



The Chemours Company
Fayetteville Works
22828 NC Highway 87 W
Fayetteville, NC 28306

June 24, 2019

Sheila Holman
Assistant Secretary for the Environment
1601 Mail Service Center
Raleigh, NC 27699-1601
sheila.holman@ncdenr.gov

Re: Submission of Site Associated PFAS Fate and Transport Study Pursuant to Consent Order Paragraph 27

Dear Ms. Holman,

Enclosed, please find a PDF copy of the *Site Associated PFAS Fate and Transport Study* for the Chemours Fayetteville Works. This document presents an evaluation the fate and transport of PFAS associated with the Site in the environment using the best currently available data and information. The evaluation includes a description of physical and chemical mechanisms and compound properties that will influence fate and transport in the environment. The evaluation also presents available empirical data about hexafluoropropylene oxide dimer acid (HFPO-DA) physical properties and fate and transport characteristics. This document meets the requirements of Paragraph 27 of the Consent Order dated February 25, 2019. Geosyntec Consultants of NC, PC has been approved as the third-party consultant by NCDEQ as required under Paragraph 27 of the Consent Order.

As always, if you have any questions or need any additional information concerning this report, or the Consent Order implementation generally, please contact me at Brian.D.Long@chemours.com.

Sincerely,

A handwritten signature in black ink that reads "Brian D. Long".

Brian D. Long
Plant Manager
Chemours – Fayetteville Works

Enclosure

Site Associated PFAS Fate and Transport Study Report

Cc:

William F. Lane, DEQ
Francisco Benzoni, NC DOJ
Michael Abraczinskas, DAQ
Michael Scott, DWM
Linda Culpepper, DWR
David C. Shelton, Chemours
John F. Savarese, WLRK
Kemp Burdette, CFRW
Geoff Gisler, SELC



Geosyntec Consultants of NC, PC

SITE ASSOCIATED PFAS FATE AND TRANSPORT STUDY CHEMOURS FAYETTEVILLE WORKS

Prepared for

The Chemours Company
Fayetteville Works
22828 NC Highway 87 W
Fayetteville, NC 28306

Prepared by

Geosyntec Consultants of NC, P.C.
2501 Blue Ridge Road, Suite 430
Raleigh, NC 27607

Project TR0795

June 2019

TABLE OF CONTENTS

1. INTRODUCTION	1
2. PFAS CHEMISTRY	2
2.1 Site Associated PFAS.....	2
3. ENVIRONMENTAL PROCESSES INFLUENCING PFAS FATE AND TRANSPORT	5
3.1 Physical Transport Processes	5
3.1.1 Advection	5
3.1.2 Diffusion.....	6
3.2 Chemical Processes	6
3.2.1 Volatilization and Influence of Dissolution	7
3.2.2 Partitioning between Environmental Media.....	7
3.2.3 Potential PFAS Transformation in the Environment	10
3.3 Summary of Site Associated PFAS Fate and Transport Pathways	11
4. PFAS CHARACTERISTICS INFLUENCING FATE AND TRANSPORT	12
4.1 Isomer type	12
4.2 Fluorination	12
4.3 Presence and number of ether bonds.....	12
4.4 Chain length	13
4.5 Number and type of functional groups.....	13
5. EMPIRICAL FATE AND TRANSPORT DATA.....	14
5.1 HFPO-DA Empirical Data	14
5.2 Liquid Chromatography Retention Times.....	14
6. DISCUSSION AND SUMMARY	15
7. REFERENCES	16

LIST OF TABLES

Table 1:	Classification of Site Associated PFAS
Table 2:	Empirically Measured Data for hexafluoropropylene oxide dimer acid (HFPO-DA)
Table 3:	Site Associated PFAS Liquid Chromatography Elution Times

ACRONYMS AND ABBREVIATIONS

C	Carbon
°C	degrees celsius
CAS	Chemical Abstracts Service
Chemours	The Chemours Company FC, LLC
CO	Consent Order
DEQ	North Carolina Department of Environmental Quality
DuPont	E.I. du Pont de Nemours and Company
E1	Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether
Geosyntec	Geosyntec Consultants of NC, PC
HFPO	Hexafluoropropylene oxide
HFPO-DA	Hexafluoropropylene oxide dimer acid
LC	Liquid chromatograph
NCDEQ	North Carolina Department of Environmental Quality
Pa	Pascals
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyl
PFAS	Per- and polyfluoroalkyl substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
pKa	Negative logarithm of the acid dissociation constant
PVF	Polyvinyl fluoride
USEPA	United States Environmental Protection Agency

1. INTRODUCTION

This document has been prepared by Geosyntec Consultants of NC P.C. (Geosyntec) for The Chemours Company FC, LLC (Chemours) to address requirements specified in Paragraph 27 of the Consent Order (CO) between Chemours and the North Carolina Department of Environmental Quality (NCDEQ) with the Cape Fear River Watch as intervenor. Geosyntec has been approved by NCDEQ to prepare this document, which analyzes the fate and transport of per- and polyfluoroalkyl substances (PFAS) originating from Chemours Fayetteville Works (the Site; the Facility). Specifically, Paragraph 27 of the CO states:

Chemours shall fund development by a third party contractor(s) of a study, based on the best available data and information, analyzing the fate and transport of identified PFAS originating from the Facility in air, surface water and groundwater. Chemours' contractor(s) shall (i) be approved by DEQ, and (ii) submit the completed study to DEQ for review by June 30, 2019.

The objective of this report is to evaluate the fate and transport of PFAS associated with the Site in the environment using the best currently available data and information. Based on available data, this report presents a qualitative description of the fate and transport of these PFAS, including a description of physical and chemical mechanisms and compound properties that will influence fate and transport in the environment. At present, only a qualitative description is possible since published measured fate and transport properties are scarce for PFAS associated with the Site. The remainder of this report is organized as follows:

1. **Introduction.** This section describes the purpose and overview of this document.
2. **PFAS Chemistry.** This section presents an overview of PFAS chemical structures and then introduces Site Associated PFAS and their chemical characteristics.
3. **Environmental Processes Influencing PFAS Fate and Transport.** This section reviews the currently known physical and chemical mechanisms that control PFAS fate and transport in the environment.
4. **PFAS Characteristics Influencing Fate and Transport.** This section describes how chemical characteristics of Site Associated PFAS are expected to influence their fate and transport in the environment.
5. **Empirical Fate and Transport Data.** This section presents the available empirical data at the time of publication of this report for the PFAS related to the Site.
6. **Discussion and Summary.** This section summarizes earlier sections of this document.

2. PFAS CHEMISTRY

PFAS is a term used for a group of man-made carbon-based chemicals composed of a fully or partially fluorinated chain of carbon atoms (referred to as a “tail”) and a nonfluorinated, polar functional group (referred to as a “head”) at one end of the carbon chain. Numerous variations of fluorinated tails and functional groups exist, including for Site Associated PFAS (Table 1).

The term “PFAS” is most correctly used when referring to a perfluoroalkyl and polyfluoroalkyl chemicals (Mueller and Yingling, 2018a). When many fluorine atoms are bonded to the carbon atoms of the tail, the prefix “poly” is used in the name of the chemical compound. When all potential fluorination locations on the carbon tail are fluorinated, i.e. there are no hydrogen-carbon bonds, the prefix “per” is used in the name of the compound. The properties of per- and polyfluoroalkyl substances are sufficiently similar that they are considered jointly and referred to as PFAS (Mueller and Yingling, 2018a).

