QUANTIFYING EXCHANGEABLE DISSOLVED ORGANIC CARBON (EDOC) IN HURRICANE HARVEY (2017) AND HURRICANE FLORENCE (2018) RAINWATER

By

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ABSTRACT

Exchangeable dissolved organic carbon (EDOC) refers to the pool of dissolved organic compounds that are available for diffusion across the air-water interface. This study addresses the rainwater organic carbon deposited on land by two hurricanes, Hurricanes Harvey (2017) and Florence (2018). Samples were analyzed for total dissolved carbon (TDC), non-purgeable organic carbon (NPOC), and dissolved inorganic carbon (DIC). From the TDC, NPOC, and DIC measurements, EDOC was calculated as follows: EDOC = TDC – NPOC – DIC. In Pearland, Texas, during Hurricane Harvey TDC ranged from approximately 0.31-3.6 mg L^{-1} (VWA 1.8 mg L^{-1}) and NPOC ranged from 0.26-3.6 mg L^{-1} (VWA 0.99 mg L^{-1}). Calculations for EDOC yielded results of 0-0.9 mg L^{-1} (VWA 0.88 mg L^{-1}). In League City, Texas, TDC ranged from approximately 0.65-1.9 mg L^{-1} (VWA 1.1 mg L^{-1}) and NPOC ranged from 0.37-1.6 mg L^{-1} (VWA 0.82 mg L^{-1}). Calculations for EDOC yielded results of 0.2-0.3 mg L^{-1} (VWA 0.28 mg L^{-1}). For both Pearland and League City, EDOC comprised approximately 30% of the total dissolved carbon in rainwater. Samples collected during Hurricane Florence in Winterville, North Carolina, had TDC concentrations of approximately 0.2-1.1 mg L^{-1} (VWA 0.8 mg L^{-1}), NPOC concentrations of 0.5-0.6 mg L-1 (VWA 0.53 mg L^{-1}), and EDOC concentrations of 0.3-0.6 mg L^{-1} (VWA 0.37 mg L^{-1}). EDOC comprised approximately 53% of the total dissolved

carbon in rainwater in Winterville during Hurricane Florence. In general, though rainwater NPOC varied as a function of rainfall, EDOC concentrations remained steady throughout each storm. Lack of EDOC measurements in rainwater DOC may lead to large errors in the air/water exchange of carbon and to an incomplete understanding of the global carbon cycle. Moving forward it is imperative that this carbon pool be quantified and characterized for its composition and reactivity.

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List of Symbols and Abbreviations

aq	aqueous
DOC	Dissolved Organic Carbon
DIC	Dissolved Inorganic Carbon
EDOC	Exchangeable Dissolved Organic Carbon
H	Henry's Law Constant
HTCO	High Temperature Catalytic Oxidation
l	liquid
NPOC	Non-Purgeable Organic Carbon
OC	Organic Carbon
POC	Particulate Organic Carbon
TC	Total Carbon
TDC	Total Dissolved Carbon
TOC	Total Organic Carbon
VOC	Volatile Organic Carbon
VWA	Volume-Weighted Average

I. <u>Introduction</u>

The atmosphere of the Earth plays an important role in global cycling of various constituents, including carbon. Atmospheric carbon concentrations affect both air quality and climate (Muller et al., 2008; O'Dowd et al., 2004; Williams, 2004). Organic carbon (OC) is ubiquitous in the atmosphere, with both biogenic and anthropogenic sources (Figure 1). Some of this atmospheric OC is oxidized to inorganic forms (e.g., CO, CO_2), but a majority is removed from the atmosphere by wet and dry deposition (Dachs et al., 2005). Air-water gas exchange, by both volatilization (water-to-air) and diffusion (air-to-water), can also significantly affect OC concentrations in the atmosphere and on land and surface waters (Dachs et al., 2005; Hauser et al., 2013; Liss and Slater, 1974; Ruiz-Halpern et al., 2010).
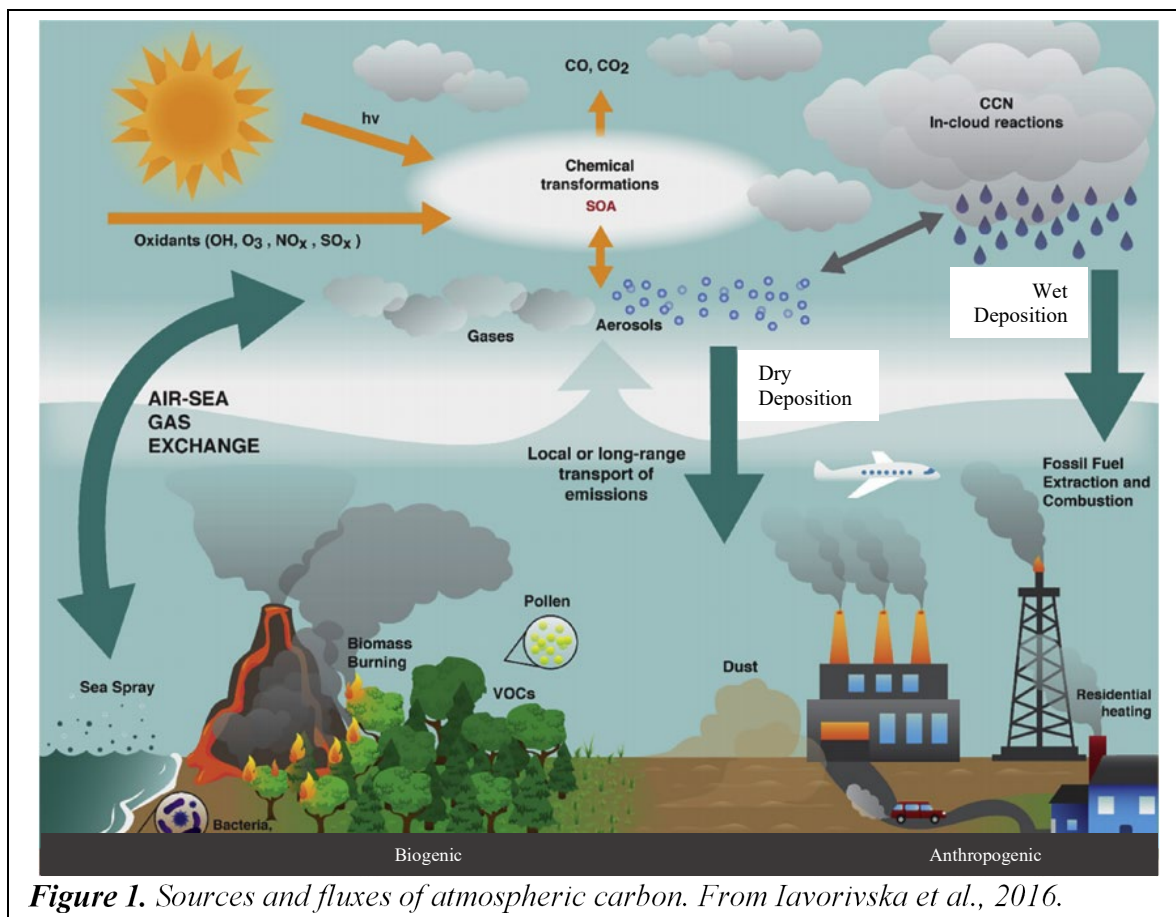
Figure 1. *Sources and fluxes of atmospheric carbon. From Iavorivska et al., 2016.*

In 2000, Willey et al. published a seminal study quantifying dissolved organic carbon (DOC) in rainwater. The researchers estimated that DOC in rainwater, with a global flux of $4.3 \pm 1.5 \times 10^{14}$ g C yr^{-1}, was greater than the rainwater flux of nitric and sulfuric acids combined. About half of the DOC in rainwater is readily available to microbes, and it could be an important source for fueling secondary productivity (Avery et al., 2003; Bao et al., 2018). In fact, rainwater DOC has been found to be up to seven times more bioavailable than river water (Avery et al., 2003). Indeed, a recent global inventory of DOC in rainwater by Iavorivska et al. (2016) underscores the importance of understanding the role of the atmosphere in the biogeochemical cycling of OC.

Current estimates of rainwater DOC flux do not include exchangeable dissolved organic carbon (EDOC). In general, non-purgeable organic carbon (NPOC) which does not include the more labile and volatile EDOC, is measured and used as the operational definition for DOC in rainwater (Avery et al., 2003; Avery et al., 2006; Mullaugh et al., 2013; Willey et al., 2000). However, not specifically quantifying EDOC leads to an inaccurate representation of DOC biovailability in surface waters. For example, EDOC in rainwater may be contributing to heterotrophic respiration in remote areas which only receive nutrient and carbon inputs via atmospheric processes (Jurado et al., 2008). Moreover, EDOC, if revolatilized, may affect the atmosphere directly by acting as precursors to secondary organic aerosols. These secondary organic aerosols may act as cloud condensation nuclei as well as aerosol pollutants. Thus, omission of EDOC in atmospheric carbon budgets may lead to a misunderstanding of the role of this compartment in the global carbon cycle.

There have been some studies aimed at quantifying EDOC in surface waters which have determined that EDOC can comprise a significant portion of the total DOC pool (Figure 2). For

example, Dachs et al. (2005) found EDOC in the coastal and open ocean surface for the subtropical northeastern Atlantic was 30-40% of the total DOC concentration. The fraction of EDOC in their samples was measured by purging 1L of seawater with ultra-high purity nitrogen for 5-8 minutes and equilibrating the outgased products in 40 mL of acidified pure high

Figure 2. Studies that have measured EDOC have determined that EDOC comprised 11-56% of the total DOC.
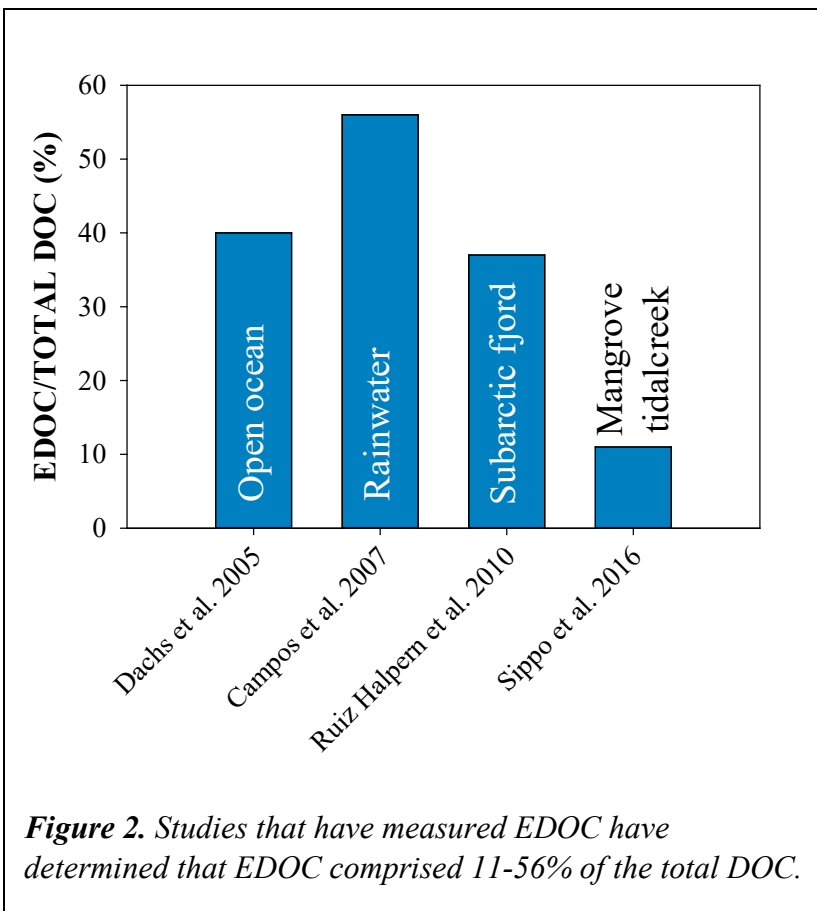
pressure liquid chromatography grade water. That water was then analyzed for dissolved organic carbon. Using a similar method, Ruiz-Halpern et al. (2010) determined that EDOC concentrations represented approximately 37% of the total DOC of a water column within a subarctic fjord. A similar method was used to determine EDOC concentrations and flux in outwelling mangrove waters, where EDOC was found to comprise approximately 11% of the DOC with a flux from the atmosphere to the ocean of 3.1 Tg C yr^{-1} (Sippo et al., 2016).

There have been few studies aimed at quantifying EDOC in rainwater, albeit using slightly different methods compared to the studies noted above. Studies by Campos et al. (2007) and Godoy-Silva et al. (2017) used high temperature catalytic oxidation (HTCO) to determine that EDOC (incorrectly identified as VOC in their studies) represented as much as 53-56% of the

total DOC pool in precipitation in São Paulo, Brazil. The air in São Paulo State is impacted by biomass burning at sugar cane plantations, which may have led to the high DOC and EDOC at their sampling sites via vapor phase scavenging of low molecular weight compounds during precipitation (Campos et al., 2007; Godoy-Silva et al., 2017; Leister and Baker, 1994). In Wilmington, North Carolina, Avery et al. (2009) analyzed six rain events for DOC and EDOC. Only one sample had detectable concentrations of EDOC. However, in that one sample EDOC comprised 20% of the total DOC.

The objective of this research was to quantify EDOC in two Atlantic Hurricanes. Wet deposition of OC from hurricanes can transmit massive amounts of marine OC into terrestrial ecosystems in relatively short amounts of time (Mitra et al., 2013; Mullaugh et al., 2013; Raymond, 2005). Moreover, hurricane events are expected to intensify in the coming years due to climate change (Knutson et al., 2015; Trenberth et al., 2018). Thus, quantifying EDOC in coastal rainwater, specifically hurricanes, can improve our understanding of air-water fluxes of OC and help refine estimates of those fluxes.

I quantified rainwater EDOC in two major coastal storms, Hurricane Harvey (2017) and Hurricane Florence (2018). Numerous researchers have quantified DOC concentration and composition in hurricane rainwater (Willey et al., 2000; Mitra et al., 2013; Mullaugh et al., 2013). However, there have been no attempts to quantify EDOC in hurricane rainwater. Hurricanes and their associated excessive winds and precipitation over short periods of time, can serve as end-members for atmospheric carbon loading Earth's surface.

Analytical approaches to quantifying EDOC in seawater and by association, rainwater, are not trivial. Thousands of organic compounds are known to exist in the atmosphere and in surface waters (Kawamura & Kaplan, 1983; Graedel & Mcgill, 1986; Cottrell et al., 2013).

