The Chemours Company
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PFAS NON-TARGETED ANALYSIS AND METHODS INTERIM REPORT #7

Process and Non-Process Wastewater and Stormwater

Prepared by

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ACRONYMS AND ABBREVIATIONS

Chemours	The Chemours Company FC, LLC
Facility	Chemours Fayetteville Works, North Carolina
LC	liquid chromatography
PFAS	per- and polyfluoroalkyl substances
QToF	quadrupole time-of-flight
TFA	trifluoroacetate

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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 seventh interim report.

First Interim Report - Summary

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). 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) as a result of 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 tentative empirical formulas of the five most abundant unknown PFAS in each sample category were:

- General Facility Discharge Samples - $C_4H_5F_3O_2$, $C_4H_2F_4O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$; and

- Chemours Process Wastewater Samples - $C_8H_2F_{14}O_7S$, $C_8HF_{13}O_4$, $C_8H_5F_{13}O_6S$, $C_9H_2F_{14}O_6$ and $C_6HF_{11}O_4$.

None of the identified five potential PFAS in the General Facility Discharge samples were represented in the five potential PFAS in the Chemours Process Wastewater samples. These ten (10) unknown PFAS were advanced to the next step in the program - identifying molecular structures (defined as the arrangement of the atoms into a molecule).

Second Interim Report - Summary

General Facility Discharge Samples

Investigation into the five most abundant unknown PFAS in the General Facility Discharge samples revealed that four ($C_4H_5F_3O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$) coeluted from the LC (Chemours, 2020b). These compounds have different molecular weights and were therefore expected to be chromatographically resolved. Examination of the empirical formulas showed that the four compounds are related by C_2HF_3, that is, the addition of C_2HF_3 (trifluoroethylene, which is a potential impurity in tetrafluoroethylene, a feedstock at the Facility) to each compound generates the empirical formula of the following compound. This suggested that these four compounds may represent a single compound, $C_4H_5F_3O_2$, which, upon elution from the LC, undergoes adduction[1] of C_2HF_3 in the ion source of the mass spectrometer. Furthermore, the single compound $C_4H_5F_3O_2$ itself could be generated from a reaction between C_2HF_3 and acetate (CH_3COO^-, present in the LC eluent) in the ion source of the mass spectrometer. The fifth unknown PFAS, $C_4H_2F_4O_2$, was not present in the samples at high enough concentrations to analyze by the QToF mass spectrometer.

Chemours Process Wastewater Samples

Investigation into the five most abundant unknown PFAS in the Chemours Process Wastewater samples concluded:

- $C_8H_2F_{14}O_7S$ - the molecular structure was determined to be CF_3-CF(COOH)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H;
- $C_8HF_{13}O_4$ - a molecular structure was tentatively identified for this unknown PFAS, however, background interference in the samples had to date interfered with confirmation of the tentatively identified structure;
- $C_8H_5F_{13}O_6S$ - the molecular structure was determined to be HO_3S-CF_2-CF_2-O-CF(CF_3)-CF_2-O-CHF-CF_2-OCH_3;
- $C_9H_2F_{14}O_6$ - the molecular structure was tentatively determined to be HOOC-CF_2-CF_2-O-CF(CF_3)-CF_2-O-CF(CF_3)-COOH; and

[1] Adduction is the process of the direct addition of two or more distinct molecules that results in a single reaction product referred to as an adduct which contains all atoms of the initial reaction molecules.

- $C_6HF_{11}O_4$ - a molecular structure was not yet identified; background contamination in the samples had to date interfered with confirmation of a tentatively identified molecular structure.

Third Interim Report - Summary

General Facility Discharge Samples

The five most abundant unknown "PFAS" were identified to be sodium or potassium adducts of acetate clusters. They do not contain fluorine and are consequently not PFAS (Chemours, 2021a). They were therefore eliminated from the list of unknown PFAS in the General Facility Discharge samples.

Chemours Process Wastewater Samples

For the three remaining unidentified PFAS (of the five most abundant unknown PFAS):

- $C_8HF_{13}O_4$ - identified as EVE Acid, and was therefore no longer unknown;
- $C_8H_5F_{13}O_6S$ - the tentatively identified molecular structure was found to not match an existing authentic standard, and therefore another molecular structure needs to be proposed; and
- $C_6HF_{11}O_4$ - tentatively identified as CF_3-O-CF_2-O-CF_2-CF_2-CF_2-COOH.