In general, fluorination of the carbon chain renders it hydrophobic (i.e., unlikely to associate with water molecules) and lipophobic (i.e., unlikely to associate with nonpolar carbon-based molecules), while the polar head group is hydrophilic (i.e., likely to associate with water molecules). In other words, the fluorinated tail does not have strong affinity for either polar or non-polar phases while the head group does have affinity for polar phases (Mueller and Yingling, 2018b). These primary characteristics (fluorinated tail and polar functional group) control much of the environmental properties of PFAS. Specific variations in chain length, molecular weight, head group, and other structural features of PFAS also influence transport, toxicity, and reactivity in the environment (Ahrens et al., 2011).

2.1 Site Associated PFAS

Chemours manufactures per- and polyfluoroalkyl ether compounds and polymers at the Site. The Site is located within a 2,177-acre property approximately 15 miles southeast of the city of Fayetteville in North Carolina. The Site was originally purchased by E.I. du Pont de Nemours and Company (DuPont) in 1970 for production of nylon strapping and elastomeric tape. Presently Chemours is the Site owner with leased tenants DuPont and Kuraray. The Site has five manufacturing areas:

- Area 1- Chemours Monomers IXM;
- Area 2- Chemours Polymer Processing Aid;
- Area 3 - Kuraray Butacite[®];
- Area 4 - Kuraray SentryGlas[®]; and
- Area 5 - DuPont Company polyvinyl fluoride (PVF) resin manufacturing unit.

In addition to the manufacturing operations, Chemours operates two natural-gas-fired boilers and a wastewater treatment plant for the treatment of process wastewaters from the Kuraray and

DuPont manufacturing facilities and sanitary wastewaters from all three facilities. At present all Chemours process wastewater is sent offsite for disposal.

PFAS from the Site have been identified by non-targeted mass spectrometry analyses performed by Chemours, the United States Environmental Protection Agency (USEPA), and researchers within the University of North Carolina System. Non-targeted mass spectrometry is a specialized technique used to identify unknown compounds, particularly when analytical standards of these compounds may not exist. These non-targeted studies identified perfluorinated ether compounds. The term “ether” refers to compounds with an ether bond. An ether bond is two carbon atoms linked by oxygen atom; this bond can also be referred to as “ether linkages”. These ether compounds have been detected in environmental samples of soil, groundwater, surface water and rainwater (Sun et al., 2016; Hopkins et al., 2018; McCord and Strynar, 2019). To date, Chemours has identified 24 PFAS associated with the Site in water and soil-based samples. In this document these 24 PFAS are referred to as the “Site Associated PFAS” and they are presented in Table 1. Analytical standards have been developed for these compounds to allow for quantitative measurement in certain Site media (groundwater, surface water and rainwater). The analytical method developed to quantify these Site Associated PFAS is referred to as "Table 3+". Currently two commercial analytical laboratories can analyze samples using this method. Eurofins TestAmerica Sacramento and Eurofins Lancaster can quantitate 20 of these compounds. Presently a second method is being developed to quantitate the remaining 4 compounds (MTP, MMF, DFSA, and PPF Acid).

Consistent with work published by McCord and Strynar (2019), Chemours has identified chemical formulas, although not structures, for an additional 22 PFAS through non-targeted analysis of wastewater samples collected prior to June 21, 2017 the date when Chemours began diverting certain process wastewaters for offsite disposal. As part of Consent Order Paragraph 11a, Chemours is performing non-targeted analysis on samples of stormwater and process water as described in the *PFAS Non-Targeted Analysis and Methods Development Plan* (Chemours, 2019) to identify PFAS potentially present in these samples which are in addition to the 24 PFAS that have had their structures identified and standards synthesized. Chemours will then develop analytical standards and methods for any newly identified PFAS compounds as part of Paragraph 11a efforts.

Site Associated PFAS described in this document are those detected in soil, groundwater, surface water and rainwater samples. Some Site Associated PFAS compounds have been transported offsite via aerial transport and deposition. These compounds can then be transferred to water and transported to groundwater. Two additional perfluorinated compounds, Hexafluoropropylene oxide (HFPO) and Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether (E1), have been detected in air samples collected to measure concentrations of PFAS in air emissions; these compounds have not been detected in water or soil based samples. Upon emission to air, HFPO and E1 become dispersed in the global atmosphere (Yarwood, 2018a; Yarwood, 2018b). They are transformed after reaction with atmospheric hydroxyl radicals (Yarwood, 2018a; Yarwood, 2018b). Other per-

and polyfluorinated compounds have been potentially emitted to air but have not been quantified to date in air samples. HFPO and E1 are not associated with water and hence have not been detected in non-targeted analyses of groundwater, surface waters, or process waters by Chemours or other researchers.

The current group of 24 Site Associated PFAS that have been detected in soil or water samples are the focus of this Fate and Transport study. The 24 Site Associated PFAS differ from each other based on the following properties:

- Degree of fluorination
- Isomer type
- Functional groups
- Chain length
- Presence of ether groups.

These attributes and chemical structures are shown in Table 1, and the anticipated relative effect that each attribute will have on the compounds fate and transport in the environment is described in Section 4.

The Site Associated PFAS that has been studied most to date is hexafluoropropylene oxide dimer acid (HFPO-DA; CAS 13252-13-6). HFPO-DA is one of a group of related chemicals. When either hexafluoropropylene oxide dimer acid fluoride (“HFPO-DA fluoride”, CAS 2062-98-8) or hexafluoropropylene oxide dimer acid ammonium salt (CAS 62037-80-3) enter water, HFPO-DA is formed (Hogue, 2018). HFPO-DA fluoride is manufactured from HFPO (CAS 428-59-1) in controlled conditions (Hogue, 2018). The same is true for the formation of HFPO-DA ammonium salt from HFPO-DA fluoride. Because of the rapid reaction that transforms HFPO-DA fluoride and HFPO-DA ammonium salt to HFPO-DA, HFPO-DA is the chemical with environmental relevance. Accordingly, because the Table 3+ method and the McCord and Strynar (2019) methods are designed for liquid samples, they measured HFPO-DA, not HFPO-DA ammonium salt. Consequently, HFPO-DA is the only one of these related chemicals to be considered as a Site Associated PFAS in this report.

HFPO-DA is the only Site Associated PFAS for which environmentally relevant experimental data exist. These results are presented in this document and summarized in Section 5.1 and Table 2.

3. ENVIRONMENTAL PROCESSES INFLUENCING PFAS FATE AND TRANSPORT

The environmental fate and transport of Site Associated PFAS will result from a combination of physical and chemical factors and processes acting on individual PFAS. Physical processes involve the mixing and transport of environmental media and chemicals within media while chemical processes include interactions between compounds and environmental media or changes in the compounds themselves. This section describes the physical and chemical factors and processes that influence fate and transport.

3.1 Physical Transport Processes

Physical processes involve the movement of compounds in response to environmental gradients (e.g., pressure or chemical gradients). Advection and diffusion are the two physical processes that will affect Site Associated PFAS.

