The Chemours Company
Fayetteville Works
22828 NC Highway 87 W
Fayetteville, NC 28306

PFAS NON-TARGETED ANALYSIS AND METHODS INTERIM REPORT #9

Process and Non-Process Wastewater and Stormwater

Prepared by

The Chemours Company FC, LLC

Fayetteville Works

22828 NC Highway 87 W

Fayetteville, NC 28306

June 26, 2024

The Chemours Company
Fayetteville Works
22828 NC Highway 87 W
Fayetteville, NC 28306

TABLE OF CONTENTS

The Chemours Company
Fayetteville Works
22828 NC Highway 87 W
Fayetteville, NC 28306

LIST OF TABLES

ACRONYMS AND ABBREVIATIONS

Chemours	The Chemours Company FC, LLC
Facility	Chemours Fayetteville Works, North Carolina
HFPO-TA	hexafluoropropylene oxide trimer acid
LC	liquid chromatography
NMR	nuclear magnetic resonance
Orbitrap	Thermo Scientific Orbitrap Exploris 240 mass spectrometer
PFAS	per- and polyfluoroalkyl substances
PFO_6TeA	pentadecafluoro-2,4,6,8,10,12-hexaoxatetradecan-14-oic acid
RHDA	RSU/HFPO Diadduct
QToF	quadrupole time-of-flight
TFA	trifluoroacetate

The Chemours Company
Fayetteville Works
22828 NC Highway 87 W
Fayetteville, NC 28306

1 INTRODUCTION

This interim report has been prepared by The Chemours Company FC, LLC (Chemours) to provide an update on the characterization of previously unidentified per- and polyfluoroalkyl substances (PFAS) in aqueous samples collected from process wastewater, non-process wastewater (i.e., non-contact cooling water) and stormwater at the Chemours Fayetteville Works, North Carolina site (the Facility). This work is being conducted pursuant to Paragraph 11 subpart (a) in the Consent Order executed 25 February 2019 between Chemours and the North Carolina Department of Environmental Quality with the Cape Fear River Watch as intervenor. The overall purpose of this program is to identify previously unknown PFAS that may be present in samples of collected water and to develop standards and methods to facilitate the quantitative analysis of these PFAS, as described in the PFAS Non-Targeted Analysis and Methods Development Plan, Version 2 (Chemours and Geosyntec, 2019). This is the 9th interim report.

The samples assessed via the non-targeted program were divided into two categories:

- General Facility Discharge Samples - samples of stormwater, treated non-Chemours process wastewater and/or non-contact cooling water discharging to the Cape Fear River. These samples were collected at five locations; and
- Chemours Process Wastewater Samples - samples of process wastewater from Chemours manufacturing areas. These samples were collected at two locations.

Samples were analyzed by liquid chromatography (LC) coupled to high-resolution quadrupole time-of-flight (QToF) mass spectrometry (Chemours, 2020a). Potential unknown PFAS were assigned a tentative empirical formula (defined as the number of atoms present in a compound but not the arrangement of the atoms) from unidentified chromatographic peaks with a signal-to-noise level greater than six and using the atomic mass defect of fluorine as the molecular feature. An atomic mass defect refers to the phenomenon that the mass of an atom is not exactly equal to the number of subatomic particles (protons and neutrons) or the atomic mass number (except for carbon-12 by definition) due to differences in mass lost (as energy) when the atomic nucleus is formed for each isotope. Fluorine is well-known to have a negative mass defect, where the exact mass is slightly less than the mass number. When the QToF mass spectrometer is operated in the negative mode, one can select fluorine-containing features and empirical formulas using available software provided by the instrument vendor.

