2017. 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 October 30 and November 6, 2017. The NTA analysis focused on concentration estimates for nine novel PFAS that have been identified in soil and vegetation samples reported previously. The nine PFAS listed in Table 2 are congeners of chloro-perfluoro-polyether-carboxylate (ClPFPECA).

The current data report is intended to provide a simple representation and summary of the analysis results. Therefore, the description of methods, results and quality assurance are brief and high-level. Additional reports and/or publications are being developed that will include a more detailed description of methods, results, quality assurance procedures, and statistical interpretation of the data. As study partners/collaborators, we anticipate that NJ DEP and Region 2 will assist in preparation of these reports and publications.

Methods in Brief. The sediment samples were extracted and analyzed according to methods documented within an approved Quality Assurance Project Plan (QAPP)[1]. These methods are also generally described in Washington *et al*. (2014, 2015). PFAS were identified and quantified using a non-targeted analysis approach. Non-targeted analysis differs from targeted analysis in that chemical identification and quantification does not have the benefit of being based on an authentic standard for each compound.

[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.

In brief, each sample was divided into three ~l g aliquots and extracted individually. Samples were extracted with 90%:10% acetonitrile:water followed by a liquid/liquid cleanup. Extracts were first analyzed by ultra performance liquid chromatography (UPLC)/mass spectrometry using a Waters Acquity UPLC coupled to a Waters Xevo quadrupole time-of-flight (QToF) mass spectrometer to identify the previously unknown PFAS. After PFAS were identified, the extracts were analyzed using a Waters Acquity UPLC coupled to a Waters Quattro Premier tandem mass spectrometer providing semi-quantitation.

PFAS concentrations were estimated by manual integration of chromatographic peaks in each of the 3 replicates. Peak areas were compared to $^{13}C_5$-labeled perfluorononanoic acid (M5PFNA), the matrix internal standard, by simple peak-area ratios. The quantitation of the non-targeted analyte assumes that the mass spectrometer responds to M5PFNA as it does to the reported analyte yielding identical chromatographic peak areas for a given concentration. Even though the absolute concentration estimate will be uncertain, relative comparisons between samples for a given congener will be much less uncertain. Any application of NTA results should consider this inherently greater uncertainty with NTA than those performed by routine laboratory analysis with authentic standards.

The limit of detection (LOD) and the reporting limit (RL) for sample concentrations are defined using a two-mean, one-tailed Student's t-test[2] to verify a significant difference between chemical abundance averaged for the 3 aliquots and that observed in the laboratory process blanks. This approach establishes unique limits for each sample arising from the sample-specific standard deviation among the three aliquot replicates. Samples with no observed peak area in any aliquot are reported as Non-Detect ("ND"). A sample is less than LOD if a peak area was observed in one more aliquots but the t-statistic for aliquot replicates was less than $t_{critical=.0.05}$ and is reported as "<LOD" in Table 3. A sample is below the RL if the t-statistic is greater than $t_{critical=0.05}$ but less than $t_{critical=.0.01}$ and is flagged as "U" in Table 3.

Summary of Results. The mass spectral features of the ClPFPECA congeners as well as PFOA, and PFNA for comparison are provided in Table 2, including carbon chain length and ethyl, propyl group. We have high confidence in the identification of the ClPFPECA congeners considering a combination of evidence including mass spectral data, consistency of our detection in other media (i.e., water, dispersions, soil, and vegetation), and literature reports of Wang *et al.* (2013) establishing these PFAS in products produced by Solvay who also has a facility located within the geographic area of sampling.

Concentration estimates for the ClPFPECA congeners are provided in Table 3. Results are given by sample IDs assigned by NJ DEP. Sample values are reported as process-blank corrected, (i.e., reported sample concentrations are analytical concentrations minus mean process blank values), and are adjusted to dry weight.

Eight of the nine PFAS ClPFPECA congeners that were reported for soil and vegetation samples in Report #2[3] were also identified in the sediment samples. Samples varied in abundance of ClPFPECA compounds, but one or more of the congeners was present in every sample in

[2] 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), Amendment #1 D-EMMD-0031345-QP-1-1. May 2, 2018.