3.1.1 Advection

Advection in environmental fluids induces turbulence and consequent dispersion that can mix chemicals into the flowing fluid. Advection of PFAS can occur in air, groundwater and surface water. To the extent that Site Associated PFAS volatilize, become airborne associated to particulates or dissolve (discussed below), they will be subject to advection.

Historically some Site Associated PFAS have been emitted to the atmosphere. Transport of compounds via air will be affected by local meteorology, precipitation, terrain and surface characteristics. Additionally, source-specific parameters such as buoyancy, flow rate, exhaust temperature, release height, etc. also influence fate and transport of a compound in the atmosphere. Air transport also includes the airborne transport of particles that contain Site Associated PFAS. These may originate from the land surface, from dust accumulation on industrial areas, or from particulate emissions that are part of industrial processes. Literature studies have documented airborne PFAS accumulating to measurable levels on soil surface and in surface water through dry or wet atmospheric deposition (Dreyer et al., 2010; Taniyasu, Yamashita et al. 2013, Rankin et al., 2016).

Site Associated PFAS are expected to be soluble in water (see Section 3.2.1), so compounds that enter surface water or groundwater will be transported via advection. Dispersion in porous media will cause PFAS concentrations to become distributed along the direction of flow and perpendicular to flow direction. Sorption to either aquifer material or air-water interfaces will retard groundwater transport. Advection in surface waters will also transport Site Associated PFAS. Surface waters transport particles in both stormwater runoff and stream flow, and so surface water transport of Site Associated PFAS will include both dissolved and particulate PFAS species. When compounds sorb to organic and inorganic particles and those particles are immobile in calm

water (either as a stream bed or as a suspended load that settles), this may result in retardation during surface water transport.

3.1.2 Diffusion

Diffusion transports chemicals through fluids (e.g. air and water) in response to concentration gradients. Where advection is negligible, diffusion can be the primary mechanism of mass transport in environmental media. Effective diffusion, the amount of diffusion that occurs in groundwater, is controlled by temperature, porosity, permeability, soil grain tortuosity, molecular size of chemical compounds, and intermolecular interactions. It can be inhibited by interactions between molecules and particles (i.e., aquifer material). Although diffusion coefficients for Site Associated PFAS are not presently known, diffusion is expected to be of minor importance for the transport of these chemicals because the groundwater, surface water, and air are not static in the vicinity of the Site and so advection is expected to be the dominant transport mechanism over diffusion.

One scenario in which diffusion may be relevant is back diffusion. This occurs following multiple separate processes. First, concentrations of chemicals in groundwater of low-permeability aquifer formations (e.g., a clay formation) slowly increase due to diffusion of chemicals contained in groundwater in neighboring, higher-permeability formations (e.g., a sand formation or surface water). Over time the concentrations in the higher permeability formations decreases (e.g., due to a discontinuation of contamination and ongoing groundwater advection or due to treatment). When this occurs, the higher concentrations of compounds are in the low-permeability formation, and diffusion will occur to achieve equilibrium. This process is referred to as “back diffusion”. This process can result a long-term, low-level source for chemicals to the groundwater in the permeable aquifer formation and thus potentially result in continued detections in the environment. Rates of back diffusion for Site Associated PFAS will depend not only on presently unknown diffusivities but also on the aquifer and clay soil properties of the Site.

3.2 Chemical Processes

Chemical processes involve interactions between chemical compounds and environmental media. Chemical processes can alter transport of chemicals, including PFAS, in environmental media by transferring them between media with different transport velocities. For example, if a chemical load is introduced to surface water and a fraction of that load reacts with sediment particles, then downstream transport of the total introduced load will be retarded. Conversely, chemical reactions can result in mobilization of sediment-associated chemicals into more mobile phases (e.g., water or air). The following subsections describe specific processes that are expected to influence Site Associated PFAS.

3.2.1 Volatilization and Influence of Dissolution

Volatilization is the process by which liquids become gases and can influence fate and transport in groundwater, surface water and air. Volatilization of most carbon-based compounds occurs at the liquid-to-gas transition phase. Dissolution is the process by which a compound forms a chemical bond with a solvent (e.g., water) such that it behaves as though it is part of the solvent. In environmental media, dissolution of a compound in water hinders the volatilization of that compound. Nonpolar and light compounds are highly volatile, whereas heavier and polar compounds are less volatile because of their propensities to bond with each other and with water. Polarity also facilitates dissolution in water. The volatility of a compound in liquid form can be described by its vapor pressure, and the solubility of a compound describes its likelihood of dissolving. Generally, PFAS vapor pressures are low and water solubilities are high. Most PFAS have negatively charged head groups, so they are likely to be relatively mobile in the subsurface due to the affinity of the head group for water molecules (Mueller and Yingling, 2018b).

All Site Associated PFAS contain at least one polar head group. Many Site Associated PFAS also contain additional polar head groups or one or more ether bonds, yet some of them are also short-chain compounds. These two characteristics are likely to offset one another, with increased polarity decreasing volatility while decreased chain length increasing volatility. For example, the vapor pressure of HFPO-DA, which contains a six-member chain with one ether (i.e., oxygen) linkage and a carboxylic acid head group, is 133 Pascals (Pa) at 25°C (DuPont, 2011). This indicates a lower volatility than the linear six-carbon perfluorohexanoic acid (vapor pressure = 264 Pa at 25°C; National Center for Biotechnology Information, 2019) yet a higher volatility than the linear eight-carbon perfluorooctanoic acid (vapor pressure = 70 Pa at 25°C; EPA, 2017). The Site Associated PFAS have a chain length range (carbon and oxygen atoms) of 3-11 atoms with a wide range of structural variation that includes ether linkages, polar head groups, and double bonds, all of which will decrease volatilization of these PFAS when in pure liquid form (Table 1). Vapor pressures and solubilities for Site Associated PFAS other than HFPO-DA have not been measured, but they are expected to span a range of values due to the variation of chain length and other structural features. Most Site Associated PFAS are ethers, which are expected to be less volatile and more soluble than non-ether PFAS of equivalent chain length due to the polar oxygen atoms included in their structures.

3.2.2 Partitioning between Environmental Media

After compounds enter the environment in a given medium (e.g., surface water), chemical interactions will result in their total mass being divided between the environmental media (e.g., water, soils, sediments, air). This process is called partitioning. Partitioning can influence fate and transport in groundwater and surface water. One of the most important partitioning processes is sorption, which is the association of atoms or molecules with the surfaces of environmental media (e.g., air, particles, or organic carbon). Most often, sorption refers to the chemical “sticking” or association of low-concentration chemicals to the particles that make up sediment (including

suspended sediment in surface waters) or soil. Sorption retards transport when dissolved atoms or molecules become attached to sediment particles that are less mobile than water. In the subsurface, organic carbon in aquifer material is generally not mobile, so sorption will retard transport. Similarly, in surface waters, sediment in river beds moves downstream more slowly than the water in rivers, so sorption here also retards transport. This section examines the effect of partitioning through four different processes that are particularly relevant to PFAS:

- Sorption to Organic Carbon,
- Electrostatic Interactions,
- Air-Water Interface Partitioning, and
- Formation of Micelles.

