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CAPE FEAR RIVER PFAS MASS LOADING CALCULATION PROTOCOL

Chemours Fayetteville Works

Prepared for

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Project Number TR0795

August 2020





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LIST OF ABBREVIATIONS

CFR	Cape Fear River
CFR-BLADEN	Bladen Bluffs
CFR-KINGS	Kings Bluff
CFR-TARHEEL	Tar Heel Ferry Road bridge
СО	Consent Order
DEQ	Department of Environmental Quality
DSI	Dynamic Solutions International
EFDC	Environmental Fluid Dynamics Code
kg	Kilograms
L/s	liters per second
mg/s	Milligrams per second
Mass Loading Protocol	PFAS Mass Loading Protocol
NC	North Carolina
ng/L	nanograms per liter
PFAS	Per- and polyfluoroalkyl substances
SOP	Standard Operating Procedures
USGS	United States Geological Survey



1 INTRODUCTION

Geosyntec Consultants of NC, PC (Geosyntec) has prepared this per- and polyfluoroalkyl substances (PFAS) Mass Loading Protocol ("Mass Loading Protocol") on behalf of The Chemours Company FC, LLC (Chemours) pursuant to the requirements of Paragraph 1 (a) and (b) of the Addendum to Consent Order Paragraph 12 (CO Addendum). The objective of this Mass Loading Protocol document is to describe the sampling and measurement activities, calculation methods and reporting requirements associated with the following mass loading programs:

- Cape Fear River PFAS Mass Load Sampling;
- Bladen Bluffs and Kings Bluff PFAS Sampling; and
- Cape Fear River PFAS Mass Loading Model Pathway Sampling.

The CO Addendum specifies that PFAS mass loading calculations estimate the mass loading for each of the PFAS compounds listed in Attachment C of the CO (February 25, 2019). The calculations presented in this document are suitable for evaluating the mass loads of any given set of selected PFAS. For the purposes of calculations and reporting for Paragraph 1 of the CO Addendum, the set of PFAS will be those listed in Attachment C of the Consent Order and listed in Table 1.

The remainder of this document is organized as follows:

- Section 2 Description of PFAS Mass Loads which presents an overview of the three types of PFAS Mass Loading quantities described by this protocol document;
- Section 3 Sampling and Measurement Locations and Frequency which presents the sampling requirements for the mass loads;
- Section 4 Calculations which present the protocol by which the mass loads will be calculated; and
- Section 5 Reporting which describes how the results of the protocol will be reported.



2 DESCRIPTION OF PFAS MASS LOADS

This section provides first an overview of terms used in this document and then an overview of each of the sampling, calculation and reporting activities for the three mass loading programs.

2.1 Mass Loading Terminology

The following mass loading terms are used in this document:

- Mass Load the quantity in kilograms (kg; mass) of PFAS present in a pathway over a period of time (e.g., 5 kg from a pathway over a certain number of days). This quantity is used to assess the total amount of PFAS that have reached the Cape Fear River;
- Mass Discharge the quantity in milligrams per second (mg/s; mass over time) of PFAS present in a pathway at a specific point in time. This quantity is used for assessing the relative loadings from the different pathways in the Mass Loading Model and the loading of PFAS at Bladen Bluffs and Kings Bluff raw water intakes.

2.2 <u>Cape Fear River PFAS Mass Load</u>

The Cape Fear River PFAS Mass Load focuses on PFAS mass loads measured in the river, and loads prevented from reaching the Cape Fear River from the Fayetteville Works Facility. Specifically, three loads are assessed:

- 1. The "In-River Mass Load" which is the total measured in-river PFAS mass load that reached the river as measured in kg over a period of time based on timeweighted concentrations of PFAS from samples collected at the Tar Heel Ferry Road bridge (CFR-TARHEEL) and Cape Fear River flow volumes;
- 2. The "Captured Mass Load" which is the PFAS mass load, measured in kg, prevented from reaching the Cape Fear River by remedies implemented by Chemours; and
- 3. The "Baseline Mass Load" which is the sum of the River Mass Load and the Captured Mass Load. The Baseline Mass Load will be used to assess PFAS Mass Loading reductions to surface water achieved over time.

2.3 Bladen Bluffs and Kings Bluff PFAS Sampling

The Bladen Bluffs and Kings Bluff PFAS sampling will collect monthly samples to measure PFAS loadings in the Cape Fear River adjacent to the Bladen Bluffs and Kings



Bluff points in time from discrete water samples. The loadings are expressed as mass per unit time, i.e., mg/s.

2.4 <u>Cape Fear River PFAS Mass Loading Model</u>

The Cape Fear River PFAS Mass Loading Model will estimate the mass discharge of PFAS from nine potential PFAS transport pathways to the Cape Fear River. The potential pathways are listed below, and are shown on the conceptual diagram provided in Figure 1:

- **Transport Pathway 1**: Upstream Cape Fear River and Groundwater This pathway is comprised of contributions from non-Chemours related PFAS sources on the Cape Fear River and tributaries upstream of the Site, and upstream offsite groundwater with PFAS present from aerial deposition;
- **Transport Pathway 2**: Willis Creek Groundwater and stormwater discharge and aerial deposition to Willis Creek and then to the Cape Fear River;
- Transport Pathway 3: Direct aerial deposition of PFAS on the Cape Fear River;
- **Transport Pathway 4**: Outfall 002 Comprised of (i) water drawn from the Cape Fear River and used as non-contact cooling water, (ii) treated non-Chemours process water, (iii) Site stormwater, (iv) steam condensate, and (v) power neutralization discharge, which are then discharged through Outfall 002;
- **Transport Pathway 5**: Onsite Groundwater Direct upwelling of onsite groundwater to the Cape Fear River from the Black Creek Aquifer;
- **Transport Pathway 6**: Seeps Onsite groundwater seeps A, B, C and D above the Cape Fear River water level on the bluff face from the facility that discharge into the Cape Fear River;
- **Transport Pathway 7**: Old Outfall 002 Groundwater discharge to Old Outfall 002 and stormwater runoff that flows into the Cape Fear River;
- **Transport Pathway 8**: Adjacent and Downstream Offsite Groundwater Offsite groundwater adjacent and downstream of the Site upwelling to the Cape Fear River; and,
- **Transport Pathway 9**: Georgia Branch Creek Groundwater, stormwater discharge and aerial deposition to Georgia Branch Creek and then to the Cape Fear River.

Results of the mass loading model assessments are expressed as both the PFAS mass discharge (in mg/s) per pathway and the relative estimated mass discharge per pathway.



3 SAMPLING AND MEASUREMENT LOCATIONS AND FREQUENCIES

This section describes sampling and measurement locations and frequencies for the mass loading programs. The field methods to be used for the sampling programs is provided in Appendix A.

3.1 Cape Fear River PFAS Mass Load Sampling

To assess the Cape Fear River PFAS In-River and Baseline Mass Loads (Section 2.2), a 24 hour composite sample of the Cape Fear River will be collected twice per week using an autosampler placed at CFR-TARHEEL (Figure 2). Additional sampling will be conducted within 24 hours of rain events when these rain events are predicted two days before and with at least a 70% likelihood and to be of 1 ½ inches or greater in a 24 hour period. Such additional sampling will be conducted up to twice per month for any month in which there are two or more such rain events. River flow volumes corresponding to collected samples will be determined using Cape Fear River flows as reported by the United States Geological Survey (USGS).

Remedies implemented or to be implemented by Chemours (e.g. onsite seeps interim remedies, Outfall 002 remedy) will prevent PFAS mass loads from reaching the Cape Fear River. For certain remedies, specific sampling frequency and methods and flow measurements will be specified in sampling plans or other sampling requirements (e.g. NPDES permits) for such remedy.

Sampling will be conducted for a period of five years. At the end of each reporting year, Chemours may apply to DEQ for modification of this protocol.

3.2 Bladen Bluffs and Kings Bluff PFAS Sampling

To sample the PFAS mass loading near the Bladen Bluffs and Kings Bluff Intakes (Section 2.3), grab samples will be collected on a monthly basis from the Cape Fear River adjacent to both intakes (Figure 2). For the Bladen Bluffs Intake sample location, flows as reported by the United States Geological Survey (USGS) river gauging station at the W.O. Huske Dam will be used to determine river flow volumes corresponding to collected samples. For the Kings Bluff Intake sample location, flows as reported by the USGS river gauging station at Cape Fear River Lock & Dam #1 will be used to determine river flow volumes corresponding to collected samples.

Sampling will be conducted for a period of five years. At the end of each reporting year, Chemours may request to DEQ for modification of the protocol.



