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PFAS NON-TARGETED ANALYSIS AND METHODS INTERIM REPORT #2

Process and Non-Process Wastewater and Stormwater

Prepared by

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ACRONYMS AND ABBREVIATIONS

CFRW – Cape Fear River Watch

DEQ – Department of Environmental Quality

LC – liquid chromatograph

MS-MS – tandem mass spectrometry

NCCW – non-contact cooling water

PFAS – per- and polyfluoroalkyl substances

Q-TOF-MS – quadrupole time of flight mass spectrometry

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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 [NCCW]) and stormwater at the Chemours Fayetteville Works, North Carolina site (the Facility; Figure 1). 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 (DEQ) with the Cape Fear River Watch (CFRW) 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 (the Development Plan; Chemours and Geosyntec, 2019) and the June 30, 2020 PFAS Non-Targeted Analysis and Methods Interim Report (Chemours, June 2020). This is the second interim report for the program.

In the first interim report (Chemours, June 2020), the 5 most abundant unknown PFAS from General Facility Discharge samples (samples of stormwater, treated non-Chemours process wastewater and/or non-contact cooling water discharging to the Cape Fear River) and in Chemours Process Wastewater samples (samples of process wastewater from Chemours manufacturing areas) were proposed to be advanced to the next step in the program (identifying molecular structures). This second interim report provides an update on this step.

The 5 most abundant unknown PFAS in the General Facility Discharge samples were identified as:

- $C_4H_5F_3O_2$
- $C_4H_2F_4O_2$
- $C_6H_6F_6O_2$
- $C_8H_7F_9O_2$
- $C_{10}H_8F_{12}O_2$

The 5 most abundant unknown PFAS in the Chemours Process Wastewater samples were identified as:

- $C_8H_2F_{14}O_7S$
- $C_8HF_{13}O_4$
- $C_8H_5F_{13}O_6S$
- $C_9H_2F_{14}O_6$
- $C_6HF_{11}O_4$

Of note, none of the identified 5 potential PFAS compounds in the General Facility Discharge samples were represented in the 5 potential PFAS compounds in the Chemours Process Wastewater samples.

The remainder of this report consists of:

- Section 2: Methods;
- Section 3: Results; and
- Section 4: Discussion and Next Steps.

2 METHODS

2.1 Sample Collection

Samples were collected from 7 locations (Figure 2). Five sampling locations (Locations 4, 8, 9, 20 and 42) represent a combination of stormwater, treated non-Chemours process wastewater and/or non-contact cooling water. Two locations (16 and 17B) represent Chemours process wastewater. Some locations were sampled more than once; a total of 18 samples were collected. Samples were collected according to the methods outlined in the May 2019 PFAS Characterization Sampling Plan (Geosyntec, 2019) along with modifications to the sampling program to collect stormwater samples as outlined in Version 2 of the *PFAS Non-Targeted Analysis and Method Development Plan* (Chemours, 2019). Samples from locations 4, 9 and 42 were stormwater samples, and were collected during rain events.

2.2 Sample Preparation and Analysis

Samples were prepared for non-targeted analysis by filtration through a 0.2-micrometer filter and were not diluted. Following filtration, the samples were injected directly into the analytical instrument for analysis by liquid chromatography followed by Q-TOF-MS (Agilent). Structural information was deduced by fragmenting ions via tandem mass spectrometry. Candidate structures that fit the fragmentation requirements for a particular unknown PFAS were then constructed.

3 RESULTS

3.1 General Facility Discharge Samples

Investigation into the 5 potential PFAS compounds in the General Facility Discharge samples showed that 4 of the compounds ($C_4H_5F_3O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$) coeluted from the liquid chromatograph (LC). This result was not expected. These compounds as previously identified would have different chain lengths and were therefore expected to be chromatographically resolved. Examination of the empirical formulas shows that the four

compounds are related by the fragment C_2HF_3, that is, the addition of that fragment to each compound generates the empirical formula of the following compound. Taken together, this information suggests that these 4 compounds may represent a single compound, $C_4H_5F_3O_2$, eluting from the LC which undergoes adduction[1] of the C_2HF_3 fragment during the tandem mass spectrometry (MS-MS) step. The $C_4H_5F_3O_2$ itself may be generated from a reaction between C_2HF_3 and acetate (present in the LC eluent) in the MS.

A structure for the single compound ($C_4H_5F_3O_2$) has not yet been identified.

The fifth unknown PFAS in the General Facility Discharge samples, $C_4H_2F_4O_2$, was not present in the samples at high enough concentrations to analyze by MS-MS.