Quantifying each exchangeable organic compound in rainwaters or surface waters is an unrealistic endeavor given the sheer number and variety of organic compounds in rainwater and surface water. However, the gas sparging method used by Dachs et al., (2005), Ruiz-Halpern et al., (2010), and Sippo et al., (2017), is extremely similar to the method I developed for this research in order to quantify EDOC in rainwater from Hurricanes Harvey and Florence. *Therefore, I hypothesized that the EDOC in Hurricane Harvey and Hurricane Florence, operationally-defined as described below, would be similar in magnitude with other studies quantifying EDOC in surface waters (10-40% of the total dissolved organic carbon).*

II. Background and Theory

A. The Role of the Atmosphere in the Global Carbon Cycle

Carbon is exchanged between many different reservoirs, including the ocean, land, and atmosphere (Figure 3). Carbon transfer occurs on a variety of time scales. For example, the residence time of carbon in the atmosphere (days to years) is much shorter than the residence time of carbon in deep ocean sediments (millenia) (Carlson et al., 2001). While the ultimate fate of carbon is burial in the lithosphere, proper accounting of carbon requires an examination of the pathways that different carbon molecules travel between reservoirs. Atmospheric carbon is a diverse, sometimes highly reactive carbon reservoir (Figure 1).
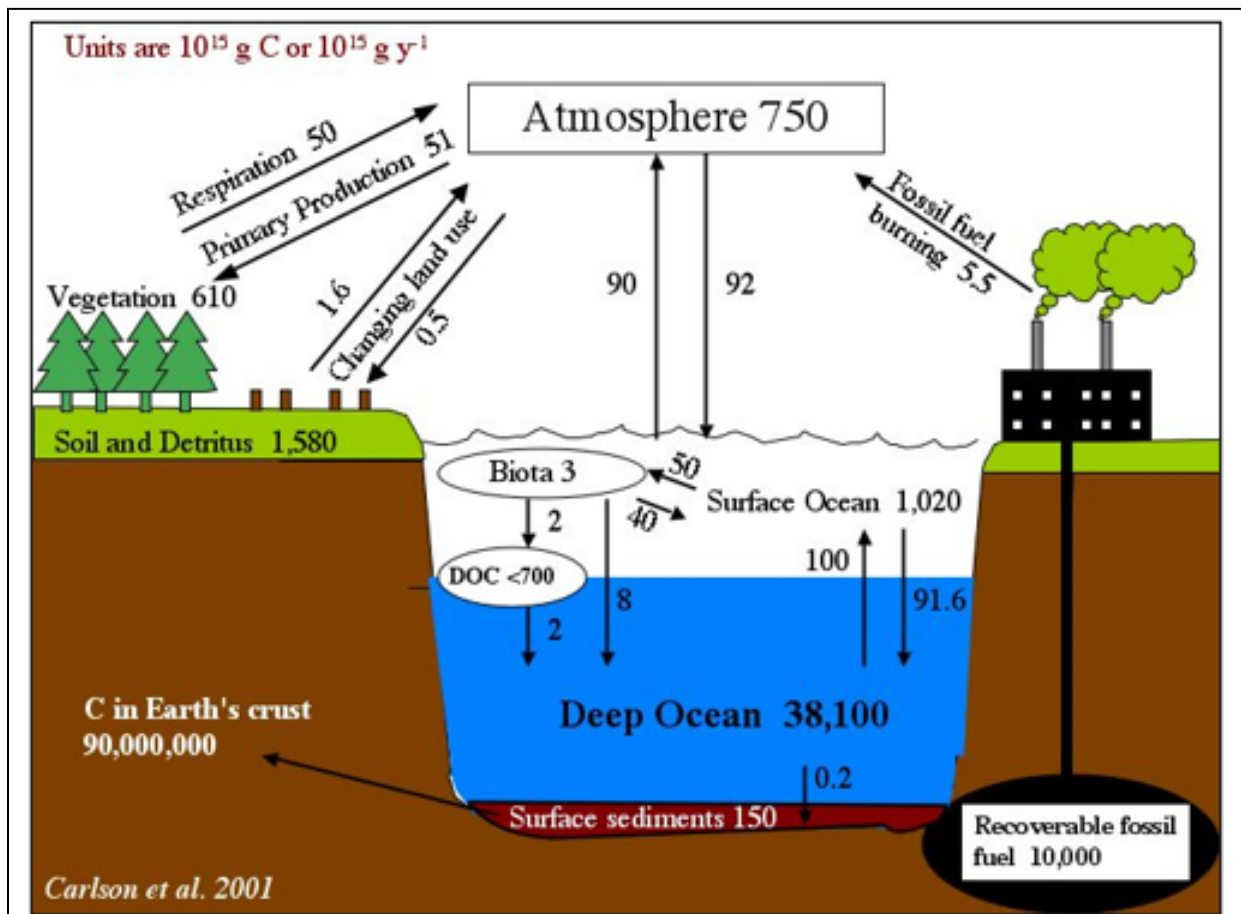
Figure 3. *Major reservoirs and exchanges of pools of carbon on Earth. From Carlson et al., 2001.*

Carbon in the Earth's atmosphere is comprised of both inorganic and organic pools. Total organic carbon (TOC) consists of particulate organic carbon (POC) and dissolved organic carbon (DOC). Particulate organic carbon refers to constituents that are insoluble in water. POC and DOC are isolated using operationally-defined size-cutoffs via filtration or via centrifugation. Dissolved organic carbon (defined as organic compounds that are soluble in water) potentially makes up 80 – 84% of the TOC in the atmosphere (Likens et al., 1983; Willey et al., 2000; Iavorivska et al., 2016).

Carbon exchange between the atmosphere and the Earth's surface occurs via three mechanisms: dry deposition, wet deposition, and gas exchange. Dry deposition occurs as particulates and gases from the atmosphere settle to the surface of Earth as a function of gravitational settling (Warneck, 2000). Wet deposition refers to material arriving at the surface of the Earth, scavenged by precipitation. Of the approximately 1108 Tg C yr^{-1} of gaseous and particulate OC emitted to the atmosphere, between 305 and 950 Tg C are deposited to the surface of Earth annually (Iavorivska et al., 2016a). Wet atmospheric deposition is the dominant removal mechanism for this OC (Kanakidou et al., 2005), annually depositing between 306 and 580 Tg of atmospheric OC to the surface of Earth (Avery et al., 2009; Iavorivska et al., 2016; Kanakidou et al., 2012; Willey et al., 2000). In rainwater, 67-98% of OC is water-soluble (Iavorivska et al., 2017).

Organic carbon is incorporated into precipitation by particle or vapor-phase scavenging, either during droplet formation (in-cloud scavenging) or as the hydrometeor falls through the atmosphere (below-cloud scavenging) (Scott, 1981; Slinn, 1983) (Figure 4). Physical processes controlling bulk aerosol particle scavenging include meteorology and cloud physics of each rain event as well as size and chemical composition of the particles (Ligocki et al., 1985). In contrast,
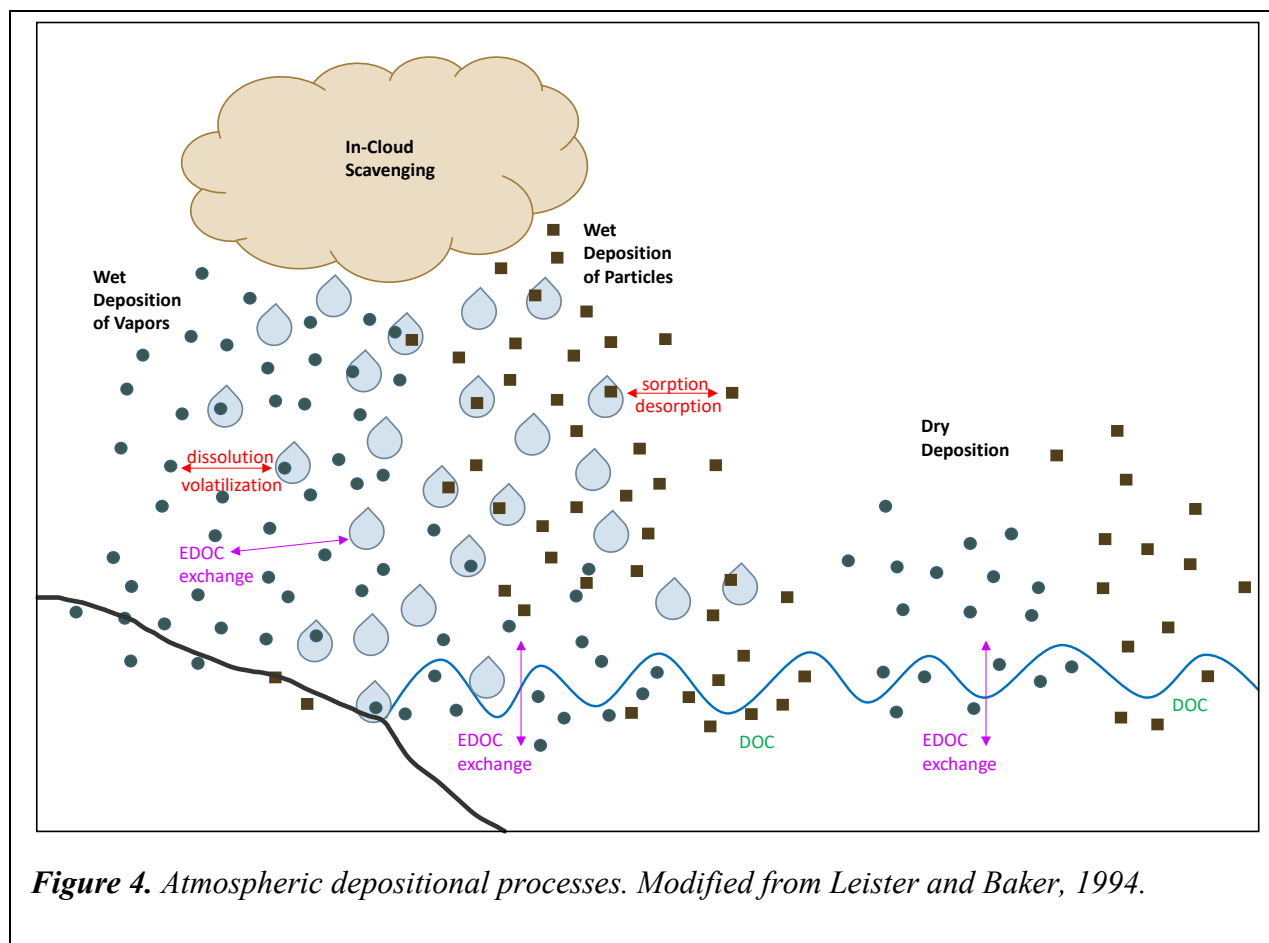
Figure 4. *Atmospheric depositional processes. Modified from Leister and Baker, 1994.*

concentrations and fluxes of atmospheric gases scavenged by precipitation are dependent on surface area of water droplets, concentrations of the compounds, and their physicochemical characteristics such as Henry's law constant, which is influenced by temperature (Bidleman, 1988; Junge, 1977; Ligocki and Pankow, 1989).

Organic compounds comprising rainwater and oceanic DOC can be subdivided into non-exchangeable and exchangeable portions, depending on Henry's Law constants. Non-exchangeable DOC (also called non-purgeable OC or NPOC) stays in solution, while exchangeable DOC (EDOC) is the semi-volatile, purgeable portion that is available for diffusion across the air-water interface (Dachs et al., 2005) (Figures 4 & 5). In other words, NPOC is typically particle-associated and EDOC is either a gas or in a truly dissolved form (Ligocki and

Pankow, 1989; Poster and Baker, 1996). Hauser et al. (2013) separated EDOC from volatile organic compounds (VOCs) based on Henry's Law constants (H). VOCs have high H (H $\gg$ 0.1 L atm mol^{-1}) and are water-limited, meaning they prefer to remain in a gaseous state. EDOC compounds have low Henry's law constants (H $\ll$ ~0.1 L atm mol^{-1}), and are therefore air-limited, favoring a dissolved state. Scavenging by rainwater preferentially removes low-H compounds from the atmosphere because of their higher aqueous solubility (Ligocki et al., 1985).
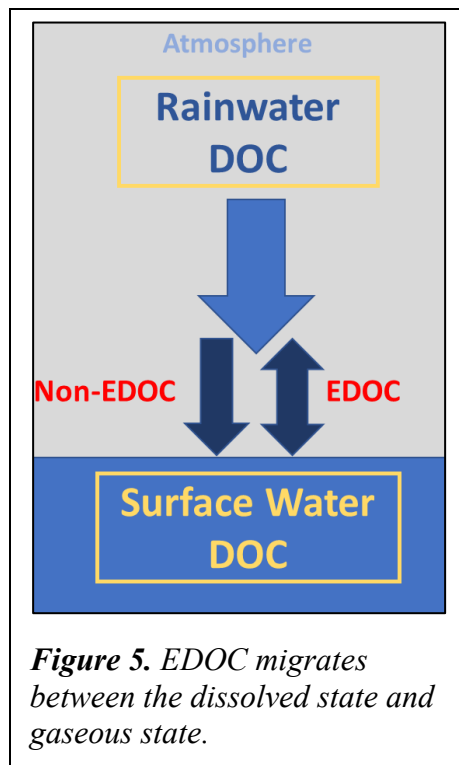
Figure 5. EDOC migrates between the dissolved state and gaseous state.

B. Sources of Atmospheric Carbon

There are two dominant sources of OC to the atmosphere: 1) biogenic emissions (Guenther et al., 1995), which account for 70-80% of the primary OC sources (De Gouw and Jimenez, 2009; Donahue et al., 2009), and 2) anthropogenic emissions (Piccot et al., 1992). The biogenic fraction contains both marine and terrestrial OC; sources include sea spray, dust, biological debris, biogenic gases, forest fires, pollen, and spores. Oceanic gross primary production alone accounts for nearly half of the total global primary production (Del Giorgio and Williams, 2005). Anthropogenic primary sources include fossil fuel combustion, human-induced biomass burning, direct industrial release, cooking operations, and agriculture emissions. Approximately 25% of DOC in rainwater collected in coastal areas of North Carolina and Connecticut, USA is derived from fossil fuel sources (Avery et al., 2009; Avery et al., 2006; Raymond, 2005).

C. Quantifying EDOC

In this research, I developed a method to quantify EDOC in rainwater using a Shimadzu TOC Analyzer. I applied a "scaffolding" approach to a rainwater sample, either eliminating or isolating a pool of carbon, and then measuring and accounting for the residual pool of carbon in

Figure 6. *Schematic for EDOC isolation in a rainwater sample. Process 1 – fitration, 2 – acidification, and 3 – gas sparging.*
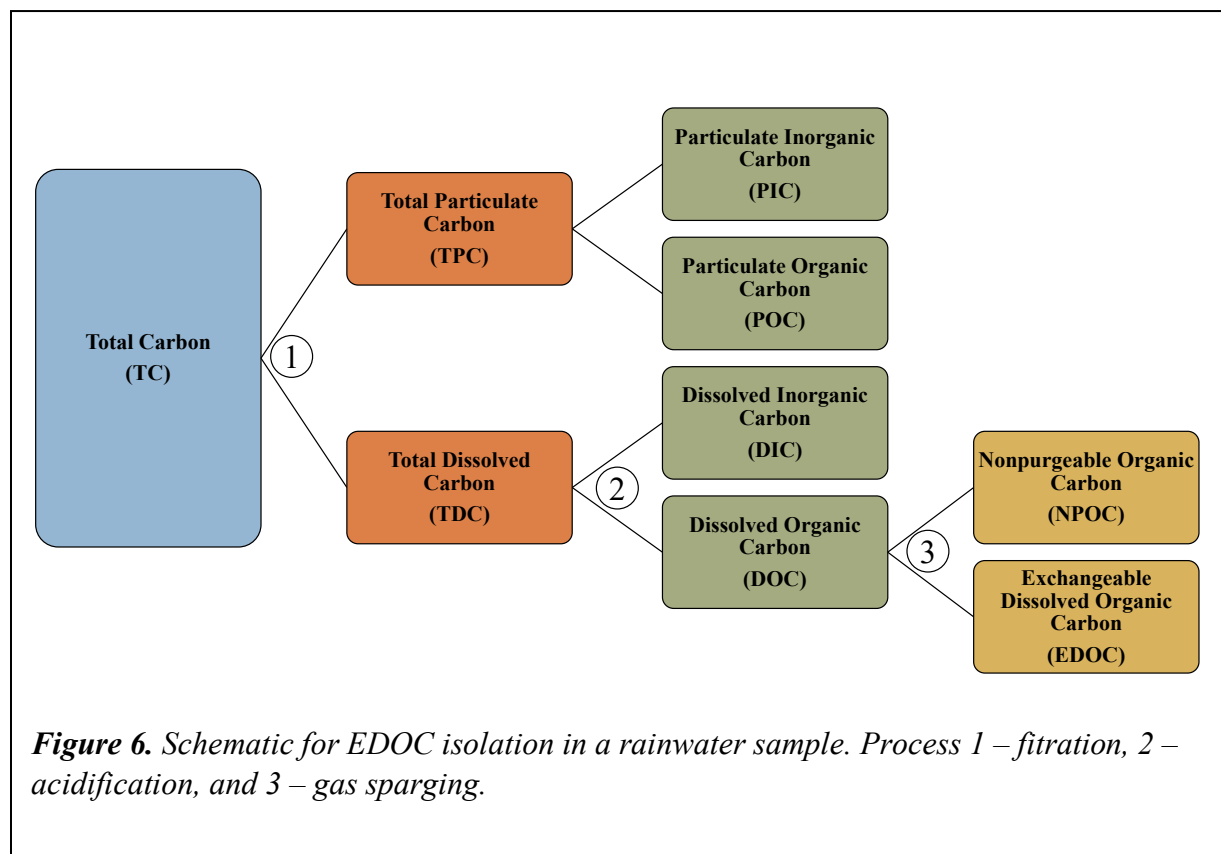
that sample (Figure 6). Total carbon (TC) includes all of the particulate (TPC) and dissolved (TDC) carbon present in an aqueous sample. Mathematically, the relationship of these pools of carbon can be represented by Equation 1:

$$TC = TPC + TDC \qquad \text{[Equation 1]}$$

The TPC is separated from TDC by filtration or centrifugation. TPC consists of the subfractions particulate inorganic carbon (PIC) and particulate organic carbon (POC) (Equation 2), but will not be addressed in this study.

$$TPC = POC + PIC \qquad \text{[Equation 2]}$$

Conventionally, the cutoff for particulate and dissolved materials has been operationally-defined via filtration using 0.7 µm, 0.45 µm, or 0.2 µm pore size cutoff filters (Campos et al., 2007; Willey et al., 2000; Coelho et al., 2008; Godoy-Silva et al., 2017; Mead et al., 2013; Mullaugh et al., 2013). The filtrate, or total dissolved carbon (TDC) was quantified by high temperature catalytic oxidation (HTCO) and includes the soluble portions of both dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC).

$$TDC = DIC + DOC \qquad \text{[Equation 3]}$$

Species of DIC include CO_2, HCO_3^-, H_2CO_3, and CO_3^{2-}. Acidifying a water sample converts all DIC to CO_2 as demonstrated by the carbonate equilibria reactions shown below (Stumm and Morgan, 1996).