3.3 Cape Fear River PFAS Mass Loading Model Sampling

To assess the relative mass loading of PFAS to the Cape Fear River from the potential PFAS mass loading pathways (Figure 1), pathway inputs to the Mass Loading Model will be sampled. The following pathways and locations will be sampled (Figures 3 and 4)¹,²:

- Transport Pathway 1: Upstream Cape Fear River;
- Transport Pathway 2: Willis Creek;
- Location: Intake River Water at Facility;
- Transport Pathway 4: Outfall 002;
- Transport Pathway 5: Onsite Groundwater (Table 2)³;
- Transport Pathway 6: Onsite Seeps (Seeps A through D);
- Transport Pathway 7: Old Outfall 002;
- Transport Pathway 9: Georgia Branch Creek; and
- Location: CFR-TARHEEL;

Where Site access and Site conditions permit, samples will be collected as 24-hour composite samples. Flow rates will be measured after sample collection at seep and creek locations specified in Table 2. Flow rates will be measured using flumes at the seeps and using flow velocity gauging at Willis Creek and Georgia Branch Creek. Flow will then be used to calculate volumetric flow rates. Flow data for the Intake River Water at Facility location and Outfall 002 will be obtained from facility discharge monitoring reports. Flow data, adjusted for travel time, recorded at the USGS river gauge at the W.O. Huske Dam will be used for CFR-TARHEEL and CFR-BLADEN. Flow data recorded at the USGS river gauge at Cape Fear Lock and Dam #1 will be used for CFR-KINGS.

The travel time adjustment calculations were based on a calibrated hydrodynamic model using the Dynamic Solutions International (DSI) version of the Environmental Fluid

¹ Transport pathway 3, direct aerial deposition, is estimated based on modeling calculations and therefore is not sampled.

² Transport pathway 8, adjacent and downstream groundwater, is estimated based on transport pathway 1, upstream Cape Fear River and is therefore not sampled for pathway estimation purposes. The downstream river is sampled to evaluate the PFAS mass loading to the Cape Fear River.

³ This list of groundwater wells to be sampled is derived from the Corrective Action Plan (Geosyntec, 2019b) with wells INSITU-02 and BLADEN-1S removed as these wells are perennially dry.



Dynamics Code (EFDC). The model domain runs from downtown Fayetteville, North Carolina to Lock and Dam #1 near Kelly, North Carolina. The model was calibrated to flow data from the USGS gauges at W. O. Huske Dam and Lock and Dam #1 and water surface elevation data (from the USGS Gauges at Fayetteville, NC and the W. O. Huske Dam) for two periods: January-February 2017 and May-June 2018.

To estimate travel times from W. O. Huske Dam to the Bladen Bluffs Intake, a dye release was modeled for 5 hours from Huske Dam at the following flow rates based on real flow data from calendar year 2017. Travel times were estimated based on first arrival as defined by the point where the concentration at the arrival point reaches 10% of the maximum concentration at the indicated location. The travel time to river flow relationships to locations CFR-BLADEN, CFR-TARHEEL and CFR-KINGS (i.e., regressions) had R^2 values of 0.997, 0.997, and 0.943, respectively.

The sampling of the inputs to the Mass Loading Model will be conducted for a period of one year on a monthly basis and then for the next four years on a quarterly basis. At the end of each reporting year, Chemours may apply to DEQ for modification of the protocol.

3.4 Potential Adjustments to Sampling Program

Planned sampling outlined in this protocol document will be conducted where locations are safely, logistically and legally accessible. The sampling and measurement protocols described in this section have been outlined based on the present understanding of Site conditions. If conditions change, modifications may need to be made to this protocol. Additionally, during a field program, the field team may need to modify the sampling program outlined in this protocol. Modifications to the sampling protocol will be described in submitted reports described in Section 5.

4 CALCULATION METHODOLOGIES

This section presents the calculation methodologies to be applied to estimate the mass loading quantities for the three mass loading programs.

4.1 <u>Cape Fear River PFAS Mass Load Calculation Methodology</u>

This subsection presents the calculation methodology for calculating the Cape Fear River PFAS Baseline Mass Load, In-River Mass Load and Captured Mass Load.

4.1.1 Baseline Mass Load Calculation Methodology

The Baseline Mass Load is calculated following Equation 1 below:

Equation 1: Total PFAS Baseline Mass Load

 $M_{CFR} = m_{CFR} + m_{Remedies}$



where,

- M_{CFR} = is the Baseline Mass Load of PFAS compounds in the Cape Fear River, including the mass load prevented from reaching the Cape Fear River by implemented remedies, measured in kg;
- m_{CFR} = is the River Mass Load estimated using PFAS concentrations in samples taken in the Cape Fear River downstream of the Site where the river is well mixed and using measured river flow volumes; and
- $m_{Remedies}$ = is the Captured Mass Load prevented from reaching the Cape Fear River by remedies implemented by Chemours;

There have been numerous interim and permanent actions taken to limit PFAS reaching the Cape Fear River prior to this baseline period, i.e., air abatement measures (installation of the thermal oxidizer and carbon beds, etc.), grouting of the terracotta pipe, sediment removal from channels, among others, and these may not be captured in this baseline load calculation methodology but should be considered in the overall assessment of PFAS reductions.

4.1.2 In-River Mass Load Calculation Methodology

The In-River Mass Load is the estimated mass, in kilograms, that has reached the Cape Fear River over a period of time. The River Mass Load, m_{CFR} , is calculated using primarily composite samples from the Cape Fear River and corresponding river flow volumes. The In-River Mass Load is calculated for a given time period following Equation 2 below:

Equation 2: In-River Mass Load

$$m_{CFR} = \sum_{n=1}^{N} \sum_{i=1}^{I} C_{CFR,n,i} \times V_{CFR,n}$$

where,

- m_{CFR} = is the Total PFAS mass load estimated from PFAS concentrations in samples taken in the Cape Fear River downstream of the Site where the river is well mixed and measured river flow volumes;
- n = represents individual time intervals during a monitoring period;
- N = is the total number of time intervals in a monitoring period;
- i = represents each of the PFAS constituents being evaluated;



I = represents total number of PFAS constituents included in the summation;

- $c_{CFR,n,i}$ = is the measured or estimated concentration of PFAS for each baseline mass loading time interval based on samples collected from the Cape Fear River; and
- $V_{CFR,n}$ = is the volume of Cape Fear River water that flowed passed the sampling point during the baseline mass loading time interval.

4.1.2.1 Calculation of Time-Weighted Average Concentrations

During a time period, multiple samples will be collected, most of them being composite samples and some potentially being grab samples. The calculation methodology outlined here considers all collected samples in the time period, including cases where samples are collected contemporaneously with each other and cases where composite sample collection events do not occur successively, as is the case with twice weekly 24 hour composite samples. To facilitate this calculation, the overall time period is separated into discrete time intervals with corresponding time-weighted concentrations calculated for each interval. The time intervals are defined as the duration in time between two sampling events, where sampling events consist of:

- Beginning of a composite sample collection;
- End of a composite sample collection; or
- Collection of a grab sample.

Equation 3 shows the formula used to calculate the total flow volume for each interval.

Equation 3: Mass Load Time Interval Concentration

$$C_{CFR,n,i} = \sum_{k=1}^{K} C_{CFR,n,i,k} \times w_k$$
$$= \sum_{k=1}^{K} C_{CFR,n,i,k} \frac{\frac{t_n}{t_k}}{\sum_{k=1}^{K} \frac{t_n}{t_k}}$$

where,

 $C_{CFR,n,i}$ = is the measured or estimated concentration of PFAS for each baseline mass loading time interval based on samples collected from the Cape Fear River;



- n = represents individual time intervals during a monitoring period;
- i = represents each of the PFAS constituents being evaluated;
- k = represents a concentration sample considered in the mass load time interval;
- K = is the total number of concentration samples considered in the mass load time interval;
- $C_{CFR,n,i,k}$ = is the measured concentration of PFAS for each sample result considered in calculating the time-weighted average concentration for a mass load time interval; and
- w_k = is the weighting factor calculated for and applied individually to each concentration, where,
- t_n = the length of time of the mass load time interval; and
- t_k = the length of time of the collected sample. For composite samples, t_k is the total length of the composite sample collection period. If $t_k < t_n$, i.e., the composite sample collection time is less than the interval time, or a grab sample was collected, then t_k is set to equal the interval time for the purposes of concentration weighting.

