

## ABSTRACT

KOROPECKYJ-COX, LYDIA JOAN. Quantifying the Transport of Per- and Polyfluoroalkyl Substances (PFAS) from Groundwater to Surface Water Near the Chemours Property in Bladen County, NC. (Under the direction of Dr. David Genereux).

Per- and polyfluoroalkyl substances (PFAS) are widely used in fire-fighting foams, non-stick surfaces, food-contact paper coatings, and other applications, and they are emerging nationally as persistent, mobile, and toxic environmental contaminants. Along with other PFAS, “GenX” has contaminated surface water and groundwater surrounding the Chemours Company chemical manufacturing plant near Fayetteville, North Carolina. Contamination of residential groundwater wells and the Cape Fear River (CFR) has degraded drinking water quality for thousands of NC residents. It is possible that PFAS input to CFR tributaries via groundwater discharge could continue over a decades-long timescale, which could mean long-term contamination of a major drinking water source.

This research involved the collection of groundwater samples from beneath the streambeds of contaminated streams and targeted liquid chromatography mass spectrometry (LCMS) analysis of groundwater samples for concentrations of 20 to 30 PFAS. Water flux was measured at these same points in the streambeds, and these measurements in combination with the groundwater PFAS concentration data yielded the PFAS flux from groundwater to streams through the streambeds. Chemical dilution stream gaging and measurement of PFAS concentrations in stream water were used to quantify the export of PFAS from streams near Chemours.

The streams sampled in summer 2018 and October 2018 were gaining at all streambed measurement points except for three points in Georgia Branch (22 October 2018). Water flux measurements combined with results from LCMS analyses of groundwater samples showed that

PFAS-contaminated groundwater was discharging into the streams. The mean total PFAS fluxes from groundwater to the streams sampled in summer 2018 ranged from  $0.43 \text{ mg m}^{-2} \text{ d}^{-1}$  (Willis Creek) to  $4.17 \text{ mg m}^{-2} \text{ d}^{-1}$  (Georgia Branch). The mean total PFAS fluxes from groundwater to the streams sampled in October 2018 were  $3.01 \text{ mg m}^{-2} \text{ d}^{-1}$  for Georgia Branch and  $2.12 \text{ mg m}^{-2} \text{ d}^{-1}$  for Mines Creek. GenX concentrations exceeded the NC state health goal of  $140 \text{ ng L}^{-1}$  in all but one of the groundwater samples collected from beneath the two streams in October 2018. GenX concentrations also exceeded the state health goal in stream water samples collected from Georgia Branch and two unnamed tributaries located east of the CFR (February 2019).

Total groundwater PFAS discharge (summer 2018, October 2018) and total PFAS stream export (October 2018, February 2019) values were used to estimate the contribution from the sampled streams to concentrations of PFAS CFR. Results from the February 2019 data likely provide the most reliable snapshot of the cumulative input of PFAS to the CFR near Chemours as they account for input from five watersheds near the plant. The five streams sampled in February 2019 were found to contribute  $1.72 \text{ ng L}^{-1}$  to the GenX concentration and  $7.84 \text{ ng L}^{-1}$  to the total measured PFAS concentration in the CFR on the sampling days. Results based on PFAS discharge estimates (summer 2018, October 2018) suggest that groundwater discharge to tributaries could be a significant source of PFAS contamination for the CFR and may account for the PFAS levels persisting in the river water.

The data collected in this study suggest it is likely that PFAS contamination of the CFR could continue in the future even though Chemours has stopped discharging process wastewater directly to the river. PFAS-contaminated groundwater in the tributary watersheds near Chemours is discharging to the tributary streams and is almost certainly reaching the CFR. Additional research is being done to characterize the age and travel time of groundwater reaching streams to

better understand the timescale over which PFAS will be flushed out from the surficial aquifer to the CFR.

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Quantifying the Transport of Per- and Polyfluoroalkyl Substances (PFAS) from Groundwater to  
Surface Water Near the Chemours Property in Bladen County, NC

by  
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## **DEDICATION**

In dedication to my loving family, my wonderful partner, and my humble companion, Flint, who have supported me along the way.

## **BIOGRAPHY**

Lydia Koropecyj-Cox was born in Philadelphia, PA and grew up in Gainesville, FL. She earned her B.A. in Geology in May 2017 from Mount Holyoke College in South Hadley, MA.

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## 1. Introduction

Per- and polyfluoroalkyl substances, abbreviated as PFAS, are widely used in the manufacturing of fire-fighting foams, non-stick surfaces, food-contact paper coatings, and other applications [Sun et al. 2016; Lindstrom et al. 2011]. These compounds are now emerging nationally as persistent, mobile, and toxic environmental contaminants [Sun et al. 2016; Lindstrom et al. 2011]. In humans, long-term exposure can cause immune diseases and various types of cancer [USEPA 2018; USEPA 2016c]. Along with other PFAS, “GenX” has contaminated surface water and groundwater surrounding the Chemours Company chemical manufacturing plant near Fayetteville, North Carolina [NCDEQ Select Committee on NC River Quality 2017; Sun et al. 2016].

This surface water and groundwater contamination has degraded drinking water quality for thousands of NC residents, through contamination of residential groundwater wells and the nearby Cape Fear River (CFR) [Doran 2018; CBS News 2017; Leclercq 2017; Sun et al. 2016; NCDEQ 2016]. The CFR supplies drinking water to many communities downstream, including the city of Wilmington, NC, and many residents living near the chemical plant draw their water from groundwater wells [NCDEQ 2016]. The site’s close proximity to major drinking water sources, namely the surficial aquifer and the CFR, makes environmental contamination a major human health concern.

It is possible that PFAS input to nearby streams via groundwater discharge could continue over a decades-long timescale. This discharge could leave streams in the area contaminated long after release by the plant has ceased. Since these streams flow into the CFR, this could mean long-term contamination of a major drinking water source. The goal of this research was to quantify the rate of transport of GenX and related PFAS from groundwater to

streams, as well as quantify the PFAS discharge down the stream channels, in the areas of known contamination near Chemours.

As part of this study, groundwater samples were collected from directly beneath the streambeds of contaminated streams and analyzed for concentrations of PFAS. Water flux was measured at these same points in the streambeds, and these measurements in combination with the groundwater PFAS concentration data yielded the PFAS flux from groundwater to streams through the streambeds. Chemical dilution stream gaging was also done and PFAS concentrations in stream water were measured to quantify the stream export of PFAS from watersheds near Chemours. Ideally, this information will improve the quantitative understanding of the transport of GenX and related PFAS from groundwater to surface water near the Chemours plant in the NC coastal plain.

## **2. Background on PFAS**

### **2.1. Structure & Physicochemical Properties**

PFAS consist mainly of a fluorinated carbon chain bonded to other functional groups, such as sulfate or carboxyl groups [Wang et al. 2017; CONCAWE 2016]. The fluorinated carbon chain, or alkyl group, can be long or short, and the length of the alkyl group along with the presence of different functional groups and heteroatoms affect the physicochemical properties of the compound [Wang et al. 2017]. Combinations of fluorinated carbon chains of varying lengths and functional groups are numerous, resulting in thousands of different PFAS compounds [Wang et al. 2017; Lindstrom et al. 2011]. Because the carbon-fluorine bonds are highly stable, PFAS do not degrade quickly under normal environmental conditions and remain persistent in the

environment for long periods of time [Wang et al. 2017; CONCAWE 2016; Sun et al. 2016; Wang et al. 2015; Lindstrom et al. 2011]. Although exposure studies on newer PFAS compounds are limited, existing research has shown that PFAS are toxic to humans, causing immune diseases and various types of cancer [USEPA 2018; USEPA 2016a; USEPA 2016b]. It is also possible that PFAS can bioaccumulate and biomagnify in wildlife [CONCAWE 2016; Lindstrom et al. 2011]. While little is known about the properties of newer PFAS being produced, data are available (Table 1) for some “legacy” PFAS, for which commercial production began in the 1940s.

Their toxicity and persistence in the environment mean that PFAS are of increasing concern as their production and use becomes more widespread [Wang et al.; Lindstrom et al. 2011]. They are beginning to be regulated by environmental organizations, and the United States Environmental Protection Agency (USEPA) has set a combined lifetime health advisory level of 70 nanograms per liter ( $\text{ng L}^{-1}$ ), or equivalently 70 parts per trillion (ppt), for perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) [Wang et al. 2017; USEPA 2016c]. Many of the legacy PFAS that have been manufactured since the 1940s are frequently being replaced by newer, slightly different chemicals with generally shorter fluoroalkyl chains [Wang et al. 2017; Sun et al. 2016]. The continuous production of new compounds makes regulating this class of chemicals difficult, especially because little is known regarding their environmental behavior.

**Table 1.** Physicochemical details for six legacy PFAS [from NGWA 2017].

PFAS Listed in UCMR3	CAS RN	Chemical Formula	MW g/mol	pKa at 25°C (USNLM 2017)	Solubility, g/L at 25°C (Concawe 2016)	Log Kow (Concawe 2016)	Log Koc (USNLM 2017)	USEPA Health Advisory Level for drinking water
Perfluorooctane-sulfonic Acid (PFOS)	1763-23-1	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> SO <sub>3</sub> H	500	<1.0	0.52 – 0.57	6.43	2.4 – 4.7	Individual or Combined 70 ng/L*
Perfluorooctanoic Acid (PFOA)	335-67-1	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>6</sub> COOH	414	-0.5 – 4.2	3.4 – 9.5	5.30	1.92 – 2.59	
Perfluorononanoic Acid (PFNA)	375-95-1	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> COOH	464	-0.21	9.5	5.92	5.08	No Standard
Perfluorobutane-sulfonic Acid (PFBS)	375-73-5	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H	300	-3.31	46.2 – 56.6	3.90	2.26	
Perfluoroheptanoic Acid (PFHpA)	375-85-9	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> CO <sub>2</sub> H	364	-2.29	4.2	4.67	1.52 – 2.82	
Perfluorohexane-sulfonic Acid (PFHxS)	355-46-4	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> SO <sub>3</sub> H	400	-6 – -5	2.3	5.17	1.78	

CAS RN = Chemical Abstracts Registry Number

MW = molecular weight

ng/L = nanograms per liter

g/L = grams per liter

g/mol = grams per mole

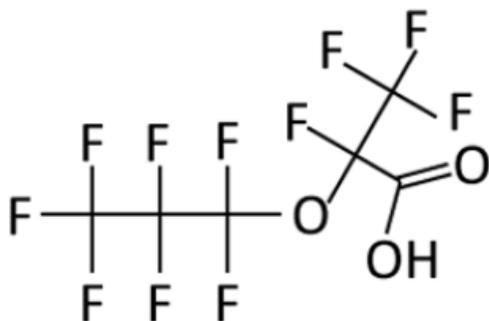
Kow = octanol/water partition coefficient

Koc = organic carbon partition coefficient

\*The USEPA Health Advisory Level for drinking water is 70 ng/L for PFOS and PFOA as individual analytes, but EPA guidance recommends application of the 70 ng/L level to the combined concentrations.

## 2.2. GenX

One type of PFAS goes by the tradename “GenX” and is emerging as a contaminant of concern, especially for the area surrounding the Chemours Company chemical manufacturing plant near Fayetteville, NC [Sun et al. 2016]. The name “GenX” may refer to perfluoro-2-propoxypropanoic acid, also called hexafluoropropylene oxide dimer acid (HFPO-DA), or just the anion of this dissociated acid, or the ammonium salt of this anion [Hopkins et al. 2018]. Given that the  $pK_a$  for the acid is predicted to be -0.77 [Hopkins et al. 2018], GenX is generally expected to occur as an anion in natural waters. The acid consists of two fluorinated carbon chains bonded to an ether oxygen atom with a carboxyl group bonded to one of the carbon chains (Fig. 1). The NC state health goal for GenX in drinking water, based on draft toxicity assessments, is 140 nanograms per liter ( $ng\ L^{-1}$ ), or 140 parts per trillion (ppt) [USEPA 2018]. While GenX was the headlining compound that inspired this research, 20 to 30 other PFAS were also analyzed in collected water samples, including an array of legacy and newer compounds.



**Figure 1.** Chemical structure of the acid form of GenX,  $C_6HF_{11}O_3$  [from [www.chemspider.com](http://www.chemspider.com), accessed March 2018].

### **3. Study Area**

#### **3.1. Location, Geology, & Climate**

The Chemours Company chemical manufacturing plant is located about 24 km south of the city of Fayetteville, North Carolina, and field research included measurements and collection of samples at points in both Cumberland and Bladen Counties. The plant is situated just west of the Cape Fear River, which flows past the plant from north to south, and all streams investigated are small tributaries to the Cape Fear. Fayetteville Works is the name of the larger property which contains the Chemours manufacturing facilities as well as those owned by other companies.

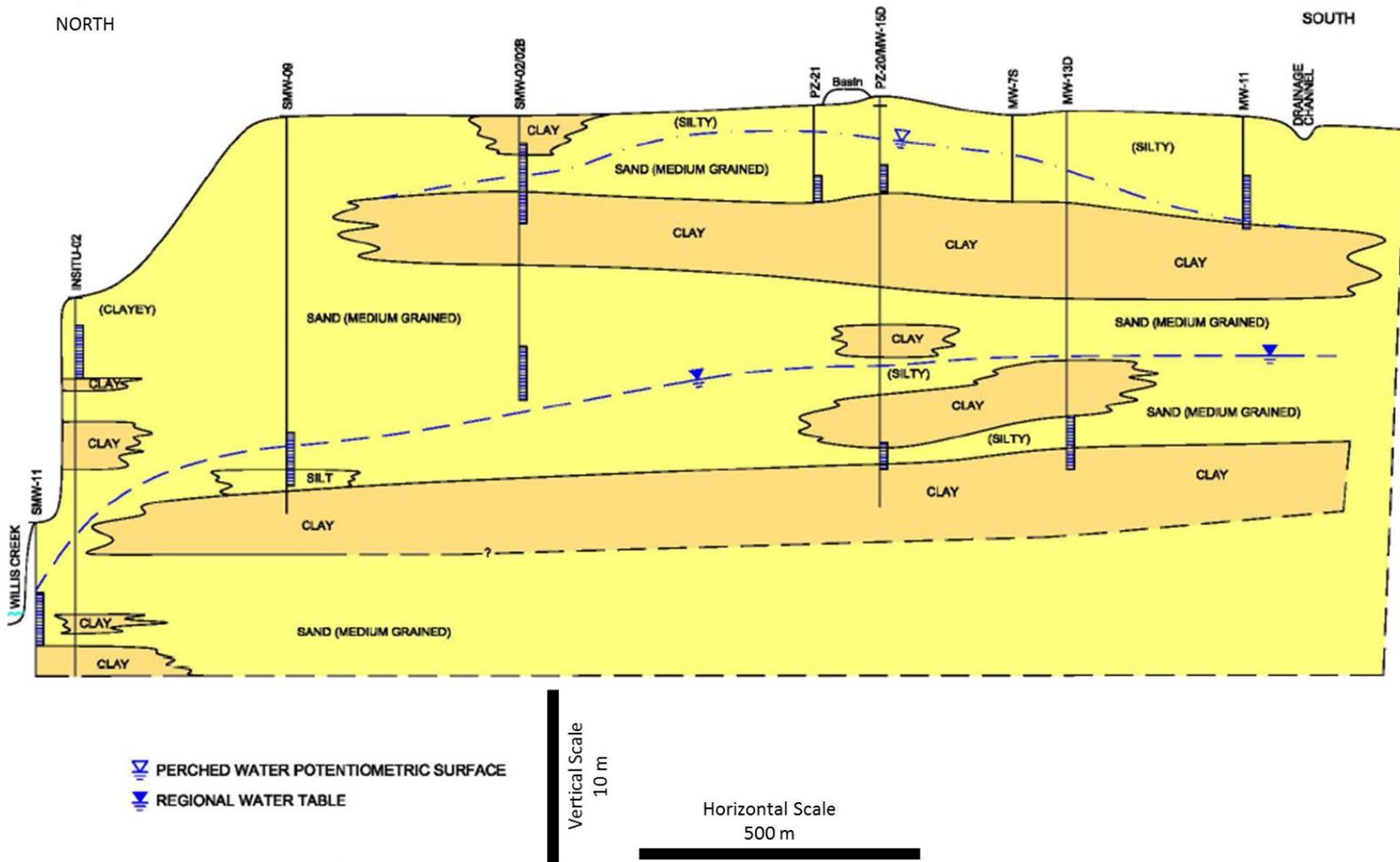
The study area is located in the Cape Fear River Basin in the coastal plain region of North Carolina. The geology of the coastal plain mainly consists of Holocene and Cenozoic sedimentary deposits, and the Cape Fear River valley contains sedimentary terraces such as the Wando and Socastee formations [Winner and Coble 1996; Soller 1988]. The streambeds in the small streams where data was gathered consisted mainly of medium- to fine-grained sand, as well as some clay beds. This observation is consistent with the measured composition of the surficial aquifer across a large area of the coastal plain [Winner and Coble 1996]. This sandy surficial aquifer is highly permeable and most of its recharge comes from rainfall infiltration, whereas streams in the region are discharge areas [Winner and Coble 1996]. Cross-sections of the stratigraphy directly beneath the Chemours property indicate that among the sandy substrate there also exist some clay lenses that may account for the clay beds in some of the streams that were sampled (Fig. 2a and 2b).

The surficial aquifer beneath the Fayetteville Works site extends approximately 18 m deep (Fig. 3) [NCDEQ 1968]. Below this surficial aquifer lie a number of deeper confined

aquifers, including the Black Creek, Upper Cape Fear, and Lower Cape Fear aquifers [Winner and Coble 1996; NCDEQ 1968]. Potentiometric surface data for the surficial aquifer in the area indicate that groundwater flows generally west to east, towards the Cape Fear River, beneath the study site [NCDEQ 2018b; Parsons 2014]. Regionally, groundwater flows coastward within the coastal plain, and the aquifers and confining layers increase in thickness towards the coast [Winner and Coble 1996].

The climate in the study area is generally temperate, with an average annual air temperature of 61.15°F, or 16.19°C [NCCO 2018]. The average annual precipitation for the area is 45.34 inches, or 115.16 centimeters [NCCO 2018]. Prevailing winds are southwest-northeast (Fig. 4).

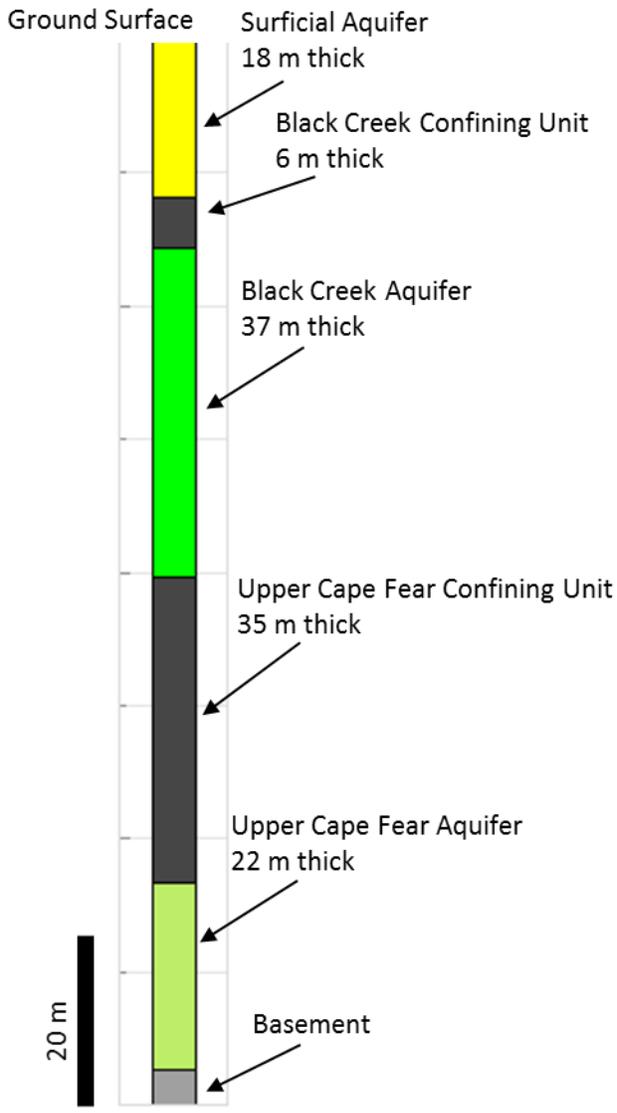




**Figure 2b.** Cross-section showing the stratigraphy of the substrate directly beneath the Chemours property along a north to south transect [from Parsons 2014]. Vertical scale has been exaggerated. Water levels based on measurements from December 2013. Parsons [2014] does not indicate in their report what the black dashed line at the bottom of the figure represents, and does not say if their boreholes reached this depth, so it cannot be assumed that this represents the base of the surficial aquifer.

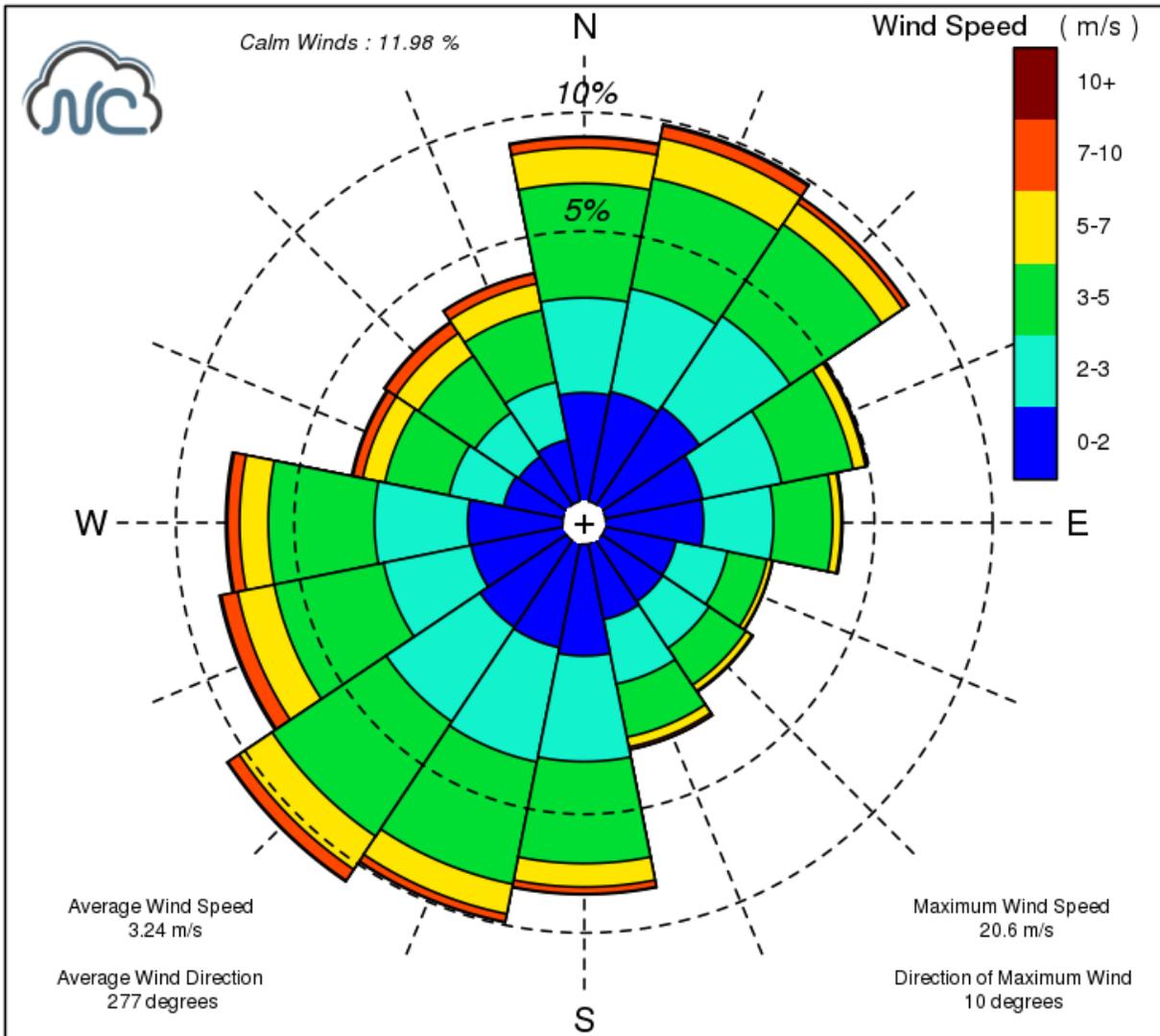


**Figure 2c.** Map showing the extent of the two cross-sections in (a) and (b) [from Parsons 2014]. The red star indicates the location of core log V42U from Figure 3. Other dots labeled with acronyms indicate wells where water samples and core data were collected as part of the Parsons (2014) investigation.



**Figure 3.** Core log V42U showing the stratigraphy of the substrate directly beneath the Chemours property and unit thicknesses in meters [from NCDEQ 1968, accessed Feb. 2019 via the web database at [https://www.ncwater.org/?page=540&quadtype=V\\*\\*42U&jmp=1&namex=Dupont\\*Corp&e=624386.01&n=121327.04](https://www.ncwater.org/?page=540&quadtype=V**42U&jmp=1&namex=Dupont*Corp&e=624386.01&n=121327.04)].