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \qquad \text{[Equation 4]}$$
$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3 \ (aq) \qquad \text{[Equation 5]}$$
$$H_2CO_3 \ (aq) \rightarrow CO_2(aq) + H_2O \ (l) \qquad \text{[Equation 6]}$$
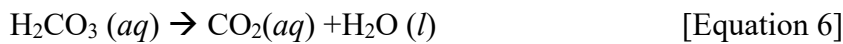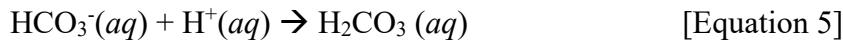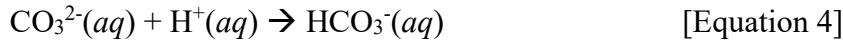
Thus, acidification and sparging can be used to remove DIC from an aqueous solution. However, the goal of this research was to determine EDOC, and acidification and sparging of a water sample would also volatilize EDOC along with dissolved inorganic carbon (DIC). Therefore, DIC was independently quantified in each sample for this study.

There are thousands of organic compounds that comprise DOC in natural systems. This paper focuses on two subcategories of DOC rather than attempting to quantify any individual compounds. NPOC is the DOC fraction that is commonly measured by HTCO. To measure NPOC, a water sample is first acidified to ~ pH 2 to convert DIC to CO_2 and then sparged to

remove DIC (see Equations 4-6). EDOC is the fraction of DOC that moves between the gaseous

phase and the aqueous phase. Since EDOC is likely removed from solution during traditional

HTCO analysis, it must be indirectly quantified. Currently, there is no standard method for

quantifying EDOC. EDOC has typically been determined on open ocean samples using a multi-

chamber gas sparging apparatus (Dachs et al., 2005; Hauser et al., 2013; Ruiz-Halpern et al.,

2010). However, such an apparatus does not lend itself to being used for lower volume water

samples such as typically isolated in rainwater. High temperature catalytic oxidation has been

used for decades as an analytical method for measuring DOC in water (Sugimura and Suzuki,

1988). By sparging an acidified rainwater sample, EDOC is released from the solution, leaving

NPOC. Quantifying that NPOC and subtracting it as well as the DIC quantified earlier from

TDC, yields EDOC as shown in Equation 7.

$$EDOC = TDC - NPOC - DIC \qquad \text{[Equation 7]}$$

III. Materials and Methods

A. Hurricane Descriptions

Hurricanes Harvey (2017) and Florence (2018) were two of the wettest storms on record for the United States (Erdman, 2018). An assessment by Kunkel and Champion (2019) demonstrated that Hurricane Harvey was the largest precipitation event in the U.S. for the period 1949-2018 and Hurricane Florence was the seventh largest for the same period. From August 25-30, 2017, Hurricane Harvey (Category 4 on the Saffir-Simpson scale) delivered approximately 1.3×10^{14} liters of water to the United States. Large areas of Texas and Louisiana received 51 to 102 cm of rain (Fritz and Samenow, 2017). Windspeeds reached a maximum of 115 kt (213 km hr^{-1}) (Blake and Zelinsky, 2018). In 2018, Hurricane Florence (Category 1 on the Saffir-Simpson scale) deposited $\sim 3.0 \times 10^{13}$ liters on the Carolinas between September 13 and 17 (Moody, 2018), with some areas receiving more than 90 cm of rain (Kunkel and Champion, 2019). When Hurricane Florence made landfall, windspeeds were at 80 kt (148 km hr^{-1}) (Stewart and Berg, 2019). Both storms caused catastrophic flooding creating devastation in their paths (Blake and Zelinsky, 2018; Kunkel and Champion, 2019; Stewart and Berg, 2019).

B. Sample Collection

Rainwater samples from Hurricane Harvey were collected at three locations in Texas: 1) in League City, approximately 35 km inland from the Gulf of Mexico, 2) in Pearland, approximately 60 km north of the Gulf of Mexico and 3) at College Station, on the southwestern side of Houston (Figure 7A). Each sample contained 20-1000 mL of
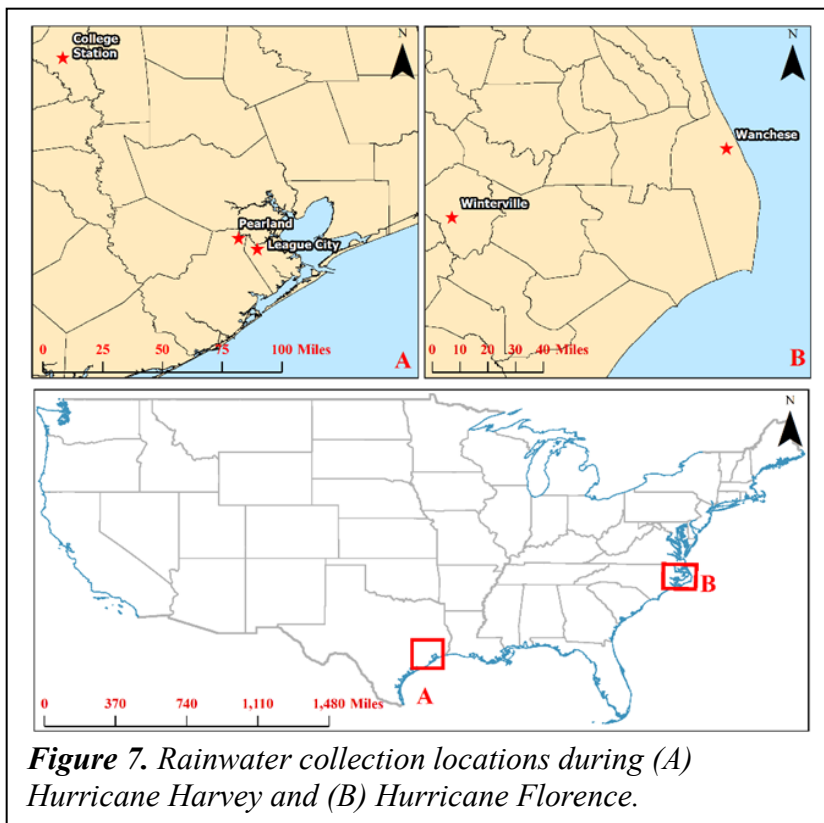
Figure 7. Rainwater collection locations during (A) Hurricane Harvey and (B) Hurricane Florence.

rainwater. Nineteen samples were collected during Hurricane Florence: eleven in Kitty Hawk, NC and eight in Winterville, NC (Figure 7B). Samples were collected approximately every six hours in Winterville, while collection times in Kitty Hawk were variable. Water was collected in pre-cleaned (washed with detergent, tap water and distilled water) glass jars or cleaned high density polyethylene (HDPE) bottles. Rainwater collected from each event was immediately frozen.

C. Back Trajectory Analysis

Airmass back trajectories for each storm were calculated using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT) model (Rolph et al., 2017; Stein et al., 2015), providing the path air masses traveled prior to sampling collection. The concentrations of

organic carbon from Hurricane Harvey and Hurricane Florence rainwater were compared to storm trajectory .

D. Quantification of each Pool of Carbon in Rainwater

Two different Shimadzu TOC instruments were used in this study. Hurricane Harvey rainwater was analyzed with a Shimadzu TOC-L. Additional analyses and Hurricane Florence rainwater were analyzed with a Shimadzu TOC-Vcph/cpn. As noted in the Results, the higher sensitivity of the TOC-L results in it being a better instrument for quantifying EDOC in rainwater. The TOC-Vcph/cpn is likely not sensitive enough to provide accurate results, even when using the high sensitivity catalyst. The limit of detection for the NPOC method was 0.1mg C L^{-1} and the limit of detection for the TDC method was 0.4 mg C L^{-1}. Both limits were calculated using the LINEST function in Excel.

DIC

Water samples were acidified with 2N HCl to convert DIC to $CO_2(g)$. Samples were analyzed with an Apollo Scitech (AS-C3) DIC Analyzer at the Virginia Institute of Marine Science, Gloucester Point, VA. The AS-C3 Analyzer quantified DIC by purging CO_2 from the water using carbon-free gas (Apollo Scitech, Newark, DE, United States). Dissolved CO_2 was quantified as $CO_2(g)$ using an LI-7000 CO_2 analyzer, a non-dispersive, infrared gas analyzer (LI-COR, Lincoln, Nebraska, United States). The detection limit of the instrument was 0.002 µmol L^{-1} (0.00003 mg L^{-1}) as calculated by the LINEST function in Excel.

TDC and NPOC

Prior to analysis, samples were thawed in a refrigerator at 4 °C. Normally the carbon analyses were completed within one or two days of thawing out the sample. Unfortunately, the COVID-19 pandemic prevented additional analyses beginning in March 2020, in the middle of a

thawing sequence. Thus, some samples could not be analyzed for carbon in a timely manner, and the results from those samples were compromised. Additional details of those compromised samples are noted in Appendix B.

Hurricane Harvey water samples were filtered with VWR polyethersulfone 0.2 μm pore size, 2 cm diameter, syringe filters. Filtering with the 0.2 μm pore size filters removed any particulate organic carbon (POC) that was present in the Hurricane Harvey water samples, ensuring that only the dissolved fraction was being measured. Hurricane Florence water samples were filtered with 0.7 μm pore-size GF/F filters attached to a Buchner funnel filtration apparatus. Since 0.7 μm pore-size GF/F filters were used for the Hurricane Florence water samples, it is possible that colloids were present in the filtrate. A tiered analysis was performed on each sample using either a Shimadzu TOC-Vcph/vpn analyzer or Shimadzu TOC-L analyzer. A high-sensitivity platinum catalyst was necessary because carbon concentrations in rainwater with marine origins are extremely low, often less than 2 mg L^{-1} (Iavorivska et al., 2016a).

First, samples were analyzed for total dissolved carbon (TDC). This fraction included both organic and inorganic species of carbon. Samples were neither acidified nor sparged before TDC analysis. Next, samples were analyzed for non-purgeable organic carbon (NPOC). This fraction included only OC. The NPOC method includes acidification with 2N HCl and sparging steps at the beginning of organic carbon analysis to remove inorganic carbon (DIC) from solution. Typically, this is the method used for DOC analysis in rainwater and oceanic studies (Avery et al., 2004; Willey et al., 2000). By acidifying and sparging the samples, however, an unknown quantity of exchangeable components of DOC (EDOC) is also removed.

E. EDOC

EDOC was calculated based on measurements of TDC, NPOC, and DIC (EDOC = TDC – NPOC – DIC).

F. Calculating Rainwater Carbon Loading and Flux

Estimates of TDC, NPOC, EDOC loading in both Hurricane Harvey and Hurricane Florence were calculated by multiplying the volume-weighted average concentration (VWA), event rainfall, and county area (Harris County, TX and Pitt County, NC) (Equation 8). For Harvey, all numbers for the calculations are from the Pearland, TX data. For Florence, all numbers for the calculations are from the Winterville, NC data.

Storm Loading = VWA * total rainfall * county area   [Equation 8]

The VWA concentration of each carbon pool at each location was calculated by using the following equation:

$$\text{Concentration} = \sum_{i=1}^{n} \frac{C_i V_i}{V_T} \qquad \text{[Equation 9]}$$

where C_i is the concentration of one sample, V_i is the volume of one sample, and V_T is total volume of rainwater collected.

G. Quality Assurance/Quality Control

All glassware was decontaminated prior to use. Glassware was soaked in an Alconox bath for 24 hours and then rinsed with DI water. After drying, glassware was placed in an oven at 450°C for 4 hours.

A preliminary experiment was conducted in order to ensure that the polyethersulfone 0.2 µm syringe filters did not leach any carbon. Solutions of potassium hydrogen phthalate ranging in concentration from about 0.2 to 2.2 mg L^{-1} of carbon were created. Solutions were split into two aliquots, designated as A and B in Table 2. Each aliquot was subdivided further into unfiltered and filtered portions (Table 2). Samples marked for filtering were filtered with the syringe filters before analysis. Both filtered and unfiltered solutions were run via the NPOC method (acidified and sparged) with the Shimadzu TOC-L analyzer.

The polyethersulfone 0.2 µm syringe filters were cleaned using the following method. First, the syringe was triple rinsed with detergent, DI water, and DDI water. Next, DDI water was pulled into the syringe (taken from a separate container than the DDI used for initial washing) and then a filter was attached to the syringe. The filter was triple rinsed with DDI water. After the syringe and filter were cleaned, a sample vial was conditioned by running a small volume of sample through the syringe and filter and into the sample vial. The conditioning sample was gently swirled around the inside of the vial. The remaining liquid was then discarded. Finally, the sample was filtered into the sample vial, and the sample vial was immediately capped.

In order to determine if sample storage in a refrigerator affected sample carbon concentrations, solutions of p-cymene, methanol, and p-cymene in methanol (50% v/v) were made and stored in glass vials. Similarly, water from the Tar River, Greenville, NC was collected, filtered with pre-washed 0.7 µm GF/F filters, and also placed in glass vials. One subsample each of each solution and river water were immediately analyzed for total dissolved carbon on a Shimadzu TOC-Vcph/cpn. The remaining sample aliquots were frozen to be analyzed at later dates.

Aqueous solutions of several organic standards varying in molecular weight (and by default Henry's Law) were quantified for carbon. Several analyses were conducted using methanol, acetaldehyde, and p-cymene. These compounds varied in molecular weight, vapor pressure, and Henry's Law constant (Table 1). Comparison of the quantity of EDOC in these standards should yield a systematic trend with $EDOC_{p\text{-}cymene} > EDOC_{acetaldehyde} > EDOC_{methanol}$, based on Henry's Law constants.

Table 1. Analysis of Organic Standards

Sample	Molecular Weight	Vapor Pressure (Pa)	Henry's Law Constant (Pa m^3 mol^{-1} at 25°C)
p-cymene	134.218	204	805
Acetaldehyde	44.052	121300	6.69-8.90
Methanol	32.042	16210	0.45

IV. Results

A. Results of QA/QC and Method Validation

Table 2 lists the results from the syringe filtering experiment. Due to the small sample size and non-parametric distribution of data, a Wilcoxon signed-rank test was used to assess the probability that the syringe filters leached carbon. The test suggested that the results between filtered and unfiltered samples were statistically insignificant ($p > 0.05$). Therefore, the polyethersulfone 0.2 µm syringe filters did not leach any carbon into the samples. Results from the storage test are presented in Figure 8. Over the period analyzed, there was not a significant change in TDC for any of the samples.