4.1.2.2 <u>Calculation of Travel Time Adjusted Flow Volumes</u>

To calculate the mass load, river flow volumes are calculated for each time interval using United States Geological Survey (USGS) reported flows at the W.O. Huske Dam. A time offset is applied to the flow data to account for travel time for the flow passing the W.O. Huske Dam to reach the CFR-TARHEEL location. River flow passing the W.O. Huske is estimated to have a travel time between 2 and 12 hours to reach CFR-TARHEEL depending on river flow (e.g., the flow rate passing W.O. Huske Dam at 8 am will arrive at CFR-TARHEEL at 11 am for a 3 hour travel time). Travel times are estimated based on the results of a numerical model of the Cape Fear River which developed a regression curve between the USGS reported gage heights at W.O. Huske Dam and travel times. Equation 4 shows the formula used to calculate the time offset. The total volume of flow for each mass loading interval is calculated as the sum of all individual flow measurements for an interval where each measurement multiplied by its corresponding 15-minute time duration. Equation 5 shows the formula used to calculate the total flow volume for each interval.

Equation 4: Travel time offset W.O. Huske Dam to Tar Heel Ferry Road Bridge

$$t_{offset} = 13,422 \cdot Q_{WOHD}^{-1} + 2.019$$

where,



- t_{offset} = is the travel time flow in the Cape Fear River takes in hours to pass from the W.O. Huske Dam to CFR-TARHEEL based on the measured flow in the Cape Fear River at the W.O. Huske Dam;
- Q_{WOHD}^{-1} = is the inverse of the measured flow rate of the Cape Fear River at W.O. Huske Dam for a given point in time in cubic feet per second (ft³/s); and
- 13,422 *and* 2.019 = are constant values, which correspond to the slope and intercept of the regression line, respectively.

Equation 5: Cape Fear River Flow Volume per Interval

$$V_{CFR,n} = \sum_{m=1}^{M} Q_{WOHD,n,m+t_{offset}} \times (t_{n,m} - t_{n,m-1})$$

where,

- $V_{CFR,n}$ = is the volume of Cape Fear River water that flowed past the sampling point during the baseline mass loading time interval;
- n = represents the baseline mass loading time intervals number for which the volume is being calculated;
- m = represents a 15-minute flow measurement recorded by the USGS station at W.O. Huske Dam during a baseline mass loading time interval "n";
- M = the total number of 15-minute flow measurements recorded by the USGS station at W.O. Huske Dam during a baseline mass loading time interval "*n*";
- $Q_{WOHD,n,m+t_{offset}}$ = is the Cape Fear River flow rate (units of volume per time) at Tar Heel Ferry Road bridge based on the recorded values at W.O.Huske Dam and adjusted for travel time as described in Equation 4; and
- $t_{n,m} t_{n,m-1}$ = is the length of time for the flow measurement durations (units of time reported typically in 15-minute intervals by USGS).

4.1.3 Captured Mass Load Calculation Methodology

Remedies implemented or to be implemented by Chemours (e.g., onsite seeps interim remedies, Outfall 002 remedy, etc.) will prevent PFAS mass loads from reaching the Cape Fear River. The specific methodology for estimating the prevented mass per remedy will be developed on a per remedy basis. The goal of such calculations will be to estimate, for a given time period, the PFAS mass diverted from reaching the Cape Fear River by the remedy that would have otherwise reached the Cape Fear River.



4.2 Bladen Bluffs and Kings Bluff Intake Calculation Methodology

This subsection presents the methodology used to calculate PFAS mass at Bladen Bluffs and Kings Bluff Intakes. Total PFAS mass is calculated as:

Equation 6: Mass at Bladen Bluffs and Kings Bluff Intakes

$$M_{BB/KB} = \sum_{i=1}^{l} M_i = \sum_{i=1}^{l} C_i \times Q$$

where,

- $M_{BB/KB}$ = Total PFAS mass in the downstream river locations (Bladen Bluffs or Kings Bluff Intakes) measured in mass per unit time [MT⁻¹], typically mg/s;
- i = represents each of the PFAS constituents being evaluated;
- *I* = represents total number of PFAS constituents included in the summation of Total PFAS concentrations;
- M_i = mass load of each PFAS constituent *i* with measured units in mass per unit time [MT⁻¹], typically mg/s;
- C_i = concentration of each PFAS constituent *i* with measured units typically in nanograms per liter; and
- Q = volumetric flow rate with measured units in volume per time [L³T⁻¹], typically liters per second (L/s). For Bladen Bluffs, the volumetric flow recorded at W.O. Huske Dam is adjusted for travel time using Equation 7.

For Bladen Bluffs, the time offset applied to the flow recorded at W.O. Huske Dam will be estimated based on the results of a numerical model of the Cape Fear River, which developed a regression curve between the USGS reported gage heights at W.O. Huske Dam and travel times (Equation 8).

Equation 7: Travel time offset W.O. Huske Dam to Bladen Bluffs

$$t_{offset} = 8,826 \cdot Q_{WOHD}^{-1} + 1.530$$

where,

- t_{offset} = is the travel time flow in the Cape Fear River takes in hours to pass from the W.O. Huske Dam to Bladen Bluffs Intake location based on the measured flow in the Cape Fear River at the W.O. Huske Dam;
- Q_{WOHD}^{-1} = is the inverse of the measured flow rate of the Cape Fear River at W.O. Huske Dam for a given point in time in cubic feet per second; and

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8,826 *and* 1.530 = are constant values, which correspond to the slope and intercept of the regression line, respectively.

4.3 Cape Fear River PFAS Mass Loading Model Calculation Methodology

This subsection presents the Mass Loading Model methodology for estimating the mass discharge of PFAS from the potential PFAS transport pathways to the Cape Fear River. The Total PFAS mass discharge entering the Cape Fear River is defined in this model as the combined mass per unit time or mass discharge (e.g., mg/s) from potential pathways. Total PFAS mass load entering the Cape Fear River is calculated as:

Equation 9: Cape Fear River Estimated Mass Discharge from Mass Loading Model

$$MD_{CFR} = \sum_{p=1}^{9} \sum_{i=1}^{I} MD_{p,i} = \sum_{p=1}^{9} \sum_{i=1}^{I} (C_{n,i} \times Q_n)$$

where,

- MD_{CFR} = Total PFAS estimated mass discharge entering the Cape Fear River, measured in mass per unit time [MT⁻¹], typically mg/s;
- p = represents each of the 9 potential PFAS transport pathways described further in Section 4.4. To facilitate model construction, the Seeps (Transport Pathway 6) were further discretized as Seep A (Transport Pathway 6A), Seep B (Transport Pathway 6B), Seep C (Transport Pathway 6C) and Seep D (Transport Pathway 6D);
- i = represents each of the PFAS constituents being evaluated;
- *I* = represents total number of PFAS constituents included in the summation of Total PFAS concentrations;
- $MD_{p,i}$ = mass load of each PFAS constituent *i* from each potential pathway *p* with measured units in mass per unit time [MT⁻¹], typically mg/s;
- $C_{p,i}$ = concentration of each PFAS constituent *i* from each potential pathway *p* with measured units in mass per unit volume [ML⁻³], typically nanograms per liter (ng/L); and
- Q_n = volumetric flow rate from each potential pathway *n* with measured units in volume per time [L³T⁻¹], typically L/s.



4.4 PFAS Mass Loading Model Pathways

The nine potential pathways representing compartments to the PFAS Mass Loading Model are described below. These pathways were identified as potential contributors of PFAS to river PFAS concentrations.

4.4.1 Upstream Cape Fear River (Transport Pathway 1)

The upstream PFAS mass discharge contribution to Cape Fear River will be estimated using measured Cape Fear River PFAS concentrations and flow rates. One water sample will be collected immediately upstream of the Site and Willis Creek at River Mile 76 to estimate upstream PFAS mass discharge contribution to Cape Fear River. River water samples will be collected at the thalweg (i.e., deepest point of the river transect) at middepth in the water column.

Volumetric flow rates for the Cape Fear River were measured at the USGS flow gauging station located at the W.O. Huske Dam, approximately 0.5 river miles downstream of the Site. The volumetric flow rate immediately upstream of the Site (River Mile 76) will be estimated using a volumetric budget accounting for flows between River Mile 76 and the W.O. Huske Dam. The volumetric flow rate at River Mile 76 will be estimated by subtracting inflows from Willis Creek, upwelling groundwater, seeps to the river, and Outfall 002 and by adding the river water intake from Chemours to the flow rate measurement from the W.O. Huske Dam (Equation 6).

Equation 6: Flow at Upstream Cape Fear River and Groundwater

$$Q_{Upstream} = Q_{WOHD} - (Q_{WC} + Q_{OF002} + Q_{Onsite GW} + Q_{Seeps}) + Q_{Intake}$$

where,

 $Q_{Upstream}$ = is the flow volume at River Mile 76;

 Q_{WOHD} = is the flow volume at W.O. Huske Dam, as reported by the USGS;

- Q_{WC} = is the flow volume at Willis Creek, as measured by the point velocity method;
- Q_{OF002} = is the flow volume at Outfall 002 as reported in Facility Discharge Monitoring Reports;
- $Q_{Onsite GW}$ = is the flow volume for onsite groundwater, as calculated based on the cross-sectional area, hydraulic gradient, and hydraulic conductivity for segments of the Black Creek Aquifer along the Cape Fear River Frontage;
- Q_{Seeps} = is the summed flow volume for Seeps A, B, C, and D, as measured using flumes; and

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 Q_{intake} = is the flow volume at the Facility intake, as reported in the Facility DMRs.