The analysis identified 21 potentially unknown PFAS present in General Facility Discharge samples and 250 potentially unknown PFAS present in Chemours Process Wastewater samples, with a total of 257 potential unique unknown PFAS (14 unknown PFAS were present in both types of samples). Two of the unknown PFAS were later identified as trifluoroacetic acid (TFA) and hexafluoropropylene oxide trimer acid (HFPO-TA), and not carried forward further in the non-targeted analysis program. Empirical formulas were determined for all unknown PFAS. This work represented the first part of the Initial Assessment step in the Development Plan. The second part

of the Development Plan, the Enhanced Assessment is to develop tentative molecular structures and subsequently, for the highest priority identified PFAS, develop authentic standards (i.e., synthesize samples of the compounds to facilitate traditional targeted analysis). To prioritize developing authentic standards for the most abundant unknown PFAS for each grouping of samples (General Facility Discharge and Chemours Process Wastewater), the 5 most abundant unknown PFAS from each group were advanced to the Enhanced Assessment step. As each group of 5 unknown PFAS from each group is resolved, the next group of 5 will be advanced to the Initial Assessment step. The status of the unknown PFAS in each group prior to this report is provided below; further details are provided in the references (Chemours, 2020a, 2020b, 2021a, 2021b, 2022a, 2022b, 2023a, 2023b).

The remainder of this 9th interim report consists of:

- Section 2: General Facility Discharge Samples;
- Section 3: Chemours Process Wastewater Samples;
- Section 4: Additional Next Steps; and
- Section 5: References.

2 GENERAL FACILITY DISCHARGE SAMPLES

The status of the 10 most abundant potential unknown PFAS (Table 1) in the General Facility Discharge samples prior to this report was:

- seven (GFD-1, -2, -3, -4, -5, -9 and -10) were identified as sodium or potassium adducts of acetate clusters. These are formed in the mass spectrometer source from sodium or potassium present in the sample matrix and acetate or sulfate present in the LC eluent buffer. The incorrect empirical formulas (containing fluorine) were generated by the computer algorithm used to determine empirical formulas and were mistakenly flagged as fluorinated compounds (Chemours, 2021a). These compounds are not PFAS and the proposed empirical formulas have been revised showing the absence of fluorine;
- one (GFD- 6) was identified as pentadecafluoro-2,4,6,8,10,12-hexaoxatetradecan-14-oic acid (PFO_6TeA) by comparison to a recently available commercial standard (this report);
- one (GFD-7) was identified as the sodium salt of a TFA acetate adduct. TFA is a known compound associated with the Facility; and
- one (GFD-8) was identified as R-EVE, which is a known PFAS associated with the Facility.

Of the 10 most abundant unknowns in the General Facility Discharge samples, 9 have been shown to not be PFAS or to be previously known PFAS. The tenth has been shown to be PFO_6TeA, for which an authentic standard is available.

Since the previous interim report (December 2023), the mass transitions for PFO_6TeA have been identified and the retention time in the existing Method 537 Mod Max has been estimated. From this desktop evaluation, it is not expected that other PFAS that may share the same mass transitions as PFO_6TeA will create interferences for the analysis of PFO_6TeA.Once PFO_6TeA can been adequately quantified, a method detection limit study will be conducted to establish a reporting limit and a matrix interference study will be conducted to assess the quantification of PFO_6TeA in environmental matrices related to the Facility. These items are underway at Eurofins-West Sacramento and will be reported in the next interim report (December 2024).

Additionally, Chemours has begun assessing next steps to identify the molecular structures of the third set of five most abundant potential unknown PFAS (GFD-11 through -15) in the General Facility Discharge samples. These peaks are quite small, and consequently Chemours may utilize a Thermo Scientific Orbitrap Exploris 240 mass spectrometer (Orbitrap), which may provide greater mass resolution than that of the QToF mass spectrometer employed in the initial analysis of the non-targeted samples, to investigate these peaks. Re-analysis of samples from Chemours Process Wastewater Location 16 (Monomers IXM Area combined processes) may be conducted with the Orbitrap, and the additional mass resolution of the Orbitrap may allow the identification of additional ionization fragments from GFD-11 through -15 which may aid in the proposal of potential structures for them.

3 CHEMOURS PROCESS WASTEWATER SAMPLES

The status of the 5 most abundant potential unknown PFAS in the Chemours Process Wastewater samples prior to this report was:

- one (CPWW-1) was identified as RSU/HFPO Diadduct (RHDA) by comparison to a standard purified from production samples;
- one (CPWW-2) was identified as EVE Acid, which is a known PFAS associated with the Facility;
- one (CPWW-3) was identified as a potential unknown PFAS, and a molecular structure has not yet been proposed; and
- two (CPWW-4 and -5) were identified as potential unknown PFAS, and molecular structures have been proposed.