Table 2. Syringe filter leaching

Sample	Unfiltered (mg C L^{-1})	Filtered (mg C L^{-1})
1A	0.189 (0.015)	0.209 (0.023)
1B	0.159 (0.017)	0.232 (0.009)
2A	0.468 (0.017)	0.564 (0.011)
2B	0.455 (0.007)	0.538 (0.017)
3A	1.18 (0.015)	1.16 (0.034)
3B	1.52 (0.030)	1.53 (0.026)
4A	2.11 (0.018)	2.07 (0.011)
4B	2.36 (0.042)	2.21 (0.029)

Figure 8. *A storage test of p-cymene, methanol, a p-cymene/methanol mixture, and river water illustrate no significant change in TDC concentrations during storage in a freezer over five months.*
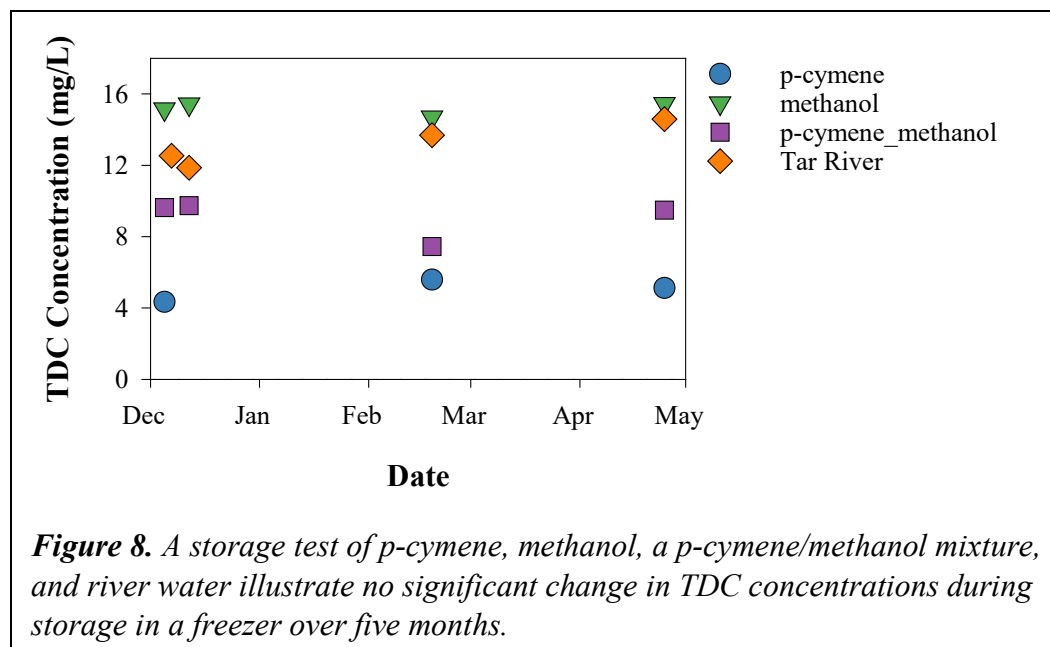
B. Hurricane Harvey

B1. Back Trajectory Analysis

The air-mass back trajectory at the onset of rainwater collection (August 25, 2017) in Pearland, TX indicates a mix of marine (Gulf of Mexico and Caribbean Sea) and terrestrial (Florida and mid-west United States) influences (Figure 9A). By early morning on August 26, 2017 the air masses transitioned to predominantly originating in the Gulf of Mexico and Caribbean Sea. The source of the air masses did not change for several hours until the evening of August 27, 2017 (Figures 9B, 9C). At that time, back trajectory analysis suggests that Hurricane Harvey was being influenced by air masses from the southeastern United States and the Atlantic Ocean (Figure 9D). The influence from the east continued during the remainder of the storm. Indeed, by the time rainwater collection ceased on August 29, 2017, there was no influence from the Caribbean Sea or Gulf of Mexico and air in the storm was exclusively derived from the eastern United States and the Atlantic Ocean (Figure 9E).

NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 26 Aug 17
GDAS Meteorological Data

A

Job ID: 120001   Job Start: Fri Oct 16 21:06:53 UTC 2020
Source 1   lat.: 29.540000   lon.: -95.267778   height: 500 m AGL

Trajectory Direction: Backward   Duration: 72 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 22 Aug 2017 - GDAS1
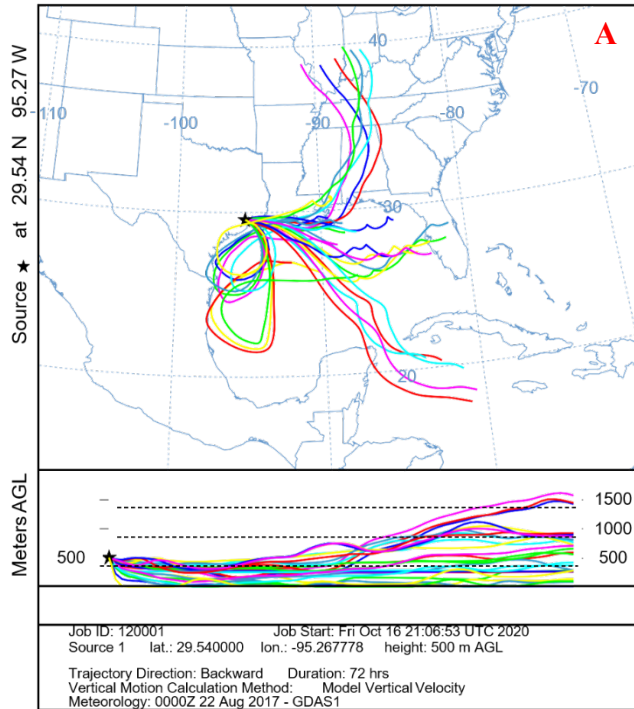
NOAA HYSPLIT MODEL
Backward trajectories ending at 0700 UTC 26 Aug 17
GDAS Meteorological Data

B

Job ID: 187729   Job Start: Mon Oct 19 16:00:08 UTC 2020
Source 1   lat.: 29.540000   lon.: -95.267778   height: 500 m AGL

Trajectory Direction: Backward   Duration: 72 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 22 Aug 2017 - GDAS1
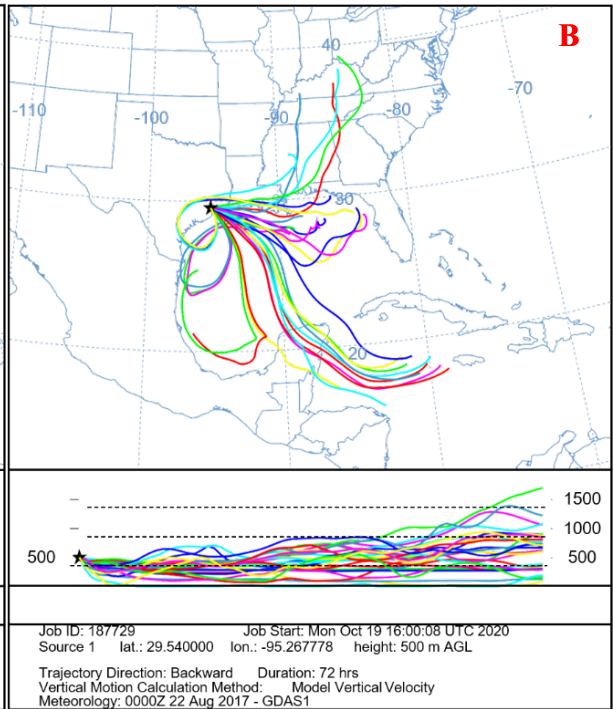
NOAA HYSPLIT MODEL
Backward trajectories ending at 1700 UTC 27 Aug 17
GDAS Meteorological Data

C

Job ID: 188646   Job Start: Mon Oct 19 16:30:59 UTC 2020
Source 1   lat.: 29.540000   lon.: -95.267778   height: 500 m AGL

Trajectory Direction: Backward   Duration: 72 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 22 Aug 2017 - GDAS1
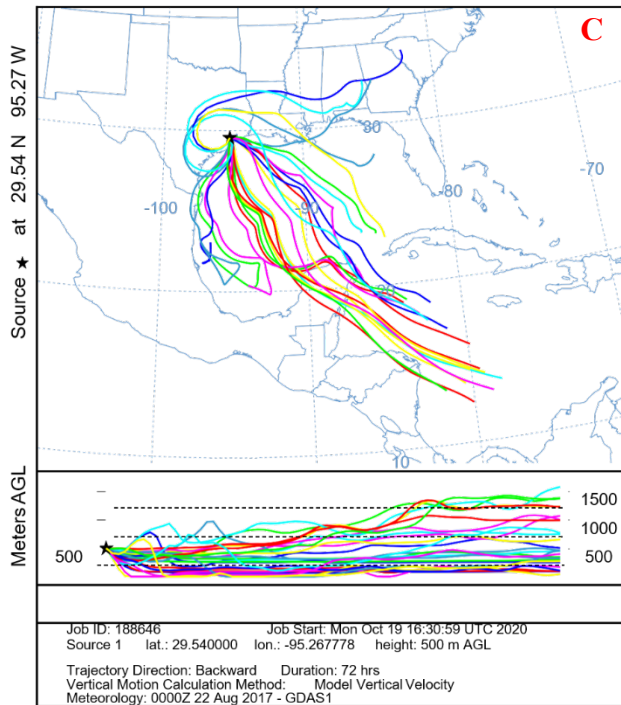
NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 28 Aug 17
GDAS Meteorological Data
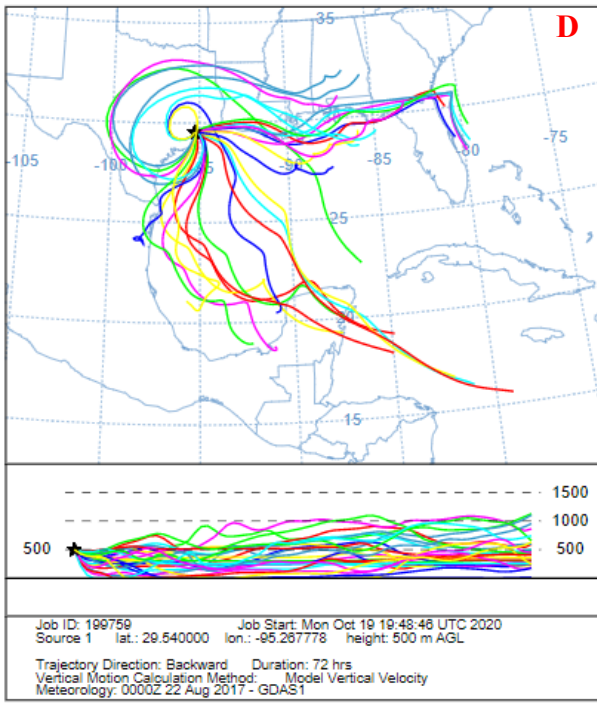
D

Job ID: 199759   Job Start: Mon Oct 19 19:48:46 UTC 2020
Source 1   lat.: 29.540000   lon.: -95.267778   height: 500 m AGL

Trajectory Direction: Backward   Duration: 72 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 22 Aug 2017 - GDAS1

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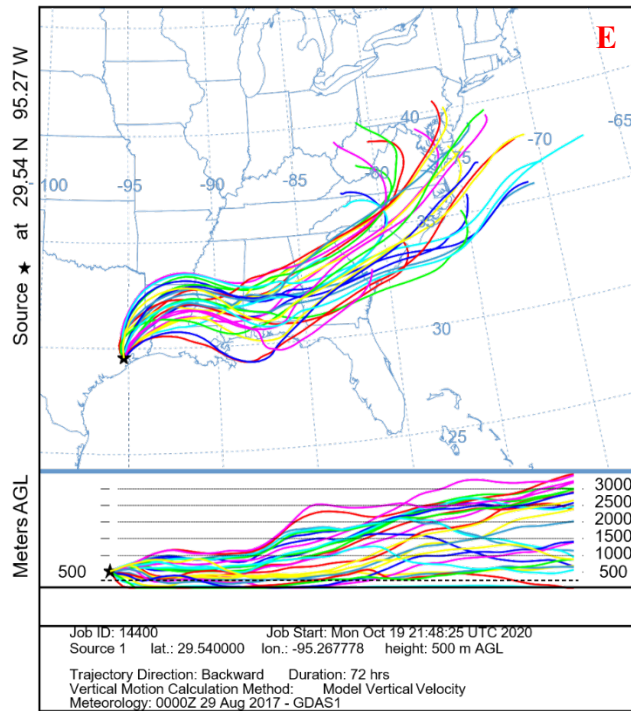
Figure 9. *Back trajectory analysis of air masses in Pearland, TX, during Hurricane Harvey. A-E denote various time periods throughout the storm.*

Figure 10. *Concentration of TDC, NPOC and EDOC as a function of time in (A) Pearland, (B) League City, and (C) College Station, Texas during Hurricane Harvey. In graph (A) the air mass transition is demarcated. The samples in section (1) have air masses dominated by the Gulf of Mexico and Caribbean Sea, the samples in section (2) have air masses dominated by the continental U.S. and the Atlantic Ocean. (T) marks samples that were collected during the transition between (1) and (2).*

B2. Rainwater Carbon Abundance

Twenty-five rainwater samples were analyzed from Pearland, Texas during Hurricane Harvey (Table 3). Collection began on the evening of 8/25/17 and continued until the rain ceased on the evening of 8/29/17 (Figure 10A). TDC concentrations ranged from 0.38-3.6 mg L^{-1}, with a volume-weighted average (VWA) of 1.8 mg L^{-1} in Pearland rainwater. NPOC was the dominant pool of carbon in all but one sample collected in Pearland (Figure 10A).

NPOC concentrations ranged from 0.26-3.6 mg L^{-1}, with a VWA of 0.99 mg L^{-1}. EDOC values

ranged from 0 to 0.88 mg L^{-1}, excluding Sample H20, an outlier with a calculated EDOC

concentration of about 11 mg L^{-1} (Figure 10A, Figure 11). EDOC comprised ~ 29% of TDC in

general. If Sample H20 is removed from the percentage calculations, EDOC made up about 8%

of TDC in Pearland rainwater (Figure 11).

Eight samples were collected in League City, Texas (Table 4). Collection began the night

of 8/26/17 and ended two days later on 8/28/17 (Figure 10B). In League City, TDC was 0.65-1.9

Figure 11. *Percentage of NPOC and EDOC in each sample collected during Hurricane Harvey. DIC was negligible compared to NPOC and EDOC.*
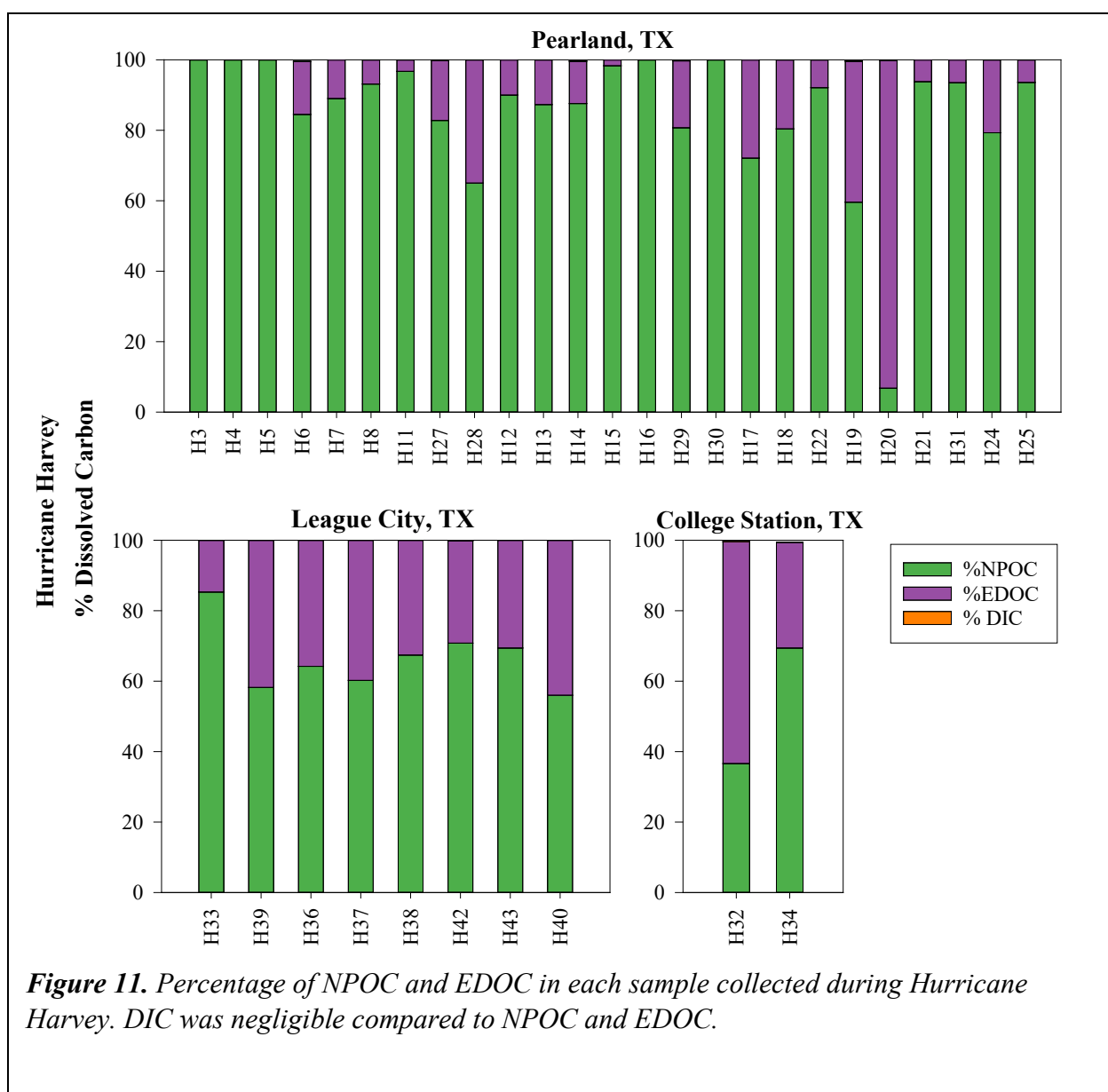
mg L^{-1} (VWA 1.1 mg L^{-1}) and NPOC was 0.37-1.6 mg L^{-1} (VWA 0.82 mg L^{-1}). The first sample

collected in League City, H33, had the highest NPOC concentration (1.61 mg L^{-1}) and the

remaining rainwater samples did not vary greatly (0.37-0.59). EDOC concentrations ranged from

0.22-0.34 mg L^{-1}. On average, TDC comprised 70% NPOC and 30% EDOC for all samples in

League City (Figure 11).