4.4.2 Tributaries – Willis Creek, Georgia Branch Creek, and Old Outfall 002 (Transport Pathways 2, 7 and 9)

The PFAS mass discharge contribution to the Cape Fear River from tributaries to the Cape Fear River (Willis Creek, Georgia Branch Creek and Old Outfall 002) will be estimated using PFAS concentrations and flow rate data. PFAS samples will be collected at each tributary at a location near the discharge point to the Cape Fear River, but still far enough upstream in the tributary where they are not potentially influenced by the Cape Fear River. Since analytical sample locations are near the discharge point to the Cape Fear River, model input for tributaries will account for loading from groundwater discharging to the tributary, onsite surface water runoff into the tributary, and direct aerial deposition on these tributaries

Volumetric discharge rates for the tributaries will be measured using a flume at Old Outfall 002 and flow velocity gauging at the creeks as outlined in the *Seeps and Creeks Investigation Report* (Geosyntec, 2019a). Detailed methods for flow measurements are presented in Appendix A.

4.4.3 Aerial Deposition to the Cape Fear River (Transport Pathway 3)

The PFAS mass discharge from direct aerial deposition of PFAS to the Cape Fear River will be estimated using air deposition modeling results for HFPO-DA from the Site (ERM, 2018). Average deposition rates to the Cape Fear River will be estimated based on the reported aerial extent and deposition contours. Estimated deposition rates will be combined with the average river surface area and estimated residence time of flowing Cape Fear River water to estimate a mass discharge from aerial deposition. The mass discharge of PFAS compounds will be estimated by using the relative concentration ratios of other PFAS to HFPO-DA based on measured concentrations from offsite wells. Supporting documentation for this estimation is included in Appendix B. The 2018 emissions reduction scenario outlined in the ERM report (ERM, 2018) is likely a conservative assumption as further air emission reductions controls have been implemented compared to the modeled scenario. As assessment of air emissions controls controls are been were formed as the performance of the transmission of a performance of the performance of the performance of the transmission of a performance of the performance of the modeled scenario. As assessment of air emissions controls have been implemented compared to the modeled scenario. As assessment of air emissions controls controls controls performance of the performance of the

4.4.4 Onsite Groundwater (Transport Pathways 5 and 6)

The Mass Loading Model describes two groundwater PFAS transport pathways to the Cape Fear River. First, the indirect pathway of groundwater to the onsite seeps which

discharge to the Cape Fear River, and second, the direct pathway of Black Creek aquifer groundwater discharging directly to the river.

4.4.4.1 Indirect Pathway – Onsite Groundwater Seeps to River (Transport Pathway 6)

Four seeps at the Site have been identified that discharge directly to the Cape Fear River: Seep A, Seep B, Seep C and Seep D (Figure 4). The PFAS mass discharge from these seeps to the Cape Fear River will be estimated using measured PFAS concentrations and volumetric discharged rates. Volumetric discharge rates will be calculated using flumes as detailed in Appendix A.

4.4.4.2 Direct Pathway – Groundwater Discharge to River (Transport Pathway 5)

The PFAS mass discharge of onsite groundwater discharge from the Black Creek Aquifer to the Cape Fear River will be estimated by calculating the sum of the PFAS mass discharge for eight segments of the Black Creek aquifer along the Cape Fear River frontage. PFAS mass discharge for each segment will be calculated based on the following parameters:

- The cross-sectional area of the Black Creek Aquifer for each segment, as determined from a three-dimensional hydrostratigraphic model of the Site;
- The hydraulic gradient for each segment, as determined from groundwater level contours in the vicinity of the river frontage;
- The hydraulic conductivity for each segment, as determined from slug tests conducted on monitoring wells representative of the Black Creek Aquifer; and
- PFAS concentrations detected in monitoring wells in the vicinity of each segment.

Further details on the onsite groundwater discharge term and associated calculations are provided in Appendix C.

4.4.5 **Outfall 002 (Transport Pathway 4)**

The PFAS mass discharge of PFAS from Outfall 002 to the Cape Fear River will be estimated using measured PFAS concentrations and measured Outfall 002 volumetric flow rates. The concentration of PFAS compounds for Outfall 002 will be adjusted for PFAS already present in the sample collected at the Intake River Water at Facility before being input into the model. The PFAS present in intake water are already accounted for in the Mass Loading Model in pathways 1, 2, and 3 (Upstream River, Willis Creek and Direct Aerial Deposition). Daily volumetric discharge from Outfall 002 to the Cape Fear River is recorded and will be used to calculate the volumetric flow rate.



4.4.6 Adjacent and Downstream Offsite Groundwater (Transport Pathway 8)

The PFAS mass discharge from adjacent (i.e., across or on the east side) and downstream offsite groundwater to the Cape Fear River will be calculated based on estimated upstream groundwater loading described in Section 4.4.1. PFAS detected in offsite groundwater originate from aerial deposition which has occurred in all directions from the Site (Geosyntec, 2019b). These aerially deposited PFAS have subsequently infiltrated to groundwater and migrate towards the Cape Fear River where they lead to upstream, adjacent and downstream offsite groundwater PFAS mass. The upstream offsite groundwater PFAS mass discharge will be estimated relatively simply by using measured river flows and concentrations at River Mile 76 upstream of the Site. Here only the upstream offsite groundwater PFAS mass discharge is present in the river at this location. Conversely, the adjacent and downstream offsite groundwater PFAS mass discharge is difficult to measure directly since many PFAS mass discharges from all other pathways are present in the river where these offsite groundwater contributions join the river. Additionally, adjacent and downstream offsite groundwater have a relatively small component of the Total PFAS mass discharge making their additional contributions to the total discharge difficult to distinguish from other discharges already present.

Therefore, since PFAS mass discharge from offsite groundwater both upstream and downstream of the Site follow the same dynamics (deposition, infiltration, migration, discharge) the adjacent and downstream PFAS mass discharge will be scaled from the upstream offsite groundwater mass discharge estimate. The downstream offsite groundwater loadings are scaled to the upstream offsite groundwater loadings based on the length of river downstream of the Site known to be in contact with offsite groundwater containing PFAS compared to the length of the river upstream also in contact with offsite groundwater containing PFAS. A description of these calculations is presented in Appendix D.

4.5 **Potential Adjustments**

The calculation methodologies described in this section have been outlined based on the present understanding of Site conditions. If conditions or methods change, modifications may need to be made to this protocol. For example, two components of the pre-design investigation, anticipated in Q3 and Q4 2020, includes installation of passive flux meters in wells along the Cape Fear River and aquifer tests in extraction wells adjacent to the Cape Fear River. Both investigations will provide a better understanding of the connection between the Black Creek Aquifer and the Cape Fear River. Accordingly, the Mass Loading Model may be modified to incorporate findings from these investigations. Modifications to the calculation methodologies will be described in submitted reports



described in Section 5. At the end of each reporting year, Chemours may request to DEQ a modification of the protocol.

5 **REPORTING**

The data and results from the three mass loading sampling programs (Cape Fear River Mass Loads, Bladen Bluffs and Kings Bluff Intakes Mass Discharge, and the Cape Fear River Mass Loading Model) will be provided to NCDEQ on a quarterly basis where outputs for the previous quarter are provided within ninety (90) days of the end of the previous quarter.

6 REFERENCES

- Geosyntec, 2019a. Seeps and Creeks Investigation Report. Chemours Fayetteville Works. 26 August 2019
- Geosyntec, 2019b. Corrective Action Plan. Chemours Fayetteville Works. December 31, 2019.