[3] NJ DEP Report #2. Detection, Evaluation, and Assignment of PFAS in Environmental Media from an Industrialized Area of New Jersey. Laboratory Data Report #2: Non-targeted Analysis of PFAS in Soil and Vegetation. U.S.EPA/ORD, March 8, 2019.

measurable concentrations. Most ClPFPECA compounds occurred at low concentrations but C8 (0,1) and C10 (1,1) occurred at relatively higher concentrations in a number of the samples (maximum concentration C8 (0,1 = 5,930 pg/g, C10 (1,1) =1,480 pg/g). On average, C8 (0,1) and C10 (1,1) constituted 63% and 21%, respectively, of the total of ClPFPECA congeners observed in the sediments. The C8 (0,1) and C10 (1,1) ClPFPECA congeners were also the most abundant compounds in soils and vegetation (Report #2).

Results for 2 field blanks (PFSDFB1 and PFSDFB2) and 2 duplicates (PFTSDDUP1 and PFTSDUP2) are provided in Table 3. None of the ClPFPECA congeners were detected in any of the field blanks. Precision was checked by computing the Coefficient of Variation (CV) among the 3 aliquots of each of the samples for each analyte. The CV of laboratory aliquots evaluates extraction and analytical precision and was within project goals of CV <50%[2] in 94% of 163 analyte/sample comparisons. Sample aliquots that did not meet the acceptance criteria are flagged as "JP1" in Table 3. Repeated measurement of the same aliquot was also performed on 5 samples to evaluate analytical precision alone. The CV of repeated measures (when concentrations in both samples were > RL) was within project goals in 97% of the 35 analyte/sample comparisons. Samples not meeting the acceptance criteria are flagged as "JP2" in Table 3.

Table 2. LC/MS/MS analytical parameters of Chloro-Perfluoro-Polyether-Carboxylate (ClPFPECA) Congeners Identified in Sediments Using Non-Targeted Analysis.

Parameter	Chloro-perfluoro-polyether-carboxylate (ClCPFPECA) congeners by group number of ethyl, propyl									Legacy compounds for comparison	
Ethyl, Propyl Groups	**0,1**	**2,0**	**1,1**	**0,2**	**3,0**	**2,1**	**1,2**	**4,0**	**0,3**	**PFOA**	**PFNA**
Carbon Length	**8**	**9**	**10**	**11**	**11**	**12**	**13**	**13**	**14**	**8**	**9**
Molecular Mass (Daltons)	461.9340	527.9257	577.9225	627.9193	643.9142	693.9110	742.9078	759.9028	793.9046	413.9737	463.9705
Anion Formula	$C_8ClF_{14}O_4$	$C_9ClF_{16}O_5$	$C_{10}ClF_{18}O_5$	$C_{11}ClF_{20}O_5$	$C_{11}ClF_{20}O_6$	$C_{12}ClF_{22}O_6$	$C_{13}ClF_{24}O_6$	$C_{13}ClF_{24}O_7$	$C_{14}ClF_{26}O_6$	$C_8F_{15}O_2$	$C_9F_{17}O_2$
Precursor Mass (Daltons/electrostatic unit)	366.9395	432.9312	482.9280	532.9249	548.9198	598.9166	648.9134	664.9083	698.9102	412.9659	462.9627
Precursor Formula	$C_6ClF_{12}O_2$	$C_7ClF_{14}O_3$	$C_8ClF_{16}O_3$	$C_9ClF_{18}O_3$	$C_9ClF_{18}O_4$	$C_{10}ClF_{20}O_4$	$C_{11}ClF_{22}O_4$	$C_{11}ClF_{22}O_5$	$C_{12}ClF_{24}O_4$	$C_8F_{15}O_2$	$C_9F_{17}O_2$
Fragment Mass (Daltons/electrostatic unit)	200.9542	200.9542	200.9542	200.9542	200.9542	200.9542	200.9542	366.9395	532.9249	368.9761	418.9729
Fragment Formula	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	C_3ClF_6O	$C_6ClF_{12}O_2$	$C_9ClF_{18}O_3$	$C_7F_{15}O$	$C_8F_{17}O$
Elution Time (m)	2.6	3.2	3.5	4.0	4.2	4.7	5.2	5.4	5.6	2.35	2.91
Dwell time (s)	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Cone potential (V)	12	12	12	12	12	12	12	12	12	14	15
Collision energy (V)	10	10	10	10	10	10	10	10	10	10	11

Table 3. Semi-Quantitative Concentrations of Chloro-Perfluoro-Polyether-Carboxylate (ClPFPECA) Congeners in Sediment Samples Determined with Non-targeted Analysis Expressed in pg/g.