Fourth Interim Report - Summary

General Facility Discharge Samples

Because the first set of five most abundant unknown "PFAS" turned out to be non-PFAS, the second set of five most abundant unknown PFAS in the General Facility Discharge samples was advanced and identification of their molecular structures was begun (Chemours, 2021b). In order of relative abundance, this resulted in the following:

- $C_8HF_{15}O_8$ was no longer detected in the original samples and, therefore, could not be further investigated. A new sample from the same location, Location 42 (Figure 1), was proposed for collection during a rain event to investigate the presence and temporal stability of this compound;
- $C_4H_2F_6O_2$ was identified as the sodium salt of a trifluoroacetate (TFA) and acetate adduct. The correct formula was identified as $C_4H_4F_3O_4Na$;
- $C_8HF_{13}O_4$ was identified as R-EVE;
- $C_4HF_9O_2S$ was identified as the sodium salt of sulfuric acid and acetate dimer adduct. The correct formula was identified as $C_4H_7SO_8Na_3$. This compound is not a PFAS; and
- $C_6H_3F_7O_2$ was identified as the sodium and potassium salt of an acetate dimer. The correct formula was identified as $C_6H_{10}O_6NaK$. This compound is not a PFAS.

Chemours Process Wastewater Samples

Of the five most abundant unknown PFAS, there was one remaining unidentified PFAS, $C_8H_5F_{13}O_6S$, for which the molecular structure identified was found to not match an existing authentic standard (Interim Report 3). A tentatively identified molecular structure for this unidentified PFAS continued to be in development.

Fifth Interim Report - Summary

General Facility Discharge Samples

A new sample was collected from Location 42 on March 17, 2022 during a rain event and analyzed (Chemours, 2022a). Initial analysis of the sample again showed that the peak (with a retention time of approximately 12.3 minutes) was not present. The sample was concentrated 100-fold using solid-phase extraction (SPE) and re-analyzed. The peak corresponding to the unknown PFAS was then observed. Further analysis of the sample by tandem mass spectrometry resulted in the proposal of the following molecular structure for $C_8HF_{15}O_8$:

- CF_3-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-COOH

Chemours Process Wastewater Samples

One unknown PFAS ($C_8H_5F_{13}O_6S$) had a previously tentatively identified molecular structure, which was found to be incorrect upon comparison to an existing authentic standard. A revised tentatively identified molecular structure was in development.

Sixth Interim Report - Summary

General Facility Discharge Samples

Since the issue of the fifth interim report, the structure proposed for $C_8HF_{15}O_8$ became commercially available (Fluoryx Labs (Carson City, NV); catalog number FC23-PFO6TeANa). The standard was purchased by Chemours with the intent to assess the peak corresponding to $C_8HF_{15}O_8$ in General Facility Discharge samples against this standard (Chemours, 2022b).

Chemours Process Wastewater Samples

The most abundant unknown PFAS in the Chemours Process Wastewater samples ($C_8H_2F_{14}O_7S$; proposed structure CF_3-CF(COOH)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H) was recognized as potentially being an intermediate product in one of the production processes at the Facility.

Two routes were proposed to confirm this:

- The development of a synthetic pathway. This is challenging, and may take considerable time to complete given the complex structure of the compound;

- Isolation of the intermediate product from production samples so that it can be further compared to the unknown PFAS.

Seventh Interim Report (this report)

This seventh interim report provides an update on the identification of $C_8HF_{15}O_8$ (from the General Facility Discharge samples) and $C_8H_2F_{14}O_7S$ (from the Chemours Process Wastewater samples)

The remainder of this seventh interim report consists of:

- Section 2: Investigation of the Second Set of Five Most Abundant Unknown PFAS in General Facility Discharge Samples
- Section 3: Investigation of the Five Most Abundant Unknown PFAS in Chemours Process Wastewater Samples; and
- Section 4: Summary and Next Steps.

2 INVESTIGATION OF THE SECOND SET OF FIVE MOST ABUNDANT UNKNOWN PFAS IN GENERAL FACILITY DISCHARGE SAMPLES

The commercial standard corresponding to the proposed structure for $C_8HF_{15}O_8$ (CF_3-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-COOH) was purchased by Chemours. During the current reporting period, this standard was purified by Chemours so that accurate assessment of the $C_8HF_{15}O_8$ peak can be undertaken.

The current status of the second set of five most abundant PFAS in the General Facility Discharge samples (as well as of the first set of five most abundant PFAS) is summarized in Table 1.