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TABLES

TABLE 1 PFAS ANALYTICAL METHODS AND ANALYTE LIST Chemours Fayetteville Works, North Carolina

Analytical Method	Common Name	Chemical Name		Chemical Formula
	HFPO-DA*	Hexafluoropropylene oxide dimer acid		C6HF11O3
	PEPA	Perfluoro-2-ethoxypropionic acid (Formerly Perfluoroethoxypropyl carboxylic acid)	267239-61-2	C5HF9O3
	PFECA-G	Perfluoro-4-isopropoxybutanoic acid	801212-59-9	C12H9F9O3S
	PFMOAA	Perfluoro-2-methoxyacetic acid	674-13-5	C3HF5O3
	PFO2HxA	Perfluoro-3,5-dioxahexanoic acid (Formerly Perfluoro(3,5-dioxahexanoic) acid)		C4HF7O4
	PFO3OA	Perfluoro-3,5,7-trioxaoctanoic acid (Formerly Perfluoro(3,5,7-trioxaoctanoic) acid)		C5HF9O5
	PFO4DA	Perfluoro-3,5,7,9-tetraoxadecanoic acid (Formerly Perfluoro(3,5,7,9-tetraoxadecanoic) acid)		C6HF11O6
Table 3+ Lab SOP	РМРА	Perfluoro-2-methoxypropionic acid (Formerly 2,3,3,3-Tetrafluoro-2-(trifluoromethoxy)propanoic)	13140-29-9	C4HF7O3
	PFO5DA	Perfluoro-3,5,7,9,11-pentaoxadodecanoic acid	39492-91-6	C7HF13O7
	PS Acid (Formerly PFESA-BP1)	Ethanesulfonic acid, 2-[1-[difluoro[(1,2,2-trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro- (Formerly PFESA-BP)	29311-67-9	C7HF13O5S
	Hydro-PS Acid (Formerly PFESA-BP2)	Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro- (Formerly PFESA-BP2)	749836-20-2	C7H2F14O5S
	PFHpA*	Perfluoroheptanoic acid	375-85-9	C7HF13O2

Notes:

 \ast - HFPO-DA and PFHpA are also analyzed by EPA Method 537 Mod.

EPA - Environmental Protection Agency

PFAS - Per- and Polyfluoroalkyl substances

SOP - Standard Operating Procedure

TABLE 2

SURFACE WATER, SEEP AND RIVER SAMPLING LOCATIONS AND AND FLOW MEASUREMENT METHODS Chemours Fayetteville Works, North Carolina

Location ID	Location Description	Sample Collection Method	Flow Measurement Method
OLDOF-1	Mouth of Old Outfall 002	24-hour composite	Flume
SEEP-A-1	Mouth of Seep A	24-hour composite	Flume
SEEP-B-1	Mouth of Seep B	24-hour composite	
SEEP-B-2	Tributary to Seep B		Flume
SEEP-B-TR1	Tributary to Seep B		Flume
SEEP-B-TR2	Tributary to Seep B		Flume
SEEP-C-1	Mouth of Seep C	24-hour composite	Flume
SEEP-D-1	Mouth of Seep D	24-hour composite	Flume
WC-1	Mouth of Willis Creek	24-hour composite	Velocity Probe
GBC-1	Mouth of Georgia Branch Creek	Grab	Velocity Probe
CFR-MILE-76	Cape Fear River Mile 76	Grab	USGS Data
CFR-BLADEN	Cape Fear River at Bladen Bluffs	Grab	USGS Data
CFR-KINGS	Cape Fear River at Kings Bluff Raw Water	Grab	USGS Data
TAR HEEL	Cape Fear River at Tar Heel Ferry Road Bridge	24-hour composite	USGS Data
W.O. Huske Dam	USGS Gauge Site No. 02105500		USGS Data
Intake River Water at	Water Drawn Through the Intake Sampled at	24 hour composite	Facility DMRs
Facility	the Power Area at the Site	24-nour composite	
Outfall 002	Outfall 002 in open channel	24-hour composite	Facility DMRs

Notes:

-- not applicable

DMRs - discharge monitoring reports

EPA - Environmental Protection Agency

PFAS - per- and polyfluoroalkyl substances

USGS - United States Geological Survey

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TABLE 3

GROUNDWATER MONITORING WELL SAMPLING AND WATER LEVEL MEASUREMENT LOCATIONS Chemours Fayetteville Works, North Carolina

Area	Hydrogeological Unit ¹	Well ID	Adjacent Surface Water Feature
Onsite	Black Creek	PIW-3D	Cape Fear River
Onsite	Floodplain	PIW-7S	Cape Fear River
Onsite	Black Creek	PIW-7D	Cape Fear River
Onsite	Floodplain	LTW-01	Cape Fear River
Onsite	Black Creek	LTW-02	Cape Fear River
Onsite	Floodplain	LTW-03	Cape Fear River
Onsite	Floodplain	LTW-04	Cape Fear River
Onsite	Black Creek	LTW-05	Cape Fear River
Onsite	Black Creek	PZ-22	Cape Fear River
Onsite	Surficial	PW-06	Georgia Branch Creek
Onsite	Surficial	PW-07	Georgia Branch Creek
Onsite	Surficial	PW-04	Old Outfall
Onsite	Black Creek	PW-11	Old Outfall
Onsite	Black Creek	PW-09	Willis Creek
Onsite	Surficial	SMW-11	Willis Creek
Onsite	Surficial	SMW-10	Willis Creek
Onsite	Black Creek	SMW-12	Willis Creek
Onsite	Floodplain	PIW-1S	Cape Fear River / Willis Creek
Onsite	Surficial	PIW-1D	Cape Fear River / Willis Creek
Offsite	Black Creek	Bladen-1D	Georgia Branch Creek

Notes:

1. Hydrogeologic units for existing wells determined based on boring log descriptions.



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FIGURES





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





Legend

- ▲ Flow Measurement Location
- Sample Location
- -- Observed Seep
- Nearby Tributary
- Site Boundary

Notes:

- The outline of Cape Fear River is approximate and is based on open data from ArcGIS Online and North Carolina Department of Environmental Quality Online GIS.
 Basemap sources: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community.

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APPENDIX A

Field Methods

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APPENDIX A

FIELD METHODS

This appendix describes the field methods and procedures that will be employed for collecting onsite seep and surface water samples, gauging stream flow, groundwater level measurements, water quality parameter assessment and sample collection.

ONSITE SEEP AND SURFACE WATER SAMPLE COLLECTION METHODS

Onsite Seep and Surface Water Composite Sampling Methods

Autosamplers will be used to collect 24-hour integrated samples from various surface water bodies and onsite Seeps. The autosamplers will collect sample aliquots once per hour. The sample tubing from the autosampler will be positioned at minimum 2 inches above the bottom of the water body flow with the open end of the sample tubing pointed in the downstream direction to minimize the potential for sediment accumulation and uptake. Autosampler materials will be consisting of highdensity polyethylene (HDPE) tubing, silicon tubing, and an HDPE sample reservoir. Water from the sample reservoir will be decanted into laboratory supplied bottles (e.g. 250-milliliter [mL] HDPE bottles for PFAS analysis) and then sent to an approved laboratory. Field parameters will be measured twice for composite samples: once during composite sampling (collected directly from the water stream), and once after composite sampling (collected from the autosampler reservoir). The following water quality parameters will be recorded:

- pH;
- Temperature (degrees Celsius [°C]);
- Specific Conductivity (microsiemens per centimeter [µS/cm]);
- Dissolved Oxygen (DO) (milligrams per liter [mg/L]); and,
- Oxidation-Reduction Potential (ORP) (millivolts [mV])

Creek and Seep Water Grab Sampling Methods

Where composite sample collection is not feasible due to access or other field conditions, creek and seep water samples will be collected as grab samples. Laboratory-supplied 250 mL HDPE sample bottles will be lowered into the flowing water of the creek to collect the sample. The bottles will be lowered into the stream either using a properly decontaminated dip rod with bottle attached with a nylon zip tie, or in shallow streams, by hand. The bottle will be lowered into the stream with the cap removed, open and facing oncoming flow. Where possible, the sample will be collected from the middle of the stream. Care will be taken to avoid collecting suspended solids or other materials in the sample. The following water quality parameters will be measured after sample collection using water from the same location in the stream:

- pH;
- Temperature (°C);
- Specific Conductivity (µS/cm);

- DO (mg/L); and
- ORP (mV).

Cape Fear River Water Grab Sampling Methods

Cape Fear River water samples will be collected using a peristaltic pump and new dedicated HDPE tubing and dedicated silicone tubing for the pump head at each location. The tubing will be lowered to the specified sampling depth below the water surface using an anchor weight and the tubing fastened to the anchor pointing upwards. Surface water will be pumped directly from the submerged tubing through the pump head to a flow-through cell. Field parameters will be monitored over a 5-minute interval, then the flow-through cell will be disconnected, the tubing cut to provide a new, clean end and a grab sample will be collected from the discharge of the peristaltic pump in new 250 mL laboratory-supplied HDPE bottles. The following water quality parameters will be measured:

- pH;
- Temperature (°C);
- Specific Conductivity (µS/cm);
- DO (mg/L); and
- ORP (mV).

FLOW GAUGING METHODS

Flow velocity will be measured after sample collection at seep and creek locations specified in Table 2. Flow velocity will be measured using flumes where they exist, otherwise flow velocity will be measured via flow meters.

Flumes

Flumes are currently installed in Seep A, Seep B, Seep C, Seep D, and Old Outfall 002 under Nationwide Permit 38 (United States Army Corps of Engineers, June 2019). Where present, they will be used to calculate flow based on the data collected by the level logger installed in the flume.