3.2 Chemours Process Wastewater Samples

Investigation into the 5 potential PFAS compounds in the Chemours Process Wastewater samples identified the following:

- $C_8H_2F_{14}O_7S$ - the following structure has been determined for this unknown PFAS:
  - CF_3-CF(COOH)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H
- $C_8HF_{13}O_4$ - a structure has been tentatively identified for this unknown PFAS, however, background contamination in the samples has to date interfered with confirmation of the tentatively identified structure
- $C_8H_5F_{13}O_6S$ - the following structure has been determined for this unknown PFAS:
  - 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 following structure has been tentatively determined for this unknown PFAS:
  - HOOC-CF_2-CF_2-O-CF(CF_3)-CF_2-O-CF(CF_3)-COOH
- $C_6HF_{11}O_4$ - a structure has not yet been identified for this unknown PFAS. Background contamination in the samples has to date interfered with confirmation of the tentatively identified structure.

These results are summarized in Table 1.

4 DISCUSSION AND NEXT STEPS

The second part of the Development Plan, the Enhanced Assessment, calls for the development of tentative molecular structures and subsequent development of authentic standards (i.e. synthesis of samples of the compounds to facilitate traditional targeted analysis) for the highest priority non-targeted PFAS identified. A summary of the next steps for each of the 10 potential PFAS compounds discussed in this interim report is provided below and in Table 1.

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

4.1 General Facility Discharge Samples

The 4 compounds that co-eluted in this assessment will be further investigated to understand the relationship between them. Planned investigations are:

- assessment of the presence of C_2HF_3 in the samples. The presence of C_2HF_3 would support the hypothesis that this group of four compounds represents only 1 compound;
- addition of C_2HF_3 to PFAS-free water to see if $C_4H_5F_3O_2$, $C_6H_6F_6O_2$, $C_8H_7F_9O_2$ and $C_{10}H_8F_{12}O_2$ are produced;
- perform the analysis using formate (a one-carbon molecule) instead of acetate (a two-carbon molecule) in the LC eluting solution. As noted above, $C_4H_5F_3O_2$ may be generated from a reaction between C_2HF_3 and acetate in the eluent. This hypothesis would be supported if $C_4H_5F_3O_2$ is not observed when formate is substituted for acetate.

The fifth compound in the General Facility Discharge samples, $C_4H_2F_4O_2$, could not be further investigated because it was not present in the samples at high enough concentrations to analyze by MS-MS. Alternative sample preparation methods that can concentrate analytes will be investigated in order to prepare samples with sufficient concentration of this compound to undergo MS-MS analysis.

4.2 Chemours Process Wastewater Samples

Authentic standard synthesis will be initiated for the 3 compounds for which structures have been identified ($C_8H_2F_{14}O_7S$ and $C_9H_2F_{14}O_6$) or tentatively identified ($C_8H_5F_{13}O_6S$). Because contamination interfered with the analysis of the remaining 2 compounds ($C_8HF_{13}O_4$ and $C_6HF_{11}O_4$), sample cleanup will be initiated so that their structures may be identified.