## Wind Rose for Fayetteville Airport (KFAY) Jan. 10, 1998 to Dec. 13, 2018

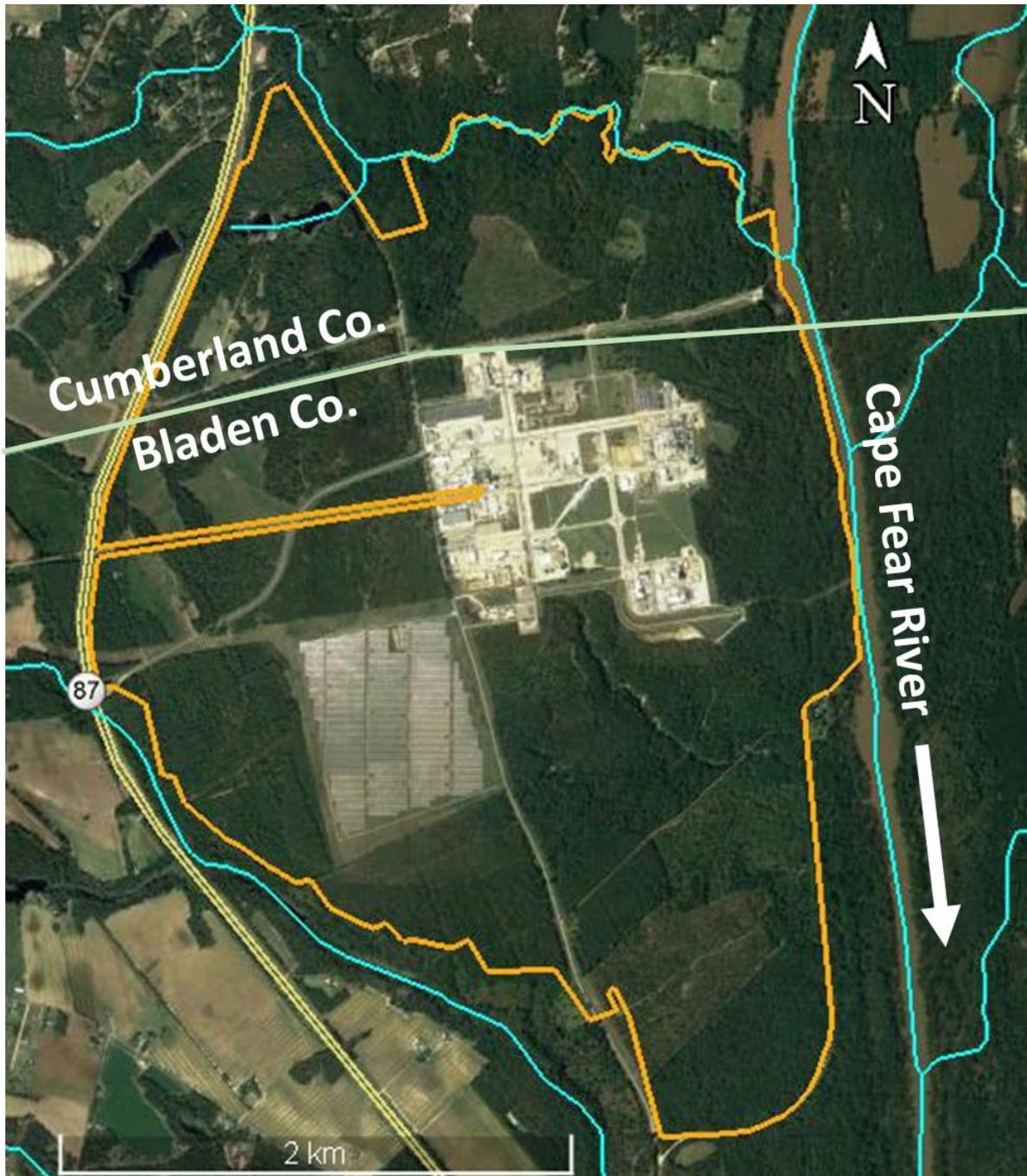


**Figure 4.** Wind rose from the climatological station at Fayetteville Regional Airport (KFAY), located about 17 km northwest of the Chemours plant [from <https://climate.ncsu.edu/windrose>, accessed Nov. 2018]. This diagram shows the direction and frequency of winds in this area, where each wedge represents wind blowing from that direction on the compass, and the length of the wedge indicates the percentage of time that winds were blowing from that direction. Colors correspond to wind speed in meters per second.

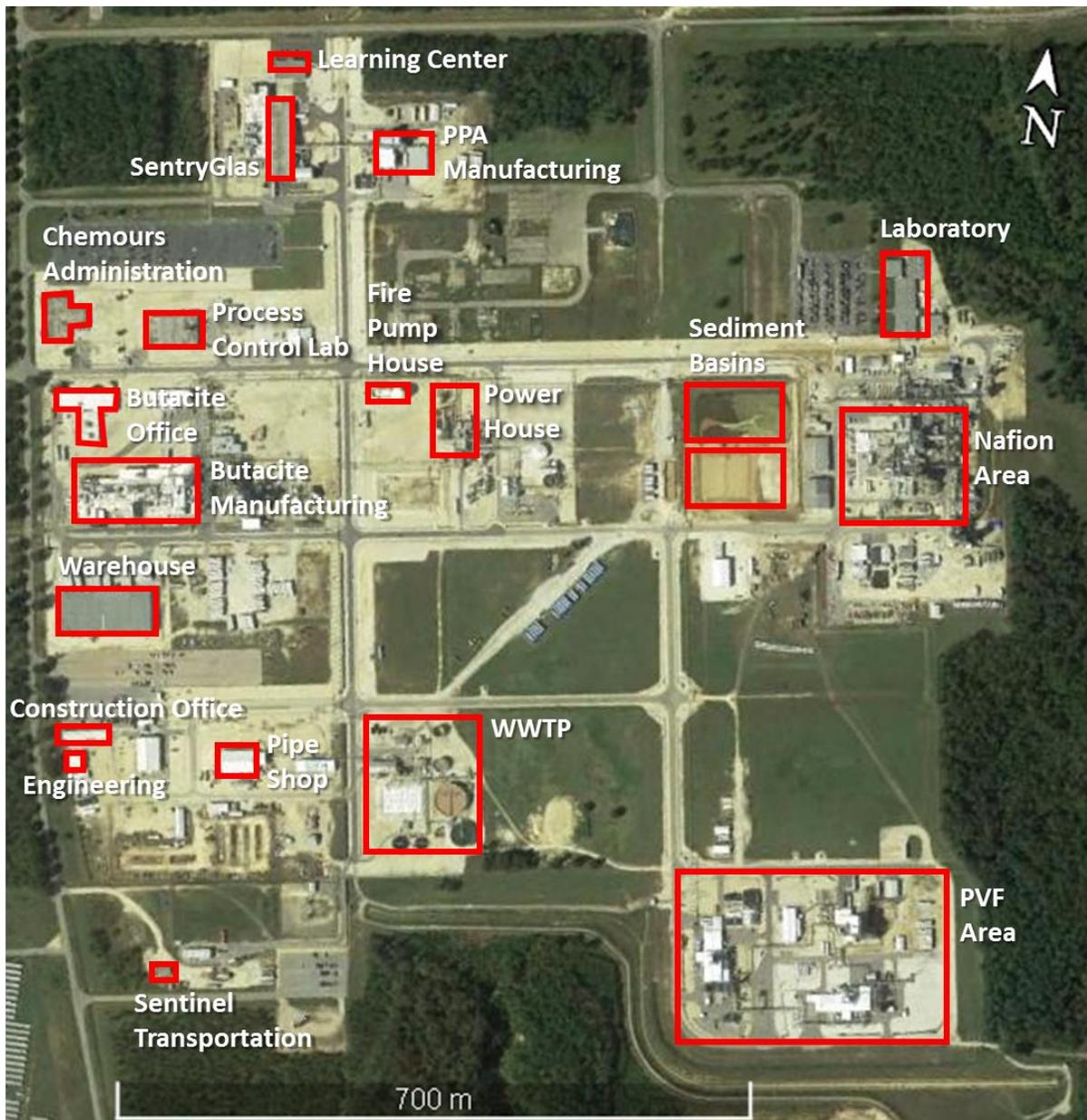
### **3.2. The Chemours Fayetteville Works Property**

The property containing the Chemours chemical manufacturing facilities is called Fayetteville Works and is located at the address 22828 NC-87, Fayetteville, NC 28306. It occupies the land between NC Highway 87 and the Cape Fear River and sits on 2,150 acres of land, 400 acres of which is developed [Chemours 2019]. Fayetteville Works has been owned by the Chemours Company since they became a spin-off of Dupont and acquired the property from DuPont in 2015 [Futch 2015]. Four separate companies have facilities on the Fayetteville Works property: Dupont, the Chemours Company, Kuraray America, Inc., and Sentinel Transportation, LLC. Chemours is the owner of the property, and Dupont and Kuraray are tenants [Futch 2015; Chemours 2019]. Sentinel is a contract hauling business and has an office on site.

From the Bladen and Cumberland County online GIS databases [Cumberland Co., NC 2017; Bladen Co., NC 2019], the property boundary of Fayetteville Works can be delineated. Since the property encompasses land in both counties, the parcels must be stitched together to create the whole property boundary (Fig. 5). It is this property outline that various third-party environmental consulting companies use in the maps in their commissioned reports (i.e. Parsons and ERM, cited in this report). Based on information gathered from these reports, and information available through online map tools, it was determined which buildings on the property serve what purposes (Fig. 6). Some of the buildings on the property house the administrative offices of the companies operating there and some house the manufacturing facilities for various chemical products and intermediates: Nafion® and intermediates of Viton® and Teflon® (Chemours); Butacite® and SentryGlas® (Kuraray); PVF resin for use in the production of Tedlar® (DuPont) [Futch 2015; Chemours 2019]. There are also structures for on-site power production and waste treatment [Chemours 2019].



**Figure 5.** Map showing the property boundaries of Chemours Fayetteville Works (outlined in orange) from the parcel maps from Bladen and Cumberland County tax records GIS databases [satellite image from Google Earth 2019; stream vector layer from US NHD 2017; Cumberland Co., NC 2017; Bladen Co., NC 2019]. The light green line represents the border between the two counties, with Bladen to the south and Cumberland to the north, and the light blue lines represent streams. The white arrow indicates the direction of flow in the Cape Fear River.



**Figure 6.** Map detail showing the different buildings on the Chemours Fayetteville Works property and their known uses [satellite imagery from Google Earth 2019; Chemours 2019; Parsons 2014].

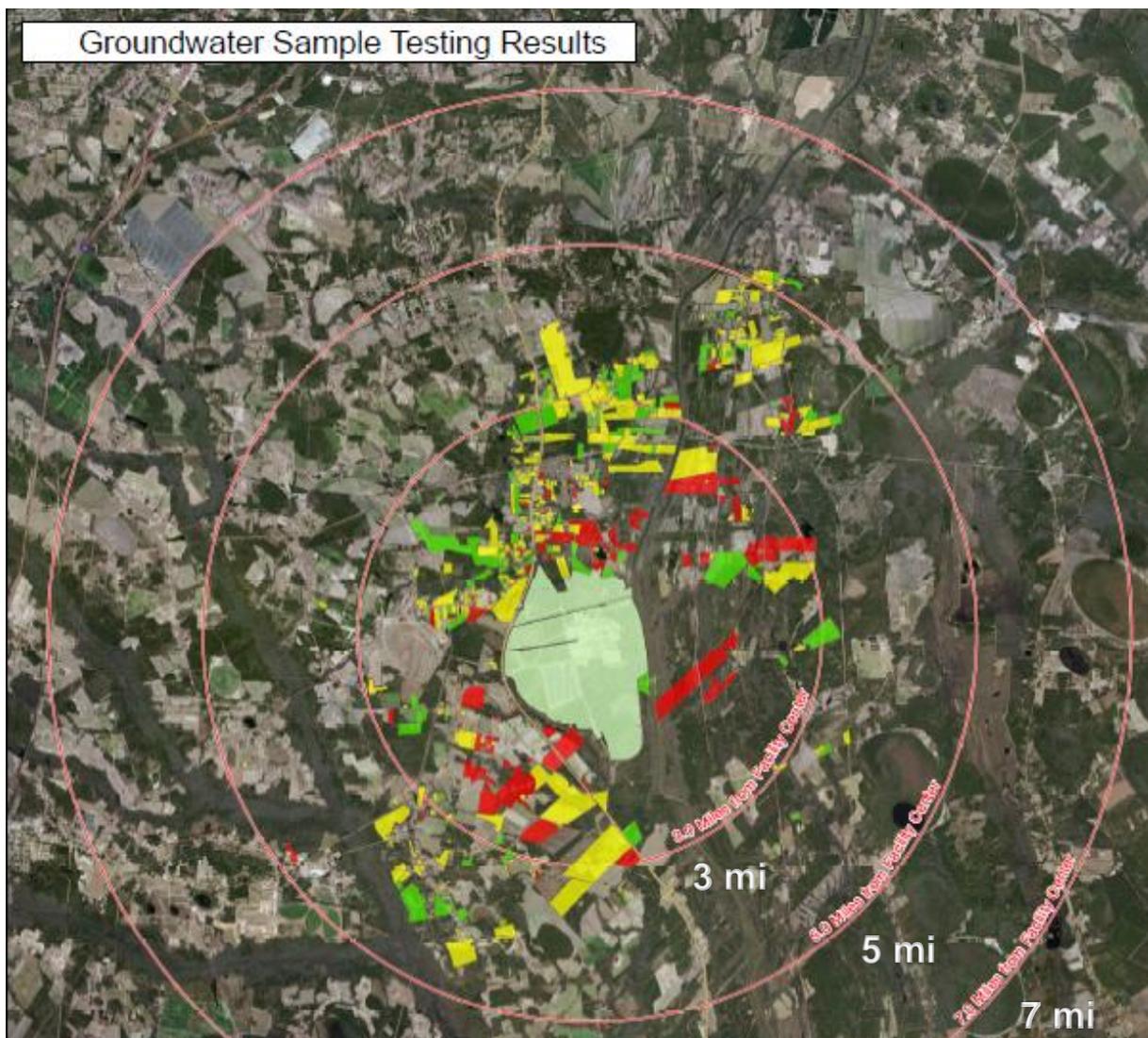
### 3.3. History of PFAS Production in the Study Area

This research focused on streams near the Chemours plant on the Fayetteville Works property located near Fayetteville, NC where groundwater is known to be contaminated with GenX and other PFAS [NCDEQ 2018a; NCDEQ Select Committee on NC River Quality 2017]. The plant, at the time owned by Dupont, started commercial production of PFAS in 1980, when the plant began generating GenX as a byproduct [WRAL 2018; Sun et al. 2016]. The plant previously released their process wastewater in part through an outflow into the adjacent Cape Fear River [WRAL 2018]. In the 1990s, the contamination of water resources was addressed, and in 2005 Dupont settled a lawsuit with the EPA regarding their release of PFAS into the environment near their site in West Virginia, which the company knew to be harmful [Doran 2018; WRAL 2018]. More recently, in June 2017, the plant's ability to release wastewater into the Cape Fear River was partially revoked – the plant has since transitioned to transporting PFAS-contaminated wastewater offsite for deep well injection in Texas but is working to establish on-site wastewater treatment capabilities [Hagerty 2019; WRAL 2018]. Since these emission reductions, concentrations of GenX and other PFAS in the Cape Fear River have decreased but are still measurable [NCDEQ 2019b].

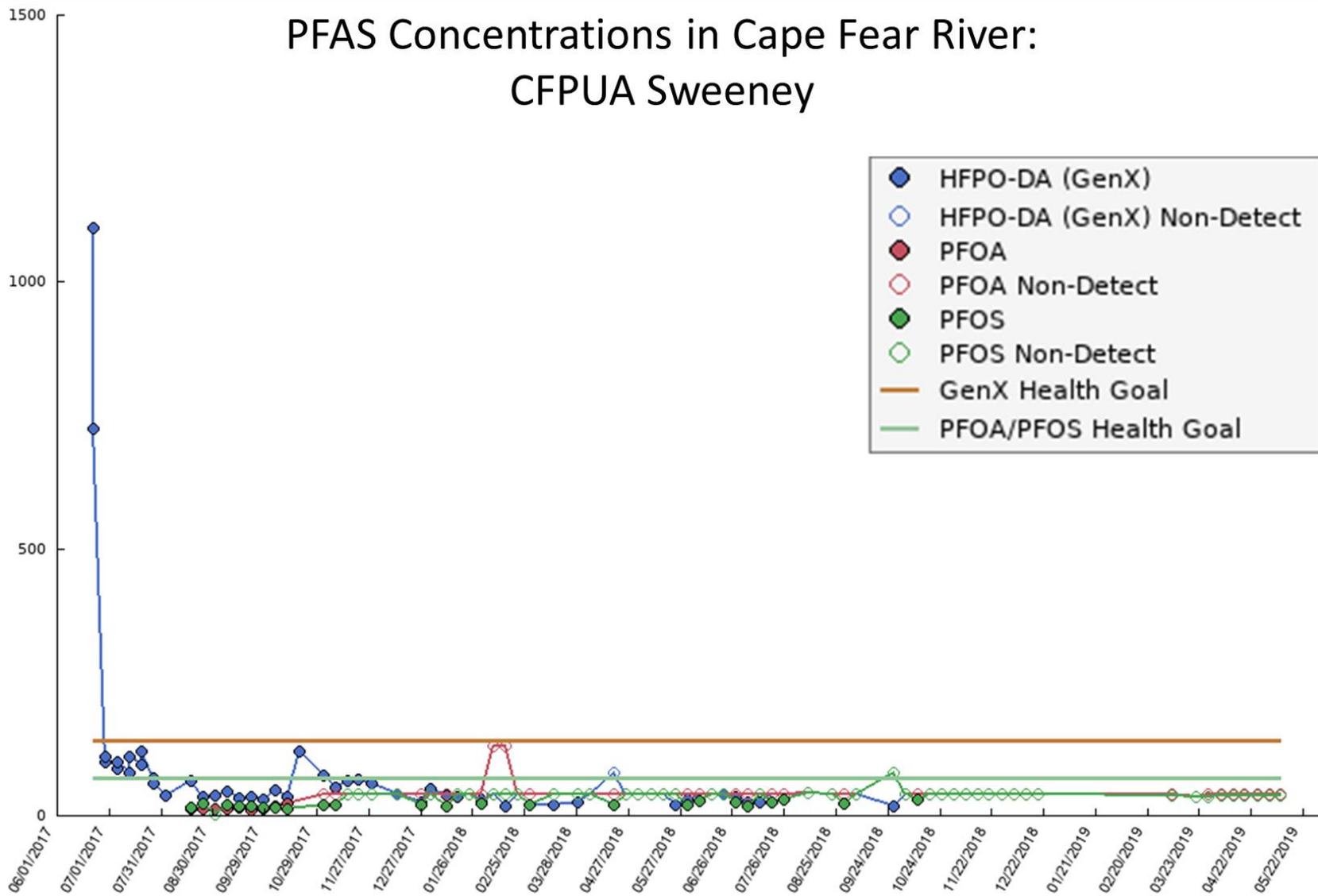
The Chemours Fayetteville Works plant has also been releasing PFAS into the atmosphere through air emissions. Along with stopping their release of wastewater into the Cape Fear, air emissions of GenX have also been reduced from the 2017 levels of about 2300 lb yr<sup>-1</sup> [Hagerty 2019; WRAL 2018; ERM 2018]. Stack testing from February 2018 indicate that emission rates of GenX were 1.6 lb hr<sup>-1</sup> at that time [Weston Solutions, Inc. 2018]. The ultimate goal for Chemours' air emissions reduction, imposed by the NC Department of Environmental Quality and the Division of Air Quality, is to reduce emissions by 99% from 2017 levels by the

end of 2020 through the installation of new treatment equipment, including a thermal oxidizer [Hagerty 2019; WRAL 2018].

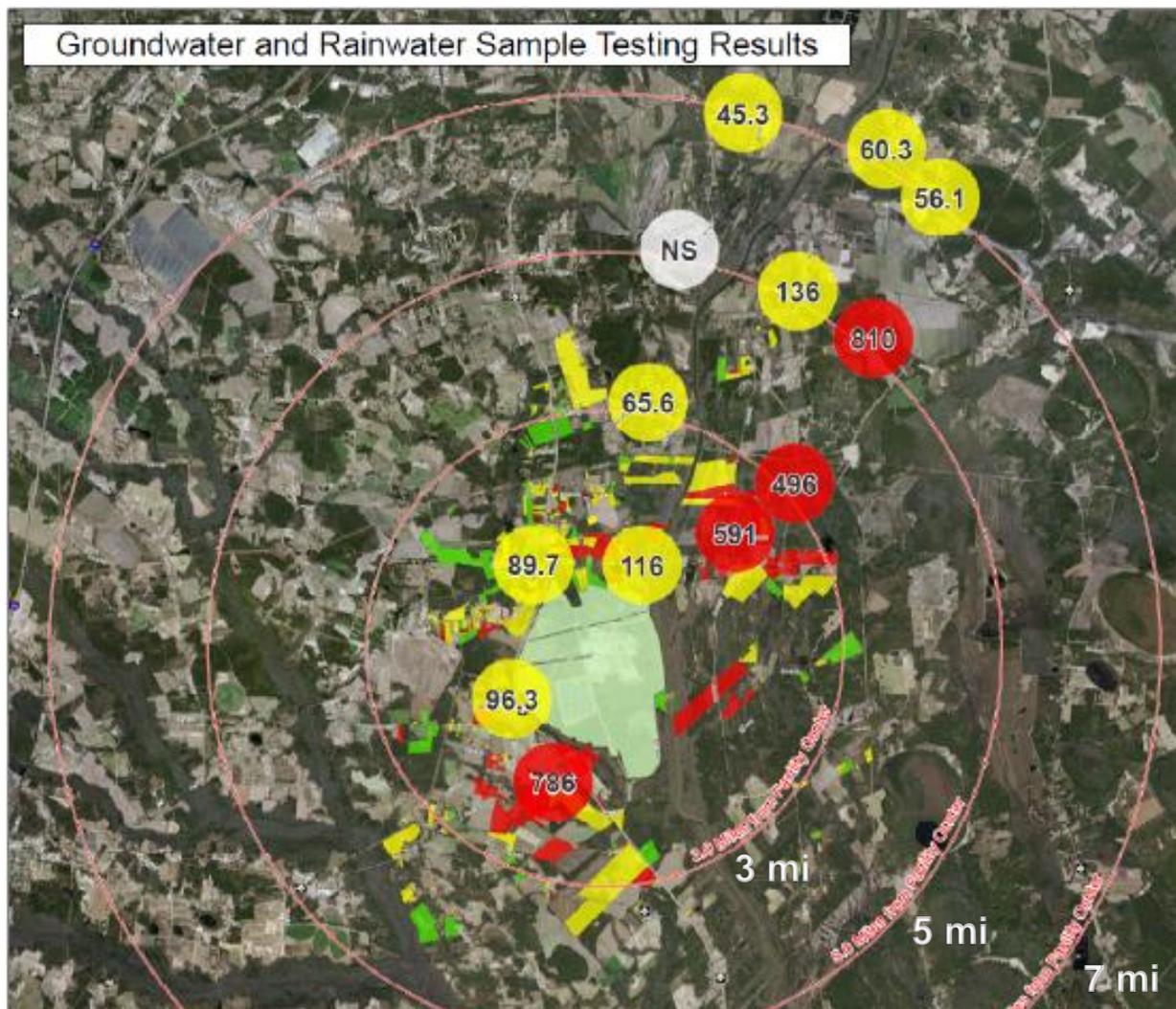
Even though the plant's release of PFAS into the environment has been reduced, and concentrations of GenX and other PFAS in the Cape Fear River have decreased, the North Carolina Department of Environmental Quality (NCDEQ) has found GenX concentrations above the state health goal in groundwater wells within seven kilometers of the plant (Fig. 7) as well as a concentration of 10 ng L<sup>-1</sup> in the Cape Fear River that persists in Wilmington, NC (Fig. 8) [NCDEQ 2019b; NCDEQ 2018a; WRAL 2018]. Groundwater contamination in the area is most likely due to the atmospheric deposition of PFAS from air emissions and subsequent infiltration into the surficial aquifer, a theory which is supported by the high concentrations of GenX found in rainwater samples collected from sites near Chemours (Fig. 9) [NCDEQ 2018c; NCDEQ 2018d]. These high concentrations in rainwater samples have decreased over time as Chemours has installed activated carbon filters to reduce their emissions to the air (Fig. 10) [NCDEQ 2019a; NCDEQ 2018d].



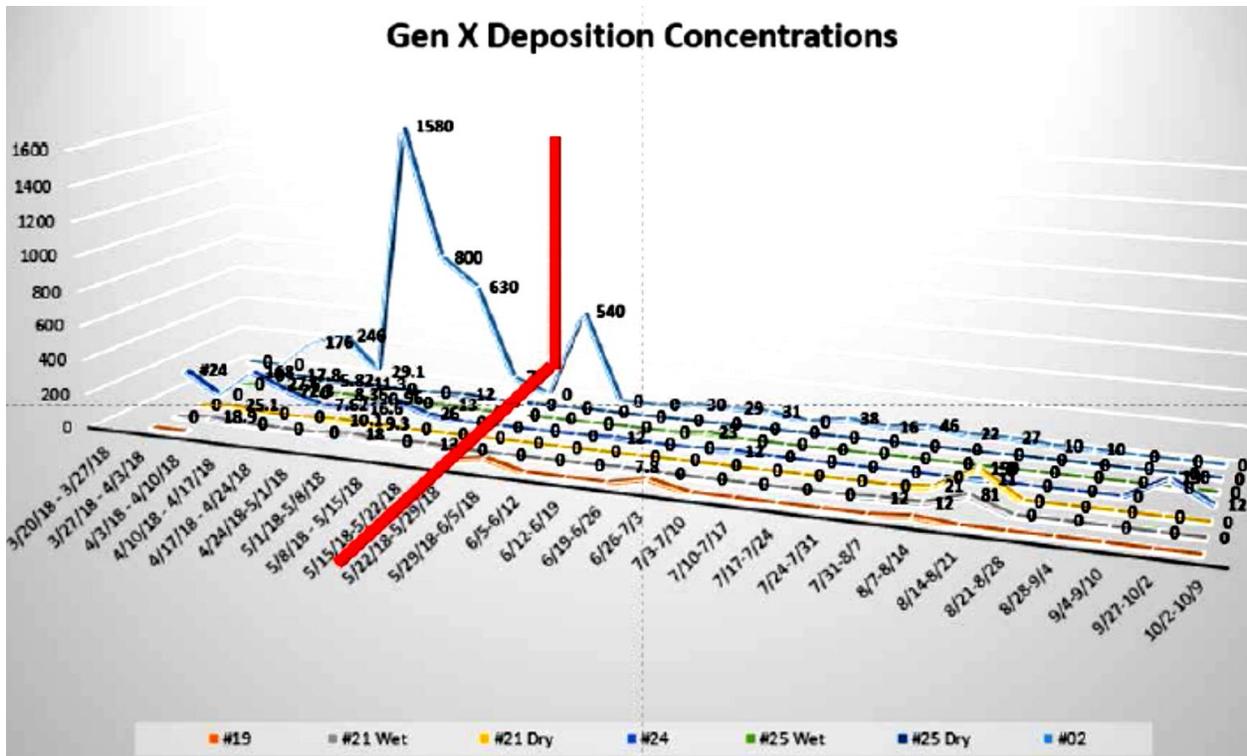
**Figure 7.** Map showing GenX concentrations in groundwater wells for the area surrounding Chemours (property shaded in pale green) within three, five, and seven-mile radii. Red parcels had groundwater GenX concentrations greater than  $140 \text{ ng L}^{-1}$ , yellow represents concentrations between  $10$  and  $140 \text{ ng L}^{-1}$ , and green represents non-detect levels [from NCDEQ 2018a].  $140 \text{ ng L}^{-1}$  is the state health goal set by the NCDEQ for drinking water in NC.