Flow Velocity Gauging

Where flumes are not installed (i.e., Willis Creek and Georgia Branch Creek), the flow rate of the stream will be measured using a submersible flow meter. The flow meter will be placed beneath the flowing stream along the cross section of the stream at regular intervals (e.g. every six inches) and the height of the water will be recorded along with the recorded water velocity. These measurements will then be used to calculate the volumetric flow of water passing through the structure based on the regular geometry and measured flow rates. Flow will be measured using two to three transects to assess variability in estimated flow. Transects that have fairly uniform cross sections that could be gauged with minimal disturbance will be selected.

SYNOPTIC WATER LEVEL MEASUREMENTS

Water level measurements for monitoring wells listed in Table 3 will be collected during a single synoptic event. At each location, notes on well condition, weather, date and time of collection, depth to bottom of well and depth to water level from top of casing will be recorded.

GROUNDWATER SAMPLING METHODS

Designated monitoring wells will be monitored as part of the quarterly monitoring activities. These wells are listed in Table 3 and Figure 3.

The groundwater samples will be analyzed for the list of Table 3+ compounds listed in Table 1. Field equipment will be inspected by the program on-Site supervisor and calibrated daily prior to use according to the manufacturer's recommended guidelines. Field parameters will be measured with a water quality meter after sample collection and will include the following:

- pH;
- Temperature (°C);
- Specific Conductivity (µS/cm);
- DO (mg/L);
- ORP (mV);
- Turbidity (nephelometric turbidity units [NTU]); and,
- Color.

Non-dedicated or non-disposable sampling equipment will be decontaminated immediately before sample collection in the following manner:

- 1. De-ionized water rinse;
- 2. Scrub with de-ionized water containing non-phosphate detergent (i.e., Alconox®); and
- 3. De-ionized water rinse.

Disposable equipment (e.g. gloves, tubing, etc.) will not be reused. New sample containers will be used for each sample.

Groundwater samples will be collected, where possible, using low-flow sampling techniques as discussed in detail in the *Long-term Groundwater Monitoring Plan* (Parsons, 2018) and briefly summarized here.

- 1. New disposable or dedicated HDPE tubing will be placed at the midpoint of the well's screened interval.
- 2. Water will be purged through a flow-through cell attached to a water quality meter capable of measuring pH, temperature, specific conductivity, dissolved oxygen, and ORP.
- 3. Water will be pumped using a peristaltic pump, with dedicated silicone tubing for the pump head, at wells with water level less than 30 feet. A submersible pump will be used for wells with water level deeper than 30 feet.

- 4. Groundwater will be pumped directly from submerged tubing through the pump head to a flow-through cell until field parameters (pH, temperature, specific conductivity, DO, ORP) and will be stabilized within ±10% over three consecutive readings within a five-minute interval. If field parameters stabilized, but turbidity remains stable yet elevated greater than 20 NTU, field personnel will purge five well volumes prior to sample collection.
- 5. Water levels in the designated wells will be monitored during purging so that minimum draw-down of the water column was maintained.
- 6. Once flow-through cell readings are stable, the flow-through cell will be disconnected, the tubing cut to provide a new clean end and samples will be collected from the discharge of the peristaltic pump in new 250 mL laboratory-supplied HDPE bottles.
- 7. Sample identification information (e.g., well/sample identification number, sample time and date, samplers' names, preservative, and analytical parameters) will be recorded on the bottle label with permanent ink after the sample will be collected.

Sample Packing and Shipping

Upon sample collection, each containerized sample will be placed into an insulated sample cooler. Wet ice will be placed around the sample containers within heavy-duty plastic bags within the sample cooler.

A chain-of-custody form was completed by the field sample custodian for each sample shipment. Sample locations, sample identification numbers, description of samples, number of samples collected, and specific laboratory analyses will be recorded on the chain-of-custody form.

Field QA/QC Samples

Field quality assurance/ quality control (QA/QC) samples will be collected as discussed in detail in the *Long-term Groundwater Monitoring Plan* (Parsons, 2018) and summarized below:

- 1. For samples collected to be analyzed by Method EPA 537 Modified, three blind duplicate samples will be collected.
- 2. For samples collected to be analyzed by Method Table 3+, three blind duplicate samples will be collected.
- 3. For samples collected to be analyzed by EPA 537, three Modified Matrix Spike and Matrix Spike Duplicate (MS/MSD) samples will be collected.
- 4. For samples collected to be analyzed by Method Table 3+, three MS/MSD samples will be collected.
- 5. For groundwater samples, equipment blanks and field blanks will be collected daily.
- 6. For surface water samples, three equipment blanks will be collected.

REFERENCES

Parsons, 2018. Long-term Groundwater Monitoring Plan. September 28, 2018.

Parsons, 2020. Fayetteville Works Health and Safety Plan.

United States Army Corps of Engineers. Nationwide Permit 6. 19 March 2017. http://saw-reg.usace.army.mil/NWP2017/2017NWP06.pdf. Accessed 30 January 2019.

United States Army Corps of Engineers. Nationwide Permit 36, 06 June 2019.

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APPENDIX B

Supporting Calculations – Direct Aerial Deposition on Cape Fear River

APPENDIX B

SUPPORTING CALCULATIONS – DIRECT AERIAL DEPOSITION ON CAPE FEAR RIVER

INTRODUCTION AND OBJECTIVE

Nine pathways (Figure 1) are identified as potentially contributing to observed Cape Fear River per- and polyfluoroalkyl substances (PFAS) concentrations. These pathways include direct PFAS aerial deposition to the Cape Fear River. This pathway is identified as Transport Pathway Number 3 in the PFAS mass loading model. The mass discharge (mass per unit time measured in milligrams per second [mg/s]) from direct aerial deposition of PFAS to the Cape Fear River will be estimated by scaling air deposition modeling results for Hexafluoropropylene oxide dimer acid (HFPO-DA; ERM, 2018). The objective of this appendix is to present the calculations for estimating aerially deposited PFAS directly on the Cape Fear River during a mass loading event.

APPROACH

HFPO-DA mass loading directly to the Cape Fear River will be estimated using the reported aerial extent and deposition contours modeled for October 2018 (ERM, 2018). As depicted in (Table B1), the HFPO-DA air loading data (micrograms per meters squared $[\mu g/m^2]$) provided from ERM (2018) will be used to calculate the net hourly deposition rate (nanograms per meters squared per hour [ng/m²/hr]) using **Equation 1** below:

Equation 1: Net Hourly Deposition Rate

$$DR_{NET} = \frac{ML_{AIR}}{t_{AIR}}$$

where:

- DR_{NET} = Net hourly deposition rate with units of mass per area per time (M L⁻² T⁻¹), typically in ng/m²/hr;
- ML_{AIR} = Air mass loading of HFPO-DA with units of mass per area (M L⁻²), typically $\mu g/m^2$; and
- t_{AIR} = time that air mass loading was modeled (T), typically hours.

Depositional area along the river will be calculated using available data for river width and computed river lengths where deposition contours were modeled (ERM, 2018). Average river width in meters (m) along sections of the Cape Fear River will be estimated in GIS. As depicted in Figures B1 through B5, five sections along the Cape Fear River (Center, Up River Sections 1 and 2, and Down River Sections 1 and 2) with HFPO-DA concentrations contours ranging from 40 to 640 μ g/m² have been identified and the length of the Cape Fear River along each of the sections will be measured. For each section, the average river width and lengths between contours shown in Figures B1 through B5 will be used to calculate cross-sectional areas (in m²) as described in **Equation** below:

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Equation 2: Cape Fear River Surface Area for Each Section

$$A_s = L_s \times W_s$$

where,

- A_s = total spatial area over which deposition occurs between contours (L²) in section "s", typically in m²;
- s = section along the Cape Fear River with HFPO-DA concentrations contours ranging from 40 to 640 μ g/m² (five sections in total);
- L = total length of river within section "s", typically in m; and
- W_s = average river width in section "s", typically in m.

Start and end deposition rates $(ng/m^2/hr)$ for each section along the Cape Fear River will be estimated based on the deposition contours and corresponding net hourly deposition rate (Table B1); a combined deposition rate for each section will be calculated as the average of the start and end deposition rates. River velocity (meters per hour [m/hr]) will be estimated from measured flow rates from USGS (2020) and the calculated river cross sectional area. Section lengths will be used to calculate HFPO-DA travel time based on the estimated river velocities. The combined deposition rate ($ng/m^2/hr$) from Table B1, section area (m^2), and travel time (hr) will be used to calculate mass HFPO-DA deposited (ng) as follows in **Equation 3** below.