Only two rainwater samples were collected in College Station during Hurricane Harvey

(Table 5). The TDC in H32 and H34 were 2.3 and 0.8 mg L^{-1}, respectively; and NPOC of H32

and H34 were 0.83 and 0.56 mg L^{-1}, respectively. EDOC was 63% and 30% of the TDC in H32

and H34, respectively (Figure 11).

In general, EDOC concentrations showed no relationship with NPOC concentrations

across each station. DIC was negligible in all rainwater samples at all locations analyzed from

Hurricane Harvey, comprising <0.5% of TDC. Thus, EDOC was essentially the difference

between TDC & NPOC (TDC – NPOC)

Table 3. Pearland carbon concentrations and precipitation

Sample	Date Collected	Time Collected	TDC (mg L^{-1})	DIC (mg L^{-1})	NPOC (mg L^{-1})	EDOC[2] (mg L^{-1})	Precipitation[3] (cm)
H1	8/25/2017	13:00-18:00	10.4 (0.052)[4]	0.0004 (4e-4)	10.70 (0.037)[4]	ND[1]	1.6
H3	8/25/2017	18:01-23:59	3.45 (0.042)	0.0004 (8e-7)	3.46 (0.032)	Calculation <0	1.6
H4	8/26/2017	00:01-04:40	3.60 (0.084)	0.0003 (1e-6)	3.63 (0.050)	Calculation <0	1.3
H5	8/26/2017	00:01-04:40	3.50 (0.011)	0.0003 (3e-7)	3.63 (0.050)	Calculation <0	1.3
H6	8/26/2017	4:40-08:45	0.996 (0.008)	0.0003 (6e-7)	0.842 (0.005)	0.15 (0.01)	4.8
H7	8/26/2017	4:40-08:45	0.779 (0.024)	0.0003 (1e-6)	0.693 (0.014)	0.085 (0.028)	4.8
H8	8/26/2017	08:45-12:35	1.27 (0.016)	0.0004 (3e-5)	1.18 (0.011)	0.088 (0.020)	0.91
H9	8/26/2017	12:35-20:00	23.5 (0.123)[4]	0.0004 (4e-5)	ND[1]	ND[1]	0.10
H10	8/26/2017	20:00-21:50	8.00 (0.025)[4]	0.0004 (3e-5)	ND[1]	ND[1]	4.2
H11	8/26/2017	21:50-22:50	1.80 (0.023)	0.0003 (4e-6)	1.74 (0.031)	0.059 (0.038)	10
H27	8/26/2017-8/27/2017	22:50-03:05	0.308 (0.010)	0.0002 (1e-6)	0.255 (0.009)	0.053 (0.013)	12
H28	8/26/2017-8/27/2017	22:50-03:05	0.518 (0.012)	0.0003 (3e-6)	0.337 (0.008)	0.18 (0.02)	12
H12	8/27/2017	03:07-08:25	1.34 (0.014)	0.0003 (1e-5)	1.20 (0.008)	0.13 (0.02)	8.4
H13	8/27/2017	08:25-12:47	0.708 (0.022)	0.0002 (6e-7)	0.618 (0.004)	0.90 (0.03)	5.0
H14	8/27/2017	08:25-12:47	0.878 (0.021)	0.0004 (2e-6)	0.770 (0.014)	0.11 (0.03)	5.0
H15	8/27/2017	12:47-17:05	1.57 (0.014)	0.0003 (2e-6)	1.54 (0.025)	0.026 (0.029)	1.8
H16	8/27/2017	17:03-23:22	2.19 (0.020)	0.0002 (2e-6)	2.74 (0.007)	Calculation <0	2.7
H29	8/27/2017-8/28/2017	23:27-06:50	2.99 (0.031)	0.0003 (1e-6)	2.41 (0.043)	0.58 (0.05)	1.1
H30	8/27/2017-8/28/2017	23:27-06:50	3.22 (0.062)	0.0003 (8e-7)	3.40 (0.035)	Calculation <0	1.1
H17	8/28/2017	06:50-9:30	0.710 (0.010)	0.0002 (1e-5)	0.512 (0.011)	0.20 (0.02)	5.7
H18	8/28/2017	09:30-10:41	0.439 (0.004)	0.0003 (1e-6)	0.353 (0.012)	0.086 (0.013)	2.4
H22	8/28/2017	9:30-10:41	0.849 (0.017)	0.0006 (1e-5)	0.782 (0.021)	0.067 (0.080)	2.4
H19	8/28/2017	10:41-13:52	2.19 (0.041)	0.002 (3e-4)	1.31 (0.023)	0.88 (0.05)	5.9
H20	8/28/2017	13:52-18:00	12.1 (0.085)	0.02 (3e-4)	0.822 (0.008)	11 (0.09)	6.9
H21	8/28/2017	18:00-21:34	0.642 (0.007)	0.0005 (1e-5)	0.602 (0.015)	0.039 (0.017)	5.4
H31	8/28/2017-8/29/2017	21:34-00:34	0.762 (0.007)	0.0002 (2e-5)	0.712 (0.017)	0.049 (0.018)	4.2
H24	8/29/2017	7:20-12:09	0.699 (0.015)	0.0004 (9e-7)	0.554 (0.008)	0.14 (0.02)	2.4
H25	8/29/2017	12:09-18:48	1.53 (0.025)	0.0003 (2e-6)	1.43 (0.006)	0.10 (0.03)	0.71

[1]Not able to be determined due to low sample volume.
[2]EDOC measurements include error propagated across each variable in equation 7.
[3]Precipitation data obtained from the Harris County Flood Warning website. Location 150:150 Clear Creek @ Country Club Drive.
[4]Analysis was completed on the sample that was thawed 2/27/20; insufficient rainwater remaining to complete another analysis.

Table 4. League City carbon concentrations and precipitation

Sample	Date Collected	Time Collected	TDC (mg L^{-1})	DIC (mg L^{-1})	NPOC (mg L^{-1})	EDOC[1] (mg L^{-1})	Precipitation[2] (cm)
H33	8/26/2017-8/27/2017	19:30 -00:40	1.89 (0.031)	0.0005 (4e-5)	1.61 (0.029)	0.28 (0.04)	28.3
H39	8/27/2017	00:40-08:20	0.729 (0.015)	0.0007 (3e-5)	0.425 (0.008)	0.30 (0.02)	23.7
H36	8/27/2017	08:20-14:00	0.650 (0.008)	0.0007 (1e-5)	0.418 (0.025)	0.23 (0.03)	7.0
H37	8/27/2017	14:00 -22:30	0.850 (0.017)	0.0006 (4e-5)	0.512 (0.007)	0.34 (0.02)	6.2
H38	8/27/2017-8/28/2017	22:30 -10:40	0.882 (0.017)	0.0006 (3e-5)	0.594 (0.012)	0.29 (0.02)	4.9
H42	8/28/2017	10:40 -14:30	0.760 (0.009)	0.0007 (2e-6)	0.538 (0.007)	0.22 (0.01)	4.9
H43	8/28/2017	14:30-20:50	0.758 (0.016)	0.0004 (3e-5)	0.526 (0.015)	0.23 (0.02)	9.2
H40	8/28/2017	20:50 -23:25	0.658 (0.009)	0.0013 (3e-5)	0.369 (0.011)	0.29 (0.01)	6.8

[1]EDOC measurements include error propagated across each variable in equation 7.
[2]Precipitation data obtained from the Harris County Flood Warning website. Location 1076:1076 Birch Creek @ Riley Road.

Table 5. College Station carbon concentrations and precipitation

Sample	Date Collected	Time Collected	TDC (mg L^{-1})	DIC (mg L^{-1})	NPOC (mg L^{-1})	EDOC[2] (mg L^{-1})	Precipitation[3] (cm)
H32	8/25/2017-8/26/2017	16:00-08:00	2.27 (0.049)	0.01 (2e-6)	0.831 (0.021)	1.4 (0.05)	8.3
H34	8/26/2017	08:00-12:00	0.800 (0.015)	0.0004 (2e-5)	0.556 (0.014)	0.24 (0.02)	1.0
H35	8/26/2017	12:00-13:35	ND[1]	0.0009 (9e-7)	ND[1]	ND[1]	0

[1]Not able to be determined due to low sample volume.
[2]EDOC measurements include error propagated across each variable in equation 7.
[3]Precipitation data obtained from the Harris County Flood Warning website. Location 110:110 Clear Creek @ I-45.

B3. Concentration vs. Precipitation

Figure 12. *Carbon concentration verses cumulative precipitation in Pearland, TX during Hurricane*
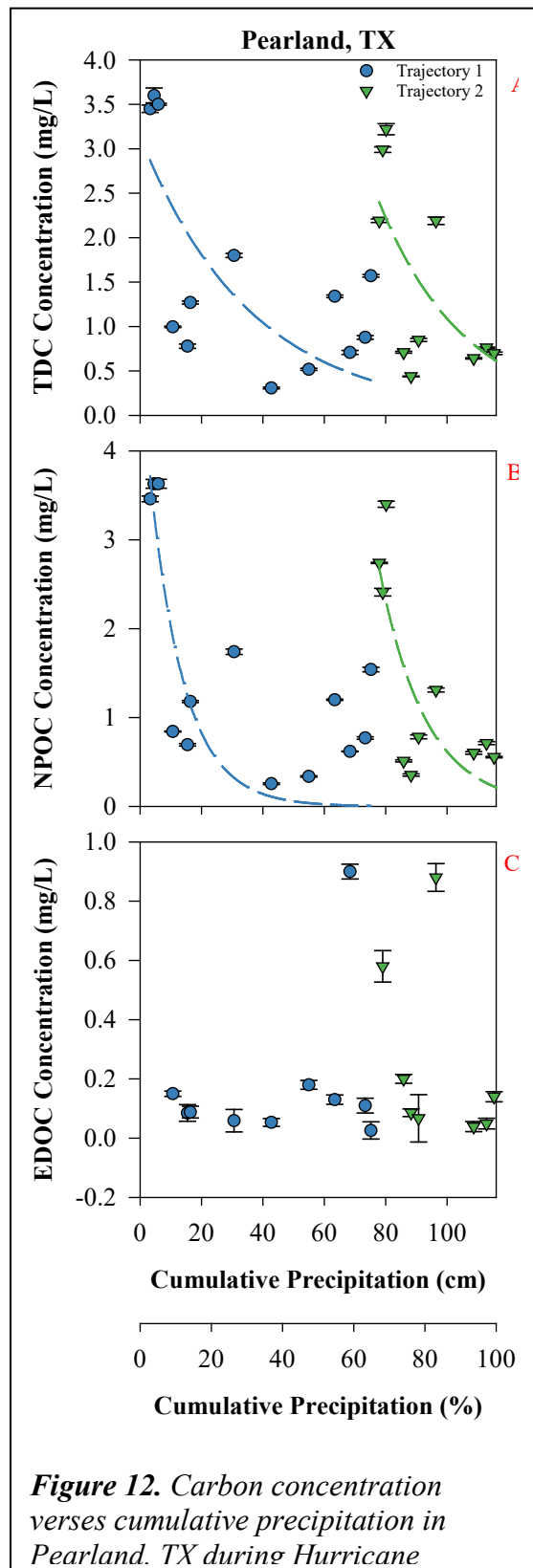
In Pearland, TX, concentrations of TDC and NPOC varied as a function of cumulative precipitation. TDC and NPOC, each at 3.6 mg L^{-1}, were highest at the start of precipitation. An exponential decay regression demonstrates that the carbon in rainwater was diluted as a function of precipitation (Figure 12A). In contrast, EDOC ranges from 0 to 11 mg L^{-1} and does not change as a function of cumulative precipitation. Note that H20 (EDOC = 11 mg L^{-1}) is not included in Figure 12, as it is an outlier. The TDC and NPOC concentrations at this site were related to the source of the air masses, as indicated by the back trajectory analyses. The change in concentrations of TDC and NPOC as a function of cumulative precipitation at this site generally follow a dilution pattern where concentration decreases as a function of cumulative precipitation; however, there are two distinct decay curves (Figures 12A & 12B). Trajectory 1 corresponds to the beginning of the storm when the air masses were predominantly coming from the Caribbean Sea and Gulf of Mexico (Figure 9B). In contrast, Trajectory 2

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corresponds to the air masses which originated from the Atlantic Ocean and southeastern United States (Figure 9E). Concentrations for TDC and NPOC are <1 mg L^{-1} for H13 and H14, the last two samples collected before the transition in air mass direction. Samples H15 and H16 correspond to the air mass change on the afternoon of August 27. H15 had concentrations of about 1.5 mg L^{-1} of TDC and NPOC while H16 had concentrations >2 for both TDC and NPOC. H15 and H16 mark the transition between airmass sources. Samples H29 and H30 see a spike in concentrations when the airmass is coming from the southeastern U.S. and the Atlantic Ocean.

At the League City, TX site, TDC, NPOC and EDOC ranged from 0.65-1.9 mg L^{-1}, 0.37-1.6 mg L^{-1}, and 0.22-0.34 mg L^{-1}, respectively as a function of cumulative precipitation. Sample collection began in League City at 7:30 pm on August 26. The first sample, H33, has the highest concentration (NPOC = 1.6 mg L^{-1}). The remainder of the rainwater samples collected at League City after have similar TDC and NPOC concentrations. As noted for rainwater collected at the Pearland site, carbon concentration versus precipitation at this site also suggests a washout effect, with the majority of dissolved organic compounds being immediately scavenged at the beginning of the storm.
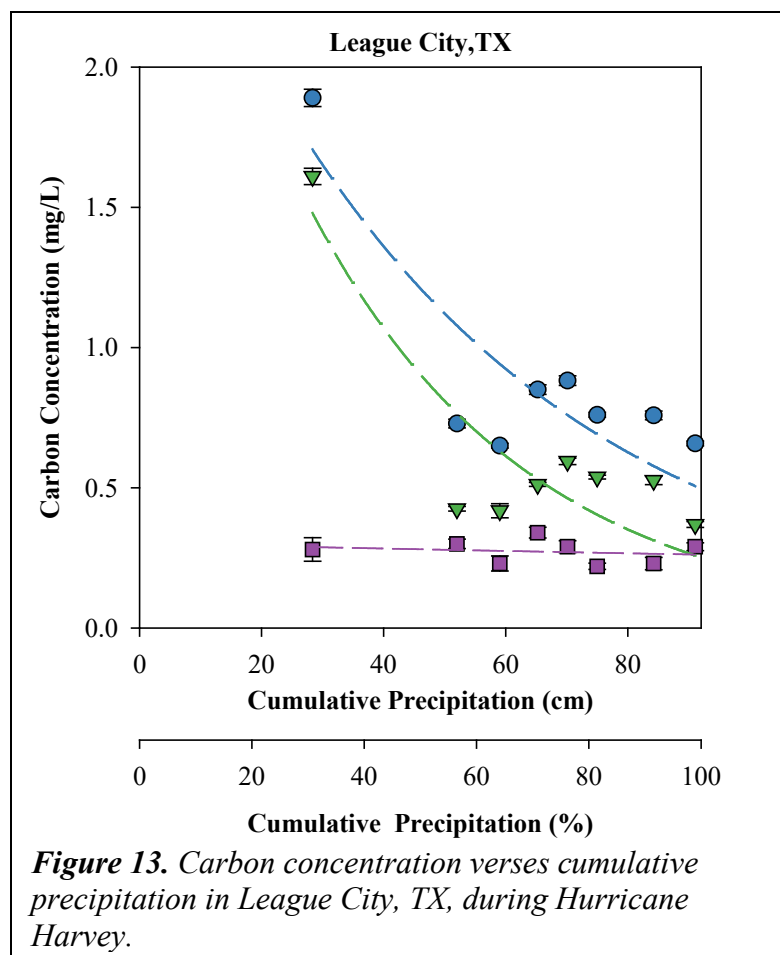
Figure 13. *Carbon concentration verses cumulative precipitation in League City, TX, during Hurricane Harvey.*

The correlation between NPOC concentration and air mass back trajectory in League City is not as evident as at the Pearland, TX site (Figure 13). There is an irregular and large gap in time between the first and second rainwater samples. Samples H33 (collected from 7:30 pm to 12:40 am on August 26th and 27th) and H39 (collected from 12:40-8:40 am on August 27th), corresponding to the beginning of the storm, had the most precipitation. During the time H33 was being collected at League City, ~28 cm of rain deposited over five hours. During the collection of H39, the next sample that was collected, ~ 24 cm of rain was deposited over eight hours at League City (Harris County Flood Control District). Thus, there were only two samples collected over a period in which 57% of the precipitation in League City occurred. Although, the period of time between H33 and H39 corresponds to when the source of air changed from the Caribbean Sea and Gulf of Mexico to the Atlantic Ocean and continental U.S, there were too few samples to correlate with the higher resolution air mass back trajectory analyses. As noted at the Pearland site, EDOC demonstrates no dependence on either precipitation amount or air mass back trajectory at the League City site.

