ROY COOPER
Governor
MICHAEL S. REGAN
Secretary
LINDA CULPEPPER
Director

NORTH CAROLINA
Environmental Quality

March 29, 2019

Christel Compton
The Chemours Company FC, LLC
22828 NC Highway 87 W
Fayetteville, NC 28306-7332

RE: Review of Consent Order Paragraph 11a

Dear Ms. Compton:

This is to convey the final list of questions from our review of the documents related to the Consent Order Paragraph 11a. Thank you for assisting with potential dates for the next few weeks to discuss the items with our staff and EPA.

Geosyntec PFAS Characterization Sampling Plan

It appears that samples may either be sent to Eurofins or TestAmerica [both are referenced in Tables 2 and 4]. Please submit the TestAmerica's SOP(s) so we can understand how any of the standard operating procedures may differ between labs.

Section 3.3.1 – Consider whether Clean Water Act approved methods [40 CFR Part 136] should be used for the Field Parameter measurements taken during sampling. If so, those SOPs should be included.

Section 3.3.2 – where are the boundaries for spatial and temporal composite sampling defined? Please reference or provide detail for consistency in sampling events and documentation requirements.

Section 3.3.2 – Do any of the markers (e.g., Sharpie and others) being used for sample labelling contain PFAS?

Section 3.3.2 – Powderless nitrile gloves should be used and changed between samples. Gore-Tex or other water-resistant, insect-resistant, or UV-protected synthetics or products should not be worn during sampling.

Section 3.4 – Define storage temperature for archived samples since we do not know how long archived samples may be stored. What type of QA/QC samples will be maintained (e.g., Field Blank) should those archived samples be analyzed at a much later date?

Section 3.4 – The section states that sample coolers will be "taped shut" and signed across the lid of the cooler. It is unclear what kind of tape is to be used. The use of custody seals is recommended, and the bill of lading is to be retained with the sample records.

Section 3.5.1 – Recommend the use of Temperature Blanks to verify proper thermal preservation during shipment.

Section 3.5.1 – The Field Blanks are required by the reference method and should be analyzed regardless.

Section 3.5.1 – Field duplicates are used to assess the precision associated with sample collection, handling and storage procedures as well as laboratory analytical processes. This statement should be added to the first sentence under *Field Duplicates*.

Section 4.2 – If SPE is used, Method Blanks should be used at a frequency of one per extraction batch rather than one per 20 samples when an extraction batch is less than 20 samples. This will test the day-to-day variability between extraction batches.

Section 4.2 – Since this is a location- and time-limited project and since the bias these matrices may attribute to these methods of analyses for these compounds is unknown, each sample location should be characterized with Matrix Spikes rather than relying on random selection during through ongoing QC requirements.

Section 4.2 – Indicate that CCVs are analyzed initially, after so many samples and at the end of each analysis batch to bracket samples analyzed.

Section 5 – Provide all associated QC results and not just case narratives.

Table 2 – There are fairly significant differences in PQLs between the two contract laboratories, TestAmerica and Eurofin Lancaster. Please describe how it is determined which lab is used. It appears that Eurofins is not using the branched isomers of PFOS, PFHxS, NetFOSAA and MeFOSAA in their calibration curves. What the rationale for that decision? Eurofins does analyze a solution at the mid-point of the curve that contains the previous analytes and their branched isomers. This is simply done for the analyst so they know how to fully integrate the analytes in real samples. As such it seems that Eurofins is capturing the linear/branches isomers when they analyze real samples, but they are not including them in the calibration. The extraction/cleanup was left out as "proprietary".

Table 4 – There is no mention of thermal preservation requirements [e.g., ≤10 degrees C without evidence of freezing] for shipment and storage. Please clarify the requirements.

Table 4 – The significant difference in hold time [i.e., 40 vs 28 days unpreserved] used by the two contract laboratories [TestAmerica and Eurofins] is concerning. Without stability validation data in the matrices of interest, it is not known whether data may be impacted by the significantly longer hold time especially if samples are not to be thermally preserved as indicated in the Sampling Plan. The conditions for storage of extracts must also be addressed.
Table 5 – Footnote 2 may need adjustment based on previous comment regarding analysis of Field Blanks and frequency of CCV based on previous comments.

