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PFAS NON-TARGETED ANALYSIS AND METHODS INTERIM REPORT

Process and Non-Process Wastewater and Stormwater

Prepared by

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June 30, 2020

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ACRONYMS AND ABBREVIATIONS

CFRW – Cape Fear River Watch

DEQ – Department of Environmental Quality

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 report has been prepared by The Chemours Company FC, LLC (Chemours) to provide an update on the characterization of previously unidentified (additional) 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). The purpose of the work 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. The work described in this report was conducted according to the PFAS Non-Targeted Analysis and Methods Development Plan, Version 2 (the Development Plan, Chemours and Geosyntec, 2019). This work is intended to address requirements specified in 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. Other parts of the Consent Order will be addressed separately by Chemours.

Non-targeted analysis refers to a procedure that searches for unknown compounds in a sample following analysis of the sample by a given analytical method; the compounds are considered to be unknown because the analytical method has not been calibrated for them (for example, because authentic standards do not exist). Analytical methods do, however, contain data (such as mass spectral data) that can be used to provide some information on unknown compounds despite the lack of calibration.

Non-targeted analysis for unknown PFAS can 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 PFAS facilitating the determination of their chemical formulas. Relevant structural information can then 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.

The remainder of this report consists of:

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

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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).

Known PFAS (i.e., compounds on the analytical lists for EPA Method 537 Modified and Table 3+ Standard Operating Procedure (SOP)) were identified and removed from consideration. Unknown PFAS[1] were identified from the remaining, unidentified chromatographic peaks with a signal-to-noise level of greater than 6 using the mass defect of fluorine as the molecular feature[2]. The empirical formula of the unknown PFAS was then determined based on the accurate mass from the mass spectral data. Results are provided in Tables 2 through 8 for Locations 4, 8, 9, 16, 17B, 20 and 42, respectively.

[1] Trifluoroacetic acid (TFA) and hexafluoropropylene oxide-trimer acid (HFPO-TA) are known PFAS compounds which have been definitively identified and for which authentic standards exist. TFA and HFPO-TA are not included on the analytical lists for EPA Method 537 Modified and Table 3+ SOP, and thus were identified as an "unknown" compound in the initial assessment.

[2] A mass defect occurs when the mass of an atom is different from the sum of the masses of its subatomic particles. In this case, fluorine is well-known to have a negative mass defect and when LC-QToF is operated in the negative mode, one can select F-containing features and empirical formulas using available software provided by the instrument vendor. The exact procedures utilized followed closely to what was outlined in the McCord & Strynar 2019 which consists of using a software workflow of Agilent ProFinder, MassHunter, and Mass Profile.

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3 RESULTS

To identify the most relevant unknown PFAS, the non-targeted results were assessed in two groups:

- General Facility Discharge samples: samples from locations that may reach the Cape Fear River (Locations 4, 8, 9, 20 and 42). Water from these locations consists of stormwater, treated non-Chemours process wastewater and/or non-contact cooling water discharging to the Cape Fear River; and
- Chemours Process Wastewater samples: samples from these locations (Locations 16 and 17B) consist of process wastewater from Chemours manufacturing areas.

Grouping the results in this way allows for the assessment of the most relevant unknown PFAS at the Facility and prioritization of which unknown PFAS should be advanced for synthesis of authentic standards.

In the General Facility Discharge samples, there were 21 unknown PFAS ranging in ion abundance from 1.8E9 to 5.5E6 (Table 9). The most abundant "unknown" PFAS was later identified as TFA. In the Chemours Process Wastewater samples, there were 250 unknown PFAS ranging in ion abundance from 7.1E8 to 5.3E6 (Table 10). Fourteen of the 21 unknown PFAS from the General Facility Discharge samples were also found in the Chemours Process Wastewater samples.

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4 DISCUSSION AND NEXT STEPS

Non-targeted analysis has identified 21 unknown PFAS present in General Facility Discharge samples and 250 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). Empirical formulas were determined for all unknown PFAS. This work represents 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 detected samples, 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 will be advanced to the Enhanced Assessment step. This is an adjustment from Chemours's prior proposal to carry the 5 most abundant unknown PFAS from each sample from the Initial Assessment step forward to the Enhanced Assessment step. This adjustment ensures that this program retains focus on unknown PFAS which were most abundant overall, whereas the 5 most abundant unknown PFAS in any given sample do not necessarily represent the most abundant unknown PFAS overall.

The 5 most abundant unknown PFAS in the General Facility Discharge samples (excluding TFA, which has been definitively identified and for which an authentic standard exists) consists of the following list:

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

The 5 most abundant unknown PFAS in the Chemours Process Wastewater samples consists of the following list:

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

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None of the 5 most abundant unknown PFAS in the General Facility Discharge samples are represented in the 5 most abundant unknown PFAS in the Chemours Process Wastewater samples, and vice versa. Therefore, the 10 unknown PFAS in the two lists are unique.

During the Enhanced Assessment step, authentic standards will be prepared and analyzed for the unknown PFAS carried forward from the Initial Assessment step. Following this, the Development Plan states that a test method will be developed for these unknown PFAS. The timeline for the Enhanced Assessment and the Test Method Development is provided in Figure 3.

5 REFERENCES

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

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