Equation 2: Total HFPO-DA Mass Discharge to Cape Fear River

$$MD_{HFPO-DA} = \sum_{s=1}^{S} DR_{AVG,s} \times A_s \times t_s$$

where,

- $MD_{HFPO-DA}$ = total mass discharge of HFPO-DA into the river across all sections, with units of mass per time (M T-¹), typically mg/s;
- s = section along the Cape Fear River with HFPO-DA concentrations contours ranging from 40 to 640 μ g/m²;
- S = total number of sections along the Cape Fear River with HFPO-DA concentrations contours ranging from 40 to 640 μ g/m², five in total;
- $DR_{AVG,s}$ = average deposition rate based from the ERM model (2018) in section "s", typically in ng/m²/hr;
- A_s = spatial area over which deposition occurs in section "s", typically in m²; and
- t_s = travel time through the river length in section "s", typically in hr.

As reported in the Corrective Action Plan (Geosyntec 2019), ten offsite groundwater seeps south of Old Outfall 002 (Seeps E to M) were identified on the west bank of the Cape Fear River south of the Site. Seeps E to M were sampled in October 2019 and Seeps E to K were sampled in March

2020. The results of both sampling events indicate that Seeps E to M show an aerial deposition PFAS signature (concentrations decrease in seeps more distant from the Site). Accordingly, the offsite seep data will used to build a relationship, i.e., scaling factor, between HFPO-DA and other PFAS compounds (Figure B6). This scaling factor will be used to estimate mass discharge of Total PFAS compounds to the Cape Fear River as shown in **Equation 4**.

Equation 4: Mass Discharge to Cape Fear River

$$MD_{PFAS} = MD_{HFPO-DA} \times R$$

where,

 MD_{PFAS} = total mass discharge of PFAS compounds into the river, typically in mg/s;

 $MD_{HFPO-DA}$ = total mass discharge of HFPO-DA into the river, typically in mg/s; and

R = average ratio of measured HFPO-DA to PFAS compounds across the nine offsite seeps.

REFERENCES

ERM, 2018. Modeling Report: HFPO-DA Atmospheric Deposition and Screening Groundwater Effects. 27 April 2018.

Geosyntec, 2019. Corrective Action Plan. Chemours Fayetteville Works. December 31, 2019.

USGS, 2020. USGS 02105500 Cape Fear River at Wilm O Huske Lock near Tarheel, NC. Available at: https://waterdata.usgs.gov/nwis/uv?site_no=02105500

Modeled Deposition Contours, October 2018 Scenario

40 µg/m²/yr

80 µg/m²/yr

160 µg/m²/yr

320 µg/m²/yr

640 µg/m²/yr

3 StatePlane North Carolina FIPS 3200 Feet; Units in Foot U

μg / m²/yr - micrograms per square meter per year

HFPO-DA deposition model contours for October 2018 from ERM, 2018, Modeling Report: HFPO-DA Atmospheric Deposition and Screening Groundwater Effects. 27 April 2018.

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Raleigh, NC

August 2020

B1

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

TABLE B1 NET HOURLY HFPO-DA DEPOSITION RATE Chemours Fayetteville Works, North Carolina

Air Loading (µg/m ²)	Air Loading (ng/m ²)	Time (year)	Time (hour)	Net Hourly Deposition Rate (ng/m ² /hr)	River Sections Within Air Loading Zones
40	40,000	1	8 760	4.6	Up River Section 2
10	40,000	1	0,700	4.0	Down River Section 2
	80,000	1	8,760	9.1	Up River Section 1
80					Up River Section 2
80					Down River Section 1
					Down River Section 2
	160,000	1			Center
160			8,760	18.3	Up River Section 1
					Down River Section 1
320	320,000	1	8,760	36.5	Not used in calculations
640	640,000	1	8,760	73.1	Not used in calculations

Notes:

1. HFPO-DA model values are from ERM (2018). Modeling Report: HFPO-DA Atmospheric Deposition and Screening

Groundwater Effects. 27 April 2018.

2. Air deposition contours are shown in Figures J-2 through J-6.

3. Net hourly deposition rates are used in the mass discharge calculations, Table J5.

Abbreviations:

HFPO-DA: Hexafluoropropylene oxide dimer acid; or dimer acid.

 $\mu g/m^2$: micrograms per meter square.

ng /L: nanograms per liter.

ng/m²/hr: nanograms per meter square per hour.

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APPENDIX C

Supporting Calculations – Onsite Groundwater Pathway

APPENDIX C

SUPPORTING CALCULATIONS - ON SITE GROUNDWATER PATHWAY

INTRODUCTION AND OBJECTIVE

Based on the conceptual site model, the Black Creek Aquifer and the Flood Plain deposits at the riverbank are the primary hydrogeologic units that are potentially in hydraulic connection with the Cape Fear River. The Cape Fear River stage is lower than the top of the Black Creek Aquifer, except during peak rainfall or flooding, indicating that the Cape Fear River is a discharge boundary for the aquifer. Onsite groundwater from the Black Creek Aquifer discharging to the Cape Fear River is therefore a potential pathway for per- and polyfluoroalkyl substances (PFAS) mass loading to the Cape Fear River. This pathway was identified as Transport Pathway Number 5 in the PFAS mass loading design in the. The objective of this appendix is to provide calculations for estimating PFAS mass loading from onsite groundwater discharge based on calculated PFAS mass flux for segments of the Black Creek Aquifer along the river frontage.

APPROACH

The PFAS mass loading from onsite groundwater discharge will be estimated as follows:

- 1. The Cape Fear River frontage will be divided into 8 segments (Figure C1). Each segment includes at least one groundwater monitoring well that is considered representative of the Black Creek Aquifer and that is included in the Corrective Action Plan (Geosyntec, 2019b).
- 2. The thickness of the Black Creek Aquifer (h) will be estimated for each segment based on the segment length and the cross-sectional area of the Black Creek Aquifer, as determined by the three-dimensional hydrostratigraphic model of the Site, constructed using CTech's Earth Volumetric Studio (EVS) software (Geosyntec, 2019b):

$$h = \frac{A}{l}$$

where h is the Black Creek Aquifer thickness [ft];

A is the cross-sectional area of the Black Creek Aquifer [ft^2]; and

l is the segment length [ft].

The EVS model output for each segment is presented in Figure C2.

3. The hydraulic gradient (i) will be derived based on the groundwater level contour map. For each segment, the gradient will be estimated based on the distance between contour lines in the vicinity of the river frontage:

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 $i = \frac{\Delta h}{d}$

where *i* is the hydraulic gradient [ft/ft];

 Δh is the head difference between two contour lines [ft]; and

d is the estimated distance between the contour lines [ft].

This approach is considered to best represent the likely groundwater fluxes discharging from the Black Creek Aquifer to the Cape Fear River. Based on hydrographs from wells along the river presented in Figure C3 hydraulic gradients in the aquifer are relatively constant over time. With the exception of large changes in the river level (over ten feet), these wells respond to river level fluctuation in a subdued manner.

- 4. The hydraulic conductivity (K) will be estimated for each segment using the results of slug tests conducted for select monitoring wells representative of the Black Creek Aquifer. The range of slug test results for LTW-02, LTW-03, and LTW-05 will be used to determine the hydraulic conductivity of segments 3,4, and 7, respectively since these wells are located in the corresponding segments. For other segments where no slug tests are performed, the range of slug test results for the entire Black Creek Aquifer will be used to determine the hydraulic conductivity. In both cases, the minimum hydraulic conductivity and the geometric mean hydraulic conductivity will be used to calculate a range of mass flux values. Table C1 provides the results of the slug tests and the minimum and geometric mean hydraulic conductivities for each segment.
- 5. The total PFAS concentration for each segment will be determined based on grab samples collected from monitoring wells within a given monitoring period. For segments with two wells, the average PFAS concentration will be used.
- 6. Mass flux for each segment, representing the PFAS mass loading to the river from groundwater, will be determined as follows:

$$Q = lhKiCf$$

where Q is the mass flux [mg/s];

l is the segment length [ft];

h is the Black Creek Aquifer thickness [ft];

K is the hydraulic conductivity of the aquifer [ft/s];

i is the hydraulic gradient [ft/ft];

C is the total PFAS concentration [ng/L]; and

f is the conversion factor between cubic feet and liters and between ng and mg.

7. The total mass flux for the groundwater pathway will be calculated as the sum of the individual mass flux results for the 8 segments.

POTENTIAL FUTURE METHODOLOGY MODIFCATIONS

Periodically, adjustments to this calculation methodology may be required based on changes in conditions or refinement of Site knowledge.

REFERENCES

Geosyntec, 2019. Corrective Action Plan. Chemours Fayetteville Works. December 2019.