MDL and IDOC studies are generally performed in laboratory water matrix. How have each of the proposed methods have been validated for analysis of PFAS in the matrices involved in this project? Were any spike studies, etc. done? The method validation is indirectly referenced for the non-targeted analyses by reference to following *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)*, but is not mentioned for the targeted analyses.

Original questions submitted to Chemours on March 22, 2019……
EPA Analytical Services Branch - Science and Ecosystem Support Division (SESD)

EPA, Science and Ecosystem Support Division (SESD) conducted a limited review of the following documents provided by Chemours to NC DEQ Division of Water as part of their consent order:

- Geosyntec's, PFAS Characterization Sampling Plan, Process and Non-Process Wastewater and Stormwater – December 28, 2018
- Chemours, PFAS Non- Targeted Analysis and Methods Development Plan
- Chemours, Determination of Table 3 Plus Compounds by LC/MS/MS, Chemours Fluoro products Analytical Method revision date 01/10/2019
- Eurofins, PFAS in Aqueous Samples by Method 537 version 1.1 using LC/MS/MS

SESD has provided the following comments:

PFAS Characterization Sampling Plan –

1. Page 4, 3.3.2 Sample Collection Procedures Common to All Locations: There are no "procedures" listed in this section nor in Table 4, Sampling Containers, Preservation, and Holding Times.

2. Page 5, first paragraph, first sentence: If the sample containers used for EPA Method 537 Mod contain Trizma® as a buffer, they should not be used to fill the flow-through cell.

3. Page 5, first paragraph, third sentence: "For each sample type" should be "For each sample" or "For each sample station".

4. Page 5, second paragraph: For consistency between sampling events, more detail of how the sampling will be conducted for each of the various media (i.e. stormwater, process water, NCCW, etc.). When temporal composite samples are being collected, the duration and interval of the aliquot collection should be specified. During storm events, the "composite samplers" may need to be reprogrammed for each storm, but it is necessary to detail the criteria for the field personnel and the regulators what information is desired for each sampling event. Additionally, the protocol used to split the composite sample and fill the nine sample containers needs to be stated.

5. Page 5, second paragraph: While it may be advantageous to collect composite samples for variable solids loading in stormwater samples, it should be acknowledged that there may be PFAS losses in the composite sampling process. From Section 3.1 Equipment and Supplies of the Interstate Technology Regulatory Council's **Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances [PFAS]**: *"Not all PFAS are hydrophilic, and some are volatile. As a result, these chemicals may sorb to sampling equipment and supplies or be lost from samples during sample collection. Preliminary data suggest that sorption may occur quickly. Additionally, volatile losses have not yet been characterized. Until they are better quantified, sampling efforts should consider whether these losses would affect project objectives and adjust accordingly."*.

   To evaluate the PFAS losses, it is recommended that a grab sample (or two) be collected in addition to one of the proposed composite sample locations for each sampling event.

6. Page 5, second paragraph, seventh sentence: Provide details for the Hach SD900 and the other composite samplers. Are they refrigerated or capable of storing samples on ice? Is there one container for the aliquots that will comprise the of temporal composite sample or are there several containers? What is the composition of the sampler's tubing and components?

7. Pages 5 & 6, Stormwater, Intake and Outfall, NCCW, Process Wastewater, and WWTP Discharge Sampling: Due to the potential stratification of PFAS in solution, the sampling location/depth in the water column needs to be specified for each sampling medium. (See Section 3.6.2 Surface Water of the ITRC's **Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances [PFAS]**).

8. Page 6, Non-Contact Cooling Water: For the spatial composite samples, the length of each ditch and the number aliquots collected needs to be stated so that data from subsequent sampling events can be appropriately assessed.