Sorption to Organic Carbon

Like many elements and chemical compounds, PFAS can sorb to particles and porous media (i.e., suspended solids and soils). In the natural environment, many particles and porous media contain organic carbon. Generally, clay and silt particles tend to be high in organic carbon, whereas sand grains are lower in organic carbon content. Particulate organic carbon (i.e., biomass) can comprise a substantial fraction of the particulate mass in many natural settings. Consequently, partitioning of low-concentration compounds, especially carbon-based compounds, in the environment is frequently controlled by sorption to organic carbon.

The tails of PFAS are made primarily of carbon atoms. They tend to be nonpolar, and so they tend to sorb to organic carbons in soil and sediment (Higgins and Luthy 2006, Guelfo and Higgins, 2013). Because PFAS tails are also lipophobic, sorption to organic carbon tends to be weaker than that of alkanes or well-studied organic contaminants (e.g., PAHs, PCBs). The sorption and retardation of PFAS will increase with increasing fluorinated tail length. For a given soil, sediment, or organic carbon type, the structure of the PFAS tail affects its interactions with organic carbon molecules. Branched isomers tend to have lower sorption affinity than linear isomers of equal chain length (Kärrman et al., 2011).

The coefficient that describes the partitioning to organic carbon (referred to as “ K_{OC} ”) of HFPO-DA has been measured as 12.0 L kg^{-1} for soil and as 12.6 L kg^{-1} for sludge (Bloxham, 2008). These measurements were performed by dissolving HFPO-DA ammonium salt into a methanol-water solution. Since HFPO-DA ammonium salt separates into HFPO-DA and an ammonium ion upon contact with water, the results reported by this study for HFPO-DA ammonium salt are taken to represent partitioning coefficients of HFPO-DA. These values are multiple orders of magnitude lower than other common carbon-based contaminants like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). While the sorption of HFPO-DA to environmental media is low, sorption to Granular Activated Carbon (GAC) will still occur to a much greater

degree than environmental media due to the high surface area of GAC relative to that of natural organic carbon.

No empirical partitioning data exist for other Site Associated PFAS outside of HFPO-DA. As with volatilization, the range of chain lengths of the Site Associated PFAS suggests a potential range of sorption affinities to organic carbon. In general, compared to other well studied PFAS (e.g., perfluorooctanoic acid [PFOA] and perfluorooctanesulfonate [PFOS]), the Site Associated PFAS are likely to have lower affinities to organic carbon. Site Associated PFAS have ether bonds and, for 5 of the 24 compounds, two charged head groups. Both of these features increase the polarity of the compounds and are likely to result in reduced sorption to organic carbon relative to non-ether PFAS, given similar geochemical settings.

Electrostatic Interactions

Electrostatic interactions determine sorption of polar or charged chemicals to charged surfaces. Site Associated PFAS are expected to have negatively charged head groups, and therefore electrostatic sorption to soil and sediment particles is possible through ion exchange with negatively charged ions on particle surfaces (Higgins and Luthy 2006). However, sorption to charged particle surfaces in common soils and sediments is expected to be negligible relative to sorption to particulate organic carbon (Higgins and Luthy 2006).

Air-Water Interface Partitioning

In addition to sorption, many PFAS partition to air-water interfaces when the hydrophobic tail of carbon atoms of PFAS associates with the air-water interface of the subsurface unsaturated zone or an above-ground water surface and the polar head group bonds to water (Brusseau et al., 2019; Krafft and Riess 2015). This partitioning has been observed to retard subsurface transport by approximately 50% in a model system with 20% air saturation (Brusseau, 2018). Other studies indicate that the unsaturated zone can be a subsurface reservoir of PFAS (Weber et al., 2017).

Partitioning of PFAS at the air water interface will be dependent on PFAS concentration and structure, the type of soils in the vadose zone and the degree of water saturation. Longer-chain length PFAS are expected to accumulate at air-water interfaces more than shorter-chain length PFAS (Brusseau et al., 2019). For Site Associated PFAS, adsorption to air-water interfaces may be a retardation mechanism for subsurface transport. At present, experimental data do not exist to assess the potential degree of retardation from this effect.

Formation of micelles

At elevated concentrations, PFAS form micelles in water. Micelles are aggregations of individual molecules (Yu et al., 2009; Du et al., 2014). Micelles represent an association of PFAS molecules with other PFAS molecules rather than surfaces or interfaces. In micelles, which are generally spherical, the hydrophilic head groups of PFAS interact with surrounding water molecules and the hydrophobic portions interact with each other on the inside of the sphere. Micelle formation

confounds the partitioning interactions described above. The branched geometries and ether bonds of Site Associated PFAS are expected to reduce the likelihood of micelle formation by providing steric and electrostatic barriers to the association of the PFAS tails, but no empirical information is currently available to quantify these effects in most Site Associated PFAS. The exception is HFPO-DA: critical micelle concentration for HFPO-DA has been reported to vary between 0.135 and 0.2 moles per liter (approximately 40 to 70 grams per liter; Table 2). These concentrations are significantly higher than observed in any groundwater or surface water sample.

3.2.3 Potential PFAS Transformation in the Environment

Current literature reviews indicate that transformation of most PFAS in the environment is negligible. An important observed environmental transformation of PFAS has been the hydrolysis of some polyfluorinated precursors to form perfluorinated compounds (Mueller and Yingling, 2018) and the biotic degradation of trifluoroacetate (e.g., Visscher et al., 1994). Components of Site Associated PFAS which may be amenable to transformation reactions that degrade the tails of these compounds are ether bonds present in 21 of 24 Site Associated PFAS, and carbon-hydrogen bonds present in 5 of 24 Site Associated PFAS. (e.g., Weber et al., 2017). With one exception, no data exist to document their transformation in surface water or groundwater. The one exception is HFPO-DA, which has been documented to persist in the environment (The Netherlands, 2019). This is consistent with research showing that perfluoroether chains are resistant to abiotic and biotic degradation under environmentally relevant conditions, similar to the perfluoroalkyl chains (Wang et al., 2015).

3.3 Summary of Site Associated PFAS Fate and Transport Pathways

The anticipated relevance of the different factors and processes described above on a transport pathway basis are summarized below.

Anticipated Relevance of Fate and Transport Processes and Mechanisms for Site Associated PFAS

Fate and Transport Process or Mechanism	Air	Groundwater	Surface Water
Physical – Advection	◆	◆	◆
Physical – Diffusion	--	◆	--
Chemical – Volatilization and Dissolution	◆	◆	◆
Chemical – Sorption to Organic Carbon / Particles	◆	◆	◆
Chemical – Electrostatic Interactions	--	--	--
Chemical – Partitioning to Air-Water Interfaces	--	◆	◆
Chemical – Formation of Micelles	--	--	--
Chemical – Transformation	--	--	--

Legend

- ◆ Process expected to have influence on fate and transport
- ◆ Process expected to have minimal influence on fate and transport
- Process expected to have negligible influence on fate and transport

4. PFAS CHARACTERISTICS INFLUENCING FATE AND TRANSPORT

The discussion above of the physical and chemical processes that are expected to control PFAS fate and transport in the environment reveals common themes across environmental media and chemical processes. This section discusses the anticipated effects of the defining chemical characteristics of the Site Associated PFAS on their fate and transport.