Since the previous interim report (December 2023), RHDA has been further purified from production samples and has been shown to be an authentic standard by nuclear magnetic resonance (NMR), and mass transitions have been identified A standard solution of 32.4% purity has been provided to Eurofins-West Sacramento. As described above for PFO_6TeA, the next steps are the assessment of RHDA analysis using existing test methods (e.g., Method 537Mod Max) to assess if it can be adequately separated and accurately quantified in the presence of other Table 3+ PFAS.

Once the analysis of RHDA has been optimized in the laboratory, a method detection limit study will be conducted to establish a reporting limit and a matrix interference study will be conducted to assess the quantification of RHDA in environmental matrices related to the Facility. RHDA is a diprotic PFAS and it is expected that the analytical performance of RHDA will be similar to the other diprotic analytes in the existing 537MM method, i.e., inaccurate analysis due to interferences by the sample matrix in both groundwater and surface water. The above items are underway at Eurofins-West Sacramento and will be reported in the next interim report (December 2024).

Since the previous interim report (December 2023), a process for synthesizing the proposed structure for CPWW-4 has been identified, and synthesis has been initiated. The synthesis will be completed in the second half of 2024, and results of the comparison of the synthesized compound to the proposed structure will be reported in December 2024.

Additionally, Chemours will continue to develop a molecular structure for CPWW-3 (so that a synthetic pathway can be developed), and to develop a synthetic pathway for CPWW-5 (so that an authentic standard can be produced). Note that the synthetic pathways are challenging, and this process may take considerable time to complete given the complex structure of these compounds.

Chemours will also begin work on identifying the molecular structures of the second set of five most abundant potential unknown PFAS (CPWW-6 through -10) in the Chemours Process Wastewater samples using the Orbitrap as described in Section 2.

4 ADDITIONAL NEXT STEPS

In the first interim report (Chemours 2020a), unidentified potential PFAS with their empirical formulas were listed in order of ion abundance for each of the General Facility Discharge and Chemours Process Wastewater samples, and work began on the most abundant unidentified potential PFAS in each group of samples. One issue that will become significant as the non-targeted program proceeds is that the abundance of the unidentified potential PFAS becomes smaller, and peaks may not be large enough to undergo the fragmentation needed to further identify the unidentified potential PFAS. While the use of the new Orbitrap may allow additional identification of unidentified potential PFAS beyond those described on Section 2 and 3, Chemours plans to conduct a mass balance of a sample from Chemours Process Wastewater Location 16 (which had the highest number of unidentified potential PFAS of the locations assessed in the first interim report) by:

- conducting a targeted analysis using Method 537 Mod Max to quantify as many known PFAS as possible; and
- conducting a Total Organic Fluorine analysis via EPA Method 1621 to quantify the total mass of organic fluorine present.

Assessing the difference in the two analyses may provide insight into the mass of potential PFAS that remains unknown.

5 REFERENCES

Chemours, 2023a. PFAS Non-Targeted Analysis and Methods Interim Report #7. June 30, 2023.

Chemours, 2023b. PFAS Non-Targeted Analysis and Methods Interim Report #8. December 29, 2023

Chemours, 2022a. PFAS Non-Targeted Analysis and Methods Interim Report #5. June 30, 2022.

Chemours, 2022b. PFAS Non-Targeted Analysis and Methods Interim Report #6. December 30, 2022.

Chemours, 2021a. PFAS Non-Targeted Analysis and Methods Interim Report #3. July 30, 2021.

Chemours, 2021b. PFAS Non-Targeted Analysis and Methods Interim Report #4. December 22, 2021.

Chemours, 2020a. PFAS Non-Targeted Analysis and Methods Interim Report. June 30, 2020.

Chemours, 2020b. PFAS Non-Targeted Analysis and Methods Interim Report #2. December 31, 2020.