3 INVESTIGATION OF THE FIVE MOST ABUNDANT UNKNOWN PFAS IN CHEMOURS PROCESS WASTEWATER SAMPLES

The proposed structure for $C_8H_2F_{14}O_7S$ (CF_3-CF(COOH)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H) was identified as potentially being present in one of the production processes at the Facility. Samples from the production process were obtained from the Facility and the peak corresponding to $C_8H_2F_{14}O_7S$ was purified by Chemours so that accurate assessment of the $C_8H_2F_{14}O_7S$ peak can be undertaken.

The current status of the five most abundant PFAS in the Chemours Process Wastewater samples is summarized in Table 1.

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4 SUMMARY AND NEXT STEPS

A summary of results to date and the next steps for the potential unknown PFAS in General Facility Discharge and Chemours Process Wastewater samples is provided below and in Table 1.

In the General Facility Discharge samples, the 10 most abundant unknown "PFAS" have been identified:

- seven 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 was identified as the sodium salt of a TFA acetate adduct;
- one was identified as R-EVE, which is a known PFAS associated with the Facility; and
- one ($C_8HF_{15}O_8$) has a proposed molecular structure, and a commercial standard for the proposed molecular structure is available. The commercial standard has been purchased by Chemours and has undergone purification by Chemours so that accurate assessment of the $C_8HF_{15}O_8$ peak can be undertaken.

The next step for the General Facility Discharge samples will be to compare the retention times and mass spectra of the $C_8HF_{15}O_8$ to the commercial standard to see if the proposed molecular structure for $C_8HF_{15}O_8$ can be confirmed.

In the Chemours Process Wastewater samples, the five most abundant unknown PFAS have been identified:

- one was identified as EVE Acid, which is a known PFAS associated with the Facility;
- one ($C_8H_2F_{14}O_7S$) was identified as potentially being present in one of the production processes at the Facility. Samples from the production process have been obtained from the Facility and have been purified to isolate the production PFAS at sufficient purity that it can be used as a standard;
- two were identified as unknown PFAS, and molecular structures have been proposed; and
- one was identified as an unknown PFAS, and a molecular structure has not yet been proposed.

The next step for the Chemours Process Wastewater samples will be to compare the retention times and mass spectra of the $C_8H_2F_{14}O_7S$ to the purified production PFAS to see if the proposed molecular structure for $C_8H_2F_{14}O_7S$ can be confirmed.

5 REFERENCES

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.