**Figure 8.** Graph showing concentration data for GenX, PFOA, and PFOS in the Cape Fear River at the Cape Fear River Utility Authority (CFPUA) Sweeney sampling location in Wilmington, NC, about 145 km southeast of Fayetteville [NCDEQ 2019b].



**Figure 9.** Map showing both concentrations of GenX in groundwater wells (colored parcels) and rainwater samples (colored circles) collected from locations near Chemours (property shaded in pale green) by NCDEQ and Division of Air Quality, within three, five, and seven-mile radii [from NCDEQ 2018d]. Red areas had GenX concentrations greater than 140 ng L<sup>-1</sup>, yellow represents concentrations between 10 and 140 ng L<sup>-1</sup>, and green represents non-detect levels. This map was used to show how the spatial distribution of groundwater contamination coincides with the spatial distribution of rainwater contamination for GenX. Concentration data are for rainwater samples collected 28 February through 2 March 2018.



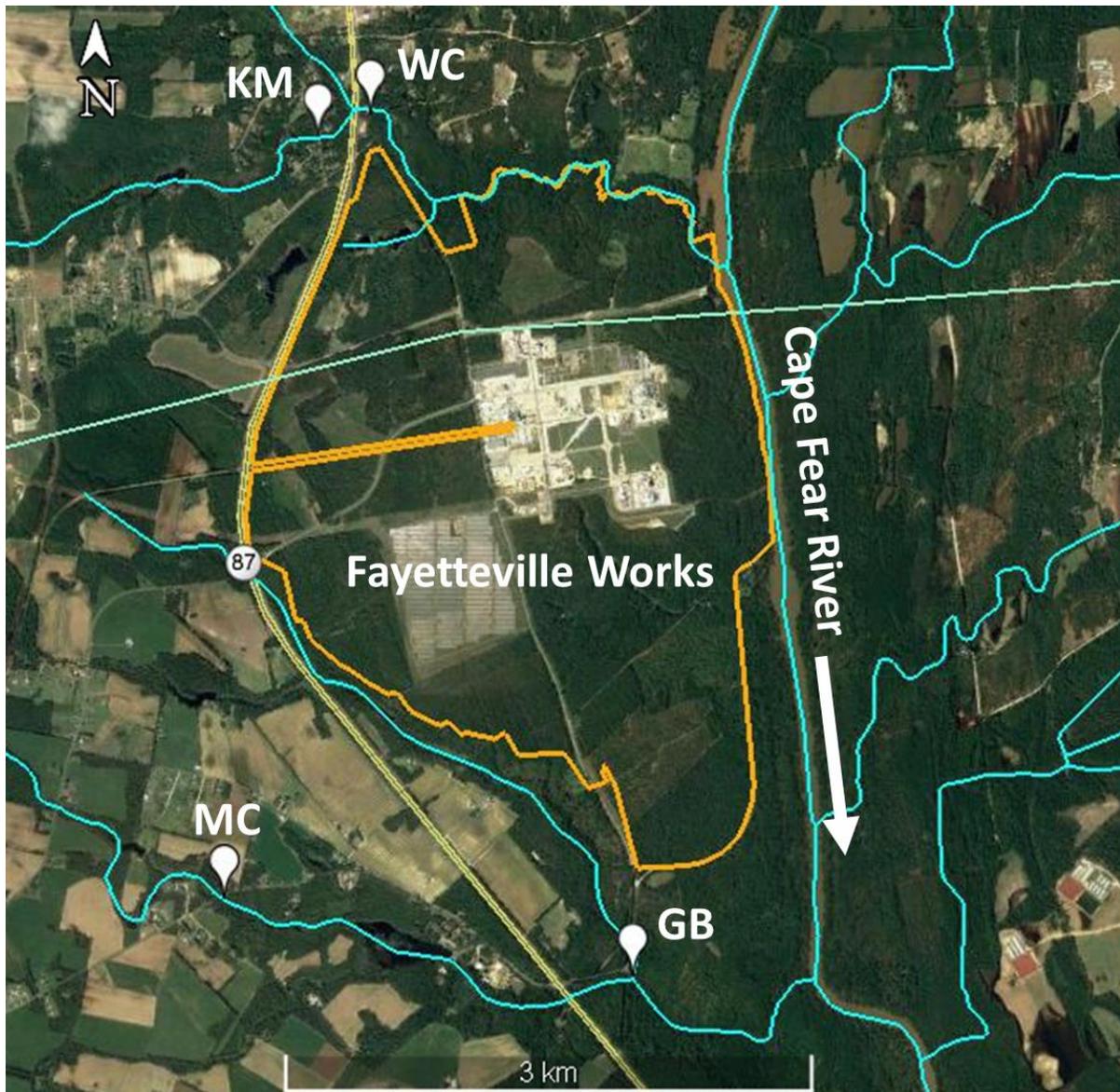
**Figure 10.** Graph of concentrations of GenX in rainwater samples collected at five sampling locations near Chemours by NCDEQ and Division of Air Quality for sampling dates from March to October 2018 [NCDEQ 2019a]. The red line indicates the point in time when Chemours’ interim GenX air emissions mitigation measures were installed in May 2018.

#### 4. Study Design

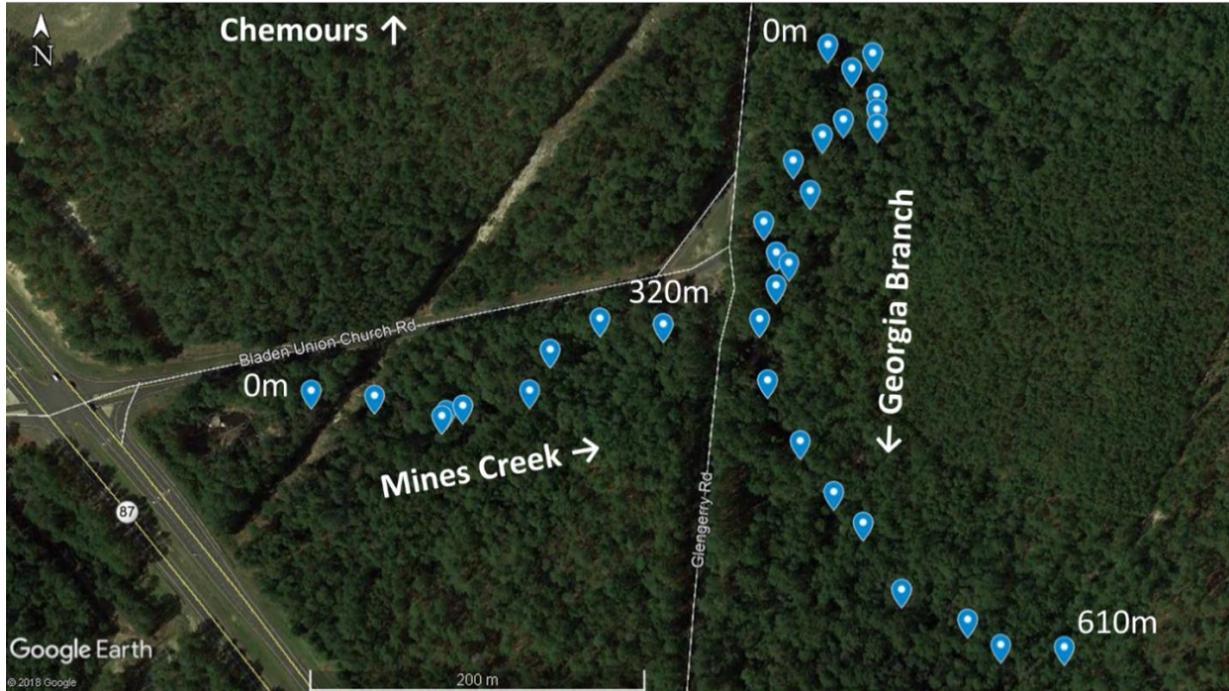
This research consisted of three phases of data collection, listed here:

1. Field reconnaissance on 5 March 2018, followed in June and August of 2018 by sampling of the groundwater-based PFAS flux to four streams at locations identified in March 2018 (Fig. 11).
2. Detailed sampling campaign measuring groundwater-based PFAS flux to Mines Creek and Georgia Branch, on 22 and 23 October 2018 (Fig. 12). The same type of streambed measurements were done as in the initial survey but with more measurement points. Chemical dilution stream gaging using NaCl was also done along with PFAS concentration analysis of stream water samples.
3. Chemical dilution stream gaging and stream water PFAS concentration analyses, on 14 and 15 February 2019 to provide a snapshot of stream PFAS export from five tributary watersheds into the Cape Fear River near the Chemours plant (Fig. 13).

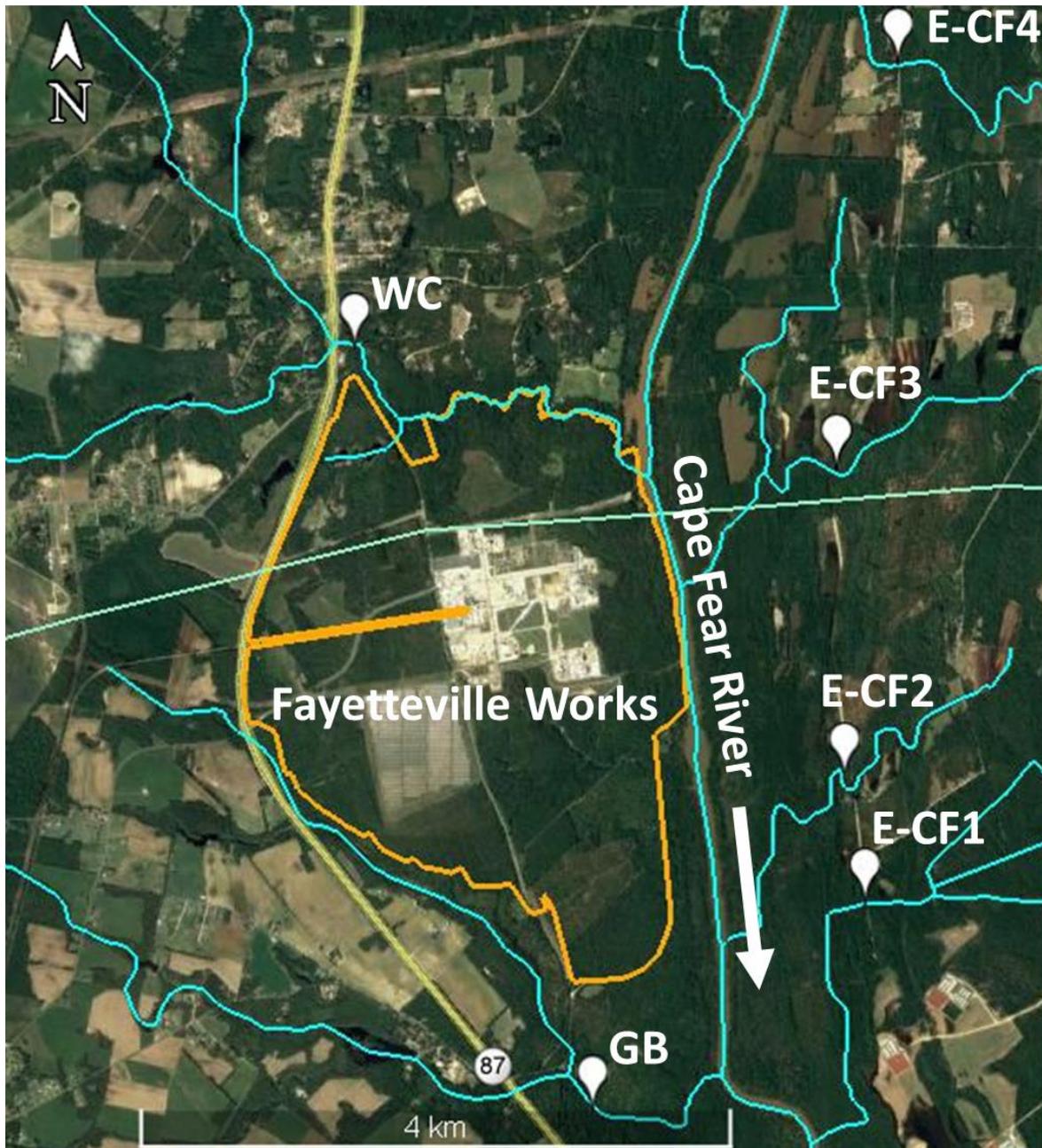
During a reconnaissance trip into the field on 5 March 2018, 13 stream sites near the Chemours plant (all west of the Cape Fear River) were investigated and evaluated for their suitability to the field research methods based on groundwater sampling and measurements in streambeds, e.g., close proximity to local roads, relatively shallow stream depth (below waist-level), permeable and sandy streambed allowing for the use of piezomanometers and field permeameters (see Section 5), and lack of obstructing vegetation or other barriers to access. Of the 13 sites that were evaluated, four were found to be feasible study sites: (1) Georgia Branch (GB) near its confluence with Mines Creek directly south of the plant, (2) Mines Creek (MC) where it flows beneath Pages Lake Road southwest of the plant, (3) Kirks Mill Creek (KM)



**Figure 11.** Map of the study area showing the four sites where the initial sampling was carried out in June and August of 2018: Kirks Mill Creek (KM), Willis Creek (WC), Mines Creek (MC), and Georgia Branch (GB) [satellite image from Google Earth 2019; streams vector from U.S. National Hydrography Dataset 2017]. The Chemours Fayetteville Works property is outlined in orange, streams are represented by light blue lines, and sampling locations are indicated by white bubble markers. The white arrow indicates the direction of flow in the Cape Fear River.



**Figure 12.** Map of the study area showing the locations of streambed sampling points (indicated with blue point markers) in Mines Creek and Georgia Branch, south of the Chemours Fayetteville Works property, during the intensive sampling on 22 and 23 October 2018 [satellite image from Google Earth 2019]. Distance measurements along the reach length begin at 0m, the upstream-most point on each stream. Stream discharge measurements and stream water samples were taken at the 0m and 320m points on Mines Creek and at the 0m and 610m points on Georgia Branch. White arrows following stream names indicate flow direction.



**Figure 13.** Map of the study area showing the locations where stream discharge measurements and stream water samples were taken 14 and 15 February 2019. E-CF1 was named but not sampled. The Chemours Fayetteville Works property is outlined in orange, streams are represented by light blue lines, and sampling locations are indicated by white bubble markers. The white arrow indicates the direction of flow in the Cape Fear River.

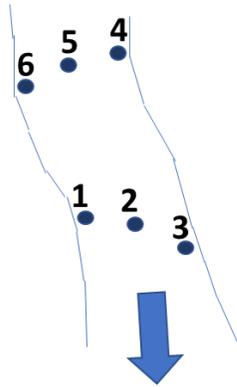
where it flows beneath Point East Drive northwest of the plant, and (4) Willis Creek (WC) where it flows beneath Crittercreek Road directly north of the plant (Fig. 11).

Mines Creek and Kirks Mill Creek were sampled on 5 June 2018, Georgia Branch was sampled on 29 June 2018, and Willis Creek was sampled on 8 August 2018. In each stream, groundwater samples were collected beneath the streambed at six different points, and vertical hydraulic head gradient and hydraulic conductivity were measured at the same six points in the streambed where groundwater samples were taken. Vertical head gradient and hydraulic conductivity were used to calculate groundwater flux through the streambed, and groundwater samples were analyzed for PFAS concentrations. For each measurement point, groundwater PFAS concentration data was multiplied by vertical water flux data to give the PFAS flux through the streambed.

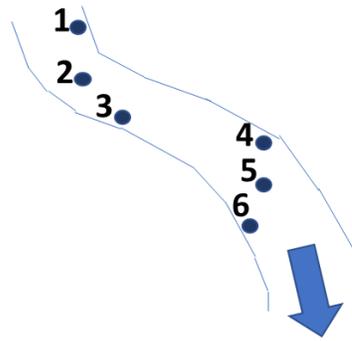
At each stream sampling site, the six streambed measurement points were arranged in two three-point clusters along a 5 to 10 m stream reach. Each cluster of three measurement points was arranged so that there was one point near the left bank of the stream (when facing downstream), one in the center, and one near the right bank (Fig. 14).



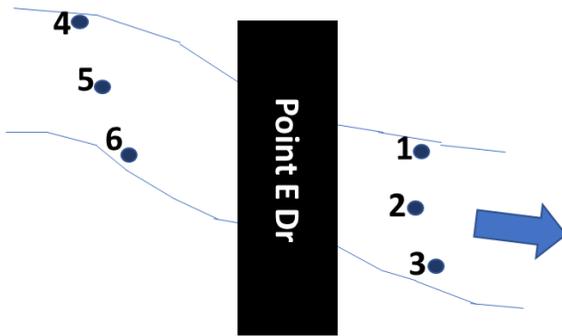
Georgia Branch (GB)



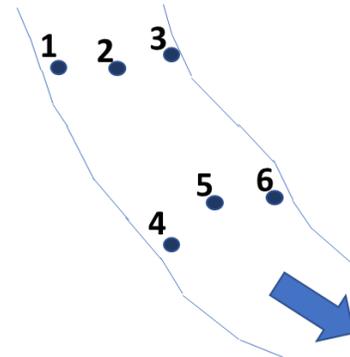
Mines Creek (MC)



Kirks Mill Creek (KM)



Willis Creek (WC)



**Figure 14.** Schematic drawings showing the arrangement of numbered streambed measurement points at each of the four stream sampling sites for the work done in summer 2018 (not to scale). Blue arrows indicate the direction of stream flow, and “Point E Dr” is the name of the road that crosses Kirks Mill Creek at that study site.

Parts of Mines Creek and Georgia Branch were later chosen for additional intensive sampling (item 2 in the list above), in part because initial groundwater samples from these stream sites yielded the highest concentrations of PFAS, including GenX. At Georgia Branch, on 22 October 2018, groundwater samples and groundwater flux measurements were taken at 22 streambed points along a 610-meter stream reach (Fig. 12). At each end of the Georgia Branch study reach, on 23 October 2018, stream discharge was also measured, and a stream water sample was collected for PFAS analysis. At Mines Creek, on 23 October 2018, groundwater samples and water flux measurements were taken at 8 points along a 320-meter reach, and stream discharge was measured and stream water samples were collected at each end of the reach (Fig. 12). Stream discharge data in combination with PFAS concentrations in the stream water yielded (1) the discharge of PFAS down the stream channel with stream flow (in other words, the stream export of PFAS from the watershed upstream of the sampling point), (2) reach-scale estimates of the PFAS flux from groundwater to each stream by difference (PFAS export at the downstream end of the reach minus PFAS export at the upstream end of the reach) for comparison with PFAS flux results from the streambed point sampling. On Mines Creek, streambed sampling points were at 40-meter intervals, save for one area where the interval was 80 meters. Point MC280 could not be sampled due to the hard clay streambed there. On Georgia Branch, points were at 20-meter intervals upstream of the Mines Creek confluence and at 40-meter intervals downstream of the confluence.

To provide a snapshot of stream PFAS export from tributary watersheds into the Cape Fear River near Chemours, chemical dilution stream gaging was done and stream water PFAS measurements were taken at five stream sites within 5 km of the Chemours plant (item 3 in the list above). On 14 February 2019, discharge measurements and stream water samples were taken

at three different tributaries located east of the Cape Fear River (Fig. 13). These streams do not have formal geographic names but will be referred to as E-CF2, E-CF3, and E-CF4, where E-CF2 is the southernmost stream sampled, E-CF3 is north of E-CF2, and E-CF4 is north of E-CF3. E-CF1 was actually the southernmost stream east of the Cape Fear River, but it was extremely narrow and shallow, so discharge could not be measured with the methods used. Willis Creek and Georgia Branch were sampled in the same way on 15 February 2019 (Fig. 13). At each stream, discharge was measured at one location and a stream water sample was collected from the same location. Together, these data were used to calculate the export of PFAS for each stream watershed and the contribution of stream export of PFAS to contamination in the Cape Fear River.

## **5. Methods**

### **5.1. Overview**

Field sampling for this research followed methods previously applied to measure the flux of nitrate and volatile organic compounds (VOCs) through streambeds [Gilmore et al. 2016; Babuin et al. 2015; Kennedy et al. 2009]. Piezomanometers and field permeameters were used to measure vertical hydraulic head gradient and hydraulic conductivity in streambeds, respectively [Genereux et al. 2008; Kennedy et al. 2007]. A steel and copper piezometer [Kennedy et al. 2009] was used to collect groundwater samples for analysis of PFAS concentrations. Additionally, streamflow was measured using salt tracer injections, following methods published by the U.S. Geological Survey (USGS) [Radtke et al. 2005; Rantz 1982]. Stream discharge data, together with measured PFAS concentrations in stream water, were used to (1) compute stream export of PFAS from watersheds (i.e., the PFAS discharge to the Cape Fear River due to stream flow in the tributary streams) and (2) the reach-scale groundwater input of PFAS to the 610-meter reach of Georgia Branch and 320-meter reach of Mines Creek mentioned in Section 4.

### **5.2. Groundwater Sampling**

At all groundwater sampling points, the steel and copper piezometer used to collect the sample was inserted so that the top of the 5 cm screen lay about 30 cm below the streambed. In another intensively studied sandy coastal plain stream, this depth was sufficient to ensure that the water collected was groundwater below the streambed and not stream water circulating in the hyporheic zone [Kennedy et al. 2007]. A total insertion depth of 35 cm (to include the length of the piezometer screen) was also used for the insertion depth of the permeameter and PVC piezomanometer to ensure that hydraulic conductivity and groundwater head measurements were taken at the same depth at which groundwater samples were collected.

### 5.3. PFAS Sampling & Laboratory Analysis

All water samples (groundwater and surface water) for analysis of PFAS concentrations were collected based on the water sampling methods (modified Method 537.1) developed by the USEPA National Exposure Research Laboratory [USEPA 2009]. The containers used to collect all water samples were 500 mL high-density polyethylene (HDPE) bottles. Each bottle was rinsed with 5 to 10 mL of methanol in the lab and then left to dry prior to sample collection. During sample collection, each bottle used for groundwater sampling was rinsed three times with 20 mL of the groundwater at that sampling point before the bottle was filled. Bottles used for stream water sampling were rinsed three times with a small volume of the stream water at the sampling point before the bottle was filled. Surface water samples were collected by dipping the bottle below the stream surface while standing on the bank or directly downstream of the sampling point so as not to interfere with sample collection. All water samples were stored in coolers – not on ice – during transport to and from the lab. After water samples were collected, labeled, and transported to the lab, they were preserved by adding 2.5 mL of 35% nitric acid to the sample using a 5 mL polypropylene pipette. Samples were stored in the lab at room temperature before being analyzed for PFAS concentrations.

A tandem liquid chromatography mass spectrometry (LCMS) system was used to detect the presence of various PFAS and measure their respective concentrations. All water sample analysis was conducted in the lab of Dr. Detlef Knappe in the Department of Civil, Construction, and Environmental Engineering at NC State University. Targeted LCMS analysis of all water samples followed a large volume direct injection approach [Sun et al. 2016; USEPA 2016d]. PFAS concentrations were determined using an isotope dilution approach [Sun et al. 2016; USEPA 2016d] for PFAS for which mass-labeled internal standards were available. For those

PFAS for which standards were not available, concentrations were determined from the analyte peak area relative to a mass-labeled internal standard with similar retention time and structure.

The 22 PFAS tested for in groundwater samples collected during the summer 2018 sampling campaign were: perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonic acid (PFOS), 6:2 fluorotelomer sulfonic acid (6:2 FTS), 1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoroethoxy)ethane sulfonate (NVHOS), perfluoropentadecanoate (PEPA), difluoro(perfluoromethoxy)acetic acid (PFMOAA), perfluoro-3,5-dioxahexanoic acid (PFO2HxA), perfluoro-3,5,7-trioxaoctanoic acid (PFO3OA), perfluoro-3,5,7,9-tetraoxadecanoic acid (PFO4DA), perfluoro-3,5,7,9,11-pentaoxadodecanoic acid (PFO5DoA), perfluoromethoxypropyl carboxylic acid (PMPA), GenX, and Nafion Byproducts 1 and 2 which are produced as a result of the Nafion production process, a registered tradename for a perfluoroether sulfonic acid.

Analysis of water samples collected in October 2018 included the same 22 compounds listed above in addition to two more PFAS: Nafion Byproduct 4 and perfluoroethoxypropanoic acid, or HydroEve, another registered compound. Water samples collected in February 2019 were analyzed for all of the same compounds as the October 2018 samples as well as five others, for a total of 29 different PFAS. These five other compounds were: perfluoropentanesulfonic acid (PFPeS), perfluoroheptanesulfonic acid (PFHpS), 4:2 fluorotelomer sulfonic acid (4:2 FTS), 9-chlorohexadecafluoro-3-oxanone-1-sulfonate (F53B), and dodecafluoro-3H-4,8-dioxanoate, also referred to as ADONA.