9. Page 6, Process Wastewater: Process wastewaters have the potential for great variability due to batch processing, process upsets, wash-downs, start-ups, etc., but grab samples are being proposed for each production area. Grab samples are appropriate where temporal variability over the course of one day is not expected at the sampling location.

10. Page 7, 3.3.3 Decontamination Procedures: Tap water and de-ionized water should be analyzed for PFAS and the one with the lower PFAS constituents should be used as the final rinse in the decontamination procedure. If they both exceed the criteria to achieve the DQOs for the project, PFAS-free water should be used as the final rinse. Decontaminated equipment should be covered with polypropylene or other PFAS-free plastic until it is ready for use.

11. Page 7, 3.4 Sample Shipping, Chain of Custody, and Holding Times, first sentence: To prevent ice melt water from potentially contaminating the samples, it is recommended that the samples be bagged in Ziplocs® or Whirl-Paks®.

12. Page 7, 3.4 Sample Shipping, Chain of Custody, and Holding Times, first sentence: Composite sampling requiring ice preservation, should have composite aliquots stored on ice or refrigerated during the sampling process.

13. Page 7, 3.5 Quality Assurance/Quality Control, second sentence: "Table 4" should be "Table 5".

14. Page 8, 3.5.1 Field QA/QC, second sentence: Insert at the beginning of the section "Criteria for achieving...". Also, "Table 3" should be "Table 2".

15. Page 8, Equipment Blanks, first sentence: Equipment blanks should also be used to demonstrate that sampling equipment is not contaminating the sample with analytes of interests. Modify the first sentence to "Equipment blanks are used to evaluate equipment and cleaning or decontamination procedures."

    The complete sampling system (containers, gloves, tubing, composite samplers, labels, bags, etc.) should be evaluated to ensure all the equipment is PFAS-free and not contributing to any PFAS detected in the samples. Initially this can be done by using the composite sampler to collect a sample from PFAS-free water and labeling, bagging, ice, and shipping to the laboratory for analyses. If PFAS are detected above the PQLs, then further investigation will be required to determine the cause.

16. Table 2: Title should be "CRITERIA FOR ACHIEVING DATA QUALITY OBJECTIVES".

17. Table 4: In the preservation column, "Ice" should be listed for each of the analytical methods.

Chemours, PFAS Non- Targeted Analysis and Methods Development Plan –

1. The planning document overall, seems sound. There should be greater emphasis given to synthesis of authentic standards by companies which maintain an arms-length relationship with Chemours. Companies which specialize in the production of high-purity analytical standards should be focused on for their expertise. This is especially important, as new compounds are discovered and methods developed for their quantification in real-world samples.

2. The use of high-field NMR would be of potential benefit in structural identification of unknown compounds.

Chemours, Determination of Table 3 Plus Compounds by LC/MS/MS –

1. Details in this SOP are minimal, with limited procedural information available. A more detailed version of the methodology is necessary for evaluation of the procedures.

2. Most of the target analytes are not available commercially. Suggest that funding be directed toward synthesis of these compounds with non-related companies which specialize in production of analytical laboratory standards so that primary and secondary source standards are available. Doing so will give greater validity to the data.

3. Page 1, Sample Preparation. The note states that the 100 ppb mixed stock standard is prepared in ultrapure water. Studies have shown that PFAS will bind to the sample container in the absence of an organic solvent. Preparing stock or mixed standards in water may cause low bias in quantitative results because of PFAS binding to the sample container.

4. The 10-point calibration curve spans a concentration range from 10 – 50,000 ng/L. This calibration range seems to span a range greater than possible with MS/MS detection. Clarify how this is performed.

5. Page 2, Sample Preparation. The QC samples are prepared at a concentration of 5 ppb (5,000 ng/L). Relative to the NC DHHS provisional health goal of 140 ng/L for HFPO-DA and the US EPA health advisory for PFOA and PFOS of 70 ng/L, the QC spike concentrations are quite high and not representative of protective health goals.

6. Page 4, QQQ Acquisition Parameters. If possible, add confirmatory ions where possible. The qualifier ion ratio and retention time criteria for selection or exclusion of a compound should be stated. This may require multiple MRM functions to obtain an adequate number of scans across peaks.