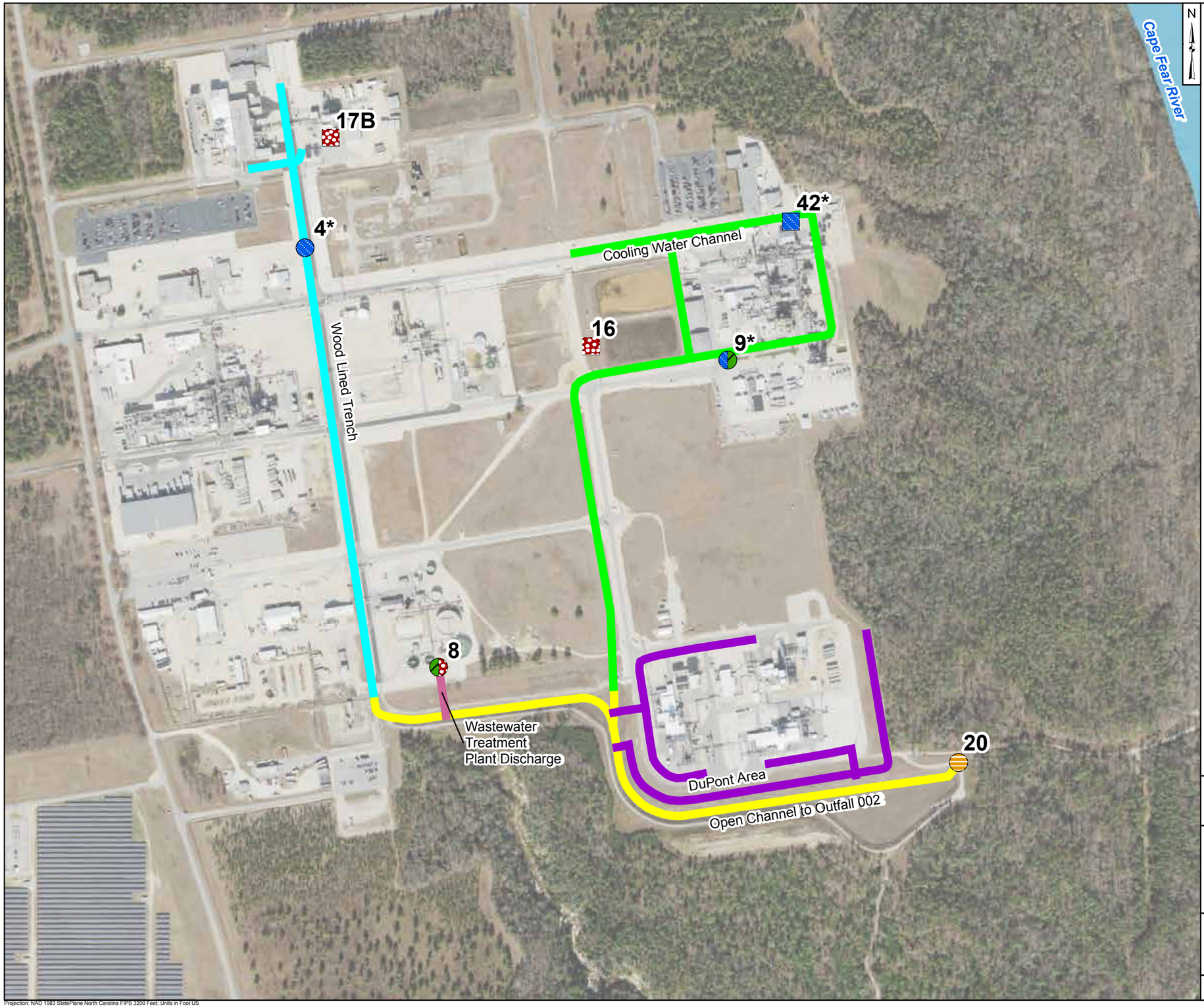
TABLE 1
STATUS OF UNKNOWN PFAS - INTERIM REPORT #7
Chemours Fayetteville Works, North Carolina

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	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
	157.9983	156.9910	$C_4H_2F_4O_2$*	$C_4H_6O_4K$		
	224.0272	223.0199	$C_6H_6F_6O_2$*	$C_6H_{10}O_6Na_2$		
	306.0302	305.0230	$C_8H_7F_9O_2$*	$C_8H_{13}O_8Na_3$		
	388.0331	387.0258	$C_{10}H_8F_{12}O_2$*	$C_{10}H_{16}O_{10}Na_4$		
	509.9432	508.9357	$C_8HF_{15}O_8$	--	CF_3-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-O-CF_2-COOH	Authentic standard now commercially available (Fluoryx Labs; catalog number FC23-PFO6TeANa) and has been purchased and purified. General Facility Discharge sample will be assessed against the purified standard.
	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
	407.9670	406.9596	$C_8HF_{13}O_4$	--	Identified as R-EVE	None
	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
	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	507.9302	506.9229	$C_8H_2F_{14}O_7S$	--	CF_3-CF(COOH)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H	May be present in a production process at the Facility. Has been purified from production process samples. Chemours Process Wastewater sample will be assessed against the purified standard.
	407.9670	406.9598	$C_8HF_{13}O_4$	--	Identified as EVE Acid	None
	475.9587	474.9515	$C_8H_5F_{13}O_6S$	--	No proposed molecular structure yet	Continue to develop a proposed molecular structure.
	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 under consideration.
	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 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



Projection: NAD 1983 StatePlane North Carolina FIPS 3200 Feet; Units in Foot US

Legend

Temporal Composite Sample

Grab Sample

Sample Location Category

Outfall 002

Process wastewater

Non-process wastewater

Stormwater

Ditch Types

Wood Lined Trench

Wastewater Treatment Plant Discharge

Cooling Water Channel

Open Channel to Outfall 002

DuPont Area

Notes:
*- Locations 4, 9, and 42 are collected during rain events only.

Sample numbers 4, 8, 9, 16, 17B and 20 correspond to locations identified in the May 2019 PFAS Characterization Plan. Sample number 42 corresponds to the location identified in the September 2019 Stormwater Grab Sampling Workplan.

500 250 0 500 Feet

Paragraph 11(a) Non-Targeted Analysis Sample Locations

Chemours Fayetteville Works, North Carolina

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Figure 1

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