4.1 Isomer type

Isomers are chemicals with identical formulas but distinct structures. The concept of varying chemical structure is important in the Site Associated PFAS because some have a single chain of carbon and oxygen atoms in the tail whereas others have branched tails (Table 1). The existence of branching in a compound can be determined visually by starting at the head group and examining each atom of the chain, for example in Table 1 compare PFO5DA a linear compound to Hydro-EVE Acid a branched compound. Branching occurs when a given carbon atom has more than two carbon or oxygen atoms bonded to it and additional examination is required to determine which atom is part of the chain and which is a smaller “branch” to the chain. In the 12 branched Site Associated PFAS, all branches consist of a single carbon atom with three fluorine atoms bonded to it.

Linear and branched PFAS differ in their partitioning behavior to particles. Isomerization also results in significant differences in biochemical reactions and bioaccumulation (Mueller and Yingling 2018b). For compounds with similar chain lengths and functional groups, branched isomers sorb less than linear isomers in sediment (Houde et al., 2008; Chen et al., 2015) and municipal sludge (Filipovic and Berger, 2015). These studies suggest that the branched Site Associated PFAS may be more mobile in surface water and groundwater than similar linear Site Associated PFAS.

4.2 Fluorination

All Site Associated PFAS are fluorinated. However, 6 of the 24 compounds are considered polyfluorinated – not perfluorinated – because a hydrogen atom occupies one of the bonding locations that could hold a fluorine. Consequently, not all Site Associated PFAS are fluorinated to the same degree. Perfluorinated compounds tend to have higher sorption affinities to particulate organic carbon than polyfluorinated compounds (Xiao et al., 2017).

4.3 Presence and number of ether bonds

The presence of oxygen atoms in the tails of Site Associated PFAS distinguishes the Site Associated PFAS from the majority of PFAS studied in the publicly available literature. Empirical studies of the effect of ether bonds on the partitioning behavior of PFAS in the environment has not been conducted. Nonetheless, treatability studies using powdered activated carbon showed that replacing a carbon (and its two bonded fluorine atoms) in the tail of a PFAS with an ether oxygen

decreases the sorption affinity of that compound (Sun et al., 2016). This suggests that PFAS tails with ether oxygens have increased tail polarity and decreased affinity for nonpolar organic carbon compared to a PFAS with the same tail length but only with carbon atoms in the tail.

4.4 Chain length

Shorter-chain, linear PFAS without ether linkages have lower partitioning affinities to organic carbon than similar compounds with longer chains. This implies that shorter-chained PFAS may be transported from in groundwater at a faster rate (Sepulvado et al., 2011). It is expected in the environment that perfluorinated and polyfluorinated ether compounds of varying chain length will exhibit the same trends of greater mobility with short chains and less mobility with longer chains.

4.5 Number and type of functional groups

The number and type of functional groups in PFAS may affect partitioning affinity and micelle formation due to the differing electrostatic and hydrophobic interactions and strengths of these interactions. Site Associated PFAS that have one or two sulfonic and/or carboxylic head groups are expected to exist in deprotonated form at natural pH based on reported pKa values for HFPO-DA (Table 2). PFAS with two head groups (any combination of carboxylic or sulfonic acids) are referred to as diprotic compounds and will likely experience less sorption to organic carbon and are expected to be more mobile in the environment.

5. EMPIRICAL FATE AND TRANSPORT DATA

As mentioned in Section 3, to date, empirical data exist that describe the environmental behavior of HFPO-DA but not for other Site Associated PFAS. This section consolidates information from these studies and also presents chromatographic retention time data for Site Associated PFAS.

5.1 HFPO-DA Empirical Data

Laboratory measurements of several HFPO-DA physicochemical properties were performed in 2008 and 2011 by DuPont (Bloxxham, 2008; DuPont, 2011). Some of these measurements refer to HFPO-DA ammonium salt as a starting material. The HFPO-DA ammonium salt dissociates to HFPO-DA and an ammonium ion in water, therefore the results from these experiments are considered to be descriptive of HFPO-DA. Additionally, several experimental studies are summarized by The Netherlands (2019). The results of these measurements are presented in Table 2. The primary observations from these data are as follows:

- The coefficients that describe partitioning of HFPO-DA between water and the organic fractions of soil and sludge (i.e., K_{oc} values) have been estimated at 12.0 and 12.6 L/kg, respectively;
- HFPO-DA has a pK_a between 2.45 and 2.84. This indicates that it will be deprotonated at environmental pH;
- HFPO-DA and HFPO-DA ammonium salt are completely soluble in water.

These observations are consistent with the expected effects of structural properties on HFPO-DA fate and transport that are described in Section 0.

5.2 Liquid Chromatography Retention Times

Site Associated PFAS retention time data from a liquid chromatograph (LC) experiment performed by the Chemours Fluoroproducts analytical group are presented in Table 3. Retention times presented are the time required for the Site Associated PFAS to travel through an LC column with a hydrophobic stationary phase. The mobile phase is the solvent in which the PFAS were dissolved and which carried the PFAS through the LC column. Compounds that interact less strongly with the column material pass through the column more quickly. LC retention times provide an indication of relative anticipated environmental mobility between Site Associated PFAS.

The distribution of retention times suggests that Site Associated PFAS may exhibit differential mobility in soil and sediment depending on the compound. Given sufficient organic carbon to act as a sorbent, some of the PFAS compounds will migrate more rapidly through the environment while others will be subject to more sorption and retardation along transport pathways.

6. DISCUSSION AND SUMMARY

The PFAS associated with the Chemours Fayetteville Works Site are characterized primarily by the presence of ether bonds, i.e. two carbons connected by an oxygen atom. Currently, the Site associated PFAS have limited publicly available, peer-reviewed literature describing their fate and transport. The understanding of anticipated fate and transport of Site Associated PFAS presented in this report was based on combining A) peer-reviewed studies for other PFAS chemicals that are generally linear, perfluorinated, and lacking ether bonds with B) the studies that describe how different PFAS chemical features may affect their environmental fate and transport.

Given the diversity in Site Associated PFAS chain length, head groups, number of ether bonds, isomer type and fluorination, the Site Associated PFAS will span a range of mobilities in environmental media. Generally, Site Associated PFAS are expected to be mobile in the environment given the presence of charged head groups and ether bonds, but they will experience some retardation. For some Site Associated PFAS, mobility may be enhanced relative to straight-chain, non-ether PFAS by their branched structure and the presence of two charged head groups. The mobility of the Site Associated PFAS will be retarded by various chemical processes but will likely have lower retardation than long-chain PFAS without ether bonds or other well-studied carbon-based chemicals like PAHs and PCBs. Chemical processes expected to have the most impact on mobility are sorption to organic carbon and, in the unsaturated soil zone, preferential partitioning to the air water interface.

