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Fayetteville Works
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PFAS NON-TARGETED ANALYSIS AND METHODS DEVELOPMENT PLAN

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

NCCW – non-contact cooling water

ng/L – nanograms per liter

PFAS – per- and polyfluoroalkyl substances

PPA – polymer processing aid

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

SPE – solid phase extraction

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1 INTRODUCTION

This plan (the Plan) has been prepared by The Chemours Company FC, LLC (Chemours) and Geosyntec Consultants of NC, P.C. (Geosyntec) to provide information to support the characterization of additional per- and polyfluoroalkyl substances (PFAS) in aqueous samples collected from process and 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 Plan identifies the locations for samples to be collected, a schedule, and describes the approach that will be used to identify PFAS compounds. The analytical approach selected for screening the aqueous samples collected is referred to as a non-targeted analysis and this is described more below in Section 1.1. For any new PFAS identified through the non-targeted analysis Chemours plans to develop a schedule for developing test methods and laboratory standards.

This Plan is intended to address requirements specified in Paragraph 11 subpart (a) in the proposed Consent Order dated 21 November 2018 between Chemours and the North Carolina Department of Environmental Quality (DEQ) with the Cape Fear River Watch (CFRW) as intervenor. Other parts of the Consent Order will be addressed separately by Chemours. Aside from collection of samples for non-targeted analysis, at present Chemours plans to perform all other effort and reporting described in this Plan. This Plan was prepared under the direction of Dr. Lam Leung, an analytical chemist, of The Chemours Company. The purpose of the work described in this Plan is to identify previously unidentified (i.e. additional) PFAS that may be present in water and develop standards and methods to facilitate the quantitative analysis of these PFAS.

1.1 Non-Targeted Analytical Background

Non-targeted analysis for PFAS will be conducted using liquid chromatography coupled to high resolution quadrupole time of flight mass spectrometry (Q-TOF-MS). Q-TOF-MS accurately measures the mass to charge ratio of unknown analytes (i.e. candidates) facilitating the determination of their chemical formulas. Relevant structural information can be interpreted by fragmenting ions via tandem mass spectrometry, where candidates that do not fit the fragmentation requirements for a particular structure are eliminated so that the tentative structure for the molecule can be assigned. After tentative identification, the structural identity of an analyte can be further assessed by comparing the analyte's chromatographic retention time and mass spectrometry fragmentation patterns to those of an authentic standard.

1.2 Scope and Rationale

This Plan addresses requirements in Paragraph 11 subpart (a) as listed in the proposed Consent Order. Chemours plans to begin sample collection within thirty days of DEQ approval of this Plan. In parallel to this non-targeted work, samples will also be collected and analyzed for PFAS using existing laboratory methods as part of the Initial Characterization program described in the December 2018 Sampling Plan (Geosyntec, 2018). Non-targeted analysis will commence with

sample preparation by filtration, direct injection, or solid phase extraction (SPE) procedures, followed by analysis by liquid chromatography coupled to Q-TOF-MS. Initial assessment will be conducted for all additional PFAS, to determine each analyte's empirical formula and identify candidate molecular structures. Enhanced assessment will be conducted on a prioritized set of the highest abundance additional PFAS, using authentic standards for confirmation of the analyte's structural identity. Test methods will then be developed for these analytes according to EPA's Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater under EPA's Alternate Test Procedure Program (EPA, 2016). Chemours plans to prepare a report documenting the findings of the non-targeted analysis and development of laboratory standards and test methods and plans to submit this report to the DEQ by June 30, 2020.

2 SAMPLING PLAN

2.1 Sampling Locations

Aqueous samples will be collected during the non-targeted sampling events at locations shown on Figure 2 and listed in Table 1. The six identified sample locations (4, 8, 15, 16, 17, and 20) are a subset of those proposed in the December 2018 Sampling Plan (Geosyntec, 2018). These locations include water from process wastewater streams, non-process wastewater, and stormwater.

Process wastewater streams at the Chemours Monomers IXM Area (location 16) may vary temporally based on campaigns being run at different times, therefore samples at this location will be collected on a bimonthly basis for one year, concurrent with the Initial Characterization sampling events outlined in the December 2018 Sampling Plan (Geosyntec, 2018). All other non-targeted samples will be collected one time during the first sampling event, because they are not expected to show significant temporal variation.