#### 5.4. Vertical Water & PFAS Fluxes Through Streambeds

Vertical flux calculations for water and PFAS through streambeds involved first calculating the discharge rate of groundwater at the streambed interface and then multiplying this rate by the groundwater PFAS concentration measured at that same point. The methods used were exactly those used by Kennedy et al. [2009] and Gilmore et al. [2016] to quantify nitrate flux from groundwater to streams. Using Darcy's Equation,  $v=KJ$ , specific discharge of water through the streambed,  $v$ , was calculated from hydraulic head gradient,  $J$ , and hydraulic conductivity,  $K$ , at each streambed measurement point. The PVC piezomanometer was used to measure vertical  $J$  at each sampling point. This raw measurement was then corrected for the amplification factor (AF) based on the temperature-density relationships for both the oil and water [Kennedy et al. 2007].  $K$  of the streambed sediment was estimated at each streambed measurement point by conducting an in situ falling head test using a field permeameter; data analysis was based on Hvorslev's method, as used and described by Genereux et al. [2008].

After calculating specific discharge, or water flux, at a given sampling point, the flux of PFAS from groundwater into the stream was calculated by multiplying the specific discharge by the concentration of PFAS in the groundwater sample at the same point [Gilmore et al. 2016; Kennedy et al. 2009]:

$$f_{PFAS} = [PFAS]v \quad \text{Equation 1}$$

where  $f_{PFAS}$  is the flux of a particular PFAS compound from groundwater into the stream in units of  $\text{mg m}^{-2} \text{d}^{-1}$  (mg of PFAS per  $\text{m}^2$  of streambed per day),  $[PFAS]$  is the concentration of a particular PFAS detected in the groundwater sample, and  $v$  is specific discharge in  $\text{cm d}^{-1}$ . Total PFAS flux through the streambed was calculated using the sum of all detected compounds in the groundwater sample collected at a particular measurement point.

For each stream in which streambed point measurements of  $f_{PFAS}$  were made, the point values were averaged and then multiplied by the streambed area in order to estimate the mass of PFAS discharging from groundwater to the stream, or  $D_{PFAS}$ :

$$D_{PFAS} \text{ (g d}^{-1}\text{)} = f_{PFAS} \times \text{streambed area} \quad \text{Equation 2}$$

Streambed area was estimated by multiplying the total length of the reach by the average width of the channel in that reach (for the October 2018 sampling). The length between points within the reach was measured using a measuring tape laid from point to point along the channel, following the bends of the stream. The distances from point to point were added to give the total reach length. Width was estimated by averaging the width measurements of the stream channel taken at each sampling point (see Appendix D).

The streambed area for the entire length of the stream was also used to extrapolate the mean PFAS flux from point measurements for each stream sampled in summer 2018 and October 2018. Total streambed area for these streams was estimated by measuring the total feature lengths in the streams vector layer in ArcMap. For the total stream lengths, tributaries were included in the feature lengths for Willis Creek, Kirks Mill Creek, and Mines Creek but were not included in the estimate for the total length of Georgia Branch, in order to calculate a "whole-stream" value for PFAS discharge from groundwater that included only Georgia Branch (and not its tributary Mines Creek). For the length of the main stream channel of Georgia Branch, the total stream length upstream of point GB610 (the downstream-most sampling point) was used – this allowed for the comparison between  $D_{PFAS}$  and PFAS stream export values measured at GB610.

This gave estimates of the total amount of PFAS discharging from underlying groundwater to the entire length of each stream. Thus,  $D_{PFAS}$  values were generated for (1) the 620 m reach of Georgia Branch and 320 m reach of Mines Creek spanned by streambed point measurements in October 2018, (2) the full lengths of Georgia Branch and Mines Creek for October 2018, and (3) the full lengths of Georgia Branch, Mines Creek, and Kirks Mill Creek (June 2018 data) and Willis Creek (August 2018 data). Here, the phrase "full length" refers to the total stream length in the streams vector layer in ArcMap upstream of the following points of stream discharge measurement (Section 5.5): (1) the 620 m point in Georgia Branch, June 2018, October 2018, and February 2019, (2) the downstream end of Mines Creek (its confluence with Georgia Branch), June 2018 and October 2018, (3) the downstream end of Kirks Mill Creek (its confluence with Willis Creek), June 2018, and (4) the downstream end of Willis Creek (its confluence with the Cape Fear River), August 2018 and February 2019.

### **5.5. Stream Discharge**

Stream discharge was measured using the tracer injection method [Rantz 1982] at the same time that intensive groundwater sampling occurred in Georgia Branch and Mines Creek in October 2018. Stream discharge was also measured at Georgia Branch, Willis Creek, and three tributaries east of the Cape Fear River in February 2019.

Stream discharge was determined by:

1. Releasing a known amount of NaCl into the stream as a "slug" (sudden injection of salty water).
2. Measuring conductivity and temperature at measurement sites in the stream channel downstream of the injection.
3. Correcting the raw conductivity data for temperature.

4. Converting the conductivity values to NaCl concentration, [NaCl].
5. Determining the area under the NaCl breakthrough curve ([NaCl] vs. time).
6. Calculating stream discharge as the mass of NaCl released divided by the area under the NaCl breakthrough curve.

The tracer used for all injections was sodium chloride (NaCl). For each injection, a mass of 500 to 1000 grams of salt was used and was measured beforehand with an Ainsworth M-310 scale (accurate to 0.001g). The known mass was then mixed with 5.5 to 9.5 liters of stream water in a large plastic bucket at the injection site. Prior to pouring the salt solution into the stream, a HOBO conductivity logger (Model U24-001, HOBOWare 3.7.15, <https://www.onsetcomp.com>) was programmed to collect conductivity and temperature data every 10 seconds and placed at each measurement station downstream of the injection site (Table 2). At each station, the conductivity logger was deployed in the center of the channel by attaching it to a wooden stake inserted into the sandy streambed. To obtain background stream water conductivity, data logging was initiated at each station 30 minutes to one hour before the salt solution was poured quickly (within one to two seconds) into the stream at the injection site.

**Table 2.** List of stream sites used in the work on chemical dilution stream gaging along with the date discharge measurements were taken, the mass of salt released into the stream at the injection site, and distance from the tracer injection site to each measurement station (measured along the stream channel). The Georgia Branch (GB) and Mines Creek (MC) sampling sites are shown in Figure 11. The sampling sites at Georgia Branch (GB), Willis Creek (WC), and the E-CF2, 3, and 4 tributaries to the east of the Cape Fear River are shown in Figure 13.

<b>Measurement Station ID</b>	<b>Date</b>	<b>Mass of NaCl (g)</b>	<b>Distance from Injection Site (m)</b>
<b>GB – station 1</b>	10/23/2018	1000.0072	35
<b>GB – station 2</b>			645
<b>MC – station 1</b>	10/23/2018	751.0788	30
<b>MC – station 2</b>			350
<b>E-CF2</b>	2/14/2019	500.8769	50
<b>E-CF3</b>	2/14/2019	500.4372	40
<b>E-CF4</b>	2/14/2019	499.9581	45
<b>GB</b>	2/15/2019	500.8655	45
<b>WC</b>	2/15/2019	500.0141	40

A temperature correction was applied to the raw conductivity data to estimate the conductivity at 25°C ( $S_{25}$ ) [Radtke 2005]:

$$S_{25} = \frac{S}{1+0.019(T-25)} \quad \text{Equation 3}$$

where  $T$  is the temperature of the stream water in degrees Celsius,  $S$  is the raw conductivity measured by the logger, and  $S_{25}$  is the temperature-corrected conductivity of the stream water in  $\mu\text{S cm}^{-1}$ .

Temperature-corrected conductivity was then converted to [NaCl] using an empirical linear regression determined in the lab (see Appendix C). Calibration tests were done using stream water collected at the site with varying concentrations of added salt. The relationship was defined as:

$$[\text{NaCl}] = (S_{25} - S_{25}^{\circ}) \cdot \text{slope} \quad \text{Equation 4}$$

where  $S_{25}^{\circ}$  represents the background conductivity (at 25°C) of the stream water collected in the field and taken back to the lab, [NaCl] is the salt concentration in  $\text{kg L}^{-1}$ , and "slope" represents the slope of a best-fit line from linear regression.

Stream discharge was then calculated by plotting [NaCl] versus time, integrating the area under the breakthrough curve, and dividing the tracer mass by this area:

$$Q (\text{m}^3 \text{ s}^{-1}) = \text{mass NaCl (kg)} / \text{area under curve (kg s m}^{-3}) \quad \text{Equation 5}$$

## 5.6. Stream Export of PFAS

Stream discharge measurements collected from Georgia Branch and Mines Creek in October 2018 were used to calculate the stream export of PFAS from the contributing watersheds upstream of the stream measurement stations – this was also done with the stream discharge

measurements collected from five tributaries in February 2019 (Fig. 11). Export of PFAS from these streams was calculated as:

$$E_{\text{PFAS}} (\text{g d}^{-1}) = Q[\text{PFAS}] \quad \text{Equation 6}$$

### **5.7. Reach Mass-Balance Approach to Estimating PFAS Discharge from Groundwater to Streams Near Chemours**

Steady-state mass-balance relationships were used to estimate the following variables at the scale of the October 2018 stream reaches (610 m for Georgia Branch and 320 m for Mines Creek): (1) the groundwater discharge to the stream reach, (2) the amount of PFAS discharging to the stream reach from groundwater, and (3) the flow-weighted mean [PFAS] in the groundwater discharging into the stream reach.

By subtracting the volumetric discharge at station 1 from that at station 2, total groundwater discharge ( $Q_{\text{gw}}$ ) over the reach was estimated for Mines Creek, where station 1 is situated upstream from station 2.

$$Q_{\text{gw}} (\text{m}^3 \text{ s}^{-1}) = Q_2 - Q_1 \quad \text{Equation 7a}$$

Groundwater discharge for the Georgia Branch reach was calculated similarly after subtracting the input from Mines Creek, taken as the discharge measured at MC station 2 near the downstream end of Mines Creek ( $Q_{\text{MC2}}$  below), because Mines Creek flows into Georgia Branch between GB stations 1 and 2.

$$Q_{\text{gw}} (\text{m}^3 \text{ s}^{-1}) = Q_2 - Q_1 - Q_{\text{MC2}} \quad \text{Equation 7b}$$

This mass-balance approach was also used to calculate the flow-weighted concentration of PFAS in the groundwater discharging into each stream based on measured concentrations in stream water samples collected at each station. For Mines Creek, this was calculated as

$$Q_{gw}[PFAS]_{gw} \text{ (g d}^{-1}\text{)} = Q_2[PFAS]_2 - Q_1[PFAS]_1 = D_{PFAS,R} \quad \text{Equation 8a}$$

where [PFAS] represents the concentration of a particular PFAS compound in the stream water in ng L<sup>-1</sup>, and  $Q_{gw}[PFAS]_{gw}$  represents the estimated mass discharge of PFAS from groundwater to the stream reach using the mass-balance approach.

For Georgia Branch, the same mass-balance calculation was done by subtracting the PFAS discharge at MC station 2.

$$Q_{gw}[PFAS]_{gw} \text{ (g d}^{-1}\text{)} = Q_2[PFAS]_2 - Q_1[PFAS]_1 - Q_{MC2}[PFAS]_{MC2} = D_{PFAS,R} \quad \text{Equation 8b}$$

$Q_{gw}[PFAS]_{gw}$  was divided by the area of the streambed in the reach and compared to the individual values of  $f_{PFAS}$  measured at each point in the streambed and to the mean  $f_{PFAS}$  of all the streambed measurement points in the study reach.

$$f_{PFAS,R} \text{ (mg m}^{-2} \text{ d}^{-1}\text{)} = \frac{Q_{gw}[PFAS]_{gw}}{\text{Streambed Area}} \quad \text{Equation 9}$$

where  $f_{PFAS,R}$  is the reach-scale estimate of groundwater PFAS flux based on the reach mass-balance approach and the area of the streambed within the study reach.

The steady-state reach mass-balance relationship between the stream discharge and the concentration of PFAS was used to estimate the reach-scale flow-weighted mean (FWM) concentration of PFAS in the groundwater discharging into the stream. For Mines Creek, this was calculated as

$$[PFAS]_{gw,R} \text{ (ng L}^{-1}\text{)} = \frac{Q_2[PFAS]_2 - Q_1[PFAS]_1}{Q_2 - Q_1} \quad \text{Equation 10a}$$

where  $[PFAS]_{gw,R}$  is the estimated FWM concentration of PFAS in the groundwater discharging into the stream reach estimated based on the reach mass-balance approach. For Georgia Branch,  $[PFAS]_{gw,R}$  was calculated as

$$[PFAS]_{gw,R} \text{ (ng L}^{-1}\text{)} = \frac{Q_2[PFAS]_2 - Q_1[PFAS]_1 - Q_{MC2}[PFAS]_{MC2}}{Q_2 - Q_1 - Q_{MC2}} \quad \text{Equation 10b}$$

Each reach-scale FWM estimate of  $[PFAS]_{gw,R}$ , for Mines Creek and Georgia Branch, was compared to the mean and the FWM  $[PFAS]_{gw}$  values measured at streambed sampling points in the same reach, where the FWM groundwater PFAS concentration at the streambed measurement points ( $[PFAS]_{gw,FWM}$ ) involves weighting each individual streambed  $[PFAS]$  value by the specific discharge ( $v$ ) at the same point:

$$[PFAS]_{gw,FWM} \text{ (ng L}^{-1}\text{)} = \frac{\sum f_{PFAS}}{\sum v} \quad \text{Equation 11}$$

where  $\sum f_{PFAS}$  is the sum of all point measurements of PFAS flux in the reach and  $\sum v$  is the sum of all point measurements of specific discharge in the same reach.

## 5.8. PFAS Contribution to the Cape Fear River from Contaminated Groundwater & Streams Near Chemours

PFAS export from the tributary streams ( $E_{PFAS}$ ), and PFAS discharge from groundwater to the streams ( $D_{PFAS}$ ), were used together with discharge data for the Cape Fear River (CFR) to calculate the approximate contribution to river water PFAS concentration due to inputs from the contaminated groundwater and streams near Chemours:

$$[PFAS]_{CFR} \text{ (ng L}^{-1}\text{)} = \frac{\sum E_{PFAS}}{Q_{CFR}} \quad \text{Equation 12}$$

$$[\text{PFAS}]_{\text{CFR}} (\text{ng L}^{-1}) = \frac{\sum D_{\text{PFAS}}}{Q_{\text{CFR}}} \quad \text{Equation 13}$$

where  $[\text{PFAS}]_{\text{CFR}}$  is the estimated contribution to the concentration of PFAS in the Cape Fear River,  $\sum E_{\text{PFAS}}$  is the sum of the PFAS exports from the sampled tributary streams (mass per time),  $\sum D_{\text{PFAS}}$  is the sum of the PFAS discharges from groundwater to streams over the entire streambed area of each stream, and  $Q_{\text{CFR}}$  is the discharge of the Cape Fear River in  $\text{m}^3 \text{s}^{-1}$ .

The sums in equations 12 and 13 were over:

- 4 streams in summer (June and August) 2018: Georgia Branch, Mines Creek, Kirks Mill Creek, and Willis Creek ( $D_{\text{PFAS}}$  only)
- 2 streams in October 2018: Georgia Branch and Mines Creek ( $D_{\text{PFAS}}$  and  $E_{\text{PFAS}}$ )
- 5 streams in February 2019: Georgia Branch, Willis Creek, E-CF2, E-CF3, and E-CF4 ( $E_{\text{PFAS}}$  only).

River discharge values ( $Q_{\text{CFR}}$ ) came from data at the nearest USGS gaging station on the Cape Fear River (William O. Huske Lock and Dam, USGS gaging station 02105500) [USGS 2019].

For Equation 13, the mean  $f_{\text{PFAS}}$  from streambed point measurements in each stream was extrapolated over the entire streambed area of that same stream, with the assumption that fluxes measured in the study reach could be applied to the entire length of the stream.

## 6. Results

### 6.1. PFAS Concentrations

Among the groundwater samples collected beneath four streams in summer 2018, 17 of the 22 compounds included in the targeted LCMS analysis were detected at concentrations above the minimum reporting level (MRL) of 10 ng L<sup>-1</sup> (Table 3); the other five compounds were not detected above the MRL in any of the samples. Of these 17 compounds, eight made up over 98% of all PFAS detected in the June and August 2018 groundwater samples. The eight “major” compounds, with their associated percentages of the total PFAS concentration, were: GenX (28.6%), PMPA (27.9%), PEPA (15.7%), PFO2HxA (13.5%), PFMOAA (6.1%), PFO3OA (3.5%), Nafion Byproduct 2 (1.7%), and PFO4DA (1.1%). The most common compounds detected were PEPA and GenX, which were found in all but one or two samples, respectively. Of the four streams sampled in summer 2018, Georgia Branch had the highest concentrations of all PFAS detected in the groundwater samples taken from below the streambed. The mean total PFAS concentration in groundwater was 2701 ng L<sup>-1</sup> beneath Georgia Branch (n = 6), 1521 ng L<sup>-1</sup> beneath Mines Creek (n = 6), 598 ng L<sup>-1</sup> beneath Kirks Mill Creek (n = 6), and 602 ng L<sup>-1</sup> beneath Willis Creek (n = 6). Means were calculated by averaging the total detected PFAS concentrations among all streambed measurement points for each stream, where concentrations less than MRL were treated as equal to zero.

For the groundwater samples collected beneath Georgia Branch and Mines Creek in October 2018, 11 of the 24 compounds included in the LCMS analysis were detected above the MRL of 10 ng L<sup>-1</sup> in more than one groundwater sample (Tables 4 and 5). Of these 11, six compounds made up over 96% of all detected PFAS. The six “major” compounds for this phase of the study, with their associated percentages, were: PMPA (38.7%), GenX (24.6%), PFO2HxA

(15.9%), PEPA (11.6%), PFMOAA (3.7%), and Nafion Byproduct 4 (2.4%). The mean total PFAS concentration in the groundwater beneath Georgia Branch was 2306 ng L<sup>-1</sup> (n = 22), and the mean for Mines Creek was 1533 ng L<sup>-1</sup> (n = 8). The flow-weighted mean concentration for each compound was lower than the average concentration among the sampling points in Georgia Branch (except for GenX), with percent differences ranging from 1% to 76%. For Mines Creek, the flow-weighted mean concentration for each compound was lower than the average (except for GenX and PFO2HxA), with percent differences ranging from 0.1% to 70%.

For the stream water samples collected in October 2018, 10 of the 24 compounds included for analysis were detected above the MRL of 10 ng L<sup>-1</sup> in at least one sample (Table 6). Of these 10, seven compounds made up over 98% of all detected PFAS. These compounds were: PMPA (36.5%), GenX (26.9%), PFO2HxA (17.6%), PEPA (10.8%), PFMOAA (3.6%), Nafion Byproduct 4 (1.7%), and Nafion Byproduct 2 (1.1%).

For the stream water samples collected from five tributaries to the east and west of the CFR in February 2019, 12 of the 29 compounds included in the targeted LCMS analysis were detected above the MRL of 10 ng L<sup>-1</sup> in at least one sample (Table 7). Of these 12, eight compounds made up over 99% of all detected PFAS. These compounds were: PMPA (44.7%), GenX (21.1%), PFO2HxA (13.3%), PEPA (10.7%), PFMOAA (4.5%), Nafion Byproduct 4 (2.0%), PFO3OA (1.6%), and Nafion Byproduct 2 (1.3%).

**Table 3.** PFAS concentrations for groundwater samples collected beneath the streambeds of Kirks Mill Creek (KM), Willis Creek (WC), Mines Creek (MC), and Georgia Branch (GB) in June and August 2018. All concentrations are in ng L<sup>-1</sup>. The minimum reporting level (MRL) is 10 ng L<sup>-1</sup>. A mean of “na” indicates that a mean could not be calculated due to all samples reading <MRL.

Point ID	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS	6:2 FTS	GenX
GB1	17	14	<MRL	11	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	1116
GB2	20	17	<MRL	17	<MRL	<MRL	<MRL	<MRL	<MRL	143	<MRL	903
GB3	20	19	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	937
GB4	17	20	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	884
GB5	15	19	<MRL	11	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	754
GB6	17	23	15	15	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	888
MC1	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	375
MC2	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	475
MC3	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	299
MC4	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	211
MC5	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	341
MC6	11	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	675
KM1	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	50
KM2	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	70
KM3	<MRL	<MRL	<MRL	<MRL	<MRL	12	29	<MRL	<MRL	17	<MRL	139
KM4	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	10	<MRL	<MRL	<MRL	<MRL	97
KM5	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	22	15	<MRL	11	<MRL	173
KM6	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	182
WC1	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
WC2	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
WC3	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	140
WC4	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	127
WC5	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	216
WC6	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	253

**Table 3 (continued)**

<b>Point ID</b>	<b>PFBA</b>	<b>PFPeA</b>	<b>PFHxA</b>	<b>PFHpA</b>	<b>PFOA</b>	<b>PFNA</b>	<b>PFDA</b>	<b>PFBS</b>	<b>PFHxS</b>	<b>PFOS</b>	<b>6:2 FTS</b>	<b>GenX</b>
<b>GB – Mean</b>	18	19	15	13	na	na	na	na	na	143	na	914
<b>MC – Mean</b>	11	na	na	na	na	na	na	na	na	na	na	396
<b>KM – Mean</b>	na	na	na	na	na	12	21	15	na	14	na	119
<b>WC – Mean</b>	na	na	na	na	na	na	na	na	na	na	na	184

**Table 3 (continued)**

<b>Point ID</b>	<b>Nafion Byp 1</b>	<b>Nafion Byp 2</b>	<b>NVHOS</b>	<b>PEPA</b>	<b>PFMOAA</b>	<b>PFO2HxA</b>	<b>PFO3OA</b>	<b>PFO4DA</b>	<b>PFO5D0A</b>	<b>PMPA</b>	<b>Total</b>
<b>GB1</b>	<MRL	56	12	602	152	342	163	41	<MRL	696	3222
<b>GB2</b>	<MRL	47	10	554	174	309	121	54	<MRL	704	3072
<b>GB3</b>	<MRL	39	11	504	156	343	119	47	<MRL	730	2926
<b>GB4</b>	<MRL	52	11	531	151	353	101	53	<MRL	678	2850
<b>GB5</b>	<MRL	36	<MRL	451	166	366	104	35	<MRL	<MRL	1956
<b>GB6</b>	<MRL	44	11	476	184	377	99	33	<MRL	<MRL	2182
<b>MC1</b>	<MRL	22	<MRL	207	89	250	42	11	<MRL	802	1798
<b>MC2</b>	<MRL	38	<MRL	233	77	255	54	19	<MRL	646	1797
<b>MC3</b>	<MRL	29	11	146	67	112	25	<MRL	<MRL	427	1115
<b>MC4</b>	<MRL	17	<MRL	118	34	150	20	11	<MRL	485	1047
<b>MC5</b>	<MRL	39	11	171	69	173	54	12	<MRL	493	1363
<b>MC6</b>	<MRL	58	<MRL	291	100	237	87	31	<MRL	516	2005
<b>KM1</b>	<MRL	<MRL	<MRL	33	33	68	<MRL	<MRL	<MRL	212	396
<b>KM2</b>	<MRL	10	11	36	19	41	<MRL	<MRL	<MRL	188	374
<b>KM3</b>	<MRL	11	<MRL	42	37	70	13	<MRL	<MRL	195	564
<b>KM4</b>	<MRL	<MRL	<MRL	54	57	96	13	<MRL	<MRL	235	563
<b>KM5</b>	<MRL	13	<MRL	102	70	146	20	<MRL	<MRL	299	870
<b>KM6</b>	<MRL	<MRL	<MRL	95	73	138	20	<MRL	<MRL	317	823
<b>WC1</b>	<MRL	<MRL	<MRL	13	<MRL	<MRL	<MRL	<MRL	<MRL	90	102
<b>WC2</b>	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	20	20.3
<b>WC3</b>	<MRL	<MRL	<MRL	83	52	102	13	<MRL	<MRL	275	664
<b>WC4</b>	<MRL	<MRL	<MRL	70	42	86	<MRL	<MRL	<MRL	263	589
<b>WC5</b>	<MRL	14	<MRL	129	95	158	25	<MRL	<MRL	388	1025
<b>WC6</b>	<MRL	14	<MRL	155	103	217	34	10	<MRL	428	1213

**Table 3 (continued)**

<b>Point ID</b>	<b>Nafion Byp 1</b>	<b>Nafion Byp 2</b>	<b>NVHOS</b>	<b>PEPA</b>	<b>PFMOAA</b>	<b>PFO2HxA</b>	<b>PFO3OA</b>	<b>PFO4DA</b>	<b>PFO5DoA</b>	<b>PMPA</b>	<b>Total</b>
<b>GB – Mean</b>	na	46	11	520	164	348	118	44	na	702	2701
<b>MC – Mean</b>	na	34	11	194	73	196	47	17	na	562	1521
<b>KM – Mean</b>	na	12	11	60	48	93	16	na	na	241	598
<b>WC – Mean</b>	na	14	na	90	73	141	24	10	na	244	602

**Table 4.** PFAS concentrations for groundwater samples collected beneath the streambed of Georgia Branch on 22 October 2018. All concentrations are in ng L<sup>-1</sup>. The minimum reporting level (MRL) is 10 ng L<sup>-1</sup>. A mean of “na” indicates that a mean could not be calculated due to all samples reading <MRL. “Mean<sub>FW</sub>” refers to the flow-weighted mean PFAS concentration.