7. REFERENCES

- Ahrens, L., L. W. Y. Yeung, S. Taniyasu, P. K. S. Lam and N. Yamashita (2011). "Partitioning of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonamide (PFOSA) between water and sediment." *Chemosphere*, 85(5): 731-737.
- Bloxham, P. A. (2008). Estimation of the Adsorption Coefficient (K_{oc}) of HFPO Dimer Acid Ammonium Salt on Soil and Sludge. Newark, Delaware, USA, DuPont de Nemours and Company.
- Brusseau, M. L. (2018). "Assessing the potential contributions of additional retention processes to PFAS retardation in the subsurface." *Science of The Total Environment* 613-614: 176-185.
- Brusseau, M. L., N. Yan, S. Van Glubt, Y. Wang, W. Chen, Y. Lyu, B. Dungan, K. C. Carroll and F. O. Holguin (2019). "Comprehensive retention model for PFAS transport in subsurface systems." *Water Research* 148: 41-50.
- Chemours (2019). "PFAS Non-Targetted Analysis and Methods Development Plan Process and Non-Process Wastewater and Stormwater" January 30, 2019
- Chen, X., L. Zhu, X. Pan, S. Fang, Y. Zhang and L. Yang (2015). "Isomeric specific partitioning behaviors of perfluoroalkyl substances in water dissolved phase, suspended particulate matters and sediments in Liao River Basin and Taihu Lake, China." *Water Res* 80: 235-244.
- Dreyer, A., V. Matthias, I. Weinberg and R. Ebinghaus (2010). "Wet deposition of poly-and perfluorinated compounds in Northern Germany." *Environmental Pollution* 158(5): 1221-1227.
- Du, Z., S. Deng, Y. Bei, Q. Huang, B. Wang, J. Huang and G. Yu (2014). "Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—A review." *Journal of Hazardous Materials* 274: 443-454.
- DuPont (2011). Discussion of Results: FRD903 Physical and Chemical Data and FRD902 Physical and Chemical Data. DuPont Document PM-W-726.
- EPA (2017). Technical Fact Sheet - Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA). Accessed online at: https://www.epa.gov/sites/production/files/2017-12/documents/ffrrofactsheet_contaminants_pfos_pfoa_11-20-17_508_0.pdf.
- Eurofins (2019). "Client Specific: Table 3 Compounds by Direct Injection Using LC/MS/MS." T-PFAS-WI201 27, Rev 2. April 12, 2019.

Filipovic, M. and U. Berger (2015). "Are perfluoroalkyl acids in waste water treatment plant effluents the result of primary emissions from the technosphere or of environmental recirculation?" *Chemosphere* 129: 74-80.

Guelfo, J. L. and C. P. Higgins (2013). "Subsurface Transport Potential of Perfluoroalkyl Acids at Aqueous Film-Forming Foam (AFFF)-Impacted Sites." *Environmental Science & Technology* 47(9): 4164-4171.

Higgins, C. P. and R. G. Luthy (2006). "Sorption of Perfluorinated Surfactants on Sediments." *Environmental Science & Technology* 40(23): 7251-7256.

Hogue, C. (2018). "Confronting Fluoroethers." *Chemical and Engineering News* 12 February 2018, 28-34.

Hopkins, Z. R., M. Sun, J. C. DeWitt, and D. R. U. Knappe (2018). "Recently detected drinking water contaminants: GenX and other per- and polyfluoroalkyl ether acids." *Journal of the American Water Works Association* 110(7): 13-28.

Houde, M., G. Czub, J. M. Small, S. Backus, X. Wang, M. Alaei and D. C. G. Muir (2008). "Fractionation and Bioaccumulation of Perfluorooctane Sulfonate (PFOS) Isomers in a Lake Ontario Food Web." *Environmental Science & Technology* 42(24): 9397-9403.

Krafft, M. P. and J. G. Riess (2015). "Selected physicochemical aspects of poly- and perfluoroalkylated substances relevant to performance, environment and sustainability-part one." (1879-1298 (Electronic)).

Kärrman, A., K. Elgh-Dalgren, C. Lafossas and T. Møskeland (2011). "Environmental levels and distribution of structural isomers of perfluoroalkyl acids after aqueous fire-fighting foam (AFFF) contamination." *Environmental Chemistry* 8(4): 372-380.

McCord, J. and M. Strynar (2019). "Identification of per- and polyfluoroalkyl substances in the Cape Fear River by high resolution mass spectrometry and nontargeted screening." *Environ Sci Technol* 53(9): 4717-4727.

Mueller, R. and V. Yingling (2018a). "Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS)". Interstate Technology Regulatory Council.

Mueller, R. and V. Yingling (2018b). "Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances". Interstate Technology Regulatory Council.

National Center for Biotechnology Information (2019). PubChem: Perfluorohexanoic Acid (Compound). Accessed online at <https://pubchem.ncbi.nlm.nih.gov/#query=Perfluorohexanoic-acid/>.

Rankin, K., S. A. Mabury, T. M. Jenkins and J. W. Washington (2016). "A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence." *Chemosphere* 161: 333-341.

Sepulvado, J. G., A. C. Blaine, L. S. Hundal and C. P. Higgins (2011). "Occurrence and Fate of Perfluorochemicals in Soil Following the Land Application of Municipal Biosolids." *Environmental Science & Technology* 45(19): 8106-8112.

Sun, M., E. Arevalo, M. Strynar, A. Lindstrom, M. Richardson, B. Kearns, A. Pickett, C. Smith and D. R. Knappe (2016). "Legacy and emerging perfluoroalkyl substances are important drinking water contaminants in the Cape Fear River Watershed of North Carolina." *Environmental science & technology letters* 3(12): 415-419.

Taniyasu, S., N. Yamashita, H.-B. Moon, K. Y. Kwok, P. K. Lam, Y. Horii, G. Petrick and K. Kannan (2013). "Does wet precipitation represent local and regional atmospheric transportation by perfluorinated alkyl substances?" *Environment international* 55: 25-32.

TestAmerica (2019). "Title: Determination of Table 3 Compounds by LC/MS/MS Chemours Fluoroproducts" SOP No. WS-LC-0031, Rev 2.1 April 03, 2019.

The Netherlands (2019). "Annex XV Report: Proposal for identification of a substance of very high concern on the basis of the criteria set out in REACH Article 57." March 2019. Accessed online at <https://echa.europa.eu/documents/10162/ef1b1606-b234-2ce5-e159-2ab89d61bfbc>.

Visscher, P. T., C. W. Culbertson and R. S. Oremland (1994). "Degradation of trifluoroacetate in oxic and anoxic sediments." *Nature* 369(6483): 729-731.

Wang, Z., I. T. Cousins, M. Scheringer and K. Hungerbuehler (2015). "Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors: Status quo, ongoing challenges and possible solutions." *Environment International* 75: 172-179.

Weber, A. K., L. B. Barber, D. R. LeBlanc, E. M. Sunderland and C. D. Vecitis (2017). "Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts." *Environmental Science & Technology* 51(8): 4269-4279.

Xiao, X., B. A. Ulrich, B. Chen and C. P. Higgins (2017). "Sorption of Poly- and Perfluoroalkyl Substances (PFASs) Relevant to Aqueous Film-Forming Foam (AFFF)-Impacted Groundwater by Biochars and Activated Carbon." *Environmental Science & Technology* 51(11): 6342-6351.

Yarwood, G. 2018a. Atmospheric lifetime and degradation products of CF₃CHF-O-CF₂CF₂CF₃ (E1). Memorandum to Joel Goss, Arnold & Porter, 30 March 2018.

Yarwood, G. 2018b. Atmospheric lifetime and degradation products of hexafluoropropylene oxide (HFPO). Memorandum to Joel Goss, Arnold & Porter, 3 April 2018.