Process wastewater at the Chemours PPA Area (location 17) is pumped in a closed loop directly into trailers within secondary containment. The sample collection point for this PPA will be determined at a later date, but is expected to be a grab sample from each of the waste trailer tanks.

2.2 Sampling Schedule

The proposed sampling, analysis, evaluation and reporting schedule is provided in a Gantt Chart (Figure 3).

2.3 Sampling Procedures

Samples will be collected as part of the Initial Characterization sampling for the December 2018 Sampling Plan (Geosyntec, 2018). Samples will be collected according to the same procedures outlined in the December 2018 Sampling Plan, including field parameter monitoring, decontamination procedures, and documentation. Sample collection procedures for non-targeted analysis are summarized in Table 2.

2.4 Sample Shipping and Chain of Custody

Samples will be shipped under chain of custody in the same manner as described in the December 2018 Sampling Plan (Geosyntec, 2018). Coolers with samples for non-targeted analysis will be shipped to the following address:

The Chemours Company
Attn: Lam Leung
Experimental Station 402/5323
200 Powder Mill Road
Wilmington, DE 19803
USA

2.5 Quality Assurance/ Quality Control

A field duplicate will be collected at each sampling location shown on Figure 2 and listed in Table 1. The duplicates will be archived for potential future analysis to confirm analyte identities after compound identification described below in Section 3.3.

3 NON-TARGETED LABORATORY ANALYSIS

3.1 Sample Preparation

Preparation of water samples for non-targeted PFAS analysis may be accomplished by filtration, direct injection, or SPE procedures. Direct injection will be conducted first, and SPE will be used if enhanced sensitivity is required. SPE is widely used to extract, clean up, and concentrate complex water samples for detection of PFAS at nanogram per liter (ng/L) levels (Nakayama et al., 2010). Various SPE sorbent materials will be evaluated to optimize the SPE extraction efficiency in the water samples.

3.2 Instrumental Analysis

3.2.1 Liquid Chromatography

All analytes in extracted samples will be separated by liquid chromatography. Liquid chromatography enables separation of analytes in complex sample matrices based on their relative affinity for the solid phase and liquid phase of the chromatographic column, significantly improving selectivity and sensitivity when coupled to mass spectrometry. Chromatographic conditions and column materials will be optimized to further improve the current detection methodology.

3.2.2 Quadrupole Time of Flight Mass Spectrometry

Following separation by liquid chromatography, the mass to charge ratio of individual analytes will be determined by Q-TOF-MS: samples are ionized, then analytes pass through a series of quadrupoles that select for one mass to charge ratio at a time. Analytes then undergo further focusing in a time of flight chamber, so that ions of different mass to charge ratios reach the detector at different times.

3.3 Compound Identification

All detectable additional PFAS will be tentatively identified through an initial assessment. The molecular identity of select compounds will then be confirmed through enhanced assessment.

3.3.1 Initial Assessment

The spectra obtained from Q-TOF-MS analysis will be used to quantify known analytes with authentic standards and determine the empirical formula for unknown analytes. Because fluorine has a unique negative mass defect, the presence and empirical formula for fluorinated compounds can be determined with a high level of confidence.

Structural information will also be interpreted for unknown compounds by performing tandem mass spectrometry: following initial mass to charge separation, precursor ions are broken down (fragmented) into product ions, and the spectra for the product ions can provide information on the structure of the precursor ions. Through this method, tentative molecular structures will be assigned.

3.3.2 Enhanced Assessment

Chemours will prioritize unknowns with the highest abundance for enhanced assessment, where the structural identity of the analyte will be assessed by preparing and analyzing an authentic standard. The retention times and spectra for the tentatively identified analytes will be compared to those of the authentic standard to confirm their chemical identity. If standards for a given compound are not commercially available, standards will be synthesized by Chemours or a contract laboratory. If the spectra for a standard does not match an unknown analyte's spectra, alternative structures will be considered.

3.4 Test Method Development

Test methods will be developed for additional PFAS compounds identified by the non-targeted assessment. Test methods will be developed according to EPA's Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater under EPA's Alternate Test Procedure Program (EPA, 2016). Depending on the number of additional PFAS identified through the non-targeted analysis and the availability of authentic standards for the additional PFAS, test method development may continue past the planned report submission date of June 30, 2020 discussed below in Section 4.