7. Page 5, Data Processing, Calibration. No mention is made of the minimum number of scans required across a chromatographic peak. A minimum of eight and preferably ten scans are required to produce quantitative data.

8. Performing two calibration curves; one prior to sample analysis and one following the sample sequence is not a technique typically seen. This may have the potential to introduce bias to the determinations, especially if absolute instrument sensitivity has been lost during analysis. If the practice is retained, precision and accuracy criteria should be developed to judge acceptability of the closing calibration curves with respect to the opening calibration.

9. Page 5, Data Processing, Blanks. As currently written, method blanks are optional (e.g., and/or). The requirement for a method blank is mandatory.

10. Page 5, Data Processing. Suggest adding a positive control spiked at a concentration equal to the minimum reporting limit to verify method performance at the limit of quantitation. A 5% frequency is reasonable (One per batch of 20 samples).

11. There is no mention of a method detection limit study. Suggest implementation of an MDL study.

12. Page 5, Data Processing, Duplicates. Suggest eliminating the RPD 50% criterion and using a single 25% criterion for all duplicates.

Eurofins, Polyfluorinated Alkyl Substances (PFAS) in Aqueous Samples by Method 537 Version 1.1 Modified Using LC/MS/MS -

1. The use of isotope dilution, where allowed, is to be commended. Isotope dilution and extracted internal standards allow recoveries of target analytes to be corrected for losses during sample processing.

2. The dependencies between internal standards (ISTDs) and the compounds they are used to quantitate seems reasonable. Chemistry and chain length of ISTDs generally corresponds to target compounds.

3. Branched isomers not in ICAL – are they included elsewhere? Integration of samples should include both linear and branched chain isomers, where present. This is implied in section D.12 (page 16) but needs clarification. If branched chain isomers are not included during integration, the potential for underestimation of results exists.

4. No MRL confirmation performed. Recommend that a positive control sample spiked at the MRL concentration be carried through the process to verify method performance.

5. With respect to the SOP title, and the use of “Modified” 537 1.1: The allowed changes to Method 537 are limited and clearly stated. Once those allowed changes are exceeded, the method is no longer considered Method 537. There have been major chemistry changes made to this SOP when compared to Method 537. The title connotates something that this method is not; this method can no longer be considered Method 537.

6. Redaction of certain SOP elements as proprietary make evaluation of the method in its entirety impossible. The SPE and cleanup sections are critical to full evaluation of the method.

7. There is no mention of HFPO-DA (aka, GenX) within the document. Presumed to not be a target compound.

8. Page 5, Precaution to minimize method interference. This section is redacted as proprietary content. No evaluation can be made.

9. Pages 6 – 7, Sample collection/preservation. Trizma is not added to samples unless they originate from a chlorinated source. Method 537 uses Trizma as both a buffer and free-chlorine scavenger. Its use in 537 increased recoveries for several compounds using SDVB SPE (unpublished data). It is impossible to know what effect Trizma will have on the samples analyzed by this method because of the (1) major differences in chemistry and (2) the addition of compounds relative to Method 537.

10. Page 10, Initial Calibration (A.2). States there must be a detection of all analytes in the MDL standard. If there is a signal-to-noise requirement for this criterion, state it.

11. Page 10, Initial Calibration (A.1/A.4). Section A.1 requires a minimum of five calibration points. Section A.4 provides for the allowance of a second-order (quadratic) calibration model. While not stated in Method 537, quadratic calibration requires a minimum of six calibration points. Likewise, a first-order model requires a minimum of five calibration points. These requirements should be stated in the SOP.

12. Page 11, Continuing Calibration (7.B.1.a) The requirement for use of the CS3 level standard is stated. Method 537 §10.3 states “The beginning CCC of each analysis batch must be at or below the MRL in order to verify instrument sensitivity prior to any analyses.”

13. Page 11, Procedure, Sample Preparation (A.1) State how many significant figures are necessary during weighing. Also applies to page 12, section A.3.j, and elsewhere.