Yu, Q., R. Zhang, S. Deng, J. Huang and G. Yu (2009). "Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study." *Water Research* 43(4): 1150-1158.

TABLES

**TABLE 1
CLASSIFICATION OF SITE ASSOCIATED PFAS
Chemours Fayetteville Works, North Carolina**

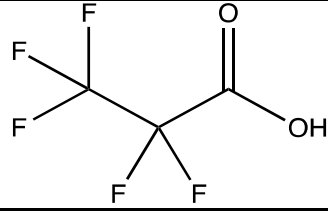
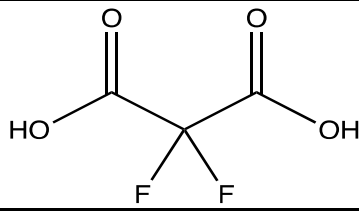
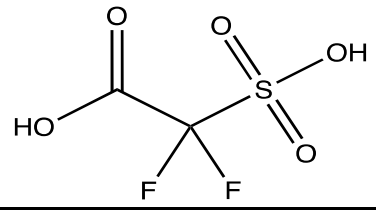
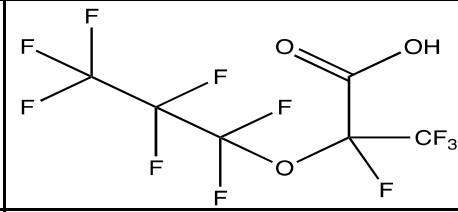
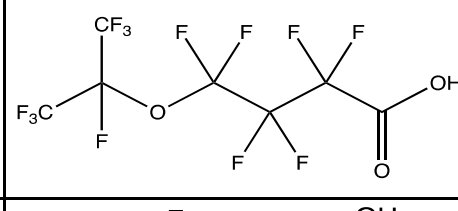
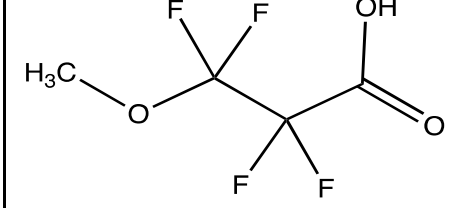
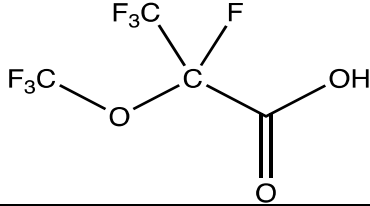
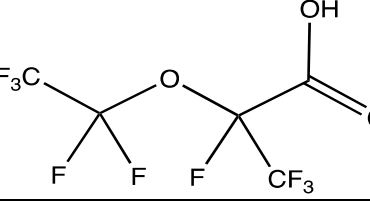
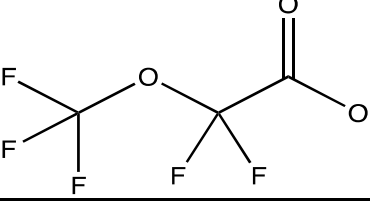
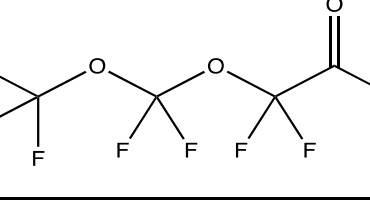
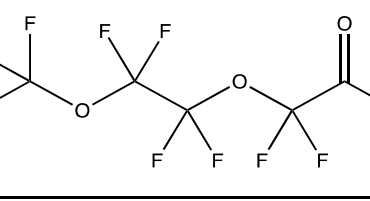
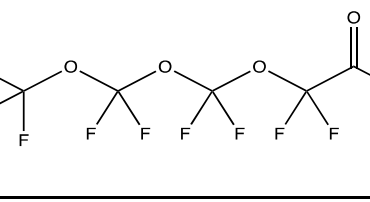
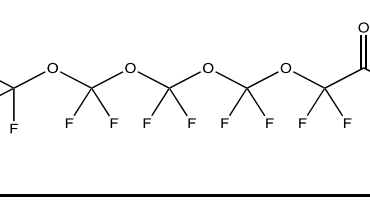
Common Name	Chemical Name	CAS #	Formula	Degree of Fluorination	Ether Bonds	Isomer type	Functional Groups			Diprotic ^d	Structure
							R-C=C ^a	R-CO ₂ H ^b	R-SO ₃ H ^c		
<i>PFAS without ether linkages</i>											
PPF Acid	Perfluoropropionic acid	422-64-0	C ₃ HF ₅ O ₂	Per	0	Linear	--	✓	--	--	
MMF	Difluoromalonic acid	1514-85-8	C ₃ H ₂ F ₂ O ₄	Per	0	Linear	--	✓	--	✓	
DFSA	Difluoro-sulfo-acetic acid	422-67-3	C ₂ H ₂ F ₂ O ₅ S	Per	0	Linear	--	✓	✓	✓	
<i>Per- and polyfluoroalkyl ether carboxylic acids (PFECAs)</i>											
HFPO-DA	Hexafluoropropylene oxide dimer acid	13252-13-6	C ₆ HF ₁₁ O ₃	Per	1	Branched	--	✓	--	--	
PFECA-G	Perfluoro-4-isopropoxybutanoic acid	801212-59-9	C ₇ H ₁ F ₁₃ O ₁	Per	1	Branched	--	✓	--	--	
MTP	Perfluoro-2-methoxypropanoic acid	93449-21-9	C ₄ H ₄ F ₄ O ₃	Poly	1	Linear	--	✓	--	--	

TABLE 1
CLASSIFICATION OF SITE ASSOCIATED PFAS
Chemours Fayetteville Works, North Carolina

Common Name	Chemical Name	CAS #	Formula	Degree of Fluorination	Ether Bonds	Isomer type	Functional Groups			Diprotic ^d	Structure
							R-C=C ^a	R-CO ₂ H ^b	R-SO ₃ H ^c		
PMPA	Perfluoromethoxypropyl carboxylic acid	13140-29-9	C ₄ HF ₇ O ₃	Per	1	Branched	--	✓	--	--	
PEPA	Perfluoroethoxypropyl carboxylic acid	267239-61-2	C ₅ HF ₉ O ₃	Per	1	Branched	--	✓	--	--	
PFMOAA	Perfluoro-2-methoxyacetic acid	674-13-5	C ₃ HF ₅ O ₃	Per	1	Linear	--	✓	--	--	
PFO2HxA	Perfluoro(3,5-dioxaheptanoic) acid	39492-88-1	C ₄ HF ₇ O ₄	Per	2	Linear	--	✓	--	--	
PFECA B	Perfluoro-3,6-dioxaheptanoic acid	151772-58-6	C ₅ HF ₉ O ₄	Per	2	Linear	--	✓	--	--	
PFO3OA	Perfluoro(3,5,7-trioxaoctanoic) acid	39492-89-2	C ₅ HF ₉ O ₅	Per	3	Linear	--	✓	--	--	
PFO4DA	Perfluoro(3,5,7,9-tetraoxadecanoic) acid	39492-90-5	C ₆ HF ₁₁ O ₆	Per	4	Linear	--	✓	--	--	