4 REPORTING

Chemours plans to submit a report to the DEQ by June 30, 2020. The report will summarize the findings of the non-targeted analysis and identify any additional PFAS detected in process wastewater, non-process wastewater, and stormwater at the Facility, and provide copies of the test methods that have been developed. The schedule of activities described in the report is shown in Figure 3.

5 REFERENCES

(EPA) United States Environmental Protection Agency, 2016. Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program. https://www.epa.gov/sites/production/files/2016-03/documents/chemical-new-method-protocol_feb-2016.pdf; Accessed January 17, 2019.

Geosyntec Consultants, 2018. PFAS Characterization Sampling Plan. December 28, 2018.

Nakayama, S. F.; Strynar, M. J.; Reiner, J. L.; Delinsky, A. D.; Lindstrom, A. B. "Determination of Perfluorinated Compounds in the Upper Mississippi River Basin." Environ. Sci. Technol. 2010, 44 (11), 4103−4109.

Tables

TABLE 1
DESCRIPTION OF SAMPLING LOCATIONS
Chemours Fayetteville Works, North Carolina

Sample Number	Sample Location Description	Sampling Method	Sample Category			
			Outfall	Process Wastewater	Non-process wastewater (i.e., NCCW)	Stormwater
4*	Combined stormwater discharge from Kuraray northern leased area and Chemours PPA area	Temporal Composite				✓
8	Outfall 001 non-Chemours treated process wastewater discharge to open channel to Outfall 002	Temporal Composite		✓	✓	
15*	Combined stormwater and NCCW discharge from eastern portion of the Facility	Temporal Composite			✓	✓
16	Chemours Monomers IXM Area combined process wastewater	Grab		✓		
17	Chemours PPA Area combined process wastewater	Grab		✓		
20*	Outfall 002 to Cape Fear River	Temporal Composite	✓			

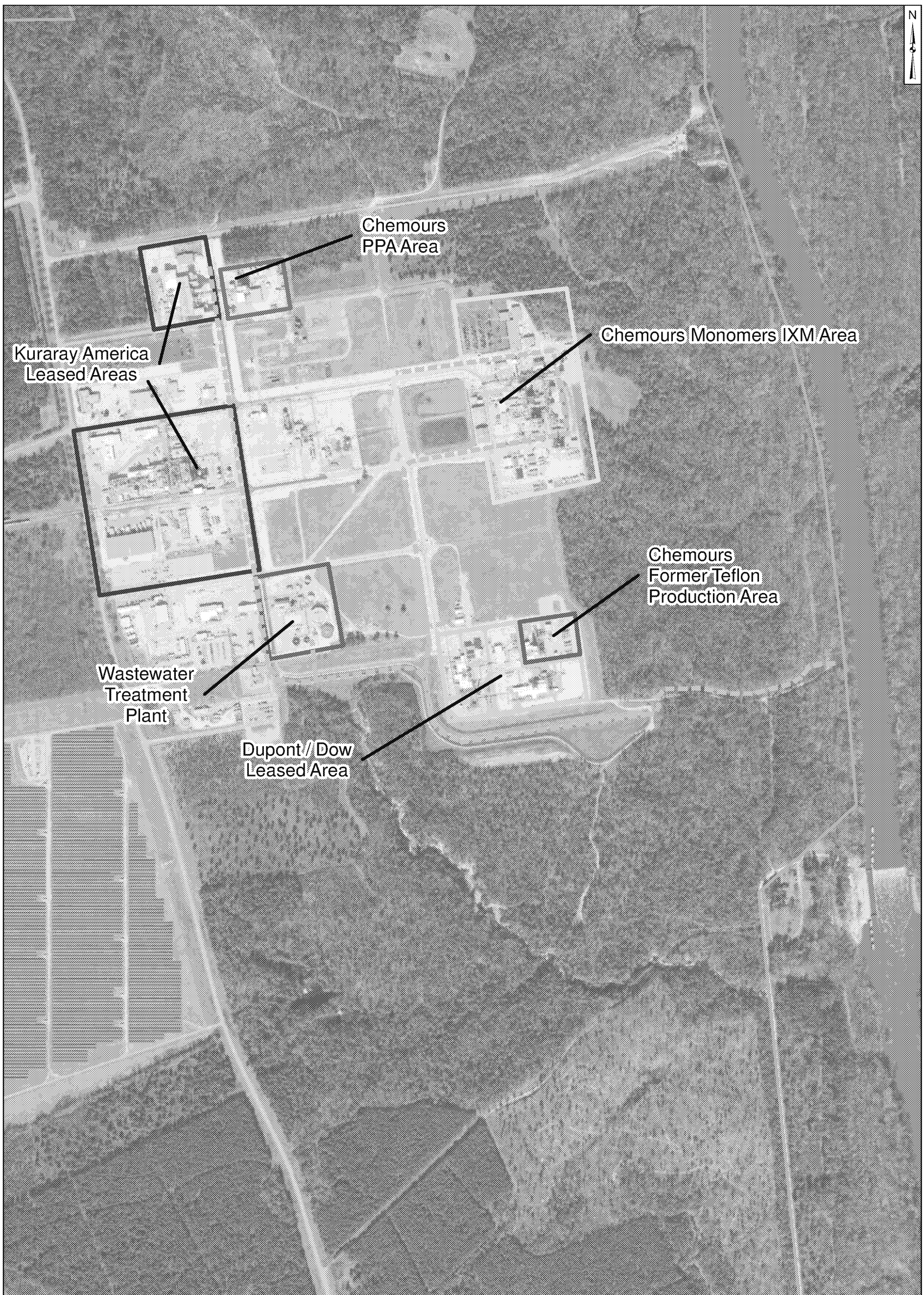
Notes
Sample numbers refer to locations identified in Figure 2 and correspond to locations identified in the December 28, 2018 Sampling Plan (Geosyntec, 2018).
NCCW - non-contact cooling water
PPA - polymer processing aid
* - sample must be collected during a rain event