Point ID	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS	6:2FTS	NVHOS
GB20	20	16	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB50	15	10	<MRL	<MRL	<MRL	<MRL	11	<MRL	<MRL	<MRL	<MRL	<MRL
GB70	17	12	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB90	11	<MRL	<MRL	<MRL	<MRL	<MRL	11	<MRL	<MRL	<MRL	<MRL	<MRL
GB110	12	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB130	18	15	<MRL	<MRL	<MRL	<MRL	10	<MRL	<MRL	<MRL	<MRL	<MRL
GB150	36	24	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB170	19	18	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB190	16	17	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB210	23	19	<MRL	<MRL	<MRL	<MRL	11	<MRL	<MRL	<MRL	<MRL	<MRL
GB230	17	13	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB250	19	16	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB270	12	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB290	22	16	<MRL	<MRL	<MRL	<MRL	12	<MRL	<MRL	<MRL	<MRL	<MRL
GB330	23	19	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB370	17	12	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB410	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB450	14	10	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB490	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB530	13	10	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB570	17	12	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
GB610	17	13	<MRL	<MRL	<MRL	<MRL	13	<MRL	<MRL	<MRL	<MRL	<MRL
Mean	18	15	na	na	na	na	11	na	na	na	na	na
Mean <sub>FW</sub>	15	10	na	na	na	na	1	na	na	na	na	na

Table 4 (continued)

Point ID	Nafion Byp 1	Nafion Byp 2	Nafion Byp 4	PFMOAA	PMPA	PEPA	GenX	PFO2HxA	PFO3OA	PFO4DA	PFO5DoA	Hydro Eve	Total
GB20	<MRL	25	55	96	1138	357	945	563	<MRL	<MRL	<MRL	<MRL	3216
GB50	<MRL	<MRL	23	62	678	220	330	183	<MRL	<MRL	<MRL	<MRL	1532
GB70	<MRL	36	61	132	694	219	504	361	56	<MRL	<MRL	<MRL	2091
GB90	<MRL	26	30	<MRL	507	138	203	89	<MRL	<MRL	<MRL	<MRL	1014
GB110	<MRL	14	30	<MRL	684	170	273	105	<MRL	<MRL	<MRL	<MRL	1287
GB130	<MRL	25	51	140	1300	419	888	555	<MRL	<MRL	<MRL	<MRL	3421
GB150	<MRL	22	239	272	1069	339	726	711	58	<MRL	<MRL	<MRL	3494
GB170	<MRL	27	52	168	1168	431	976	620	78	<MRL	<MRL	<MRL	3559
GB190	<MRL	24	52	119	1049	353	919	537	<MRL	<MRL	<MRL	<MRL	3084
GB210	<MRL	25	80	101	1113	312	795	596	<MRL	<MRL	<MRL	<MRL	3074
GB230	<MRL	20	67	69	942	255	527	345	<MRL	<MRL	<MRL	<MRL	2254
GB250	<MRL	25	54	185	1204	422	1098	642	101	<MRL	<MRL	<MRL	3766
GB270	<MRL	13	24	77	597	184	416	277	<MRL	<MRL	<MRL	<MRL	1599
GB290	<MRL	27	68	189	1231	442	1062	667	84	<MRL	<MRL	<MRL	3818
GB330	<MRL	21	135	120	1046	337	590	542	82	<MRL	<MRL	<MRL	2915
GB370	<MRL	17	42	<MRL	816	219	520	316	<MRL	<MRL	<MRL	<MRL	1958
GB410	<MRL	<MRL	<MRL	11	149	26	70	25	<MRL	<MRL	<MRL	<MRL	287
GB450	<MRL	16	34	<MRL	621	139	350	183	<MRL	<MRL	<MRL	<MRL	1367
GB490	<MRL	<MRL	12	19	347	77	110	37	<MRL	<MRL	<MRL	<MRL	603
GB530	<MRL	19	53	82	750	221	412	281	<MRL	<MRL	<MRL	<MRL	1840
GB570	<MRL	27	44	57	868	253	607	388	<MRL	<MRL	<MRL	<MRL	2273
GB610	<MRL	22	43	66	866	246	592	397	<MRL	<MRL	<MRL	<MRL	2274
Mean	na	23	57	109	856	263	587	383	76	na	na	na	2306
Mean <sub>FW</sub>	na	19	44	69	792	236	548	334	17	na	na	na	2085

**Table 5.** PFAS concentrations for groundwater samples collected beneath the streambed of Mines Creek on 23 October 2018. All concentrations are in ng L<sup>-1</sup>. The minimum reporting level (MRL) is 10 ng L<sup>-1</sup>. A mean of “na” indicates that a mean could not be calculated due to all samples reading <MRL. “Mean<sub>FW</sub>” refers to the flow-weighted mean PFAS concentration.

<b>Point ID</b>	<b>PFBA</b>	<b>PFPeA</b>	<b>PFHxA</b>	<b>PFHpA</b>	<b>PFOA</b>	<b>PFNA</b>	<b>PFDA</b>	<b>PFBS</b>	<b>PFHxS</b>	<b>PFOS</b>	<b>6:2FTS</b>	<b>NVHOS</b>
<b>MC0</b>	16	12	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>MC40</b>	14	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>MC80</b>	16	14	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>MC120</b>	12	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>MC160</b>	11	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>MC200</b>	15	13	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>MC240</b>	16	16	<MRL	<MRL	<MRL	<MRL	11	<MRL	<MRL	<MRL	<MRL	<MRL
<b>MC320</b>	16	14	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>Mean</b>	15	14	na	na	na	na	11	na	na	na	na	na
<b>Mean<sub>FW</sub></b>	14	9	na	na	na	na	1	na	na	na	na	na

**Table 5 (continued)**

<b>Point ID</b>	<b>Nafion Byp 1</b>	<b>Nafion Byp 2</b>	<b>Nafion Byp 4</b>	<b>PFMOAA</b>	<b>PMPA</b>	<b>PEPA</b>	<b>GenX</b>	<b>PFO2HxA</b>	<b>PFO3OA</b>	<b>PFO4DA</b>	<b>PFO5DoA</b>	<b>Hydro Eve</b>	<b>Total</b>
<b>MC0</b>	<MRL	17	44	67	653	218	417	285	<MRL	<MRL	<MRL	<MRL	1729
<b>MC40</b>	<MRL	<MRL	35	<MRL	564	147	222	111	<MRL	<MRL	<MRL	<MRL	1093
<b>MC80</b>	<MRL	20	31	91	703	205	487	333	<MRL	<MRL	<MRL	<MRL	1900
<b>MC120</b>	<MRL	<MRL	21	<MRL	436	97	267	54	61	<MRL	<MRL	<MRL	948
<b>MC160</b>	<MRL	14	21	<MRL	561	123	205	53	<MRL	<MRL	<MRL	<MRL	988
<b>MC200</b>	<MRL	11	43	<MRL	679	179	303	174	<MRL	<MRL	<MRL	<MRL	1417
<b>MC240</b>	<MRL	<MRL	40	110	868	280	347	316	<MRL	<MRL	<MRL	<MRL	2003
<b>MC320</b>	<MRL	<MRL	31	63	1117	309	341	234	64	<MRL	<MRL	<MRL	2188
<b>Mean</b>	na	16	33	83	697	195	324	195	63	na	na	na	1533
<b>Mean<sub>FW</sub></b>	na	10	33	43	697	193	340	200	19	na	na	na	1559

**Table 6.** PFAS concentrations for stream water samples collected at each end of the study reaches in Mines Creek and Georgia Branch on 23 October 2018. All concentrations are in ng L<sup>-1</sup>. The minimum reporting level (MRL) is 10 ng L<sup>-1</sup>. A mean of “na” indicates that a mean could not be calculated due to all samples reading <MRL.

Site ID	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS	6:2FTS	NVHOS
<b>GB – station 1</b>	20	18	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>GB – station 2</b>	18	14	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>MC – station 1</b>	16	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>MC – station 2</b>	17	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>Mean</b>	18	16	na	na	na	na	na	na	na	na	na	na

**Table 6 (continued)**

<b>Site ID</b>	<b>Nafion Byp 1</b>	<b>Nafion Byp 2</b>	<b>Nafion Byp 4</b>	<b>PFMOAA</b>	<b>PMPA</b>	<b>PEPA</b>	<b>GenX</b>	<b>PFO2HxA</b>	<b>PFO3OA</b>	<b>PFO4DA</b>	<b>PFO5DoA</b>	<b>Hydro Eve</b>	<b>Total</b>
<b>GB – station 1</b>	<MRL	30	58	164	1190	395	1011	620	69	<MRL	<MRL	<MRL	3574
<b>GB – station 2</b>	<MRL	22	41	108	870	285	662	455	<MRL	<MRL	<MRL	<MRL	2473
<b>MC – station 1</b>	<MRL	31	32	71	790	192	462	351	<MRL	<MRL	<MRL	<MRL	1945
<b>MC – station 2</b>	<MRL	21	33	<MRL	627	152	429	247	<MRL	<MRL	<MRL	<MRL	1526
<b>Mean</b>	na	26	41	114	869	256	641	418	69	na	na	na	2379

**Table 7.** PFAS concentrations for stream water samples collected from E-CF2, E-CF3, E-CF4, Willis Creek, and Georgia Branch on 14 and 15 February 2019. All concentrations are in ng L<sup>-1</sup>. The minimum reporting level (MRL) is 10 ng L<sup>-1</sup>. A mean of “na” indicates that a mean could not be calculated due to all samples reading <MRL.

Site ID	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	4:2 FTS	6:2 FTS	NVHOS
<b>E-CF 2</b>	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>E-CF 3</b>	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>E-CF 4</b>	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>GB</b>	15	12	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>WC</b>	10	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
<b>Mean</b>	12	12	na	na	na	na	na	na	na	na	na	na	na	na	na

**Table 7 (continued)**

<b>Site ID</b>	<b>Nafion Byp 1</b>	<b>Nafion Byp 2</b>	<b>Nafion Byp 4</b>	<b>PFMOAA</b>	<b>PMPA</b>	<b>PEPA</b>	<b>GenX</b>	<b>PFO2HxA</b>	<b>PFO3OA</b>	<b>PFO4DA</b>	<b>PFO5DoA</b>	<b>Hydro Eve</b>	<b>Adona</b>	<b>F53B</b>	<b>Total</b>
<b>E-CF 2</b>	<MRL	17	24	44	476	92	130	101	11	<MRL	<MRL	<MRL	<MRL	<MRL	895
<b>E-CF 3</b>	<MRL	26	44	77	677	161	345	218	29	<MRL	<MRL	<MRL	<MRL	<MRL	1577
<b>E-CF 4</b>	<MRL	19	32	60	510	118	238	161	20	<MRL	<MRL	<MRL	<MRL	<MRL	1157
<b>GB</b>	<MRL	22	28	78	936	256	539	295	40	13	<MRL	<MRL	<MRL	<MRL	2233
<b>WC</b>	<MRL	<MRL	<MRL	20	204	41	72	57	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	404
<b>Mean</b>	na	21	32	56	561	134	265	166	25	13	na	na	na	na	1253

## 6.2. Vertical Water Fluxes

Based on the point measurements of vertical water flux through the streambeds of four streams sampled in June and August 2018, it was found that all four streams were gaining in the study reaches – groundwater was flowing up into the stream from the sandy surficial aquifer. Across the four stream sites, vertical water flux ranged from 0.3 cm d<sup>-1</sup> to 480 cm d<sup>-1</sup>, depending on the stream and point location (Fig. 15). The median water flux among all sampling locations was 74.5 cm d<sup>-1</sup> (n = 24). The mean vertical groundwater flux was 138 cm d<sup>-1</sup> at Georgia Branch (n = 6), 90.3 cm d<sup>-1</sup> at Mines Creek (n = 6), 87.1 cm d<sup>-1</sup> at Kirks Mill Creek (n = 6), and 61.9 cm d<sup>-1</sup> at Willis Creek (n = 6) (Table 8).

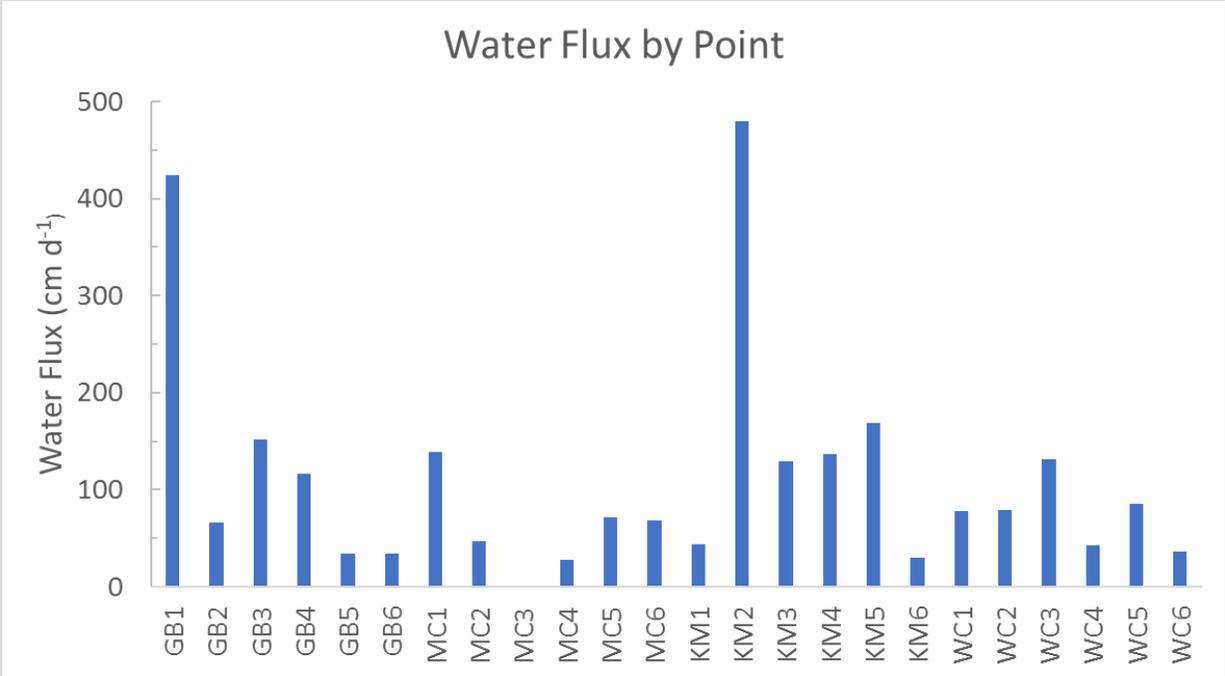
**Table 8.** Vertical water flux ( $v$ ) results for each streambed measurement point in the streams sampled in June and August 2018: Georgia Branch (GB), Mines Creek (MC), Kirks Mill Creek (KM), and Willis Creek (WC). Relative measurement point locations are shown in Figure 13.

<b>Point ID</b>	<b><math>v</math> (cm d<sup>-1</sup>)</b>
<b>GB1</b>	424
<b>GB2</b>	66.0
<b>GB3</b>	152
<b>GB4</b>	117
<b>GB5</b>	34.5
<b>GB6</b>	34.4
<b>MC1</b>	139
<b>MC2</b>	46.7
<b>MC3</b>	0.297
<b>MC4</b>	28.0
<b>MC5</b>	71.3
<b>MC6</b>	67.8
<b>KM1</b>	43.6
<b>KM2</b>	480
<b>KM3</b>	129
<b>KM4</b>	137
<b>KM5</b>	169
<b>KM6</b>	30.0
<b>WC1</b>	77.7
<b>WC2</b>	78.7
<b>WC3</b>	131
<b>WC4</b>	43.0
<b>WC5</b>	85.3
<b>WC6</b>	35.9

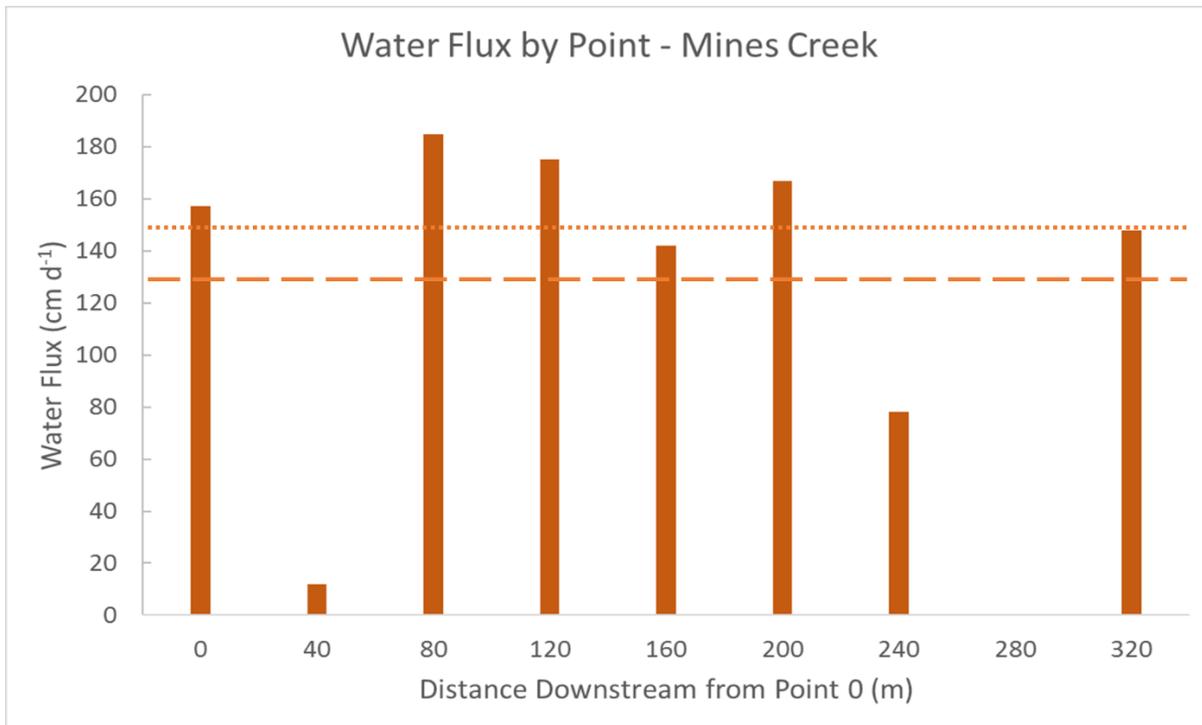
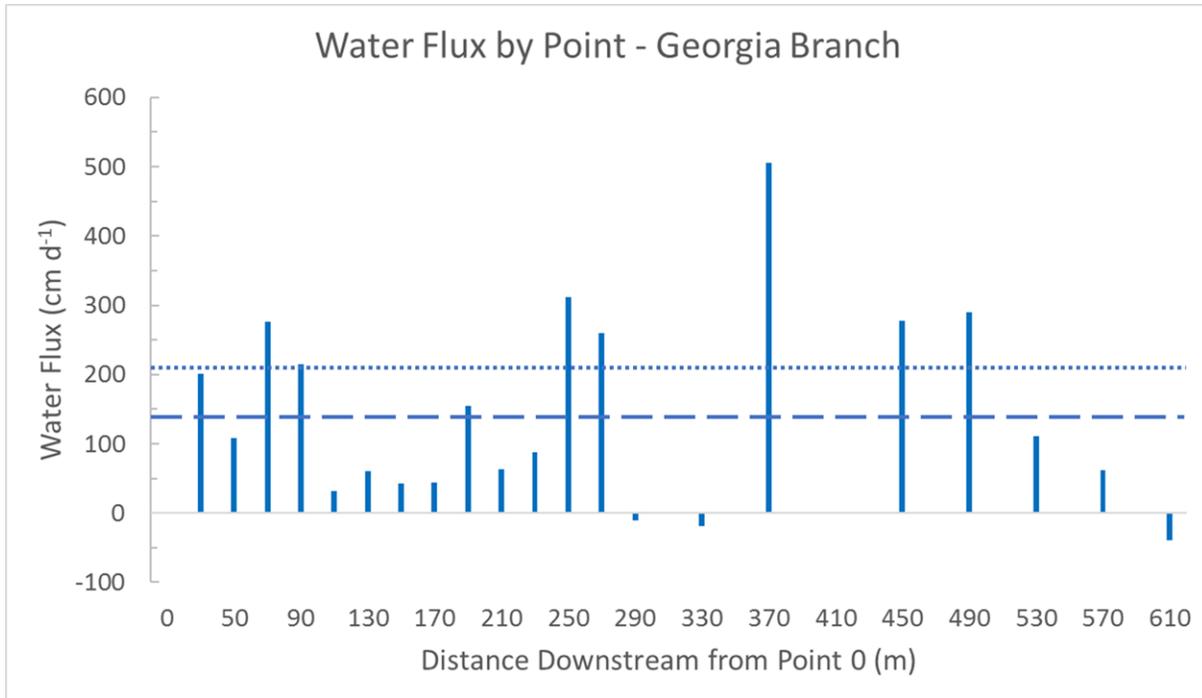
During the October 2018 stream sampling, Mines Creek and Georgia Branch were gaining at most measurement points. Georgia Branch was losing at three measurement points – water was flowing out of the stream and into the surficial aquifer at these points. The mean vertical water flux from the point measurements in Mines Creek was 133 cm d<sup>-1</sup> (n = 8), and in Georgia Branch it was 146 cm d<sup>-1</sup> (n = 21) (Table 9; Fig. 16).

**Table 9.** Vertical water flux ( $v$ ) results for each streambed measurement point in the streams sampled in October 2018: Georgia Branch (GB) and Mines Creek (MC). GB410 has a water flux of “na” because this point measurement was thrown out – the piezomanometer was not left to equilibrate for long enough at this point.

<b>Point ID</b>	<b><math>v</math> (cm d<sup>-1</sup>)</b>	<b>Point ID</b>	<b><math>v</math> (cm d<sup>-1</sup>)</b>
<b>GB20</b>	201	<b>MC0</b>	157
<b>GB50</b>	108	<b>MC40</b>	11.9
<b>GB70</b>	276	<b>MC80</b>	185
<b>GB90</b>	215	<b>MC120</b>	175
<b>GB110</b>	31.8	<b>MC160</b>	142
<b>GB130</b>	60.8	<b>MC200</b>	167
<b>GB150</b>	43.0	<b>MC240</b>	78.2
<b>GB170</b>	44.0	<b>MC320</b>	148
<b>GB190</b>	155		
<b>GB210</b>	63.4		
<b>GB230</b>	88.0		
<b>GB250</b>	312		
<b>GB270</b>	260		
<b>GB290</b>	-11.3		
<b>GB330</b>	-18.7		
<b>GB370</b>	506		
<b>GB410</b>	na		
<b>GB450</b>	278		
<b>GB490</b>	290		
<b>GB530</b>	111		
<b>GB570</b>	61.4		
<b>GB610</b>	-39.4		



**Figure 15.** Vertical water flux for each streambed point in Georgia Branch (GB), Mines Creek (MC), Kirks Mill Creek (KM), and Willis Creek (WC). Flux measurements were calculated from data from the June 2018 (GB, MC, KM) and August 2018 (WC) sampling campaigns.



**Figure 16.** Water flux at each sampling point in Georgia Branch (above) and Mines Creek (below), 22 and 23 October 2018, respectively. Dotted lines represent estimates of groundwater flux through the streambeds based on the reach mass-balance approach (Section 7.3), and dashed lines represent mean water fluxes from the streambed point measurements. Negative values indicate that water is flowing out of the stream and into groundwater. There is no bar for MC280 because it was not possible to insert a piezomanometer at that point (hard clay streambed).

### 6.3. Groundwater PFAS Fluxes

For each of the four tributaries sampled in June and August 2018, the total PFAS flux through the streambed was calculated for each measurement point using the sum of all PFAS detected at that point and the groundwater flux through the streambed at the same point. For this calculation, “MRL” concentration results were considered equal to zero. The mean total PFAS flux from groundwater to each stream, in mg of PFAS per m<sup>2</sup> of streambed per day, was 4.17 at Georgia Branch (n = 6, sd = 4.89), 1.00 at Mines Creek (n = 6, sd = 0.88), 0.87 at Kirks Mill Creek (n = 6, sd = 0.65), and 0.43 at Willis Creek (n = 6, sd = 0.38) (Table 10; Fig. 17).

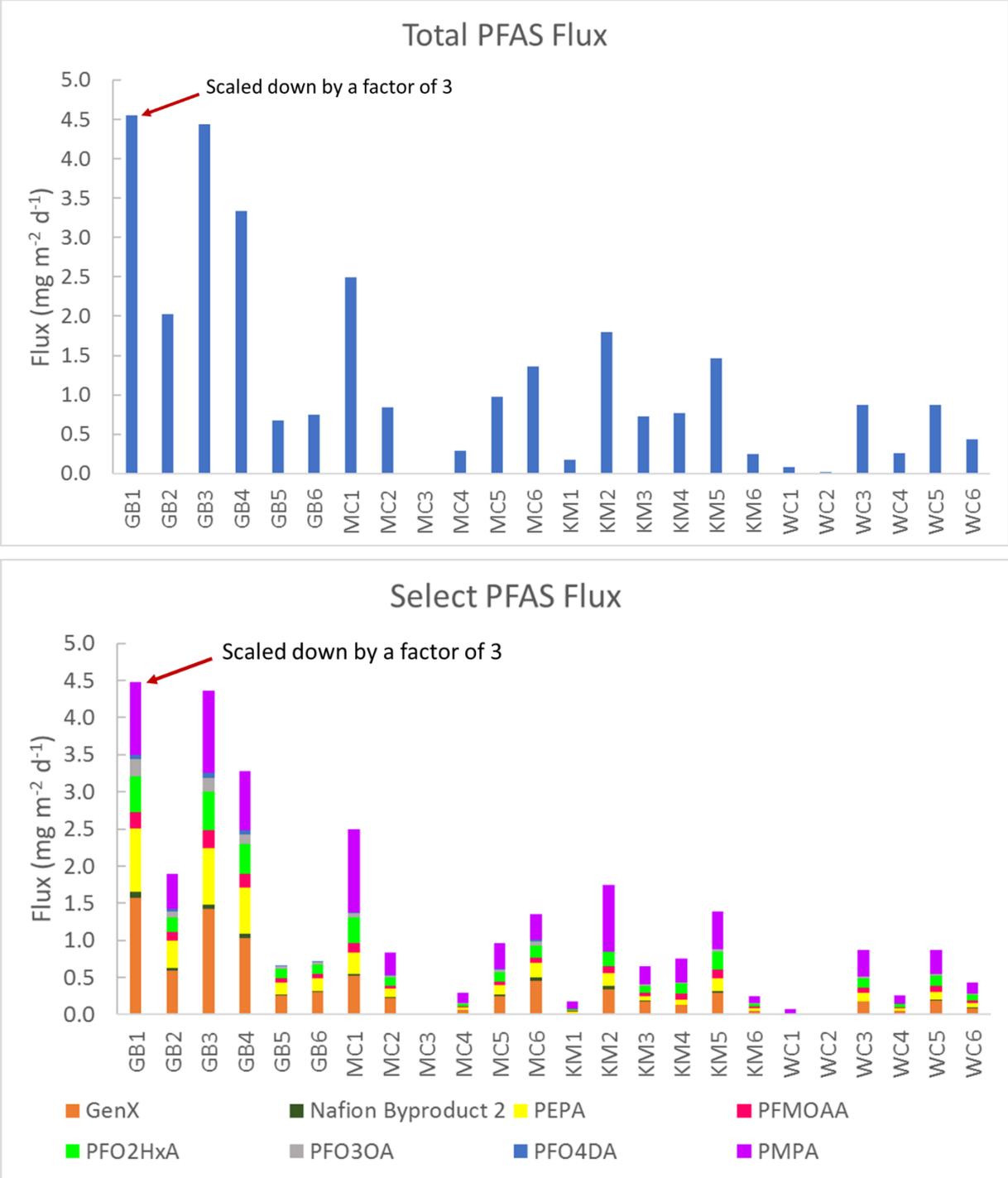
**Table 10.** Total PFAS flux from groundwater to the stream at each streambed measurement point for the streams sampled in summer 2018: Georgia Branch (GB), Mines Creek (MC), Kirks Mill Creek (KM), and Willis Creek (WC). Relative measurement point locations are shown in Figure 14.