5 REFERENCES

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

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

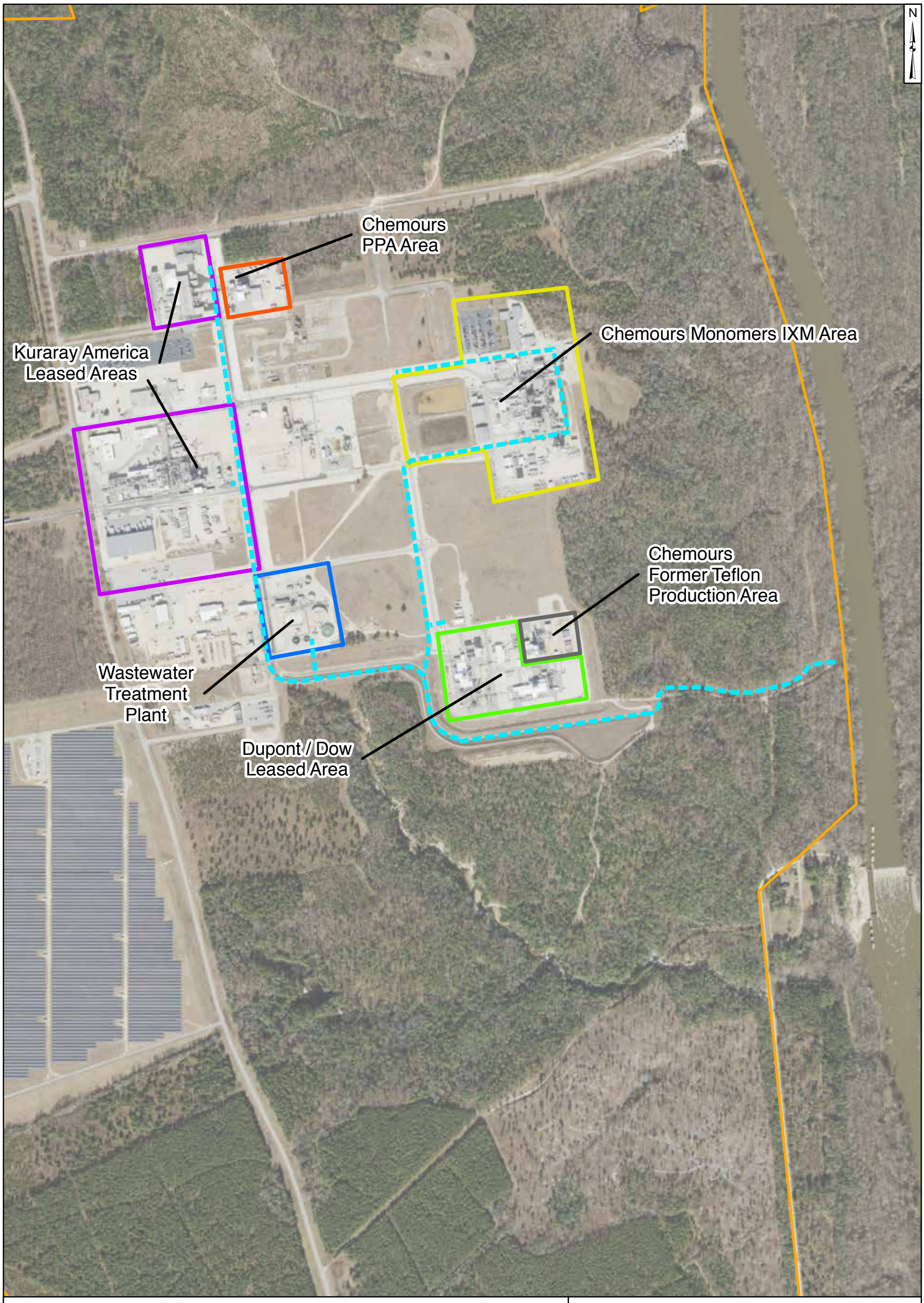
Geosyntec Consultants, 2019. PFAS Characterization Sampling Plan. Chemours Fayetteville Works. May 1, 2019.

TABLE 1
INTERIM REPORT #2 - STATUS OF 10 UNKNOWN PFAS
Chemours Fayetteville Works, North Carolina

Sample Source	Empirical Formula	Mass (amu)	Mass to Charge Ratio (m/z)	Identified Structure	Next Steps
General Facility Discharge	$C_4H_5F_3O_2$	142.0241	141.0168	Structure not yet identified	Conduct experiments to see if this is a reaction product of C_2HF_3 and acetate
	$C_4H_2F_4O_2$	157.9983	156.9910	Structure not yet identified	Concentrate sample to obtain enough of this unknown to conduct MS-MS
	$C_6H_6F_6O_2$	224.0272	223.0199	Structure not yet identified	Conduct experiments to see if this is an adduct of $C_4H_5F_3O_2$ and C_2HF_3
	$C_8H_7F_9O_2$	306.0302	305.0230	Structure not yet identified	Conduct experiments to see if this is an adduct of $C_4H_5F_3O_2$ and $(C_2HF_3)_2$
	$C_{10}H_8F_{12}O_2$	388.0331	387.0258	Structure not yet identified	Conduct experiments to see if this is an adduct of $C_4H_5F_3O_2$ and $(C_2HF_3)_3$
Chemours Process Wastewater	$C_8H_2F_{14}O_7S$	507.9302	506.9229	CF_3-CF(COOH)-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H	Initiate synthesis of authentic standard
	$C_8HF_{13}O_4$	407.9670	406.9598	Structure tentatively identified	Clean up background contamination to aid in structure identification
	$C_8H_5F_{13}O_6S$	475.9587	474.9515	Structure tentatively identified as: HO_3S-CF_2-CF_2-O-CF(CF_3)-CF_2-O-CHF-CF_2-OCH_3	Initiate synthesis of authentic standard
	$C_9H_2F_{14}O_6$	471.9630	470.9556	HOOC-CF_2-CF_2-O-CF(CF_3)-CF_2-O-CF(CF_3)-COOH	Initiate synthesis of authentic standard
	$C_6HF_{11}O_4$	345.9693	344.9620	Structure not yet identified	Clean up background contamination to aid in structure identification