TABLE 2
SAMPLING CONTAINERS AND PRESERVATION
Chemours Fayetteville Works, North Carolina

Analytical Method	Container Type and Volume	Number of Containers	Preservation
Non-targeted analysis	250 mL HDPE	4	None

Notes:
HDPE - high density polyethylene

Figures



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

Chemours Fayetteville Works, North Carolina

Geosyntec
Consultants of NC, PC
NC License No.: C-3500

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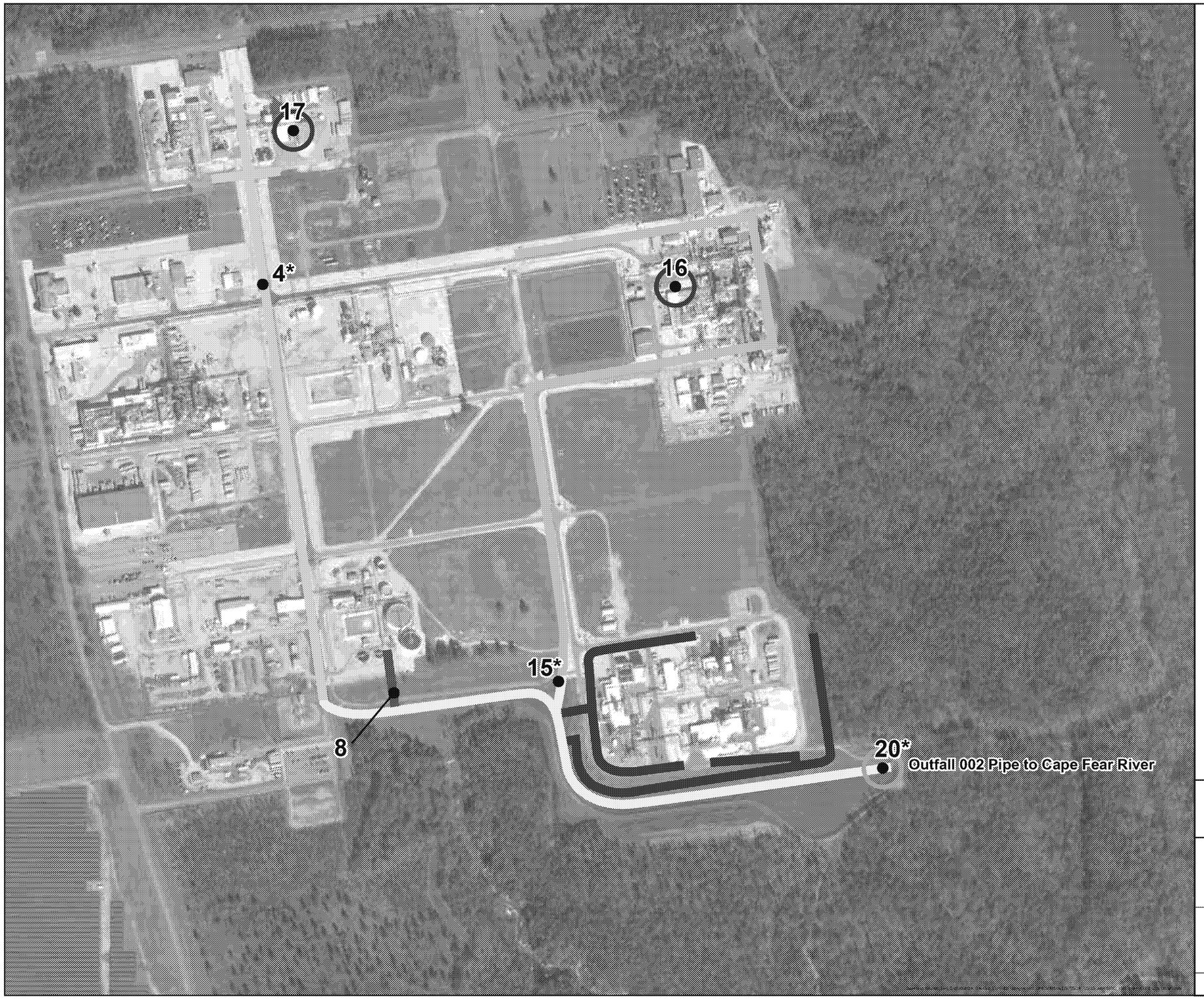
Figure
1