<b>Point ID</b>	<b>Total PFAS Flux (mg m<sup>-2</sup> d<sup>-1</sup>)</b>
<b>GB1</b>	13.7
<b>GB2</b>	2.03
<b>GB3</b>	4.44
<b>GB4</b>	3.33
<b>GB5</b>	0.675
<b>GB6</b>	0.750
<b>MC1</b>	2.49
<b>MC2</b>	0.840
<b>MC3</b>	0.003
<b>MC4</b>	0.293
<b>MC5</b>	0.972
<b>MC6</b>	1.36
<b>KM1</b>	0.173
<b>KM2</b>	1.80
<b>KM3</b>	0.730
<b>KM4</b>	0.770
<b>KM5</b>	1.47
<b>KM6</b>	0.247
<b>WC1</b>	0.080
<b>WC2</b>	0.016
<b>WC3</b>	0.872
<b>WC4</b>	0.253
<b>WC5</b>	0.874
<b>WC6</b>	0.436

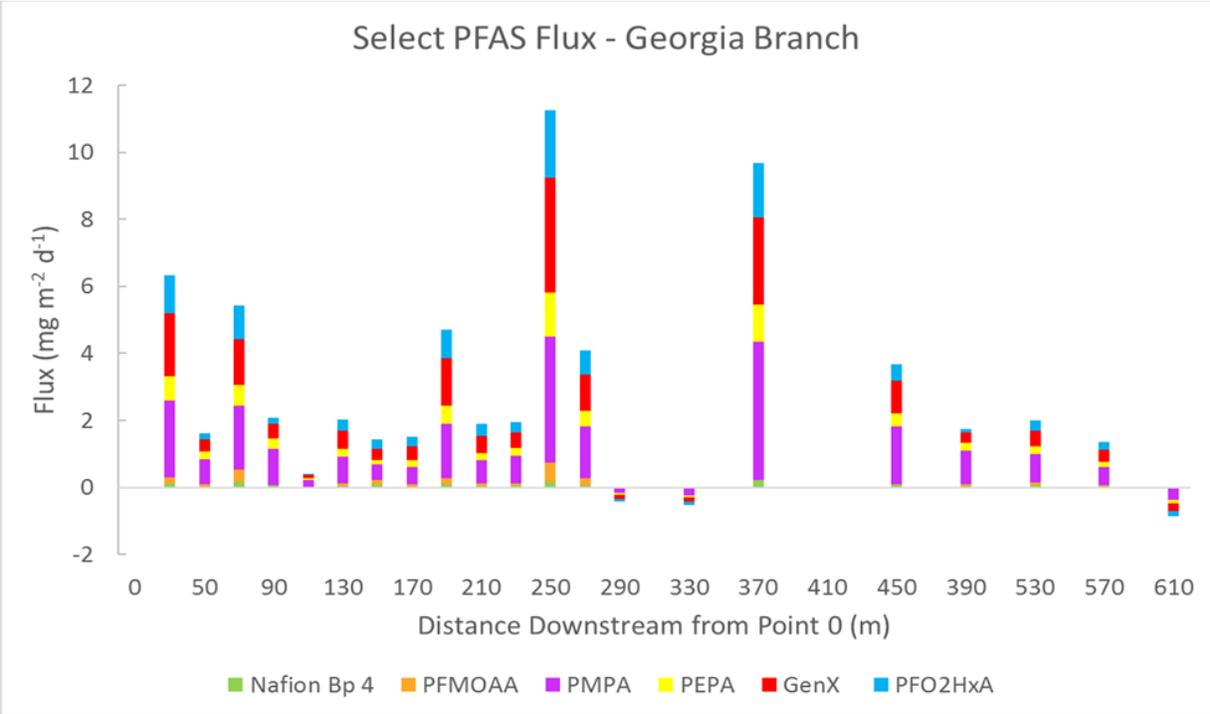
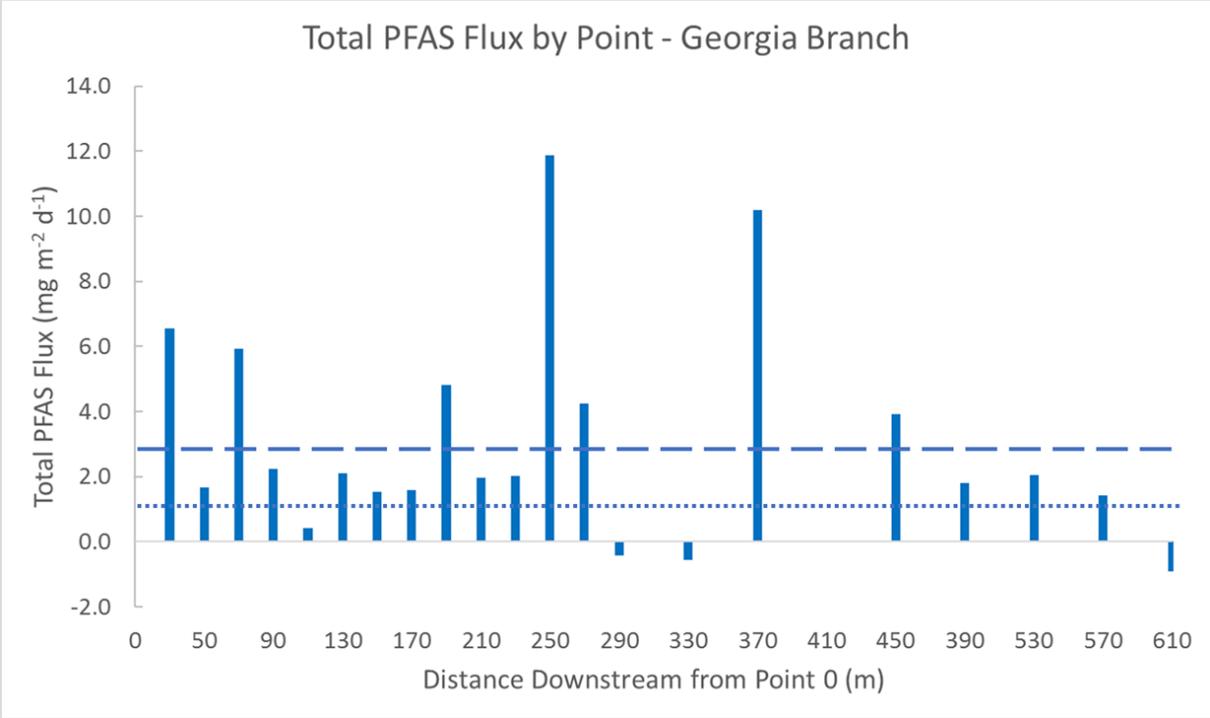
For the streams sampled in October 2018, the mean total PFAS flux from groundwater to the stream, in  $\text{mg m}^{-2} \text{d}^{-1}$ , was 3.01 for Georgia Branch ( $n = 21$ ,  $sd = 3.24$ ) (Table 11; Fig. 18) and 2.12 for Mines Creek ( $n = 8$ ,  $sd = 1.11$ ) (Table 11; Fig. 19). Based on the total PFAS fluxes and vertical groundwater fluxes at the streambed measurement points, the flow-weighted total PFAS concentration in the groundwater beneath Georgia Branch was  $2085 \text{ ng L}^{-1}$  and the flow-weighted total PFAS concentration in the groundwater beneath Mines Creek was  $1559 \text{ ng L}^{-1}$ .

**Table 11.** Total PFAS flux through the streambed at each measurement point in the streams sampled in October 2018: Georgia Branch (GB) and Mines Creek (MC). GB410 has a PFAS flux of “na” because this point measurement was thrown out – the piezomanometer was not left to equilibrate for long enough at this point.

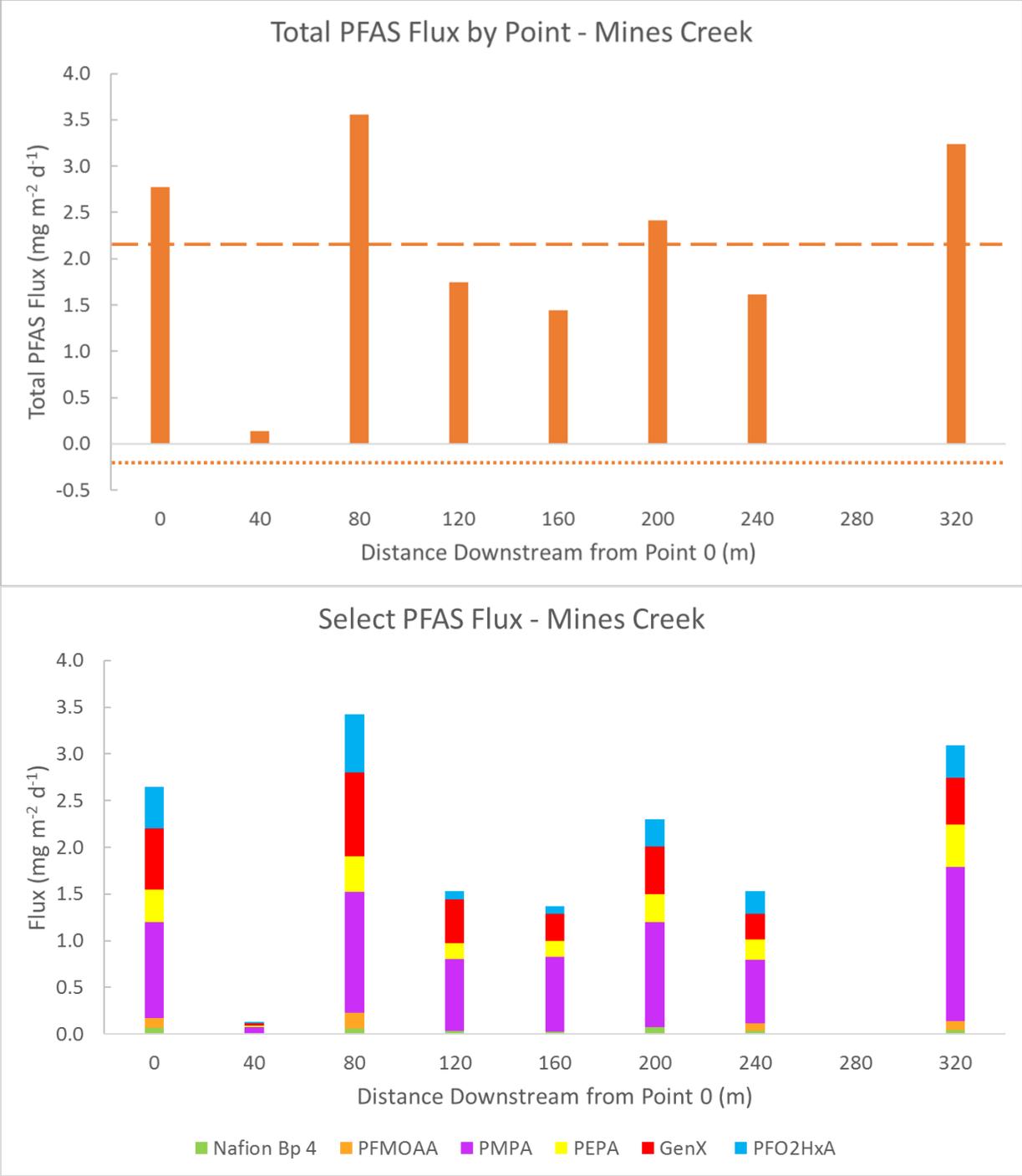
<b>Point ID</b>	<b>Total PFAS Flux (<math>\text{mg m}^{-2} \text{d}^{-1}</math>)</b>	<b>Point ID</b>	<b>Total PFAS Flux (<math>\text{mg m}^{-2} \text{d}^{-1}</math>)</b>
<b>GB20</b>	6.45	<b>MC0</b>	2.72
<b>GB50</b>	1.66	<b>MC40</b>	0.130
<b>GB70</b>	5.76	<b>MC80</b>	3.51
<b>GB90</b>	2.18	<b>MC120</b>	1.66
<b>GB110</b>	0.409	<b>MC160</b>	1.40
<b>GB130</b>	2.08	<b>MC200</b>	2.36
<b>GB150</b>	1.50	<b>MC240</b>	1.57
<b>GB170</b>	1.57	<b>MC320</b>	3.23
<b>GB190</b>	4.78		
<b>GB210</b>	1.95		
<b>GB230</b>	1.98		
<b>GB250</b>	11.8		
<b>GB270</b>	4.15		
<b>GB290</b>	-0.432		
<b>GB330</b>	-0.545		
<b>GB370</b>	9.90		
<b>GB410</b>	na		
<b>GB450</b>	3.80		
<b>GB490</b>	1.75		
<b>GB530</b>	2.05		
<b>GB570</b>	1.40		
<b>GB610</b>	-0.897		



**Figure 17.** Bar graphs showing total PFAS flux from groundwater to each stream, at each sampling point in each stream (above), and the chemical flux at each stream sampling point for the eight most abundant compounds making up 98% of all PFAS detected (below), June and August 2018. The first bar of each graph has been scaled down by a factor of three so that it could be plotted at this scale.



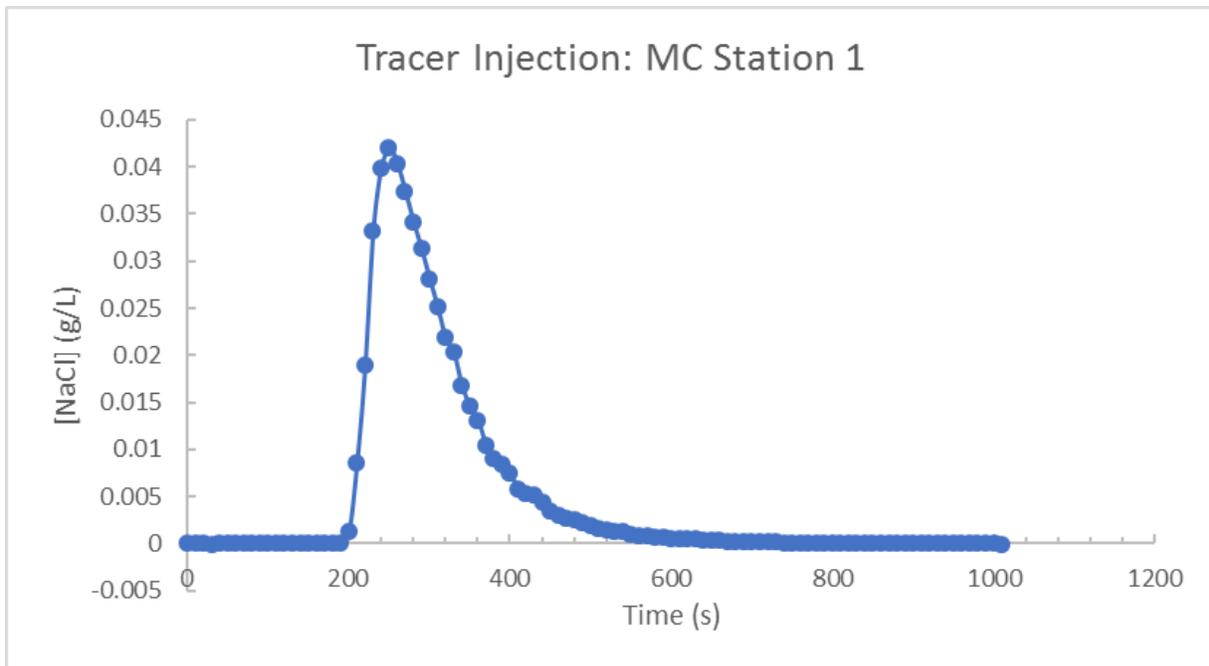
**Figure 18.** Bar graphs showing the total PFAS flux from groundwater to Georgia Branch at each measurement point (above) and the fluxes of the six most abundant PFAS (below), 22 October 2018. The dotted line represents the reach mass-balance estimate of PFAS flux from groundwater, and the dashed line represents mean total PFAS flux from streambed point measurements. Negative values indicate that PFAS-contaminated water is flowing out of the stream.



**Figure 19.** Bar graphs showing the total PFAS flux from groundwater to Mines Creek at each measurement point (above) and the fluxes of the six most abundant PFAS (below), 23 October 2018. The dotted line represents the reach mass-balance estimate of PFAS flux from groundwater to the study reach, and the dashed line represents the mean total PFAS flux from point measurements. There is no bar for MC280 because it was not possible to collect a groundwater sample from that point (hard clay streambed).

## 6.4. Stream Discharge

Stream discharge was measured at each end of each stream reach during the 22 and 23 October 2018 sampling of Mines Creek and Georgia Branch (Table 12) and at one point in each of five different streams on 14 and 15 February 2019 (Table 13). This was done according to the methods described in Section 5. For example, the area under the NaCl breakthrough curve at the upstream end of the Mines Creek study reach on 23 October 2018 (Fig. 20) was found to be  $5.15 \text{ kg s m}^{-3}$ . The mass of NaCl used ( $0.7510788 \text{ kg}$ ) was divided by the area under the curve, resulting in a stream discharge of  $0.146 \text{ m}^3 \text{ s}^{-1}$ .



**Figure 20.** Breakthrough curve for MC – station 1, with [NaCl] in  $\text{kg L}^{-1}$  and time in seconds (s) and a logging interval of 10 s.

**Table 12.** Results of stream discharge measurements for Georgia Branch (GB) and Mines Creek (MC). Measurement locations are shown in Figure 9.

Site ID	Date	Discharge (m <sup>3</sup> s <sup>-1</sup> )
GB – station 1	10/23/2018	0.0776
GB – station 2	10/23/2018	0.274
MC – station 1	10/23/2018	0.146
MC – station 2	10/23/2018	0.167

**Table 13.** Results of stream discharge measurements for E-CF2, E-CF3, E-CF4, Willis Creek (WC), and Georgia Branch (GB). Measurement locations are shown in Figure 10.

Site ID	Date	Discharge (m <sup>3</sup> s <sup>-1</sup> )
E-CF 2	2/14/2019	0.0783
E-CF 3	2/14/2019	0.109
E-CF 4	2/14/2019	0.0747
GB	2/15/2019	0.309
WC	2/15/2019	0.499

## 6.5. Stream PFAS Export

Stream discharge data were used in combination with results of PFAS concentrations in stream water samples to calculate the stream export of PFAS from each watershed. This calculation was done for each measurement station in Georgia Branch and Mines Creek, sampled 22 and 23 October 2018, and for the five streams sampled in February 2019.

The stream export of PFAS in Georgia Branch and Mines Creek in October 2018 was calculated at each stream discharge measurement location as the product of stream discharge and stream PFAS concentration at the same location (Table 14). Based on this method, the total export of PFAS from the Georgia Branch watershed upstream of the downstream-most measurement point (GB – station 2), an area of 21.3 km<sup>2</sup> which includes the Mines Creek watershed, was 58.6 grams of PFAS per day (2473 ng L<sup>-1</sup> of total PFAS (Table 6) times stream discharge of 0.274 m<sup>3</sup> s<sup>-1</sup>, with appropriate unit conversions). The export of GenX alone from

this same watershed was 15.7 g d<sup>-1</sup>. Dividing these export rates by the 21.3 km<sup>2</sup> watershed area yields total PFAS export and GenX export rates, per square kilometer of watershed, of 2.8 g km<sup>-2</sup> d<sup>-1</sup> and 0.74 g km<sup>-2</sup> d<sup>-1</sup>, respectively.

Total PFAS stream export was also calculated for the five streams sampled in February 2019. Total PFAS export for these five streams ranged from 6.05 to 59.5 g d<sup>-1</sup> (Table 15). Together, these five tributary watersheds exported 105 grams of total PFAS per day and 23.1 grams of GenX per day to the Cape Fear River during the sampling period, 14 to 15 February 2019.

**Table 14.** Total PFAS export and GenX export at measurement points in Georgia Branch (GB) and Mines Creek (MC), October 2018.

Site ID	Date	Total PFAS Export (g d <sup>-1</sup> )	GenX Export (g d <sup>-1</sup> )
GB – station 1	10/23/2018	24.0	6.78
GB – station 2	10/23/2018	58.6	15.7
MC – station 1	10/23/2018	24.5	5.82
MC – station 2	10/23/2018	22.0	6.20

**Table 15.** Total PFAS export and GenX export at measurement points in E-CF2, E-CF3, E-CF4, Willis Creek (WC), and Georgia Branch (GB), February 2019.

Site ID	Date	Total PFAS Export (g d <sup>-1</sup> )	GenX Export (g d <sup>-1</sup> )
E-CF 2	2/14/2019	6.05	0.878
E-CF 3	2/14/2019	14.8	3.23
E-CF 4	2/14/2019	7.47	1.54
GB	2/15/2019	59.5	14.4
WC	2/15/2019	17.4	3.08

## **7. Discussion**

### **7.1. Overview**

The results outlined in Section 6 were used to estimate key transport rates for PFAS in the contaminated area near Chemours. Mean total PFAS flux from point measurements in the sampled streams were extrapolated across their entire respective streambed areas to estimate the discharge of total detected PFAS from groundwater to the streams. This rough calculation was done to estimate the scale of PFAS discharge via groundwater in the contaminated area near Chemours. These values were also then compared to stream export and reach mass-balance estimates in addition to determining a rough estimate of the contribution of these streams to the PFAS concentration in the Cape Fear River.

### **7.2. Discharge of PFAS from Groundwater to Streams Near Chemours**

Point measurements of PFAS flux through the streambeds of each stream sampled in June, August, and October 2018 were used to estimate the total amount of PFAS discharging to those streams across their entire estimated streambed areas (Table 16). Total stream lengths were estimated using the feature lengths of the stream vector layer in ArcMap. Average channel widths were based on measurements taken at each point cluster location (for the streams sampled in summer 2018) and at each streambed measurement point location (for Georgia Branch and Mines Creek in October 2018). The mean channel width for the Georgia Branch study reach in October 2018 was 2.0 m (n = 22, sd = 0.83 m) and the mean channel width for the Mines Creek study reach was 2.0 m (n = 8, sd = 0.96 m) (Appendix D).

**Table 16.** Stream channel characteristics for the streams sampled in summer 2018 and October 2018, including the average channel width within the study reach, the total estimated length of the stream, and the resulting streambed area.

<b>Stream Name</b>	<b>Width (m)</b>	<b>Total Estimated Length (m)</b>	<b>Total Estimated Streambed Area (m<sup>2</sup>)</b>
<b>Georgia Branch</b>	2.0	5900	11800
<b>Mines Creek</b>	2.0	5800	11600
<b>Kirks Mill Creek</b>	2.5	5190	12975
<b>Willis Creek</b>	3.0	3360	10080

Estimates of PFAS mass discharge were used to provide a snapshot of the collective groundwater discharge of PFAS from streams near Chemours and to estimate the effect of input from these streams on concentrations of PFAS in the Cape Fear River. This calculation might be seen as only a rough estimate of total PFAS discharge from the streams, because it involved the extrapolation of point measurements across the entire estimated streambed area of each stream, and data from the measurement points may or may not be representative of other reaches within the same stream. However, this provided a useful snapshot view of groundwater discharge of PFAS to the sampled streams that compared well to the export measurements (Section 6.5), as discussed below.

It was estimated that the total mass discharge of PFAS to the main stream channel of Georgia Branch from the underlying groundwater was 48.9 grams of PFAS per day (June 29, 2018), for Mines Creek total PFAS discharge was 11.5 g d<sup>-1</sup> (June 5, 2018), for Kirks Mill Creek it was 11.2 g d<sup>-1</sup> (June 5, 2018), and for Willis Creek it was 4.3 g d<sup>-1</sup> (August 8, 2018). Taking Georgia Branch and Mines Creek together as the two main channels of the Georgia Branch watershed gives 60.4 grams of PFAS per day from groundwater to the stream channel network in that watershed.

The same calculations were done for Georgia Branch and Mines Creek in October 2018 for both the reach streambed area and the total estimated streambed area. Using the reach streambed area, the total discharge of PFAS from groundwater to the stream was 1.33 grams of PFAS per day for the 320-meter study reach in Mines Creek (23 October 2018) and 3.68 g d<sup>-1</sup> for the 610-meter reach in Georgia Branch (22 October 2018). Across the total estimated streambed area, the PFAS discharge from groundwater was 24.0 g d<sup>-1</sup> for Mines Creek and 35.5 g d<sup>-1</sup> for Georgia Branch. Totaled, the groundwater beneath Mines Creek and Georgia Branch discharged approximately 59.6 grams of PFAS per day to the two streams on the sampling days, very similar to the June 2018 estimate (60.4 g d<sup>-1</sup>) mentioned above.