1,000 50	0 0	1,000 Feet		
Black Creek Aquifer Segments for Groundwater Pathway Chemours Fayetteville Works, North Carolina				
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TABLE C1 HYDRAULIC CONDUCTIVITY RESULTS Chemours Favetteville Works, North Carolina

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			Observed	Minimum	Geometric Mean
Segment	Woll	Slug Test	Hydraulic	Hydraulic	Hydraulic
beginent	Well	Slug Test	Conductivity	Conductivity	Conductivity
			(ft/sec)	(ft/sec)	(ft/sec)
	BCA-01	T1	2.1E-04	2.1E-04	2.8E-04
		T1*	3.7E-04	-	
		T2	2.2E-04	_	
		T2*	3.7E-04	-	
		T3	2.1E-04	-	
		T3*	3.6E-04	-	
		T4	2.2E-04	-	
		T4*	3.9E-04		
	BCA-02	T1	4.6E-04	3.1E-04	5.4E-04
		T1*	1.0E-03		
		T2	4.2E-04		
		T2*	9.1E-04		
		T3	3.4E-04		
		T3*	7.4E-04	-	
		T4	3.3E-04		
		T4*	7.4E-04		
		T5	3.1E-04		
		T5*	6.8E-04		
	BCA-04	T1	1.1E-03	1.1E-03	1.4E-03
		T1*	1.6E-03	-	
		T2	1.1E-03	-	
		T2*	1.7E-03	-	
		T3	1.1E-03	-	
		T3*	1.6E-03	-	
		T4	1.1E-03	-	
		T4*	1.7E-03	-	
		T5	1.2E-03	-	
		T5*	2.3E-03		
3	LTW-02	T1	3.0E-04	3.0E-04	4.0E-04
-		T1*	4.8E-04		
		T2	3.2E-04		
		T2*	4.9E-04		
		T3	3.1E-04	-	
		T3*	4.7E-04		
		T4	3.9E-04	-	
		T4*	5.5E-04	-	
		T5	3.0E-04	-	
		T5*	4.5E-04	-	
4	LTW-03	T1	6 5E-05	2.00E-05	4 6E-05
	2111 05	T2	2 4E-05	2.001 05	1.02 05
		T3	2.4E 05	-	
		T/	2.6E-04	-	
		T5	2.0E 04	-	
7	I TW-05	T1	2.0E-05	1.8E-05	4.8E-05
,	L1W-05	T1*	2.4E-05	1.01-05	4.01-05
		T7	1.8E-05	-	
		T2*	2 5E 05	-	
		12 ¹	5.3E-03		
		14 T4*	7.4E-03	-	
Demoining		14'	1.3E-04		
Remaining $(1, 2, 5, 6)$	All DCA Walls			1 95 05	2 25 04
Segments $(1, 2, 3, 0,$	All DCA wells			1.6E-03	3.2E-04
$and \delta$				1	1

Notes

* - Screen length used for aquifer thickness

BCA - Black Creek Aquifer

ft/sec - feet per second

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APPENDIX D

Supporting Calculations –Adjacent and Downstream Offsite Groundwater

Appendix D

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APPENDIX D

ADJACENT AND DOWNSTREAM OFFSITE GROUNDWATER

This appendix presents the methodology for calculating the PFAS mass discharge from adjacent and downstream offsite groundwater to the Cape Fear River. PFAS detected in offsite groundwater originate from aerial deposition which has occurred in all directions from the Site (CAP Geosyntec, 2019g). These aerially deposited PFAS have subsequently infiltrated to groundwater and migrate towards the Cape Fear River where they lead to upstream, adjacent and downstream offsite groundwater PFAS mass. The upstream offsite groundwater mass discharge is estimated relatively simply by using measured river flows and concentrations at River Mile 76 upstream of the Site. Here, only the upstream offsite groundwater mass discharge is present in the river at this location. Conversely, the adjacent and downstream offsite groundwater PFAS mass discharge is difficult to measure directly since many PFAS mass discharges from all other pathways are present in the river where these offsite groundwater contributions join the river. Additionally, downstream offsite groundwater has a relatively small component of the Total PFAS mass discharge making its additional contributions to the total discharge difficult to distinguish from other discharges already present.

Therefore, since PFAS mass discharge from offsite groundwater upstream, adjacent, and downstream of the Site follow the same dynamics (deposition, infiltration, migration, discharge) the adjacent and downstream PFAS mass discharge is scaled from the upstream offsite groundwater mass discharge estimate. The downstream offsite groundwater loadings are scaled to the upstream offsite groundwater loadings based on the length of river adjacent and downstream of the Site known to be in contact with offsite groundwater containing PFAS compared to the length of the river upstream also in contact with offsite groundwater containing PFAS. The volume of river flow is assumed to be constant immediately upstream and downstream of the Site for the purposes of this calculation. This adjacent and downstream offsite mass discharge will be calculated using Equation 1 below:

Equation 1: Total PFAS Mass Discharge Adjacent and Downstream Offsite Groundwater

$$MD_{adj-d-gw} = \sum_{i=1}^{l} (C_{up-gw,i} \times Q_{CFR}) \times f_{adj-d}$$

where,

 $MD_{adj-d-gw}$ = represents the Total PFAS discharge from adjacent and downstream offsite groundwater to the Cape Fear River, units in mass per unit volume [ML⁻³], typically milligram per second;

i = represents each of the PFAS constituents being evaluated;

- *I* = represents total number of PFAS constituents included in the summation of Total PFAS concentrations;
- $C_{up-gw,i}$ = represents the upstream concentration of each PFAS constituent *i* from measured units in mass per unit volume [ML⁻³], typically nanograms per liter;
- Q_{CFR} = represents the volumetric flow in the Cape Fear River as reported by the United States Geological Survey gage at the W.O. Huske Dam, station ID 02105500 with units used in the equation expressed as volume per time [L³T⁻¹], typically liters per second; and
- f_{adj-d} = represents the unitless scaling factor to adjust offsite upstream groundwater mass discharge to offsite adjacent and downstream mass discharge. Where $f_{up-adj-d}$ is calculated following Equation 2 below:

Equation 2: Offsite Upstream Groundwater to Adjacent and Downstream Offsite Groundwater Mass Discharge Scaling Factor

$$f_{adj-d} = \frac{l_{CFR-adj} + 2l_{CFR-d}}{2l_{CFR-d}}$$

where,

- $l_{CFR-adj}$ = represents the length of the Cape Fear River adjacent to the Site (i.e., the east bank of the Cape Fear River opposite the Site) where PFAS have been detected in offsite groundwater within one mile of the river.
- $2l_{CFR-d}$ = represents the length of the Cape Fear River downstream of the Site where PFAS have been detected in offsite groundwater within one mile of the river. This quantity is multiplied by two (2) as the river has two downstream sides (east and west) from which groundwater discharge can reach the Cape Fear River (adjacent only has one side, east).
- $2l_{CFR-up}$ = represents the length of the Cape Fear River upstream of the Site where PFAS have been detected in offsite groundwater within one mile of the river. This quantity is multiplied by two (2) as the river has two upstream sides (east and west) from which groundwater discharge can reach the Cape Fear River (adjacent only has one side, east).

Figure D1 displays the quantities used in calculating the scaling factor f_{adj-d} on a map of the Cape Fear River and Table D1 provides a calculation of f_{adj-d} .

TABLE D1 Geosyntee Col ADJACENT AND DOWNSTREAM OFFSITE GROUNDWATER MASS DISCHARGE SCALING FACTOR Chemours Fayetteville Works, North Carolina

Item	Value	Unit
$l_(CFR-up)$	14.2	miles
$l_(CFR-adj)$	1.7	miles
$l_(CFR-d)$	4.5	miles
$f_(adj-d)$	0.38	

Calculation Notes for Offsite Upstream Groundwater to Adjacent and Downstream Offsite Groundwater Mass Discharge Scaling Factor $f_{adj-d} = \frac{l_{CFR-adj} + 2l_{CFR-d}}{2l_{CFR-up}}$

where,

 f_{adj-d} = represents the unitless scaling factor to adjust offsite upstream groundwater mass discharge to adjacent and downstream offsite groundwater mass discharge.

 l_{CFR-a} = represents the length of the Cape Fear River adjacent to the Site (i.e. the east bank of the Cape Fear River opposite the Site) where PFAS have been detected in offsite groundwater within one mile of the river.

 $2l_{CFR-d}$ = represents the length of the Cape Fear River downstream of the Site where PFAS have been detected in offsite groundwater within one mile of the river. This quantity is multiplied by two (2) as the river has two downstream sides (east and west) from which groundwater discharge can reach the Cape Fear River (adjacent only has one side, east).

 $2l_{CFR-up}$ = represents the length of the Cape Fear River upstream of the Site where PFAS have been detected in offsite groundwater within one mile of the river. This quantity is multiplied by two (2) as the river has two upstream sides (east and west) from which groundwater discharge can reach the Cape Fear River (adjacent only has one side, east).