Because only two samples were collected in College Station, no interpretation regarding air mass back trajectory and carbon concentrations are discussed.

C. Hurricane Florence

C1. Back Trajectory Analysis

Air masses originating over the northern Atlantic Ocean were the major contributors to Hurricane Florence, throughout the duration of the storm (Figure 14).
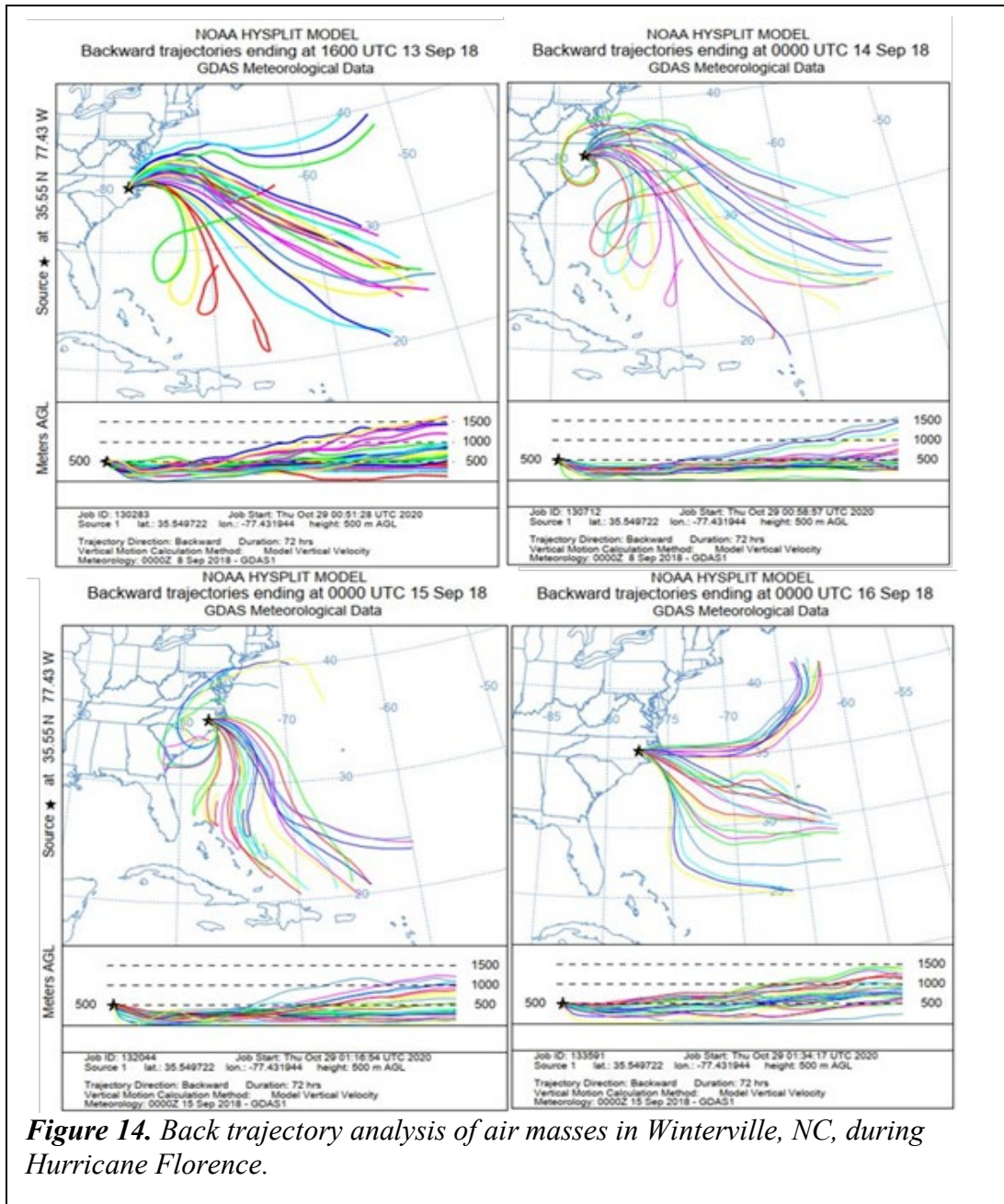
Figure 14. *Back trajectory analysis of air masses in Winterville, NC, during Hurricane Florence.*

C2. Rainwater Carbon Abundance

Figure 15 depicts carbon in Hurricane Florence rainwater samples. Much smaller volumes of rainwater were collected during Florence than in Harvey. Carbon in all rainwater

Figure 15. Time series concentration graph in Winterville, NC, during Hurricane Florence.
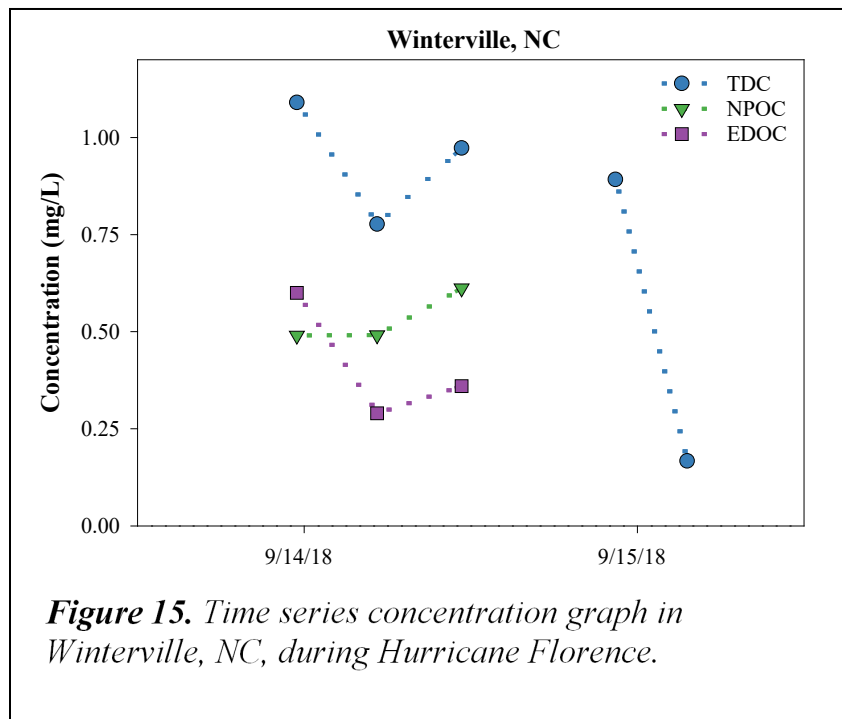
samples collected in Wanchese, NC during Hurricane Florence may have been degraded, as a result of the COVID-19 pandemic (see Appendix B). Only five samples from Winterville, NC were able to be analyzed for TDC which ranged from 0.17-1.1 mg L^{-1}

(VWA 0.8 mg L-1). Because of small volumes of rainwater, only three samples were able to be analyzed for NPOC, ranging from 0.49-0.61 mg L^{-1} (VWA 0.53 mg L^{-1}). EDOC concentrations ranged from 0.29-0.60 mg L^{-1} in those three samples. Because DIC was < 0.1% of TDC, DIC in Hurricane Florence rainwater was considered to be negligible and

Figure 16. Percentage of NPOC and EDOC in each sample collected during Hurricane Florence. As with Hurricane Harvey samples, DIC in Florence rainwater was was negliglbe relative to the other pools of carbon.
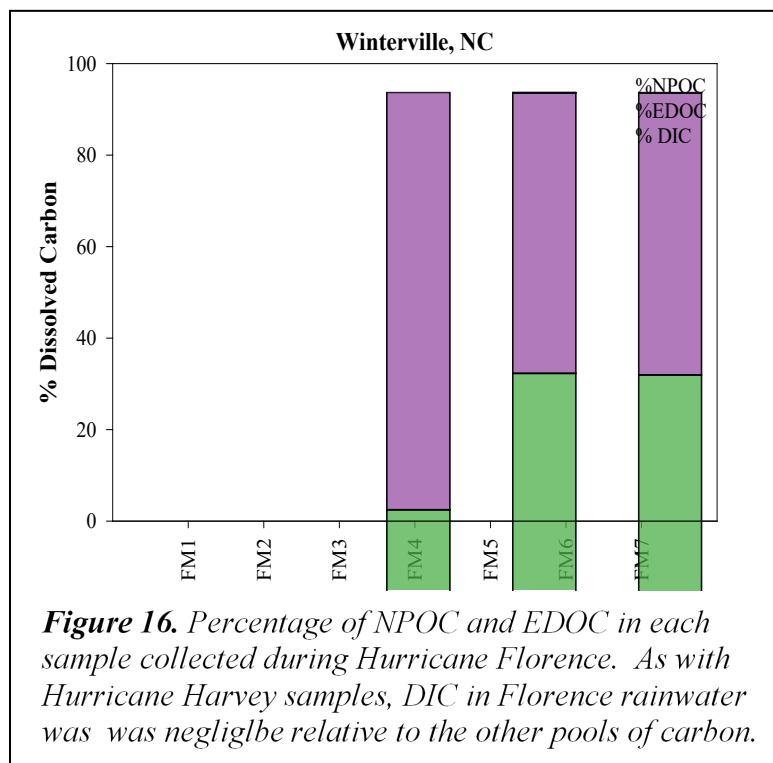
not included in the EDOC calculation. For the three samples analyzed for both TDC and NPOC, EDOC comprised approximately 44% of TDC (Figure 16).

Table 6. Winterville carbon concentrations and precipitation

Sample	Date Collected	Time Collected	TDC (mg L^{-1})	DIC (mg L^{-1})	NPOC (mg L^{-1})	EDOC[2] (mg L^{-1})	Precipitation (cm)
FM1	9/13/2018	12:26-12:38 & 14:32-20:46	13.8 (0.080)[3]	0.0007 (4e-6)	13.9 (0.026)[3]	ND[1]	0.76
FM2	9/13-9/14/2018	20:46-2:10	1.09 (0.015)	0.0006 (2e-6)	0.490 (0.007)	0.60 (0.02)	2.1
FM3	9/14/2018	2:10-8:20	0.777 (0.013)	0.0002 (2e-5)	0.491 (0.008)	0.29 (0.02)	5.0
FM4	9/14/2018	8:20-14:20	0.973 (0.007)	0.008 (5e-6)	0.612 (0.004)	0.36 (0.01)	2.9
FM5	9/14/2018	14:20-20:20	ND[1]	0.0003 (3e-5)	ND[1]	ND[1]	2.1
FM6	9/14/2018	2020:23:30	0.892 (0.016)	0.0003 (2e-6)	ND[1]	ND[1]	2.1
FM7	9/24-9/15/2018	23:30-7:30	0.167 (0.006)	0.0002 (2e-7)	ND[1]	ND[1]	1.4
FM8	9/15/2018	7:30-15:30	26.2 (0.420)[3]	0.0005 (5e-6)	ND[1]	ND[1]	2.5
FM9	9/15/2018	18:20-7:30	ND[1]	0.0003 (9e-6)	ND[1]	ND[1]	1.3
FM10	9/15/2018	7:30-18:00	ND[1]	0.0002 (4e-6)	ND[1]	ND[1]	0.71

[1]Not able to be determined due to low sample volume
[2]EDOC measurement includes the propagated error.
[3]Analysis was completed on the sample that was thawed 2/27/20; insufficient rainwater remaining to complete another analysis.

C3. Concentration vs. Precipitation

***Figure 17.** Carbon concentration verses cumulative precipitation in Winterville, NC, during Hurricane Florence.*
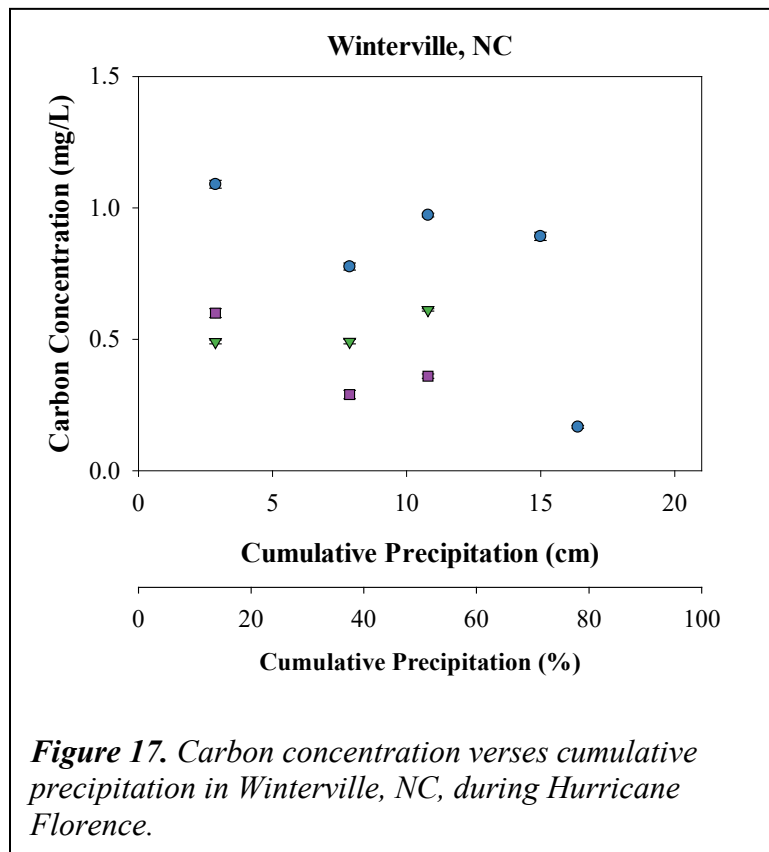
Figure 17 depicts trends in TDC, NPOC, and EDOC in Hurricane Florence rainwater samples. Although there are not enough samples to discuss trends in pools of rainwater carbon over time of collection, TDOC concentrations were between 0.17-1.1 mg L^{-1}, NPOC was between 0.49-0.61 mg L^{-1}, and EDOC was 0.29-0.60 mg L^{-1} for the samples collected.

D. Rainwater Carbon Loading and Flux

By multiplying the average concentrations of EDOC in rainwater by the total volume of rainwater deposited, estimates of the mass of TDC, NPOC, and EDOC deposited from each storm was calculated. Data from the Pearland, TX collection site indicate Hurricane Harvey deposited 2.1 g m^{-2} TDC, 1.1 g m^{-2} NPOC, and 1.0 g m^{-2} EDOC. Extrapolating to the whole area of Harris County (4600 km^2), Harvey deposited 9.6 Pg TDC, 5.3 Pg NPOC, and 4.7 Pg EDOC in the county. Hurricane Florence deposited 0.17 g m^{-2} TDC, 0.11 g m^{-2} NPOC, and 0.08 g m^{-2} EDOC. In Pitt County, NC (1700 km^2) 0.29 Pg TDC, 0.19 Pg NPOC, and 0.13 Pg EDOC were deposited.

V. Discussion

A. EDOC in Rainwater

EDOC compounds are considered semivolatile and span a large range of molecular weights and Henry's Law constants. The concentration and composition of EDOC depends on the sources of EDOC, light (photochemistry), and temperature. Compounds that might be considered EDOC include methanol, acetaldehyde, dimethylsulfide, isoprenoids, PAHs, PCBs, acetone, propanal, pyruvate, and oxalate. There are likely thousands of other compounds that also comprise EDOC that have never been quantified. Rather than attempting to identify each compound, this study aimed to use a novel method to calculate bulk concentrations of this vast pool of organic carbon.