14. Page 11, Procedure, Sample Preparation (A.3) The option for processing of an aliquot is described. Numerous workers have shown that PFAS sorption to sample containers is a source of sample loss and non-quantitative transfer. If aliquots are taken from the

original sample container, the sample must be qualified explaining the possibility for low bias in reported values.

15. Pages 12 - 13, Procedure, Solid Phase Extraction (B.1 - 16) Most (16 of 21) procedural steps of this section, which are critical to successful sample analysis have been redacted as proprietary. As such, no judgement of the extraction can be made. NOTE: EXTRACTION IS A CRITICAL STEP IN THE ANALYSIS.

16. Pages 13 - 14, Procedure, Solid Phase Extraction (B.18 -19) Steps 18 (tare bottle) and 19 (weigh bottle) appear to conflict with each other. Clarify.

17. Page 14, Procedure, Solid Phase Extraction (B.20) The SOP states that following addition of labeled internal standards, the sample is ready for instrumental analysis. However, section C (Extract Cleanup) follows this stated sample processing endpoint. Clarify the flow of the sample extract and state if Section C Extract Cleanup is optional.
    In section B.20, state what equipment is allowed or disallowed (pipette, syringe, etc.) for sample transfer.

18. Page 14, Procedure, Extract Cleanup (C) All procedural steps of this section, which are critical to successful sample analysis have been redacted as proprietary. As such, no judgement of the cleanup procedure can be made. NOTE: CLEANUP STEPS ARE CRITICAL TO THE ANALYSIS.

19. Page 14, LC/MS/MS Analysis, Mass Calibration and Tuning (D.1.b) The SOP provides a criterion for mass axis calibration to be within ± 0.5 Daltons of the true value. There is no statement indicating how this is performed. Note: Failure to maintain mass calibration will impact instrument sensitivity.

20. Page 15, LC/MS/MS Analysis, Mass Calibration and Tuning (D.3) Acquisition Method, Attachment 3 is redacted indicating it to be proprietary. Therefore, no judgement of the LC/MS/MS acquisition procedure can be made. NOTE: ACQUISITION PARAMETERS ARE CRITICAL TO THE ANALYSIS.

21. Page 15, LC/MS/MS Analysis, (D.5) The acronym L/B standard is used but undefined; assume this to be Liner/Branched-chain. Clarify.

22. Page 16, LC/MS/MS Analysis, (D.11) The use of surrogates is mentioned; however, their identity is not given. Clarify.

23. Page 16, LC/MS/MS Analysis, (D.12) The use of an MDL standard by which to judge data quality is referenced. Its use is also mentioned in section A.2 (page 10). Clarify the origin of the MDL standard.

24. Page 18, Mass Transitions AB Sciex 4500, Attachment 1. The stated transitions appear to be nominal values. Mass transitions should be optimized on an instrument-by-instrument basis. During optimization, the analyst should determine the precursor and product ion masses to one decimal place (0.1 Daltons).

25. The precursor and product transitions for PFOS (2) appears to be incorrect. The table entry *m/z* 413 > 169 should probably be 499 > 99.

EPA Office of Research and Development

Summary:

1) Groundwater analysis is not included. Comments on groundwater analysis may be provided separately.
2) In section 2 of the data quality objectives PFAS are split into 2 groups: 1) Emanating from Chemours; and 2) Not emanating from Chemours. A third group is needed: 3) contributed to by Chemours. PFAS are in the Cape Fear River, however there are legacy PFAS present contributed to by Chemours.
3) The PQLs listed in Table 2 for most of the analytes is too high at 50-120 ng/L. PQLs from laboratories have been 5-10 ng/L.
4) The plan does not incorporate any spiked field sample or spiked trip samples to assess recovery and accuracy of the intended analytes. Table 5 does indicate the plan for matrix spikes which seem to be prepared on the day of analysis. EPA and DEQ have implemented trip spikes in our project. Spiked field sample or spiked trip samples are essential. If not done it is hard to assess what happens to samples during holding times, while shipped on ice, frozen and archived and then extracted.