**TABLE 1
CLASSIFICATION OF SITE ASSOCIATED PFAS
Chemours Fayetteville Works, North Carolina**

Common Name	Chemical Name	CAS #	Formula	Degree of Fluorination	Ether Bonds	Isomer type	Functional Groups			Diprotic ^d	Structure
							R-C=C ^a	R-CO ₂ H ^b	R-SO ₃ H ^c		
PFO5DA	Perfluoro-3,5,7,9,11-pentaoxadodecanoic acid	39492-91-6	C ₇ HF ₁₃ O ₇	Per	5	Linear	--	✓	--	--	
Hydro-EVE Acid	Perfluoroethoxyspropanoic acid	773804-62-9	C ₈ H ₂ F ₁₄ O ₄	Poly	2	Branched	--	✓	--	--	
EVE Acid	Perfluoroethoxypropionic acid	69087-46-3	C ₈ HF ₁₃ O ₄	Per	2	Branched	✓	✓	--	--	
R-EVE	R-EVE	N/A	C ₈ H ₂ F ₁₂ O ₅	Per	1	Branched	--	✓	--	✓	
Per- and polyfluoroalkyl ether sulfonic acids (PFESAs)											
PES	Perfluoroethoxyethanesulfonic acid	113507-82-7	C ₄ HF ₉ O ₄ S	Per	1	Linear	--	--	✓	--	
NVHOS	Perfluoroethoxysulfonic acid	1132933-86-8	C ₄ H ₂ F ₈ O ₄ S	Poly	1	Linear	--	--	✓	--	
Byproduct 6	Byproduct 6	N/A	C ₆ H ₂ F ₁₂ O ₄ S	Poly	1	Branched	--	--	✓	--	

**TABLE 1
CLASSIFICATION OF SITE ASSOCIATED PFAS
Chemours Fayetteville Works, North Carolina**

Common Name	Chemical Name	CAS #	Formula	Degree of Fluorination	Ether Bonds	Isomer type	Functional Groups			Diprotic ^d	Structure
							R-C=C ^a	R-CO ₂ H ^b	R-SO ₃ H ^c		
Byproduct 2	Byproduct 2	749836-20-2	C ₇ H ₂ F ₁₄ O ₅ S	Poly	2	Branched	--	--	✓	--	
PFESA-BP1	Byproduct 1	29311-67-9	C ₇ HF ₁₃ O ₅ S	Per	2	Branched	✓	--	✓	--	
<i>Per- and polyfluoroalkyl ether sulfonic and carboxylic acids (PFES-CAs)</i>											
Byproduct 4	Byproduct 4	N/A	C ₇ H ₂ F ₁₂ O ₆ S	Per	1	Branched	--	✓	✓	✓	
Byproduct 5	Byproduct 5	N/A	C ₇ H ₃ F ₁₁ O ₇ S	Poly	2	Branched	--	✓	✓	✓	

Notes:

^a Carbon double bond functional group

^b Carboxylic acid functional group

^c Sulfonic acid functional group

^d Compound with two acid functional groups

TABLE 2
EMPIRICALLY MEASURED DATA FOR HEXAFLUOROPROPYLENE OXIDE DIMER ACID (HFPO-DA)
Chemours Fayetteville Works, North Carolina

Parameter	Abbreviation	Value	Unit	Notes	Reference
Organic carbon partitioning coefficient	Log K_{oc}	1.08		Measured for HFPO-DA ammonium salt in soil.	1
		1.1		Measured for HFPO-DA ammonium salt in sludge.	
Acid dissociation constant	pK_a	2.84 ± 0.021			2
		2.45			3
Density		1.683	$kg L^{-1}$	19.9°C	3
Vapor pressure		306	Pa	25°C; sources agree within 1%	2, 3
Solubility in water		fully soluble			2
Viscosity		4.39	$mm^2 s^{-1}$		3
Surface tension		59.4	$mN m^{-1}$		
Critical micelle concentration	CMC	0.135 - 0.2	M		

References:

- 1- Bloxham, P.A. 2008. Trade secret documented in Study Number DuPont-17568-1675.
- 2- The Netherlands. 2019. Annex XV Report: Proposal for identification of a substance of very high concern on the basis of the criteria set out in REACH Article 57. Accessed online at <https://echa.europa.eu/documents/10162/ef1b1606-b234-2ce5-e159-2ab89d61bfbc>. Experiments noted in this reference generally used an acid form with a purity of 98%.
- 3- DuPont. 2011. Discussion of Results: FRD903 Physical and Chemical Data and FRD902 Physical and Chemical Data. DuPont Document PM-W-726.

Notes:

°C - celsius
% - percent
 $kg L^{-1}$ - kilograms per liter
Pa - pascals
M - moles per liter

$mN m^{-1}$ - millinewtons per meter
mm - millimeters
 $mm s^{-1}$ - millimeters per second

TABLE 3
SITE ASSOCIATED PFAS LIQUID CHROMATOGRAPHY ELUTION TIMES
Chemours Fayetteville Works, North Carolina

Common Name^a	CAS #	Retention Time (min)
DFSA	422-67-3	0.268
MMF	1514-85-8	0.271
MTP	93449-21-9	0.37
PPF Acid	422-64-0	0.394
PFMOAA	674-13-5	0.437
R-EVE	N/A	0.42
Byproduct 4	N/A	0.509
Byproduct 5	N/A	0.51
PMPA	13140-29-9	0.662
PFO2HxA	39492-88-1	1.046
NVHOS	1132933-86-8	1.655
PEPA	267239-61-2	1.702
PFECA B	151772-58-6	3.027
PFO3OA	39492-89-2	3.298
HFPO-DA	13252-13-6	3.386
PES	113507-82-7	3.388
PECA G	801212-59-9	3.702
PFO4DA	39492-90-5	3.794
Hydro-EVE Acid	773804-62-9	3.825
EVE Acid	69087-46-3	3.825
Byproduct 6	N/A	3.951
Byproduct 2	749836-20-2	4.072
Byproduct 1	29311-67-9	4.084
PFO5DA	39492-91-6	4.085

^a Please see Table 1 for details about each chemical.

Method:

Elution times were provided by the Chemours Fluoroproducts Analytical Group. Elution times are based on liquid samples analyzed by liquid chromatography--tandem mass spectrometry (LC-MS/MS) utilizing the Multiple Reaction Monitoring method. Liquid chromatography was performed on an Agilent 1290 Infinity II LC with 6570 Triple Quad MS instrument with an Agilent InfinityLab Poroshell 120 EC-C18 (2.1 x 50 mm, 2.7 µm) analytical column, an Agilent Infinity Lab Poroshell 120 EC-C18 (2.1 x 5 mm, 2.7 µm) as the guard column, a Restek Ultra Aqueous C18 (4.6 x 50 mm, 5 µm) as the trapping column, and an Agilent Zorbax Eclipse Plus C18 (4.6 x 50 mm, 3.5 µm) as the delay column. Initial eluent conditions were 85% mobile phase A (2 mM Ammonium Acetate in 5:95 Acetonitrile: Water) and 15% of mobile phase B (Acetonitrile) for the first 1 mins. Then mobile phase B is ramped up to 90% at 5 mins, and held for 1.40 mins. Then Mobile phase B is ramped down again to the initial state at 6.50 mins.