Comparing between the June and October 2018 whole-stream estimates of groundwater discharge of PFAS, the October estimate was lower for the main stream channel of Georgia Branch (35.5 compared to 48.9 g d<sup>-1</sup>) and higher for Mines Creek (24.0 compared to 11.5 g d<sup>-1</sup>). The October 2018 estimates may be more reliable than the June estimates as they are based on more points: 21 for Georgia Branch and 8 for Mines Creek in October 2018, 6 for each stream in June 2018. Spatial variation may also play a role in the differences between June and October. The June measurements in Mines Creek were made about 3200 m upstream of the upstream end of the 320 m Mines Creek reach sampled in October. The June measurements in Georgia Branch were made within the October study reach, at about the 270 m location, though there was significant spatial variability in  $f_{PFAS}$  within the study reach (Fig. 18). It is also possible that hydrologic conditions may have varied between the June and October 2018 sampling campaigns due to seasonal influences, such as differences in the amount of precipitation in the area or groundwater flow paths. However, as noted above, the June and October whole-watershed

estimates that include PFAS discharge to both channels within the Georgia Branch watershed (Georgia Branch and its tributary Mines Creek) were very similar, at about 60 g d<sup>-1</sup>.

### 7.3. PFAS Discharge & Vertical Water Flux from Groundwater to Stream Reaches from Reach Mass-Balance

The reach mass-balance approach was used to estimate the net water and PFAS exchange between the stream reaches studied in October 2018 and the surrounding groundwater. This was done to gauge whether reach mass-balance was feasible for these small coastal plain streams and to compare the results from reach mass-balance and streambed point measurements for four specific variables (Table 17): water flux (cm d<sup>-1</sup>), PFAS flux (mg m<sup>-2</sup> d<sup>-1</sup>), PFAS mass discharge from groundwater to the stream reach (g d<sup>-1</sup>), and the flow-weighted total PFAS concentration in the groundwater discharging to the stream (ng L<sup>-1</sup>).

**Table 17.** Comparison of values of PFAS discharge from groundwater, total PFAS concentration, vertical water flux, and total PFAS flux for Georgia Branch and Mines Creek for the sampling days on 22 and 23 October 2018 through various methods. “RMB” refers to reach mass-balance and “conc.” refers to concentration. For Mines Creek, RMB suggests a net loss of PFAS from the stream reach to groundwater, thus the PFAS concentration in groundwater input to the reach is listed below as “na.”

Method	Georgia Branch (610 m reach)	Mines Creek (320 m reach)
<b>Water Flux from Points (cm d<sup>-1</sup>)</b>	146	133
<b>Water Flux from RMB (cm d<sup>-1</sup>)</b>	209	150
<b>Mean Total PFAS Flux from Points (mg m<sup>-2</sup> d<sup>-1</sup>)</b>	3.01	2.12
<b>Total PFAS Flux from RMB (mg m<sup>-2</sup> d<sup>-1</sup>)</b>	1.1	-0.21
<b>PFAS Discharge from Points (g d<sup>-1</sup>)</b>	3.68	1.33
<b>PFAS Discharge from RMB (g d<sup>-1</sup>)</b>	12.6	-2.5
<b>Mean Total PFAS Conc. from Points (ng L<sup>-1</sup>)</b>	2306	1533
<b>Flow-Weighted Total PFAS Conc. from Points (ng L<sup>-1</sup>)</b>	2085	1559
<b>Flow-Weighted Total PFAS Conc. from RMB (ng L<sup>-1</sup>)</b>	4996	na

Water flux from groundwater to the stream was calculated for each stream reach studied in October 2018 using the reach mass-balance approach. The resulting water flux was estimated to be 209 cm d<sup>-1</sup> for Georgia Branch and 150 cm d<sup>-1</sup> for Mines Creek. These values are overestimates compared to the vertical water flux data from the streambed measurement points, where the mean water flux was 146 cm d<sup>-1</sup> for Georgia Branch and 133 cm d<sup>-1</sup> for Mines Creek. This difference is likely due to the large uncertainty associated with this particular application of the reach mass-balance approach. While the reach mass-balance approach is reliable in some instances, in this case, it yielded groundwater inputs that represent a relatively small difference between much larger numbers. For example, the reach mass-balance calculation for the groundwater discharging to the study reach in Georgia Branch was

$$Q_{GB,gw} = Q_{GB2} - Q_{GB1} - Q_{MC2} = 0.274 \text{ m}^3 \text{ s}^{-1} - 0.078 \text{ m}^3 \text{ s}^{-1} - 0.167 \text{ m}^3 \text{ s}^{-1} = 0.029 \text{ m}^3 \text{ s}^{-1}$$

This calculation produces a groundwater discharge to the stream reach that is only about 11% of the stream discharge at the downstream-most measurement point (GB – station 2). The percent error for this  $Q_{GW}$  value was 62% (Appendix A), a relatively high uncertainty arising from the fact that this estimate based on reach mass-balance is a relatively small difference between much larger numbers. Similarly, other estimates derived from the reach mass-balance approach have relatively high uncertainties (Appendix A).

Using Equation 9, the reach-scale total PFAS flux from groundwater to the streams was estimated to be 1.1 mg m<sup>-2</sup> d<sup>-1</sup> for Georgia Branch and -0.21 mg m<sup>-2</sup> d<sup>-1</sup> for Mines Creek. These are both underestimates compared to the mean total PFAS fluxes from the streambed point measurements, where the values were 3.01 mg m<sup>-2</sup> d<sup>-1</sup> and 2.12 mg m<sup>-2</sup> d<sup>-1</sup> for Georgia Branch and Mines Creek, respectively. The large uncertainty associated with the reach mass-balance approach can be seen in this comparison: the reach mass-balance calculation for Mines Creek

resulted in a negative value, even though all of the individual streambed measurement points showed positive water flux and PFAS flux values. Using a longer reach might have reduced this uncertainty, but was not possible in this case, as site access and conditions constrained the lengths of the study reaches. Therefore, point measurements directly in the streambed were the preferred and more reliable method for this study site.

The discharge of PFAS from groundwater to each stream reach studied in October 2018 was calculated with Equations 8a and 8b. The resulting groundwater PFAS discharge was estimated to be  $12.6 \text{ g d}^{-1}$  for the study reach in Georgia Branch and  $-2.5 \text{ g d}^{-1}$  for the study reach in Mines Creek on 22 and 23 October 2018. These values are very different compared to the groundwater PFAS discharges calculated using the streambed point data, where the resulting numbers were  $3.68 \text{ g d}^{-1}$  and  $1.33 \text{ g d}^{-1}$  for Georgia Branch and Mines Creek, respectively. The reach mass-balance PFAS discharge estimate for Georgia Branch was about four times greater than the value from the streambed point measurements, and the reach mass-balance estimate for Mines Creek was negative while the value from the point data was positive. Again, the reach mass-balance results seem highly uncertain due to the small groundwater input within the reach relative to the stream discharge.

The reach mass-balance approach was also used to calculate the flow-weighted concentration of PFAS in the groundwater beneath the streams studied in October 2018. Based on this method, the flow-weighted total PFAS concentration in the groundwater beneath the study reach in Georgia Branch was  $4996 \text{ ng L}^{-1}$ . The flow-weighted PFAS concentration could not be calculated for Mines Creek using the reach mass-balance method, because the resulting groundwater PFAS discharge was negative. The estimate of  $4996 \text{ ng L}^{-1}$  from the reach mass-balance approach seems to be an overestimate compared to the flow-weighted total PFAS

concentration from the streambed sampling points in Georgia Branch (2085 ng L<sup>-1</sup>). It should be noted that the large uncertainty associated with reach mass-balance in no way affects the other results from this research (on water or PFAS flux, discharge through the streambed, or stream export of PFAS from the watersheds). The reach mass-balance results are reported here because they were obtained, but they do not constitute an important part of the results other than to show that the method was not well-suited to these stream reaches.

#### **7.4. PFAS Contribution to the Cape Fear River from Contaminated Groundwater & Streams Near Chemours**

The contribution of groundwater discharge to PFAS contamination in the Cape Fear River (CFR) was estimated based on: (1) the estimated discharge of PFAS from groundwater to the streams sampled in June and August 2018, (2) the estimated discharge of PFAS from groundwater to the streams sampled in October 2018, (3) the PFAS export from the streams sampled in October 2018, and (4) the PFAS export from the streams sampled in February 2019. These values were calculated in order to estimate the impact of groundwater discharge of PFAS to tributaries of the CFR on contamination in the river. The values (Table 18) can be compared to each other across the various methods and sampling periods.

**Table 18.** CFR discharge values from the stream gage data at Huske Lock, the values used for loading to the river, and the resulting contributions to total PFAS and GenX concentrations in the CFR.

Loading (g d <sup>-1</sup> )		CFR Discharge (m <sup>3</sup> s <sup>-1</sup> )				
		2018 Min.	2018 Max.	Mean June-Aug. 2018	Mean 22-23 Oct. 2018	Mean 14-15 Feb. 2019
		21.5	2475	128	309	155
		Contribution to Total PFAS or GenX Concentration in CFR (ng L <sup>-1</sup> )				
<b>Total PFAS Discharge from GW Summer 2018</b>	75.9	40.9	0.355	6.86		
<b>GenX Discharge from GW Summer 2018</b>	22.4	12.1	0.105	2.02		
<b>Total PFAS Discharge from GW Oct. 2018</b>	59.6	32.1	0.279		2.23	
<b>GenX Discharge from GW Oct. 2018</b>	14.6	7.86	0.068		0.546	
<b>Total PFAS Export for Oct. 2018</b>	58.6	31.5	0.274		2.19	
<b>GenX Export Oct. 2018</b>	15.7	8.44	0.073		0.587	
<b>Total PFAS Export Feb. 2019</b>	105	56.7	0.492			7.84
<b>GenX Export Feb. 2019</b>	23.1	12.4	0.108			1.72

The approach was to take estimates of GenX or total PFAS "loading" ( $\text{g d}^{-1}$ ) from each of the four sources of data listed above and divide each estimate by river discharge ( $\text{m}^3 \text{s}^{-1}$ ) in the CFR to calculate an estimated contribution from that source to the GenX or total PFAS concentration in the CFR. Discharge data for the CFR from William O. Huske Lock and Dam were used (USGS gaging station 02105500) [USGS 2019]. Discharge measurements from the time period for each sampling campaign were used to estimate the contribution to CFR concentrations for that sampling period. For example, for the summer 2018 campaign, the total GenX loading from all four streams ( $22.4 \text{ g d}^{-1}$ ) was divided by the mean CFR discharge for the months of June, July, and August of 2018 to give an estimated contribution to river water [GenX] of about  $2 \text{ ng L}^{-1}$  from groundwater discharge to the four CFR tributaries (Table 18). For the October 2018 sampling, the mean CFR discharge for the sampling days, 22 and 23 October 2018, was used. For the February 2019 sampling, the mean CFR discharge for the sampling days, 14 and 15 February 2019, was used.

To investigate a broader range of possible contributions to CFR river water GenX and total PFAS concentrations, the loadings from the four sources of GenX and total PFAS discharge listed above were also divided by the 2018 high discharge, and low discharge, of the CFR at Huske Lock. These estimates based on CFR high and low flow would be most meaningful if the mass fluxes of PFAS from the tributary streams are relatively constant in time. While this could not be firmly established in this research, there is some suggestion of consistency in PFAS fluxes in the Georgia Branch data (see Section 7.5).

Using the mean CFR discharge for the sampling period from June to August 2018, the four tributaries contributed an estimated  $6.86 \text{ ng L}^{-1}$  to the total river water [PFAS] and  $2.02 \text{ ng L}^{-1}$  to the concentration of GenX in the river. Using the extrapolation of groundwater PFAS

discharge across the total streambed areas of all four streams sampled in June and August 2018, input from these tributaries contributed  $0.36 \text{ ng L}^{-1}$  to total [PFAS] in the CFR at high flow and  $41 \text{ ng L}^{-1}$  at low flow. For GenX alone, input from the streams contributed  $0.10 \text{ ng L}^{-1}$  to the total river water [PFAS] at high flow and  $12 \text{ ng L}^{-1}$  at low flow. These are rough estimates because the calculations involved the extrapolation of six measurement points per stream within a small 5 to 10 m reach across the entire estimated area of the streambed for each stream. These six measurement points may or may not be representative of other reaches within the same stream.

Dividing the total estimated groundwater PFAS discharge into Georgia Branch and Mines Creek in October 2018 ( $59.6 \text{ g d}^{-1}$ ) by the average CFR discharge at Huske Lock on 22 and 23 October 2018 results in an estimated contribution to total river water [PFAS] of  $2.2 \text{ ng L}^{-1}$ . The same  $59.6 \text{ g d}^{-1}$  groundwater discharge of PFAS for the Georgia Branch watershed divided by the high and low river discharge at Huske Lock for 2018 gave estimated contributions of  $0.28 \text{ ng L}^{-1}$  and  $32 \text{ ng L}^{-1}$  to river water total [PFAS], respectively. For GenX alone, combined groundwater discharge from the Georgia Branch watershed contributed  $0.55 \text{ ng L}^{-1}$  on the sampling days in October 2018,  $0.068 \text{ ng L}^{-1}$  to the GenX concentration in the CFR at high flow, and  $7.9 \text{ ng L}^{-1}$  at low flow. These estimates of PFAS contributions to the CFR are probably realistic for the Georgia Branch watershed alone as they match up well with the estimates based on stream export from the October 2018 and February 2019 stream sampling of Georgia Branch at the GB610 location. However, the summer 2018 and October 2018 estimates do not take into account the possible contributions from other watersheds in the same area (on the other side of the CFR). The estimates based on the February 2019 stream measurements provide a snapshot of contributions from five CFR tributary watersheds near Chemours on both sides of the river.

Based on the export of PFAS from the streams sampled in October 2018, the contribution to the CFR total PFAS concentration from input from the Georgia Branch watershed was 2.2 ng L<sup>-1</sup> on the sampling days in October 2018, 0.27 ng L<sup>-1</sup> at high flow, and 32 ng L<sup>-1</sup> at low flow. From the export of GenX alone from the Georgia Branch watershed, the contribution to the GenX concentration in the river was 0.59 ng L<sup>-1</sup> on the sampling days in October 2018 and ranged from 0.073 ng L<sup>-1</sup> at high flow to 8.4 ng L<sup>-1</sup> at low flow. The Georgia Branch watershed (which includes Mines Creek) covers about 21.3 km<sup>2</sup>, or only 0.05% of the total area of the CFR watershed (23,700 km<sup>2</sup>). This is important to consider when estimating the contribution of the Georgia Branch watershed to PFAS concentrations in the CFR, because it represents just one small area within a much larger watershed that could contain numerous other sources of PFAS contamination for the CFR. Other sources could include leachate from old landfills that contain products made from PFAS, US Air Force bases and airports that historically used PFAS-containing fire-fighting foams, or extensive groundwater contamination on the Chemours site that will be released slowly over time from substrates with low permeability (clay lenses).

The data collected from the five tributaries in February 2019 likely provides the most accurate estimate of the contribution of PFAS to the CFR from the streams in the study area for that point in time compared to the other methods of estimation. These estimates include data collected from five stream watersheds, as opposed to one or three, and account for streams both east and west of the CFR, where the summer 2018 and October 2018 focused only on streams to the west of the river, on the same side as the Chemours plant. While the Georgia Branch watershed contributed the majority of contamination to the CFR, among the five streams sampled, E-CF3 and Willis Creek contributed 14% and 17% of the total PFAS export from all five streams (Table 19).

**Table 19.** Stream discharge measurements, total PFAS and GenX concentrations in the streams, export values used for loading to the CFR, and the resulting contributions to the total PFAS and GenX concentrations in the CFR for the mean discharge on the sampling days (14 and 15 February 2019) for the five tributary streams sampled in February 2019.

Site ID	Discharge (m <sup>3</sup> s <sup>-1</sup> )	Total [PFAS] (ng L <sup>-1</sup> )	[GenX] (ng L <sup>-1</sup> )	Total PFAS Export (g d <sup>-1</sup> )	GenX Export (g d <sup>-1</sup> )
E-CF 2	0.0783	895	130	6.05	0.878
E-CF 3	0.109	1577	345	14.8	3.23
E-CF 4	0.0747	1157	238	7.47	1.54
GB	0.309	2233	539	59.5	14.4
WC	0.499	404	71.5	17.4	3.08
<b>Total Contribution to the CFR (ng L<sup>-1</sup>)</b>				<b>7.84</b>	<b>1.72</b>

### 7.5. Comparison of PFAS Export & Discharge Values

In Section 7.4, the calculations of PFAS flux through the streambeds and PFAS stream export were treated as though either value could serve as an estimate of PFAS loading to the CFR. The reasoning for this approach is based on the assumptions that (1) measurements were made when groundwater was the only source contributing to stream flow (no overland flow or other inputs) and (2) PFAS is essentially conservative in the stream water, meaning that once a compound is discharged to the stream from the underlying groundwater, there are no biological, chemical, or physical mechanisms by which it is lost from the stream water. Since all measurements were made on clear days when there was no precipitation or runoff, assumption (1) has been met. Support for the second assumption comes from the available physicochemical data for PFAS that suggest most compounds generally do not volatilize or degrade easily [Wang et al. 2017; CONCAWE 2016; Sun et al. 2016; Wang et al. 2015; Lindstrom et al. 2011].

If both assumptions mentioned above are true, then all of the PFAS discharged from groundwater to the streams would eventually enter the CFR, and all of the PFAS entering the CFR from the streams on the sampling days would have come from groundwater. Therefore,

based on these assumptions, it would be reasonable to expect that an estimate of PFAS flux from groundwater into a stream should agree well with an estimate of stream export of PFAS (at least under baseflow conditions).

The results from the methods described in the previous sections allowed for the comparison of the amount of PFAS discharging from groundwater ( $D_{PFAS}$ ) to the total PFAS export from the sampled streams ( $E_{PFAS}$ ). Some of the results from the different methods ended up being very similar. For example, the  $D_{PFAS}$  and  $E_{PFAS}$  results for the Georgia Branch watershed from October 2018 and February 2019 were within 2% of each other (Table 20). The Georgia Branch  $D_{PFAS}$  value from summer 2018 (based on the extrapolation of six streambed measurement points in Georgia Branch and six points in Mines Creek, a tributary to Georgia Branch) was  $60.4 \text{ g d}^{-1}$ , about 3% more than the other values. This increases the level of confidence in these values, even those based on extrapolating streambed point measurements across the full streambed areas, and it suggests that  $D_{PFAS}$  is relatively consistent across different sampling periods and methods. The volumetric stream discharge measured for Georgia Branch, at location GB610, was similar for the October 2018 and February 2019 sampling periods (Tables 12 and 13), which likely contributes to the similarity in the  $E_{PFAS}$  values.

**Table 20.** Total PFAS mass discharge from groundwater to the Georgia Branch watershed upstream of GB610 based on point measurement data from June and October 2018 ( $D_{PFAS}$ ) and the total export of PFAS from the Georgia Branch watershed at stream measurement point GB610, 1100 m upstream of the confluence with the Cape Fear River, measured in October 2018 and February 2019 ( $E_{PFAS}$ ).

Georgia Branch	Method			
	$D_{PFAS}$ June 2018	$D_{PFAS}$ Oct. 2018	$E_{PFAS}$ Oct. 2018	$E_{PFAS}$ Feb. 2019
Total PFAS Mass Discharge ( $\text{g d}^{-1}$ )	60.4	59.6	58.6	59.5

For Mines Creek, the resulting values of groundwater PFAS discharge and stream PFAS export were less similar. The estimates of  $D_{PFAS}$  from the extrapolation of the October 2018 point data and  $E_{PFAS}$  from the October 2018 stream discharge data were within 10% of each other, but the  $D_{PFAS}$  estimate from the extrapolation of the June 2018 point data was 50% lower than the other two values (Table 21). This could have been due either to spatial variability in groundwater discharge along the streambed or to seasonal variability in groundwater discharge to the stream. Mines Creek was not sampled as part of the February 2019 stream sampling campaign, so a comparison across three seasons could not be made.

**Table 21.** Total PFAS mass discharge from groundwater to the Mines Creek watershed based on point measurement data from June and October 2018 ( $D_{PFAS}$ ) and the total export of PFAS from the Mines Creek watershed at stream measurement point MC320, 40 m upstream from the confluence with Georgia Branch, measured in October 2018 ( $E_{PFAS}$ ).

Mines Creek	Method		
	$D_{PFAS}$ June 2018	$D_{PFAS}$ Oct. 2018	$E_{PFAS}$ Oct. 2018
<b>Total PFAS Mass Discharge (g d<sup>-1</sup>)</b>	11.5	24.0	22.0

## 8. Summary & Conclusions

As part of this study, groundwater samples were collected from beneath the streambeds of streams near Chemours and analyzed for concentrations of PFAS. Water flux was measured at the same streambed measurement points, and these measurements combined with PFAS concentration data yielded the PFAS flux from groundwater to the streams through the streambeds. Chemical dilution stream gaging was also done and stream water PFAS concentrations were measured to quantify the export of PFAS from streams in the study area. All streams sampled as part of this research are tributaries to the CFR, and all stream study sites were located within 5 km of the Chemours plant near Fayetteville, NC. The goal of this study was to estimate the impact of groundwater upwelling and discharge from nearby streams on PFAS contamination in the CFR. The long-term goal of this work was to improve the understanding of PFAS transport in the contaminated area near Chemours.

The streams sampled in summer 2018 and October 2018 were found to be gaining at all streambed measurement points in each stream, except for three points in Georgia Branch (22 October 2018). Mean groundwater fluxes through the streambeds in summer 2018 were 138 cm d<sup>-1</sup> for Georgia Branch, 90.3 cm d<sup>-1</sup> for Mines Creek, 87.1 cm d<sup>-1</sup> for Kirks Mill Creek, and 61.9 cm d<sup>-1</sup> for Willis Creek. The mean water fluxes for the streams sampled in October 2018 were 133 cm d<sup>-1</sup> for Mines Creek and 146 cm d<sup>-1</sup> for Georgia Branch. These measurements combined with results from LCMS analyses of groundwater samples showed that PFAS-contaminated groundwater was discharging into streams within the study reaches. The mean total PFAS fluxes from groundwater into the streams sampled in summer 2018 ranged from 0.43 mg m<sup>-2</sup> d<sup>-1</sup> (Willis Creek) to 4.17 mg m<sup>-2</sup> d<sup>-1</sup> (Georgia Branch). The mean total PFAS fluxes from groundwater to the streams sampled in October 2018 were 3.01 mg m<sup>-2</sup> d<sup>-1</sup> for Georgia Branch and 2.12 mg m<sup>-2</sup>

d<sup>-1</sup> for Mines Creek. GenX concentrations exceeded the NC state health goal of 140 ng L<sup>-1</sup> in all but one groundwater sample out of all the samples collected from beneath the two streams in October 2018. GenX concentrations also exceeded the NC state health goal in the stream water samples collected from E-CF3, E-CF4, and Georgia Branch in February 2019.

Calculations for the streams sampled in October 2018 showed that groundwater input to Georgia Branch and Mines Creek was not sufficient to obtain reach mass-balance results with low uncertainty. The results from this approach represent a relatively small difference between much larger numbers, making the resulting uncertainty large ( $\pm 49\%$  for the groundwater discharge to Mines Creek and  $\pm 62\%$  for the groundwater discharge to Georgia Branch). The streams may not be well-suited for use of the reach mass-balance method unless longer reaches can be defined and used. In such an environment, the streambed point measurement method and measurements of stream export were and are more productive.

Comparing results across the various methods and sampling periods showed that  $D_{PFAS}$  and  $E_{PFAS}$  were relatively consistent for Georgia Branch across the sampling periods in summer 2018, October 2018, and February 2019 (Table 19) which improves the confidence in the values. The estimates of  $D_{PFAS}$  and  $E_{PFAS}$  from the October 2018 and February 2019 sampling were within 2% of each other, and  $D_{PFAS}$  for the June 2018 sampling was about 3% more than the other values. Similarity in PFAS export estimates between the October 2018 and February 2019 sampling periods is likely due at least in part to the similar stream discharge in Georgia Branch on those two days ( $0.274 \text{ m}^3 \text{ s}^{-1}$  on 23 October 2018 and  $0.309 \text{ m}^3 \text{ s}^{-1}$  on 15 February 2019).

Results from  $D_{PFAS}$  (summer 2018, October 2018) and  $E_{PFAS}$  (October 2018, February 2019) calculations were used to estimate the contribution from the sampled streams to CFR PFAS concentrations. The results from the February 2019 data likely provide the most reliable

snapshot of the cumulative input of PFAS to the CFR near Chemours. The five streams sampled in February 2019 were found to contribute  $1.72 \text{ ng L}^{-1}$  to [GenX] and  $7.84 \text{ ng L}^{-1}$  to total [PFAS] in the CFR on the sampling days (Table 20), with the largest single contribution among the five streams coming from the Georgia Branch watershed (Table 21). This watershed, which includes Mines Creek, covers just 0.05% of the total CFR watershed area but makes a significant contribution to CFR [PFAS]. Results based on  $D_{\text{PFAS}}$  estimates (summer 2018, October 2018) suggest that groundwater discharge to tributaries could be a significant source of PFAS contamination for the CFR. If, as expected, there is little to no degradation of PFAS in the tributary streams, then any PFAS discharging from groundwater to these streams will eventually be transported to the river and then downstream. Thus, it seems likely that groundwater discharge of PFAS into tributaries of the Cape Fear is contributing to the persistent low levels of GenX in the river water (Fig. 8) [NCDEQ 2019b].

The data collected in this study suggest it is likely that PFAS contamination of the CFR, a major drinking water source for thousands of NC residents, could continue in the future even though Chemours has stopped discharging process wastewater directly to the river. Groundwater in the tributary watersheds near Chemours is clearly contaminated with PFAS, and that PFAS is clearly discharging from the groundwater to the tributary streams (about 60 grams of PFAS per day to Georgia Branch) and is almost certainly reaching the CFR. More work still needs to be done to characterize the age and travel time of the groundwater reaching streams in this area to better understand the timescale over which PFAS contamination will be flushed out of the surficial aquifer and into the CFR.