3.3.2 Sample Collection Procedures Common to All Locations

Page 5, 5th line: "… archive for potential future analyses."

How are these samples going to be managed? Frozen? Extracted and archived?

3.5.1 Field QA/QC

The plan does not include spiked field samples. Chemours has all of these standards for assessment. Add: 1) spiked blank water samples and/or 2) spikes of field collected sample.

These samples should go out into the field (or are spiked in the field) and are cooled, transported

and extracted as unknown samples are managed. This will determine if there is good recovery for the chemicals analyzed, which determines accuracy. The assessment of blank contamination and duplicate precision is in the proposal but NOT accuracy. Also, this is NOT the same as the Matrix Spikes in section 4.2 below as the samples here are in the lab on the day of analysis.

Table 2: TestAmerica and Eurofins Lancaster Current PQL's are higher than expected.

Table 5: Spike sample must be included for Field samples.

PFAS Non-Targeted Analysis and Methods Development Plan
Process and Non-Process Wastewater and Stormwater

1 Introduction - What if any are the differences in how groundwater analysis is going to be conducted?

1.1. Non-Targeted Analytical Background – what will be done in the absence of an authentic standard?

1.2 Scope and Rationale – how is the "…prioritized set of the highest abundance additional PFAS," set? What is the cutoff for the highest?

2.5 Quality Assurance/Quality Control – how are the archived duplicates going to be managed? Frozen? Extracted and archived?

3.1 Sample Preparation

How is it determined what gets SPE? If after a direct injection is done and no peaks are seen or many large peaks are seen, how does the process proceed? Results can indicate many PFAS of widely varying concentrations.

3.3 Compound Identification

Direct Injection is the least sensitive approach. If no peaks are detected via direct injection how do you proceed?

3.3.2 Enhanced Assessment

Again, how is the prioritization conducted?

4 Reporting

Include that the QTOFMS datafiles will be provided to DEQ.

Determination of Table3

Sample Preparation – dilutions listed for calibration curve do not include values low enough to support 5-10 ppt PQL.

Note on mixed stock standard - has the stock stability on water been assessed, and then assessed as stored in a refrigerator?

"A 2x dilution will be appropriate for most groundwater analyses (trace levels expected)." This is not the case for Chemours groundwater nor many of the surfacewater and effluent samples.

QC sample: "… stock standard solution separate from the one used for calibration…" Is this a secondary standard prepared from the same chemical or from a secondary source?

Analytical Method
LC Operating Conditions: Column A – given a 50:50 methanol:water is injected into a 85:15 water:acetonitrile, you would expect early eluting peaks to split and not chromatograph well.

QQQ Acquisition Parameter – major concern in monitoring only one MRM for all of the compounds. Modern QQQs such as your Agilent 6470 has no problems with two MRMs for all if available, which makes ion ratios possible to evaluate. If not monitored, this is impossible. One is listed for HFPO-DA but for no others. No stable isotope labled standards are listed. Most may not be currently available but Wellington Labs does have 13C3 HFPO-DA.

Data Processing – reference indicates "The curve should be linear,…" Dr. Strynar indicates quadratic generally works better even if the data is linear. If the data is non-linear, a linear fit is not good.

Blanks – is the target analyte concentrations in all blanks defined as 0.01 ppb?

Duplicates – how will you work with data when one sample is above the LOQ and one is below the LOQ?

Appendix A – please add molecular weight as another column of information in the table.

DFSA, Byproduct 4 and Byproduct 5 – are diprotic, what about M-2H?

MMF – this compound is diprotic and low molecular weight. The MRM is for the M-H. It will be missed if it is M-2H as that MRM is not monitored for. The structure given is difluoromalonate. What about monofluoromalonate as a possible contaminant?

Cover letter dated January 30, 2019 from Brian Long "The lab standards are in the form of a 0.1% (by weight) solution in water for each compound, and Chemours can ship these standards solutions to DEQ promptly upon request." - have stability tests for standards in this solution been performed?