EDOC has previously been measured in surface waters of the Atlantic ocean, a subarctic fjord, outwelling mangrove waters, an estuary, and in non-hurricane rainwater (Dachs et al., 2005; Ruiz-Halpern et al., 2010; Sippo et al., 2016; Campos et al., 2007; Avery et al., 2009; Godoy-Silva et al., 2017). In this previous research, EDOC accounted for 11-40% of the DOC (analogous to NPOC in this study). This study was the first to quantify EDOC in hurricane rainwater. Specifically, EDOC was quantified in two of the largest hurricanes (in terms of volume of water deposited) to impact the coast of the US, Hurricane Harvey (2017) and Hurricane Florence (2018).

Traditional methods of quantifying EDOC by gas sparging require large volumes of water samples. I developed a method for EDOC analysis, based on quantification of DOC in water by HTCO (Sugimura and Suzuki, 1988; Spyres et al., 2000) which was simpler and allowed for EDOC to be quantified using smaller volumes of water, such as rainwater samples. By developing a method that quantifies EDOC in rainwater, it is possible to shed light on the

portion of rainwater DOC that consists of semi-volatile organic compounds that may be ephemeral upon deposition to the surface of the earth.

In general, EDOC comprised ~8% of DOC in Pearland, TX and ~30% of DOC in League City, TX during Hurricane Harvey. In Winterville, NC, EDOC was ~44% of DOC during Hurricane Florence. These values suggest that EDOC is an important component of rainwater OC. My hypothesis stated EDOC should be between 10-40% of the total DOC. The average range for Hurricane Harvey fell slightly below the hypothesized lower limit of 10% and the average range for Florence was above the hypothesized upper limit of 40%. Nonetheless, the general similarities in EDOC in hurricane rainwater compared to values determined in other studies conducted on surface water, suggests that the mechanisms producing EDOC in surface water and rainwater may be similar. More measurements are necessary to better constrain the range of EDOC values in rainwater and surface water.

Rainwater NPOC is demonstrably more labile than NPOC in surface waters (Avery et al., 2003; Bao et al., 2018). Thus, it stands to reason that rainwater EDOC should also be more labile and/or more mobile than surface water EDOC. Therefore, marine EDOC from hurricanes may provide food for coastal and terrestrial heterotrophs (Avery et al., 2003; Mitra et al., 2013; Jurado et al., 2008) . In addition, EDOC is exchangeable by definition. Depending on the environmental and biological characteristics of its deposition location, EDOC may be subsequently revolatized back into the atmosphere where it might influence climate by acting as a precursor to organic aerosols. Other potential fates of EDOC include eventual transport back to the ocean or sequestration. The ultimate question, "Is marine-derived EDOC respired or sequestered?" has significant implications for the global carbon cycle.

B. Method Validation

Although the method used in this study may be used to quantify EDOC in low-volume water samples, there are some limitations that must be addressed. The preliminary experiments discussed below suggest that EDOC analysis should be conducted on a Shimadzu TOC-L, rather than a Shimadzu TOC-Vcph/cpn, even if the latter instrument is used in conjunction with a high-sensitivity catalyst.

Preliminary analyses included three standards: methanol, sodium bicarbonate, and a sodium bicarbonate – methanol mixture (~ 50% v/v), each at concentrations ranging from ~5-50 mg L^{-1}. These were analyzed for TDC and NPOC using the TOC-Vcph/cpn. The purpose of this analysis was to test the accuracy of TDC and NPOC measurements with an organic compound (methanol), an inorganic compound (sodium bicarbonate), and a mixture including both an organic and inorganic compound; a normal sensitivity catalyst was used in these preliminary experiments. The results of these experiments are discussed in Appendix A, and suggest that the TOC-Vcph/cpn is well suited for NPOC analysis at these concentrations, but it is less reliable for DIC measurements (included as part of TDC).

Unfortunately, Hurricane Florence rainwater samples had already been analyzed with the TOC-Vcph/cpn, but using a high sensitivity catalyst instead of a normal sensitivity catalyst. Upon discovery of the lower sensitivity of the TOC-Vcph/cpn, the remaining rainwater samples (i.e., Hurricane Harvey) were analyzed with TOC-L in conjunction with a high sensitivity catalyst.

Figure 18. *%EDOC compared to (A) Henry's Law constant, (B) molecular weght, and (C) vapor pressure of three organic compounds.*
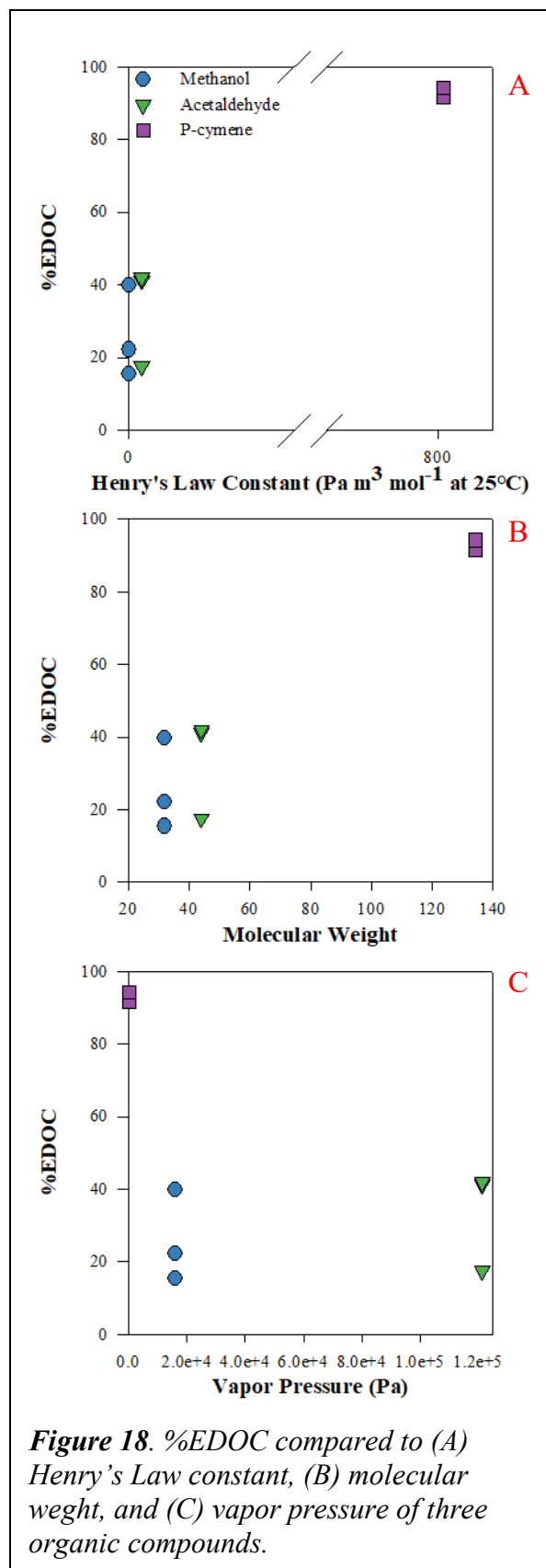
An additional limitation was that this technique was not sensitive enough to discriminate EDOC as a function of vapor pressure. Three standards at varying concentrations were analyzed for TDC and NPOC using the TOC-Vcph/cpn. EDOC was calculated as the difference between TDC and NPOC. For this analysis I used methanol, acetaldehyde, and p-cymene – organic compounds only (Table 1). Triplicates of each compound were analyzed with sample carbon concentrations ranging from ~1-4 mg L^{-1}. The standards were comprised of low concentrations of carbon in order to better reflect the concentrations of carbon in rainwater samples. Because of the low concentrations of dissolved carbon, a high sensitivity catalyst was used in the TOC. These results suggested that EDOC$_{p\text{-cymene}}$ > EDOC$_{acetaldehyde}$ > EDOC$_{methanol}$ (Figure 18). These results do correspond to the expected trend in EDOC in each compound as a function of the compounds molecular weight and Henry's Law constant.

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Ideally, I would run this same experiment using the more sensitive TOC-L. Our lab does not own the TOC-L; it was loaned by Shimadzu Laboratories (Durham, NC). At the time of this experiment, the TOC-L had already been returned to Shimadzu Laboratories. In hindsight, this experiment should have been completed before analyzing the rainwater samples.

C. Rainwater Loading of Carbon

Data from the Pearland, TX collection site indicate Hurricane Harvey deposited 2.1 g m^{-2} TDC, 1.1 g m^{-2} NPOC, and 1.0 g m^{-2} EDOC. Extrapolating to the whole area of Harris County (4600 km^2), Harvey deposited 9.6 Pg TDC, 5.3 Pg NPOC, and 4.7 Pg EDOC in the county. Hurricane Florence deposited 0.17 g m^{-2} TDC, 0.11 g m^{-2} NPOC, and 0.08 g m^{-2} EDOC. In Pitt County, NC (1700 km^2) 0.29 Pg TDC, 0.19 Pg NPOC, and 0.13 Pg EDOC were deposited. Six other studies have reported NPOC measurements from hurricane rainwater (Willey et al., 2000; Avery et al., 2004; Mitra et al., 2013; Mullaugh et al., 2013; Wang et al., 2015) and one study reported NPOC measurements from a tropical storm (Miller et al., 2008) (Table 7). In general, the average concentrations are the same order of magnitude, excepting Hurricane Irene in 2013 which had rainwater concentrations an order of magnitude greater than the other studies. The average rainwater NPOC deposition (concentration/precipitation) spanned two orders of magnitude amongst the storms. Rainwater from Hurricane Floyd and Hurricane Irene had the lowest mean depositions (0.03-0.05 g m^{-2}) and Hurricane Harvey had the greatest mean deposition (1.1 g m^{-2}). Carbon quantities deposited in Hurricane Florence was between the two extremes, with a mean deposition of 0.11 g m^{-2} of NPOC.

Table 7. Rainwater NPOC of Various Hurricanes

Reference	Sampling Location	# of Samples	Event	Precipitation (mm)	Mean Concentration (mg L^{-1})	Deposition Mean (g m^{-2})	Filter Pore Size (μm)
Willey et al. 2000	Wilmington, NC	3	Hurricanes Bertha & Fran (1996), Hurricane Bonnie (1998)	-	0.94	-	0.7
Avery et al. 2004	Wilmington, NC	1	Hurricane Fran, 4 September 1996	130	0.94 ± 0.02	0.13	0.2
Avery et al. 2004	Wilmington, NC	1	Hurricane Bertha, 12 July 1996	110	0.94 ± 0.02	0.12	0.2
Avery et al. 2004	Wilmington, NC	1	Hurricane Bonnie, 26 August 1998	240	0.94 ± 0.02	0.23	0.2
Avery et al. 2004	Wilmington, NC	1	Hurricane Floyd, 15 September 1999	490	0.13± 0.04	0.05	0.2
Miller et al. 2008	Wilmington, NC	8	Tropical Storm Ernesto, 31 August - 1 September 2006	244	VWA 0.31	0.07	-
Mitra et al. 2013	Greenville, NC	4	Hurricane Irene, 26-29 August 2011	240	2.3 ± 0.11	0.55	0.7
Mullaugh et al. 2013	Wilmington, NC	11	Hurricane Irene, 26-27 August 2011	209	VWA 0.19	0.03	0.2

Wang et al., 2015	Qingdao, Shangdong Province, China	1	Typhoon Matmo, 25 July 2014	-	0.34	-	0.7
Wang et al., 2015	Yantai, Shangdong Province, China	1	Typhoon Matmo, 25 July 2014	-	0.84	-	0.7
This Study	Pearland, TX	25	Hurricane Harvey, 25-29 August 2017	1160	VWA 0.99	1.1	0.2
This Study	League City, TX	8	Hurricane Harvey, 26-28 August 2017	910	VWA 0.82	0.75	0.2
This Study	Winterville, NC	3	Hurricane Florence, 13-16 September 2018	210	VWA 0.53	0.11	0.7

Willey et al. (2000) estimated that 2.3 g m^{-2} NPOC is deposited annually around the globe. These estimates were based on continental, oceanic, and coastal rainwater NPOC measurements. This means that Hurricane Harvey deposited nearly half of the expected annual NPOC (1.1 g m^{-2}) during a single event over a few days. Of course, Willey et al.'s estimate may need revision as more rainwater data is available now. It is also important to note that the NPOC deposition may significantly vary at a spatial level. Even so, it is clear that hurricanes move huge amounts of carbon in relatively short amounts of time.

D. Effects of Air Mass Sources

NPOC concentrations in the atmosphere during precipitation events are affected by the availability of soluble organic compounds in the local atmosphere (below-cloud scavenging or washout) as well as the transport of organic compounds within the air mass (in-cloud scavenging or rainout) (Scott, 1981; Slinn, 1983). Both washout and rainout impacted NPOC concentrations of rainwater during Hurricane Harvey. The washout effect is illustrated at each sampling location in Texas (Figure 10).

The first sample collected at each site had the highest NPOC concentration and, in general, the concentration decreased with time. Rainout is evident at the Pearland, TX sampling location. During Hurricane Harvey, the source of dominant air masses was variable (Figure 9). The NPOC concentrations of rainwater from Pearland, TX reflect the air mass changes. Two distinct decay curves indicate two dilution events during the storm (Figure 12). NPOC concentrations were greatest at the beginning of the storm when the air masses were coming from the Gulf of Mexico and the Caribbean Sea (Trajectory 1 in Figure 12). The concentrations decreased until there was a shift in the air mass source. Samples H15 and H16 demarcate the transition, when the air mass predominantly came from the Atlantic Ocean and the southeastern

United States. Samples H15 and H16 have a spike in NPOC concentrations and then concentrations decrease the remainder of the storm (Trajectory 2 in Figure 12).

Other researchers have noted NPOC washout and rainout during precipitation events. Kieber et al. (2002) noted a continuous supply of DOC, formate, and acetate in the atmosphere during New Zealand rainfall, which suggested rainout was more important than washout at their sampling site. Similarly, Avery et al. (2006) suggested that the source of the air mass controlled NPOC ^{13}C composition in Wilmington, NC. Iavorivska et al. (2016) sampled thirteen precipitation events at the Shale Hills Critical Zone Observatory. Seven events demonstrated a dilution of NPOC over the course of the storm (washout) and six events had increasing NPOC concentrations over the course of the storm. Miller et al. (2008) also found NPOC increased at the end of tropical storm Ernesto in Wilmington, NC, though washout had dominated at the beginning of the storm. Several explanations have been given for NPOC variability during storms including changing wind speeds, changing air temperatures, and shifts in cloud base height (Kieber et al., 2002; Avery et al., 2006; Miller et al., 2008; Iavorivska et al., 2016). Air mass source is clearly a major contributing factor to NPOC variability.

Unlike NPOC, EDOC concentrations generally did not vary as a function of air mass source, during either Hurricane Harvey or Hurricane Florence. Furthermore, NPOC and EDOC concentrations were not inter-correlated. This suggests differing transport and/or reaction mechanisms for NPOC versus EDOC during each hurricane. Interestingly, Avery et al. (2009) cited air mass back trajectory as a key component affecting EDOC in rainwater in Wilmington, NC. To my knowledge, Avery et al. (2009) and this study are the only studies that have examined the relationship between EDOC and air mass back trajectory in rainwater.

Though it was not the objective of this study, future research should address the composition of EDOC by complementing air mass back trajectory analysis with other proxies or rainwater composition and trajectory. For example isotope analyses, such as ^{13}C, ^{14}C, ^{18}O and ^{2}H, would help shed light on the relative influence of terrestrial vs. marine organic matter to the composition of EDOC. While some researchers have measured isotopes to complement air mass back trajectories (Avery et al., 2006; Good et al., 2014; Mitra et al., 2017), more of these methods could be applied to EDOC as well as other pools of rainwater carbon.

E. Rainwater DIC

According to calculations done by Willey et al. (2000), DIC concentrations should be ~0.2 mg L^{-1} in continental rain and ~0.17 mg L^{-1} in marine rain. The DIC concentrations in this study, ranging from 10^{-4} to 10^{-2}, are much less than the hypothesized concentrations used by Willey et al. (2000) which were based on Henry's Law and equilibrium carbonic acid dissociation constants. We did not measure rainwater pH which would be needed to calculate ideal values of rainwater DIC as a function of atmospheric CO_2. Thus, the low values of rainwater DIC measured in this study suggest that the inorganic carbon in rainwater and gas phase carbon dioxide in the atmosphere were not at equilibruium.