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## APPENDICES

## APPENDIX A. Errors & Uncertainties

This appendix explains the basis for uncertainty calculations for vertical water flux variables for streambed point measurements, for stream discharge measurements, and for the reach mass-balance calculations. Uncertainties were estimated through standard approaches to error propagation [Peters et al. 1974; Meyer 1975; Kline 1985; Genereux 1998]. For example, if  $y$  is a function of  $x_1, x_2$ , and so on, and all uncertainties in  $x$  are independent of each other, then the uncertainty in  $y$  can be calculated as

$$W_y = \sqrt{\left(\frac{\partial y}{\partial x_1} W_{x_1}\right)^2 + \left(\frac{\partial y}{\partial x_2} W_{x_2}\right)^2 + \dots + \left(\frac{\partial y}{\partial x_n} W_{x_n}\right)^2} \quad \text{Equation A1}$$

where  $W$  represents the uncertainty of each variable.

### A1. Uncertainty in Fluxes from Point Measurements

The uncertainty in the vertical water flux and total PFAS flux through the streambed depends on the uncertainty in each variable used to calculate these transport rates. The uncertainty in the hydraulic head gradient,  $J$ , was estimated based on methods described and used by Kennedy [2008] and Kennedy et al. [2007]. The uncertainty in the streambed hydraulic conductivity,  $K$ , was estimated based on methods described and used by Leahy [2007] and Genereux et al. [2008]. The uncertainties in the vertical water and total PFAS fluxes through the streambed were then estimated based on these values for each streambed measurement point.

#### A1.1. Uncertainty in $J$

The hydraulic head gradient ( $J$ ) between the stream water and the underlying groundwater was determined for each streambed measurement point based on the oil-water level measurements on the piezomanometer, the insertion depth of the piezomanometer, the densities

of the oil used ( $\rho_o$ ) and water ( $\rho_w$ ), and the amplification factor (AF) of the device. Using these parameters,  $J$  was calculated as the difference in head measurements from the manometer readings ( $\Delta h$ ) divided by the amplification factor, all divided by the length of the piezomanometer below the streambed surface,  $L$  (i.e., the insertion depth from the streambed surface to the top of the screen):

$$J = \frac{\Delta h / AF}{L} \quad \text{Equation A2}$$

AF was calculated based on the linear relationships between temperature and water density and temperature and oil density. A relationship between the density of the oil used in the piezomanometer and temperature was determined in the lab (Appendix B), and the relationship between water density and temperature was devised by Kennedy et al. [2007] based on values from Fetter [2001]. Based on these linear relationships,  $\rho_o$  and  $\rho_w$  was determined for any ambient air temperature measurement, and AF was calculated as

$$AF = \frac{\rho_w}{\rho_w - \rho_o} \quad \text{Equation A3}$$

To determine the uncertainty in  $J$  for each streambed measurement point, the uncertainties of AF,  $\rho_o$ , and  $\rho_w$  first needed to be found. The uncertainty in  $\rho_w$  ( $W_{\rho_w}$ ) was assumed to be  $0.0004 \text{ g mL}^{-1}$ , based on values from Fetter [2001] and calculations done by Kennedy et al. [2007]. The uncertainty in  $\rho_o$  ( $W_{\rho_o}$ ) was calculated by multiplying the standard error for the predicted oil density at  $20^\circ\text{C}$  (Appendix B) by the value from the Student's  $t$  distribution at the 95% confidence level ( $t_{3,2(0.05)} = 0.046$ ) [Kennedy 2008]. The standard error of the predicted  $\rho_o$  was calculated as

$$\sigma_{P(x_0)} = \sqrt{\left[ \frac{1}{m} + \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{S_{xx}} \right] MS[E]} \quad \text{Equation A4}$$

where  $x_0$  is the  $x$  value of interest (20°C),  $\bar{x}$  is the mean of all  $x$  values,  $m$  is the number of predicted values of  $y$  (one),  $n$  is the sample size (5),  $S_{xx}$  is the variance of  $x$  values in the dataset, and  $MS[E]$  is the least squares estimate of the error for the predicted  $\rho_o$  value.

Using the uncertainties in  $\rho_o$  and  $\rho_w$ , the uncertainty in AF for each streambed measurement point was estimated as

$$W_{AF} = \sqrt{\left[ \frac{\rho_w}{(\rho_w - \rho_o)^2} W_{\rho_o} \right]^2 + \left[ -\frac{\rho_o}{(\rho_w - \rho_o)^2} W_{\rho_w} \right]^2} \quad \text{Equation A5}$$

and the uncertainty in  $\Delta h/AF$  was estimated as

$$W_{\Delta h/AF} = \sqrt{\left[ \frac{1}{AF} W_{\Delta h} \right]^2 + \left[ -\frac{\Delta h}{AF^2} W_{AF} \right]^2} \quad \text{Equation A6}$$

where the uncertainty in the head difference measured on the piezomanometer ( $W_{\Delta h}$ ) is  $\pm 1$  mm, which is the accuracy with which the manometer can be read.

Then, the uncertainty in  $J$  ( $W_J$ ) was estimated using the following equation:

$$W_J = \sqrt{\left[ \frac{1}{L} W_{\Delta h/AF} \right]^2 + \left[ -\frac{\Delta h/AF}{L^2} W_L \right]^2} \quad \text{Equation A7}$$

where  $L$  is the length of the piezomanometer below the streambed, and  $W_L$  is estimated based on the standard error in  $L$  (assumed to be 1.0 cm) and the Student's  $t$  statistic at the 95% confidence level.

The resulting uncertainties in  $J$  were below 9% for all but one streambed point measurement in summer 2018 and October 2018, and the mean was 1.9% ( $n = 53$ , excluding one outlier at 50% where the measured head difference was very small).

### A1.2. Uncertainty in $K$

The hydraulic conductivity of the streambed sediment ( $K$ ) at each measurement point was determined based on a falling head test conducted *in situ* using a field permeameter inserted into the sandy streambed at each streambed measurement point [Leahy 2007]. The uncertainty in  $K$  for each point was estimated based on the uncertainties in the parameters used to calculate  $K$  [Genereux et al. 2008].

$K$  at each measurement point was estimated from the slope of the linear regression after plotting the change in the water level inside the field permeameter over time. The relationship used was

$$\ln H = (\text{slope})t + \ln H_0 \quad \text{Equation A8}$$

where  $t$  is time (s) and  $H$  is the water level inside the permeameter relative to the ambient water level in the stream prior to the falling head test (where  $H_t = H_0$  at  $t = 0$ ).

The slope of the linear regression for the falling head test data was used to find  $K$  by rearranging the following equation (based on Genereux et al. 2008):

$$\text{slope} = - \frac{K}{\frac{\pi D}{11m} + L_V} \quad \text{Equation A9}$$

where  $D$  is the diameter of the field permeameter (7.0 cm),  $m$  is the transformation ratio of horizontal ( $K_H$ ) and vertical ( $K_V$ ) hydraulic conductivity in Hvorslev's Equation ( $m = \sqrt{K_H/K_V}$ )

[1951], and  $L_V$  is the length of the sediment column contained within the permeameter (i.e. the insertion depth, or 35 cm).

The approach of Genereux et al. [2008] was used to estimate the uncertainty in  $K$  values: the uncertainties in  $D$ ,  $L_V$ , and the regression slope were estimated and added in root mean square fashion to the uncertainty arising from not knowing the exact value of  $m$ .

Uncertainty in the slope ( $W_{slope}$ ) for each measurement point was estimated through standard methods as described by Zar [1984, pp. 261-278], where the 95% confidence interval is equal to  $\pm$  the appropriate  $t$  statistic at  $n - 2$  degrees of freedom multiplied by the standard error in the slope ( $s_b$ ). To find  $s_b$ , the following equations were used:

$$s_b = \sqrt{\frac{s_{yx}^2}{\sum x^2}} \quad \text{Equation A10}$$

and

$$s_{yx} = s_y \sqrt{1 - r^2} \quad \text{Equation A11}$$

where  $s_{yx}$  is the standard error of the regression,  $s_y$  is the standard deviation of all  $y$  values used in the linear regression, and  $r^2$  is the regression coefficient.

The standard error for the diameter of the permeameter pipe ( $D$ ) was 0.0508 cm [McMaster-Carr, product #8585K21; <http://www.mcmaster.com>]. The standard error for  $L_V$  was assumed to be 1.0 cm. The uncertainties for  $D$  and  $L_V$  were estimated by multiplying their standard errors by the Student's  $t$  statistic at the 95% confidence level for large numbers (1.96). The uncertainty in  $m$  due to averaging between the assumption that  $m$  is equal to infinity and the assumption that  $m$  is equal to one was  $\pm 5\%$  [Leahy 2007].

Thus, the uncertainty in  $K$  due to uncertainty in the measurands ( $W_{K,M}$ ) was estimated first based on the uncertainties in the measurands (excluding  $m$ ) by error propagation using standard methods:

$$W_{K,M} = \sqrt{\left[-\left(\frac{\pi D}{11} + L_V\right)W_{slope}\right]^2 + \left[-\left(\frac{slope \cdot \pi}{11}\right)W_D\right]^2 + \left[-slope \cdot W_{L_V}\right]^2} \quad \text{Equation A12}$$

Then, the uncertainty in  $m$  was incorporated by adding it to  $W_{K,M}$  in root mean square fashion.

Using the methods described above, the resulting mean uncertainty in  $K$  measurements was 8.6% for all streambed point measurements in summer 2018 and October 2018 ( $n = 54$ ).

### **A1.3. Uncertainty in Vertical Water Flux**

Uncertainty in the vertical water flux at each point was estimated using the uncertainties of  $J$  and  $K$ , based on Darcy's Equation,  $v=KJ$ . To calculate the uncertainty in water flux, the following equation was used:

$$W_v = \sqrt{(K \cdot W_J)^2 + (J \cdot W_K)^2} \quad \text{Equation A13}$$

The resulting mean uncertainty in  $v$  was 9.2% for all streambed point measurements in summer 2018 and October 2018 ( $n = 53$ , excluding one outlier of 50%).

### **A1.4. Uncertainty in Total PFAS Flux**

Uncertainty in the total PFAS flux at each point was estimated using the uncertainty in  $v$ , described in the previous section, and the method uncertainty for the concentration analyses done in the lab. The uncertainty in each of the PFAS concentrations, based on repeat lab analyses of

the same sample, was  $\pm 20\%$  [pers. comm. Zachary Hopkins, March 2019]. The following equation was used to estimate the PFAS flux uncertainty for each streambed measurement point:

$$W_{f_{PFAS}} = \sqrt{(v \cdot W_{[PFAS]})^2 + ([PFAS] \cdot W_v)^2} \quad \text{Equation A14}$$

The resulting mean uncertainty in total PFAS flux was 22% for all streambed point measurements in summer 2018 and October 2018 ( $n = 54$ ).

## A2. Uncertainty in Stream Discharge & Reach Mass-Balance Calculations

Stream discharge was calculated for each measurement station based on the equation “ $Q = m/A$ ,” where  $m$  refers to the mass of NaCl (kg) used in the tracer injection and  $A$  refers to the area under the breakthrough curve when [NaCl] is plotted against time, with units of  $\text{kg s m}^{-3}$ .

Based on Equation A1, and the methods described by Hattenberger [2018], the uncertainty in  $Q$  was estimated as

$$W_Q = \sqrt{\left(\frac{1}{A} W_m\right)^2 + \left(-\frac{m}{A^2} W_A\right)^2} \quad \text{Equation A15}$$

Uncertainty in  $m$  was mostly due to the instrument precision of the balance used to measure the mass of the amount of NaCl used, which in this case was 0.001 g. Other sources of uncertainty in  $m$  may come from the process of mixing the salt slug used in the tracer injection. For example, a very small amount of salt could have clung to the plastic container when pouring the salt into the bucket used to mix the slug. However, this would represent a very small loss of the total mass of NaCl, likely less than 1 g out of the total 500 to 1000 g of salt used in the slug. Similarly, a very small amount of the salt solution could have been retained by the plastic bucket when pouring the solution quickly into the stream channel. Again, this probably represents a very

small loss of the salt solution, likely a few mL out of the approximate total 7500 mL. These very small sources of uncertainty are most likely negligible in this case.

The most significant source of uncertainty in  $Q$  then comes from the determination of the area under the NaCl breakthrough curve. To estimate the uncertainty in the area ( $W_A$ ), the  $1 \mu\text{S cm}^{-1}$  resolution of the conductivity loggers was first added to all of the raw conductivity measurement values, prior to applying the temperature correction for  $S_{25}$  and converting conductivity to  $[\text{NaCl}]$ , and then the resulting breakthrough curve was integrated to determine the maximum probable area under the curve ( $A_{\text{max}}$ ) [Hattenberger 2018]. Then,  $1 \mu\text{S cm}^{-1}$  was subtracted from all of the raw conductivity measurement values and the process was repeated to determine the minimum probable area under the curve ( $A_{\text{min}}$ ) [Hattenberger 2018]. Using these estimated values, the uncertainty in  $A$  was estimated using the following equation [Hattenberger 2018]:

$$W_A = \frac{(A_{\text{max}} - A) + (A - A_{\text{min}})}{2} \quad \text{Equation A16}$$

The uncertainties for  $m$  and  $A$  were then substituted into Equation A2.1, and  $W_Q$  was estimated for each stream discharge measurement station for the October 2018 and February 2019 stream sampling campaigns. The resulting uncertainties were all below 48% of the total discharge at each station, and the mean was 20.4% ( $n = 9$ ).

The uncertainty in  $Q$  for each station for the October 2018 sampling was then used to estimate the uncertainty in  $Q_{\text{GW}}$  calculated from the reach mass-balance approach. The following equations were used for Mines Creek and Georgia Branch, respectively:

$$W_{\text{GW.MC}} = \sqrt{(W_{\text{Q.MC2}})^2 + (W_{\text{Q.MC1}})^2} \quad \text{Equation A17a}$$

$$W_{GW.GB} = \sqrt{(W_{Q.GB2})^2 + (W_{Q.GB1})^2 + (W_{Q.MC2})^2} \quad \text{Equation A17b}$$

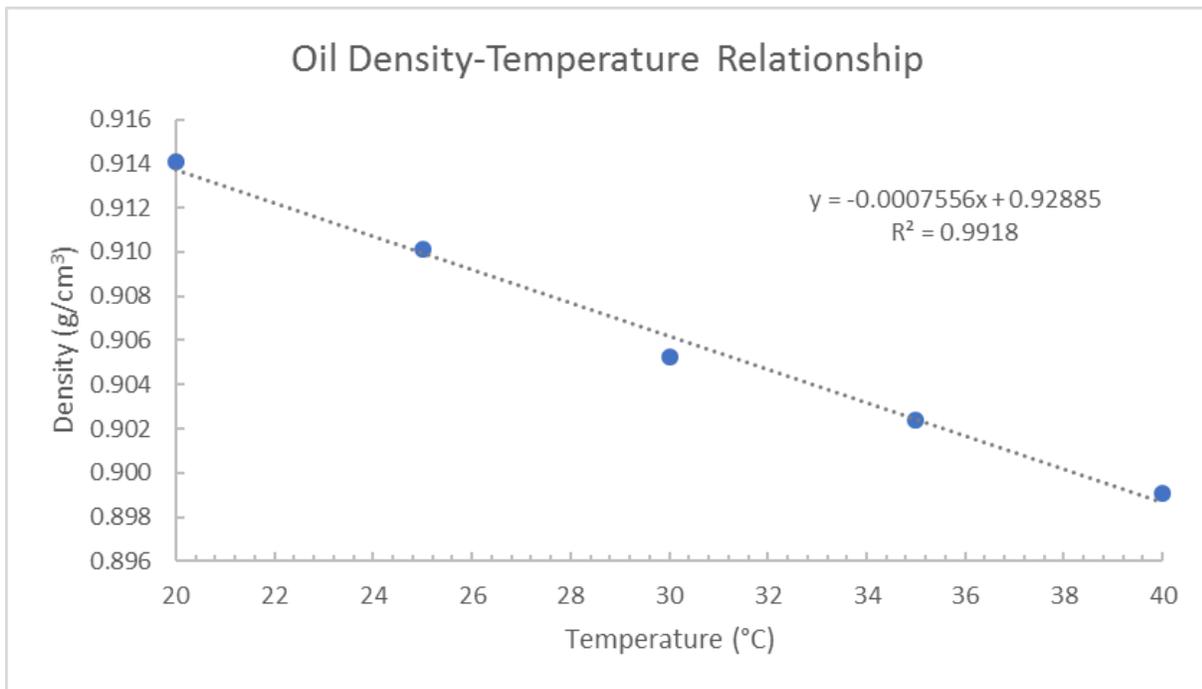
The resulting uncertainties were 49% of the estimated groundwater discharge for the reach in Mines Creek and 62% of the estimated groundwater discharge for the reach in Georgia Branch.

## **APPENDIX B. Oil Density-Temperature Relationship**

This appendix explains the process for determining the relationship between temperature and the density of a light oil used in the piezomanometers used in this study. A relationship between oil density and temperature needed to be established so that the amplification factor (AF) could be calculated (Equation A3) based on the ambient air temperature at the time of each manometer measurement in the field. To establish this relationship, an experiment was conducted in the lab where a known volume of oil was equilibrated at different temperatures and the resulting mass was measured in order to calculate density at various controlled temperatures.

First, the mass of a glass 100 mL flask was measured while it was empty. The mass was measured using an Ohaus Pioneer<sup>TM</sup> (model PA323C) balance to an accuracy of 0.001 g. Then, vegetable oil (Wesson brand soybean oil) was measured out into the flask using a plastic 5 mL pipette, and the flask with oil was moved to a temperature-controlled water bath. The water bath used was a Fisher Scientific IsoTemp® GPD 05 (model FSGPD05) with a temperature uncertainty of  $\pm 0.2$  °C. After the flask with oil was inserted into the water bath, the bath was filled sufficiently with tap water, the lid was closed, and the temperature was adjusted to the desired value. Temperature was monitored using the digital reader on the water bath as it increased to the programmed value. Once the temperature of the water bath reached the programmed value, the oil was left to equilibrate for one hour. After equilibration, the volume was adjusted to 100 mL by removing oil with the plastic pipette and the new mass of the flask with the oil was measured. By repeating these steps for multiple temperatures, data points of oil mass and volume were recorded for five different temperatures within the range of programmable temperatures for the water bath (from 20 to 40 °C). Mass of the oil was obtained by subtracting the mass of the empty flask from the total mass of the flask with oil.

The mass and volume data from this experiment were used to calculate density of the oil at each temperature, and then the data points of density versus temperature were plotted (Fig. B1). A linear regression was performed on the data points and the slope of the trendline was determined to be -0.0007556. This slope was used along with a water density-temperature relationship and the oil-water levels from the piezomanometer to calculate hydraulic head gradient at each streambed measurement point, as described in Appendix A and used by Kennedy et al. [2007].



**Figure B1.** Graph showing the density of the light oil used versus temperature.

## APPENDIX C. [NaCl]-Conductivity Relationship

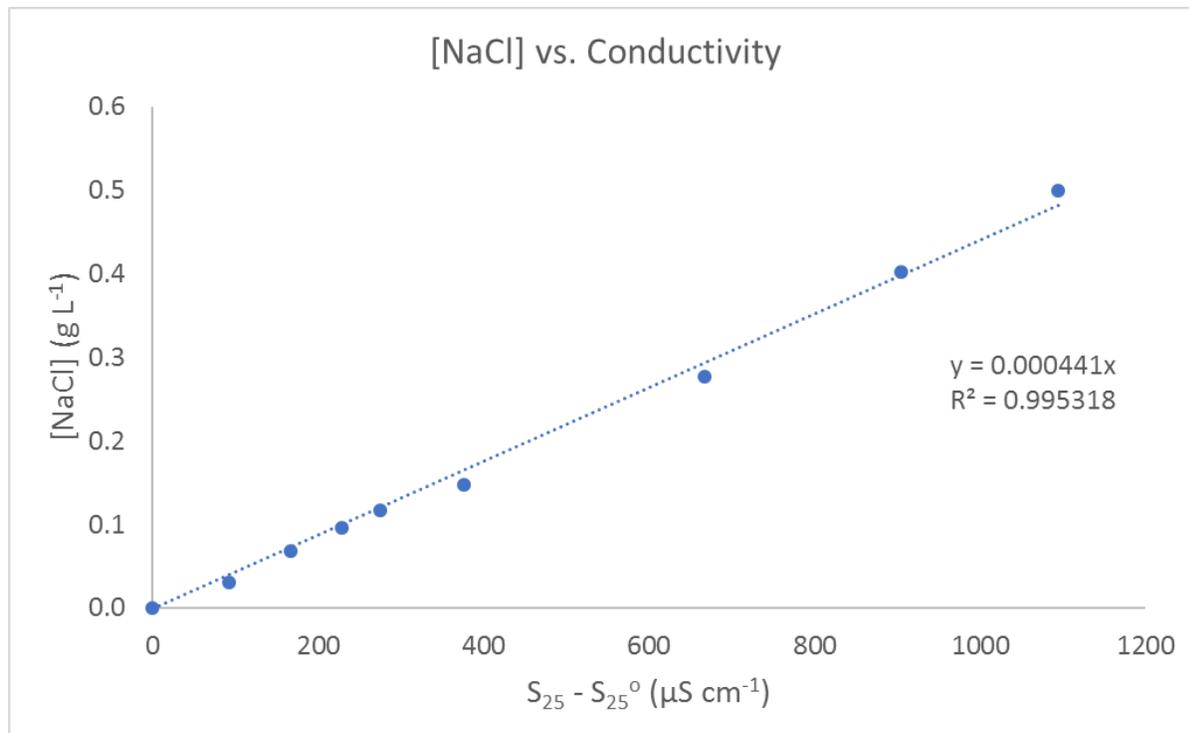
This appendix explains the process of determining a relationship between the measured conductivity of stream water and the concentration of salt, NaCl. A relationship between conductivity and [NaCl] needed to be established so that the temperature-corrected conductivity data collected with the HOBO loggers could be converted to [NaCl]. Then, these data plotted against time (breakthrough curve) were used to calculate the stream discharge at each measurement station in the October 2018 and February 2019 stream sampling.

First, small quantities of NaCl (Fisher Chemical brand sodium chloride, certified ACS crystalline, LOT 183676) were measured out in plastic weigh dishes. The mass of each empty dish was measured and recorded, and then the mass was determined for eight small quantities of NaCl ranging from 0.0103 to 0.0629 g in order to have NaCl concentrations at varying intervals between 0.0302 and 0.5004 g L<sup>-1</sup>. The balance used to measure mass was an Ainsworth M-310 with an accuracy of 0.001 g.

For the experiment, a quantity of stream water collected from the site was measured out into a 500 mL glass beaker. After stirring, a HOBO logger was inserted into the stream water in the beaker to collect background conductivity ( $S_{25}^{\circ}$ ). Then, the conductivity logger was removed and a known mass of NaCl was added. After stirring, the logger was once again inserted to collect conductivity data for the new concentration of NaCl. These steps were repeated for each of the eight known quantities of NaCl. Each time the logger was inserted into the stream water solution, it was left to collect data for at least one minute, at one-second intervals. The mean conductivity during this time period was used for each data point.

Then, the eight data points, along with the initial conductivity reading (for 0 g L<sup>-1</sup> of NaCl), were plotted after first subtracting the background conductivity from each measurement

(Fig. C1). A linear regression was performed, and the slope of the trendline was determined to be 0.000441. This slope was used to convert temperature-corrected conductivity measurements to [NaCl] for the stream discharge measurements taken during the October 2018 and February 2019 stream sampling campaigns, as described in Section 5.



**Figure C1.** Graph showing [NaCl] versus conductivity above background levels for Georgia Branch stream water.

## **APPENDIX D. Estimating Total Streambed Areas**

Total streambed areas for the streams sampled in summer 2018 and October 2018 were estimated based on width measurements made within the study reaches (Table D1) and the feature lengths in ArcMap from the streams vector layer [USGS NHD 2019]. For the four streams sampled in summer 2018, the channel width at each point cluster location was used (two clusters of three points for each stream study site). For the two streams sampled in October 2018, the channel width measured at each streambed sampling point location was used. For the streams that were sampled during both sampling periods (Georgia Branch and Mines Creek), the average channel widths from the October 2018 measurements were used in place of the summer 2018 width measurements.

**Table D1.** Channel width measurements for the streams sampled in summer 2018 and October 2018: Georgia Branch (GB), Mines Creek (MC), Willis Creek (WC), and Kirks Mill Creek (KM). MC280 could not be used as a streambed sampling point (hard clay streambed) but is still included in the channel width measurements.

<b>Stream Channel Width (m)</b>					
	<b>GB</b>		<b>MC</b>	<b>KM</b>	<b>WC</b>
<b>GB20</b>	1.2	<b>MC0</b>	1.0	2.0	2.9
<b>GB50</b>	1.0	<b>MC40</b>	1.1	3.0	3.0
<b>GB70</b>	1.4	<b>MC80</b>	2.0		
<b>GB90</b>	2.4	<b>MC120</b>	1.6		
<b>GB110</b>	3.0	<b>MC160</b>	4.0		
<b>GB130</b>	1.3	<b>MC200</b>	2.4		
<b>GB150</b>	1.9	<b>MC240</b>	2.7		
<b>GB170</b>	2.1	<b>MC280</b>	1.2		
<b>GB190</b>	3.3	<b>MC320</b>	2.3		
<b>GB210</b>	3.5				
<b>GB230</b>	2.0				
<b>GB250</b>	2.4				
<b>GB270</b>	2.3				
<b>GB290</b>	1.5				
<b>GB330</b>	1.3				
<b>GB370</b>	3.3				
<b>GB410</b>	2.7				
<b>GB450</b>	1.0				
<b>GB490</b>	1.1				
<b>GB530</b>	1.4				
<b>GB570</b>	1.5				
<b>GB610</b>	3.2				
<b>Mean</b>	<b>2.0</b>		<b>2.0</b>	<b>2.5</b>	<b>3.0</b>