Legend

Ditch Types

- Wood Lined Trench
- Waste Water Treatment Plant Discharge
- Cooling Water Channel
- Open Channel to Outfall 002
- DuPont Area Ditches

8 Sample Location

20: Outfall 002 Pipe to Cape Fear River

16: Chemours Monomers IXM Area Combined Process Water Sampling

17: Chemours PPA Area Combined Process Water Sampling

* - Samples must be collected during rain event

Sample numbers correspond to locations identified in the December 28, 2018 Sampling Plan (Geosyntec, 2018)

N

500 250 0 500 Feet

Sample Locations

Chemours Fayetteville Works, North Carolina

Geosyntec Consultants of NC, PC
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Figure 2

Project Milestone/Deliverable	2019												2020					
	01	02	03	04	05	06	07	08	09	10	11	12	01	02	03	04	05	06
Approval of Sampling Plan		✓																
Sampling Event		●		●		●		●		●		●						
Sample Preparation			○	○	○	○	○	○	○	○	○	○	○					
Instrumental Analysis					□	□	□	□	□	□	□	□	□	□	□			
Initial Data Assessment							♦	♦	♦	♦	♦	♦	♦	♦	♦			
Enhanced Assessment										‡	‡	‡	‡	‡	‡	‡		
Test Method Development													■	■	■	■	■	■
Report Submission																		×

Notes:

This schedule is based on the assumption that this Sampling Plan will be approved on February 1, 2019, and will be modified accordingly if the approval date changes.

✓ Approval of Sampling Plan.

● Bimonthly sampling event, to occur concurrently with Initial Characterization sampling events outlined in the December 2018 Sampling Plan (Geosyntec, 2018). Sample locations 4, 8, 15, 17, and 20 will be sampled once, during the first sampling event. Sample location 16 will be sampled bimonthly for one year. This schedule assumes that a storm event, as defined in C.F.R. 122.21(g)(7)(ii), will occur resulting in enough rain such that water is present at all sampling locations in the stormwater drainage network for the proposed sampling event.

○ Sample preparation by filtration, direct injection or solid phase extraction (SPE) procedures.

□ Instrumental analysis of samples by liquid chromatography coupled to quadrupole time of flight mass spectrometry (Q-TOF-MS).

♦ Initial assessment to determine the empirical formulas and tentative structural information for unknown analytes.

‡ Enhanced assessment to confirm structural identity of select analytes following preparation of authentic standards.

■ Test method development for additional PFAS identified by non-targeted analyses. Test method development is expected to be an ongoing process that may require additional time beyond June 2020.

× Report submission.

Proposed Non-Targeted Analysis Schedule
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Figure 3