Carbon Length	*C8*	*C9*	*C10*	*C11*	*C11*	*C12*	*C13*	*C13*	*C14*
Formula	$C_8ClF_{14}O_4$	$C_9ClF_{16}O_5$	$C_{10}ClF_{18}O_5$	$C_{11}ClF_{20}O_5$	$C_{11}ClF_{20}O_6$	$C_{12}ClF_{22}O_6$	$C_{13}ClF_{24}O_6$	$C_{13}ClF_{24}O_9$	$C_{14}ClF_{26}O_6$
Ethyl, Propyl Groups	**0,1**	**2,0**	**1,1**	**0,2**	**3,0**	**2,1**	**1,2**	**4,0**	**0,3**
Sample ID	**Sediment Concentration as M5PFNA (by simple ratios to matrix internal standard in pg/g dry sediment)**								
PFTSD001	795	1.3 U	54.0	23.0	1.1 U	9.9	7.2 JP2	ND	29.3
PFTSD002	5,490	61.6	1,480	391	30.2	124	73.0	ND	289
PFTSD003	1,020	4.4	97.3	37.3	3.7	16.6	7.4	ND	26.0
PFTSD004	4,620	44.5	873	214	16.8	53.2	21.6	ND	71.0
PFTSD005	4,600	46.7	1,400	530	60.6	222	66.5	ND	197
PFTSD006	969	9.2	155	28.7	1.1 U	1.5 U	<LOD	ND	ND
PFTSD007	957	9.7	320	93.1	7.4	23.9	9.3	ND	24.2
PFTSD008	188	1.4 U	90.7	34.3	2.7 U	17.5	1.8	ND	4.2
PFTSD009	38.9	ND	129	72.5	8.1	44.8	<LOD	ND	3.5
PFTSD010	5,930	52.5	924	254	25.5	101	37.2	3.4	46.7 JP1
PFTSD011	4,880	42.6	1,260	372	33.1	149	50.1	ND	73.6
PFTSD012	198	1.7 U	28	9.3	<LOD	3.9	1.0 U	ND	4.9
PFTSD013	964	12.0	297	93.2	7.5	36.5	14.0	ND	44.4
PFTSD014	98.8	5.4	297	157	20.3	94.1	11.9	ND	31.5
PFTSD015	4,500	44.8	1,200	308	29.1	108	46.0	ND	101
PFTSD016	1,590	19.8	594	276	28.6	122	29.2	ND	48.8
PFTSD017	1,010	8.3	248	94.5	10.6	43.6	13.5	ND	20.8
PFTSD018	5.8	ND	12.7	7.9	ND	4.6	ND	ND	ND
PFTSD019	4.7	ND	4.7	2.1 U	ND	ND	ND	ND	ND
PFTSD020	740	6.8	206	74.5	7.6	23.7	9.1	ND	14.5
PFTSDDUP1	4,210	44.2	1,360	378	30.7	115	62.8	ND	197
PFTSDDUP2	4,490	41.9	973	264	20.5	93.0	57.3	<LOD	199
PFSDFB1	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFSDFB2	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND No peak area observed in any aliquot.

<LOD Peak area observed but value not significantly greater than process blanks at t_{crit} = 0.05.

U Less than Reporting Limit: peak area observed but not significantly greater than process blanks at t_{crit} = .01.

JP1 Sample aliquots do not meet acceptance criteria for laboratory extraction and analytical precision.

JP2 Sample repeated measures do not meet acceptance criteria for analytical precision.

References

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