Notes:

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
amu - atomic mass units
C - carbon
F - fluorine
H - hydrogen
O - oxygen
PFAS - per- and polyfluoroalkyl substances
S - sulfur



Legend

- Drainage Network
- Site Boundary

Areas at Site

- Chemours Monomers IXM Area
- Chemours PPA Area
- Dupont / Dow Leased Area
- Chemours Former Teflon Production Area
- Kuraray America Leased Area
- Wastewater Treatment Plant

Notes:
Basemap Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

750 375 0 750 Feet

Site Location

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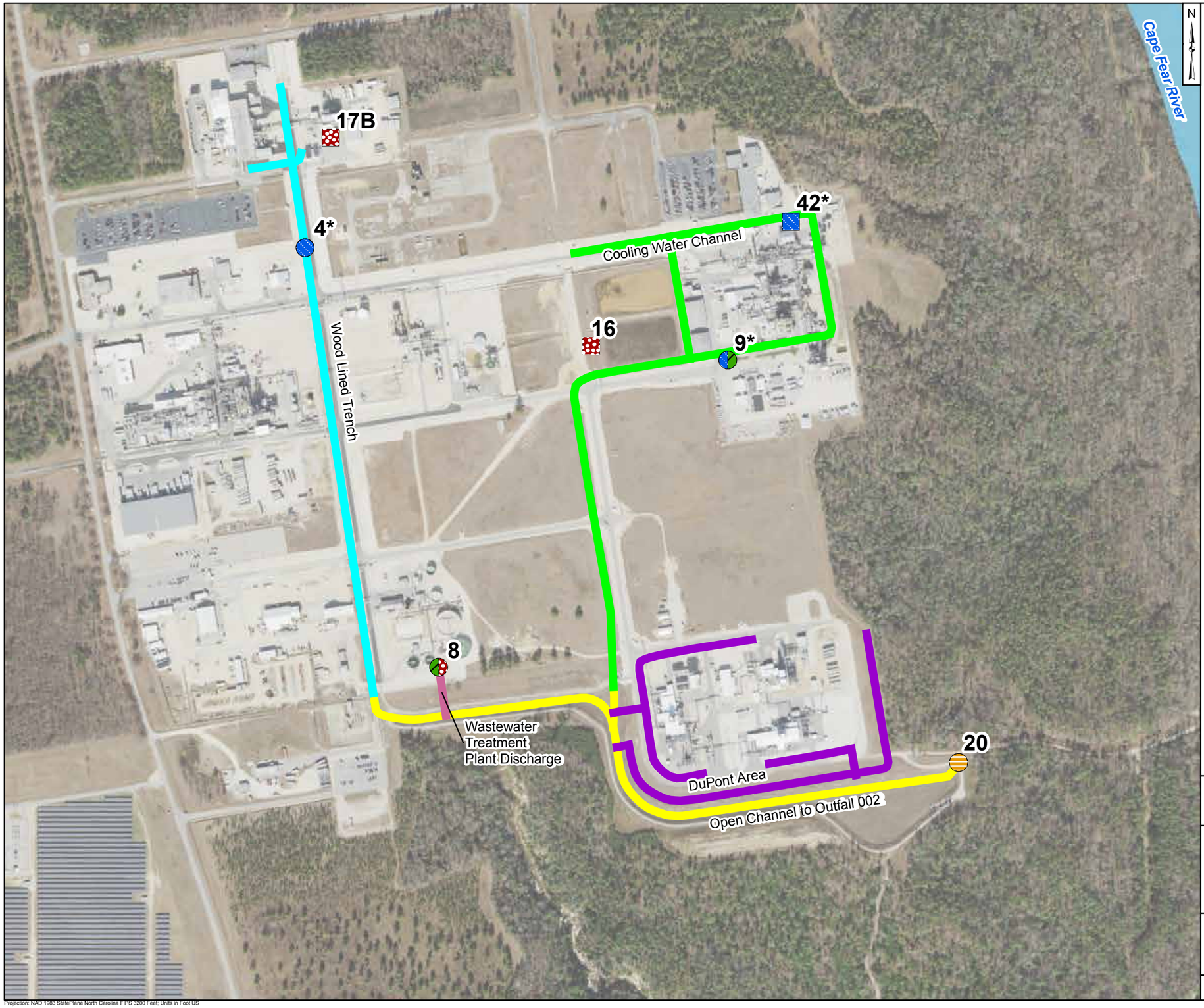
Figure

1



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

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Figure 2