Chemours and Geosyntec Consultants, 2019. PFAS Non-Targeted Analysis and Methods Development Plan. Version 2. December 5, 2019.

TABLE 1
STATUS OF UNKNOWN PFAS - INTERIM REPORT #9
Chemours Fayetteville Works, North Carolina

Sample Source	Rank (by Ion Abundance in Sample Source)	Mass (Da)	Mass to Charge Ratio (m/z)	Empirical Formula		Proposed Molecular Structure	Next Step For Identification of Unknown
				Tentative	Revised		
General Facility Discharge	GFD-1	142.0241	141.0168	$C_4H_5F_3O_2$*	$C_4H_7O_4Na$	Structures identified as sodium or potassium adducts of acetate clusters; these are formed in the MS source from sodium or potassium present in the sample matrix and acetate from the LC eluent buffer. Compounds are not PFAS.	None
	GFD-2	157.9983	156.9910	$C_4H_2F_4O_2$*	$C_4H_6O_4K$		
	GFD-3	224.0272	223.0199	$C_6H_6F_6O_2$*	$C_6H_{10}O_6Na_2$		
	GFD-4	306.0302	305.0230	$C_8H_7F_9O_2$*	$C_8H_{13}O_8Na_3$		
	GFD-5	388.0331	387.0258	$C_{10}H_8F_{12}O_2$*	$C_{10}H_{16}O_{10}Na_4$		
	GFD-6	509.9432	508.9357	$C_8HF_{15}O_8$	--	Structure identified as pentadecafluoro-2,4,6,8,12-hexaoxatetradecan-14-oic acid by comparison to authentic standard.	None
	GFD-7	195.9956	194.9884	$C_4H_2F_6O_2$*	$C_4H_4F_3O_4Na$	Structure identified as sodium salt of TFA and acetate adduct. Correct formula is $C_4H_4F_3O_4Na$	None
	GFD-8	407.9670	406.9596	$C_8HF_{13}O_4$	--	Identified as R-EVE	None
	GFD-9	283.9544	282.9471	$C_4HF_9O_2S$*	$C_4H_7SO_8Na_3$	Structure identified as sodium salt of sulfuric acid and acetate dimer adduct. Correct formula is $C_4H_7SO_8Na_3$. This compound is not a PFAS.	None
	GFD-10	240.0010	238.9937	$C_6H_3F_7O_2$*	$C_6H_{10}O_6NaK$	Structure identified as sodium and potassium salt of acetate dimer. Correct formula is $C_6H_{10}O_6NaK$. This compound is not a PFAS.	None
Chemours Process Wastewater	CPWW-1	507.9302	506.9229	$C_8H_2F_{14}O_7S$	--	Structure identified as a production intermediate, RSU/HFPO Diadduct, by comparison to authentic standard.	None
	CPWW-2	407.9670	406.9598	$C_8HF_{13}O_4$	--	Identified as EVE Acid	None
	CPWW-3	475.9587	474.9515	$C_8H_5F_{13}O_6S$	--	No proposed molecular structure yet	Re-analyze sample using Orbitrap Exploris 240 to see if structure can be proposed.
	CPWW-4	471.9630	470.9556	$C_9H_2F_{14}O_6$	--	HOOC-CF_2-CF_2-O-$CF(CF_3)$-CF_2-O-$CF(CF_3)$-COOH	Synthesis of an authentic standard is underway.
	CPWW-5	345.9693	344.9620	$C_6HF_{11}O_4$	--	CF_3-O-CF_2-O-CF_2-CF_2-CF_2-COOH	Synthesis of an authentic standard is under consideration.

Notes:

* - tentative empirical formula has been revised following further investigation
-- - revised empirical formula not required
adduct - a product of a direct addition of two or more distinct molecules resulting in a single reaction product containing all atoms of all components
- further investigation into identification of unknown not required

C - carbon
Da - dalton
F - fluorine
H - hydrogen
LC - liquid chromatograph
MS - mass spectrometer
O - oxygen
PFAS - per- and polyfluoroalkyl substances
S - sulfur