F. Implications, Future Work, and Conclusions

Hurricanes transport massive amounts of marine rain and organic matter to terrestrial ecosystems (Mitra et al., 2013; Mullaugh et al., 2013; Raymond, 2005). While it is beneficial to track the movement of NPOC and specific organic compounds in hurricane rainwater, EDOC is also a key component of carbon cycling. NPOC concentrations ranged from 0.26-3.6 mg L^{-1} during Hurricane Harvey and 0.49-0.61 mg L^{-1} during Hurricane Florence. EDOC concentrations

ranged from 0-0.88 mg L^{-1} (8-63% of the DOC) during Hurricane Harvey and 0.29-0.60 mg L^{-1}

(~44% of the DOC) during Hurricane Florence at my sampling locations. Thus, this study

accentuates the magnitude and importance of a pool of carbon that is typically not quantified by

researchers.

The tiered HTCO method used in this research is both simple and easier to implement

than the multi-chamber gas sparging apparatus used by previous researchers (Dachs et al., 2005;

Ruiz-Halpern et al., 2010; Hauser et al., 2013). Of course, there are drawbacks. For example,

unlike the previous method my method does not measure gas-phase organic carbon (GOC) in the

atmosphere. Quantification of GOC is necessary when determing diffusive air-water exchange

(Dachs et al., 2005; Ruiz-Halpern et al., 2010; Hauser et al., 2013). Having said that, concurrent

GOC and EDOC sampling may not be feasible during hurricanes.

There are several complementary analyses that can be performed with EDOC and NPOC

analyses, however. Other researchers have examined rainwater and surface water composition

by GC-MS (Cottrell et al., 2013), FTICR-MS (Cottrell et al., 2013; Mitra et al., 2013), EEMs

(Bao et al., 2018; Cottrell et al., 2013; Mitra et al., 2017), and NMR (Cottrell et al., 2013;

Pantelaki et al., 2018; Montero-Martinez et al., 2018) analyses. Each of these analyses identifies

certain types of organic compounds. Isotope analyses may also be invaluable for determining OC

origins and storm trajectories. ^{13}C and ^{14}C have been used in a few rainwater studies (Raymond,

2005; Avery et al., 2006; Mitra et al., 2013; Wang et al., 2016; Mitra et al., 2017). Carbon

isotopes can be used to elucidate OC origins (marine or terrestrial) as well as OC age

(contemporary vs. fossil fuel). ^{2}H and ^{18}O can be used to trace rain origins (marine vs. terrestrial)

(Dansgaard, 1964; Iavorivska et al., 2016b). Similarly, a multi-proxy analytical approach

including quantification of EDOC may shed more light on the specific compounds in this pool of

carbon (Cottrell et al., 2013). Lastly, bioavailability experiments should be completed to address questions such as: which pool of rainwater carbon (EDOC, NPOC, TDOC) is truly more likely to be respired or preserved by heterotrophic microbes? During this study it was assumed hurricane rainwater was mostly marine-derived and likewise, the NPOC and EDOC was largely marine-derived as well. By coupling NPOC and EDOC analysis with these other methods a clearer picture of carbon cycling in the atmosphere and during rain events will develop. Ultimately the goal is to determine which carbon is sequestered, which is oxidized, and which is released unchanged into the atmosphere.

Our current understanding of atmospheric carbon cycling is lacking, especially regarding EDOC. The absence of EDOC measurements in rain and surface waters causes inaccurate representations of DOC bioavailability, carbon flux estimates, and secondary organic aerosol formation and transport. In fact, previous studies have likely underestimated DOC in rainwater. EDOC is essentially a missing carbon pool and the measurement of EDOC in precipitation and surface water bodies may provide a major contribution to carbon science. Quantifying EDOC in hurricanes as well as other rain events can improve our understanding of air-water fluxes of OC and help refine estimates of those fluxes. As hurricanes become more intense due to climate change (Knutson et al., 2015; Trenberth et al., 2018), the study of organic matter movement during hurricanes is becoming an even more relevant topic.

VI. References

Avery, G.B., Dickson Brown, J.L., Willey, J.D., Kieber, R.J., 2009. Assessment of rainwater volatile organic carbon in southeastern North Carolina, USA. Atmos. Environ. 43, 2678–2681. https://doi.org/10.1016/j.atmosenv.2009.02.015

Avery, G.B., Kieber, R.J., Willey, J.D., Shank, G.C., Whitehead, R.F., 2004. Impact of hurricanes on the flux of rainwater and Cape Fear River water dissolved organic carbon to Long Bay, southeastern United States. Global Biogeochem. Cycles 18, 1–6. https://doi.org/10.1029/2004GB002229

Avery, G.B., Willey, J.D., Kieber, R.J., Shank, G.C., Whitehead, R.F., 2003. Flux and bioavailability of Cape Fear River and rainwater dissolved organic carbon to Long Bay, southeastern United States. Global Biogeochem. Cycles. https://doi.org/10.1029/2002GB001964

Avery, G.B.Ã., Willey, J.D., Kieber, R.J., 2006. Carbon isotopic characterization of dissolved organic carbon in rainwater: Terrestrial and marine influences. Atmos. Environ. 40, 7539–7545. https://doi.org/10.1016/j.atmosenv.2006.07.014

Bao, H., Yi, Y., Wang, C., Spencer, R.G.M., Deng, X., Guo, W., 2018. Dissolved organic matter in coastal rainwater: Concentration, bioavailability and depositional flux to seawater in southeastern China. Mar. Chem. 205, 48–55. https://doi.org/10.1016/j.marchem.2018.07.008

Bidleman, T.F., 1988. Atmospheric processes. Environ. Sci. Technol. 22, 361–367. https://doi.org/10.1021/es00169a002

Blake, E.S., Zelinsky, D.A., 2018. National Hurricane Center Tropical Cyclone Report: Hurricane Harvey (AL092017).

Campos, M.L.A.M., Nogueira, R.F.P., Dametto, P.R., Francisco, J.G., Coelho, C.H., 2007. Dissolved organic carbon in rainwater: Glassware decontamination and sample preservation and volatile organic carbon. Atmos. Environ. https://doi.org/10.1016/j.atmosenv.2007.08.017

Cottrell, B.A., Gonsior, M., Isabelle, L.M., Luo, W., Perraud, V., McIntire, T.M., Pankow, J.F., Schmitt-Kopplin, P., Cooper, W.J., Simpson, A.J., 2013. A regional study of the seasonal variation in the molecular composition of rainwater. Atmos. Environ. 77, 588–597.

Dachs, J., Calleja, M.L., Duarte, C.M., del Vento, S., Turpin, B., Polidori, A., Herndl, G.J., Agustí, S., 2005. High atmosphere-ocean exchange of organic carbon in the NE subtropical Atlantic. Geophys. Res. Lett. https://doi.org/10.1029/2005GL023799

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 4, 436–468. https://doi.org/10.3402/tellusa.v16i4.8993

De Gouw, J., Jimenez, J.L., 2009. Organic aerosols in the earth's atmosphere. Environ. Sci. Technol. https://doi.org/10.1021/es9006004

Del Giorgio, P.A., Williams, P.J., 2005. Respiration in aquatic ecosystems . Oxford University Press.

Donahue, N.M., Robinson, A.L., Pandis, S.N., 2009. Atmospheric organic particulate matter: From smoke to secondary organic aerosol. Atmos. Environ. 43, 94–106. https://doi.org/10.1016/j.atmosenv.2008.09.055

Erdman, J., 2018. Florence Sets Preliminary North Carolina and South Carolina Tropical Cyclone Rain Records; Third, Fourth States to Do So in 12 Months [WWW Document]. Weather.com. URL https://weather.com/storms/hurricane/news/2018-09-15-florence-north-carolina-tropical-rain-record

Fritz, A., Samenow, J., 2017. Harvey unloaded 33 trillion gallons of water in the U.S. - The Washington Post. Washington Post.

Godoy-Silva, D., Nogueira, R.F.P., Campos, M.L.A.M., 2017. A 13-year study of dissolved organic carbon in rainwater of an agro-industrial region of São Paulo state (Brazil) heavily impacted by biomass burning. Sci. Total Environ. 609, 476–483. https://doi.org/10.1016/j.scitotenv.2017.07.145

Graedel, T.E., Mcgill, R., 1986. Degradation of materials in the atmosphere, American Chemical Society Environ. Sci, Techno!

Guenther, A., Nicholas Hewitt, ! C, Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. J. Geophys. Res. 100, 8873–8892.

Hauser, E.J., Dickhut, R.M., Falconer, R., Wozniak, A.S., 2013. Improved method for quantifying the air-sea flux of volatile and semi-volatile organic carbon. Limnol. Oceanogr. Methods. https://doi.org/10.4319/lom.2013.11.287

Iavorivska, L., Boyer, E.W., DeWalle, D.R., 2016a. Atmospheric deposition of organic carbon via precipitation. Atmos. Environ. 153–163. https://doi.org/10.1016/j.atmosenv.2016.06.006

Iavorivska, L., Boyer, E.W., Grimm, J.W., 2017. Wet atmospheric deposition of organic carbon: An underreported source of carbon to watersheds in the northeastern United States. J. Geophys. Res. https://doi.org/10.1002/2016JD026027

Iavorivska, L., Boyer, E.W., Miller, M.P., Brown, M.G., Vasilopoulos, T., Fuentes, J.D., Duffy, C.J., 2016b. Atmospheric inputs of organic matter to a forested watershed: Variations from storm to storm over the seasons. Atmos. Environ. 147, 284–295. https://doi.org/10.1016/j.atmosenv.2016.10.002

Junge, C.E., 1977. No Title, in: Sufffet, I.H. (Ed.), Fate of Pollutants in the Air and Water Environments. Wiley, New York, pp. 7–26.

Jurado, E., Dachs, J., Duarte, C.M., Simó, R., 2008. Atmospheric deposition of organic and black carbon to the global oceans. Atmos. Environ. 42, 7931–7939. https://doi.org/10.1016/j.atmosenv.2008.07.029

Kanakidou, M., Duce, R.A., Prospero, J.M., Baker, A.R., Benitez-Nelson, C., Dentener, F.J., Hunter, K.A., Liss, P.S., Mahowald, N., Okin, G.S., Sarin, M., Tsigaridis, K., Uematsu, M., Zamora, L.M., Zhu, T., 2012. Atmospheric fluxes of organic N and P to the global ocean. Glob. Biogeochem. Cycles 26, 3026. https://doi.org/10.1029/2011GB004277

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys.

Kawamura, K., Kaplan, I.R., 1983. Organic Compounds In the Rainwater of Los Angeles. Environ. Sci. Technol. 17, 497–501.

Knutson, T.R., Sirutis, J.J., Zhao, M., Tuleya, R.E., Bender, M., Vecchi, G.A., Villarini, G., Chavas, D., Knutson, T.R., Sirutis, J.J., Zhao, M., Tuleya, R.E., Bender, M., Vecchi, G.A., Villarini, G., Chavas, D., 2015. Global Projections of Intense Tropical Cyclone Activity for the Late Twenty-First Century from Dynamical Downscaling of CMIP5/RCP4.5 Scenarios. J. Clim. 28, 7203–7224. https://doi.org/10.1175/JCLI-D-15-0129.1

Kunkel, K.E., Champion, S.M., 2019. An Assessment of Rainfall from Hurricanes Harvey and Florence Relative to Other Extremely Wet Storms in the United States. Geophys. Res. Lett. 46, 13500–13506. https://doi.org/10.1029/2019GL085034

Leister, D.L., Baker, J.E., 1994. Atmospheric deposition of organic contaminants to the chesapeake bay. Atmos. Environ. 28, 1499–1520. https://doi.org/10.1016/1352-2310(94)90210-0

Ligocki, M.P., Leuenberger, C., Pankow, J.F., 1985. Trace organic compounds in rain-II. Gas scavenging of neutral organic compounds, Atmospheric Environment (1967). https://doi.org/10.1016/0004-6981(85)90213-6

Ligocki, M.P., Pankow, J.F., 1989. Measurements of the Gas/Particle Distributions of Atmospheric Organic Compounds. Environ. Sci. Technol. 23, 75–83. https://doi.org/10.1021/es00178a009

Likens, G.E., Edgerton, E.S., Galloway, J.N., 1983. The composition and deposition of organic carbon in precipitation. Tellus B. https://doi.org/10.1111/j.1600-0889.1983.tb00003.x

Liss, P.S., Slater, P.G., 1974. Flux of gasses across the air-sea interface. Nature 247, 181–184.

Mitra, S., Osburn, C.L., Wozniak, A.S., 2017. A Preliminary Assessment of Fossil Fuel and Terrigenous Influences to Rainwater Organic Matter in Summertime in the Northern Gulf of Mexico. Aquat. Geochemistry. https://doi.org/10.1007/s10498-017-9319-5

Mitra, S., Wozniak, A.S., Miller, R., Hatcher, P.G., Buonassissi, C., Brown, M., 2013. Multiproxy probing of rainwater dissolved organic matter (DOM) composition in coastal storms as a function of trajectory. Mar. Chem. https://doi.org/10.1016/j.marchem.2013.05.013

Moody, A., 2018. Hurricane Florence: NC rain estimated at 8 trillion gallons | Raleigh News & Observer [WWW Document]. News Obs. URL https://www.newsobserver.com/news/weather/article218273350.html (accessed 2.6.19).

Mullaugh, K.M., Willey, J.D., Kieber, R.J., Mead, R.N., Avery, G.B., 2013. Dynamics of the chemical composition of rainwater throughout Hurricane Irene. Atmos. Chem. Phys. https://doi.org/10.5194/acp-13-2321-2013

Muller, C.L., Baker, A., Hutchinson, R., Fairchild, I.J., Kidd, C., 2008. Analysis of rainwater dissolved organic carbon compounds using fluorescence spectrophotometry. Atmos. Environ. 42, 8036–8045. https://doi.org/10.1016/j.atmosenv.2008.06.042

O'Dowd, C.D., Facchini, M.C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Young, J.Y., Putaud, J.P., 2004. Biogenically driven organic contribution to marine aerosol. Nature 431, 676–680. https://doi.org/10.1038/nature02959

Piccot, S.D., Watson, J.J., Jones, J.W., 1992. A Global Inventory of Volatile Organic Compound Emissions From Anthropogenic Sources. J. Geophys. Res. 97, 9897–9912.

Poster, D.L., Baker, J.E., 1996. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 2. Scavenging of polycyclic aromatic hydrocarbons by rain. Environ. Sci. Technol. 30, 349–354. https://doi.org/10.1021/es940681w

Raymond, P.A., 2005. The composition and transport of organic carbon in rainfall: Insights from the natural (13C and 14C) isotopes of carbon. Geophys. Res. Lett. 32, 1–4. https://doi.org/10.1029/2005GL022879

Rolph, G., Stein, A., Stunder, B., 2017. Real-time Environmental Applications and Display sYstem: READY. Environ. Model. Softw. 95, 210–228. https://doi.org/10.1016/j.envsoft.2017.06.025

Ruiz-Halpern, S., Sejr, M.K., Duarte, C.M., Krause-Jensen, D., Dalsgaard, T., Dachs, J., Rysgaard, S., 2010. Air-water exchange and vertical profiles of organic carbon in a subarctic fjord. Limnol. Oceanogr. https://doi.org/10.4319/lo.2010.55.4.1733

Scott, B.C., 1981. Modeling wet deposition, in: Eisenreich, S.J. (Ed.), Atmospheric Pollutants in Natural Waters. Ann Arbor Scence, Ann Arbor, pp. 3–21.

Sippo, J.Z., Maher, D.T., Tait, D.R., Ruiz-Halpern, S., Sanders, C.J., Santos, I.R., 2016. Mangrove outwelling is a significant source of oceanic exchangeable organic carbon. Limnol. Oceanogr. Lett. 2, 1–8. https://doi.org/10.1002/lol2.10031

Slinn, W.G., 1983. Air-to-sea transfer of particles, in: Liss, P.S., Slinn, W.G.N. (Eds.), Air-Sea Exchange of Gases and Particles. D. Reidel Publishing Company, Dordrecht.

Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA'S HYSPLIT ATMOSPHERIC TRANSPORT AND DISPERSION MODELING SYSTEM. Am. Meteorol. Soc. 96, 2059–2077. https://doi.org/10.1175/BAMS-D-14-00110.1

Stewart, S.R., Berg, R., 2019. National Hurricane Center tropical cyclone report: Hurricane Florence (AL062018). Natl. Hurric. Cent. 1–98.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, Third. ed. John Wiley & Sons, Incorporated, New York.

Sugimura, Y., Suzuki, Y., 1988. A High-Temperature Catalytic Oxidation Method for the Determination of Non-Volatile Dissolved Organic Carbon in Seawater by Direct Injection of a Liquid Sample, Marine Chemistry.

Trenberth, K.E., Cheng, L., Jacobs, P., Zhang, Y., Fasullo, J., 2018. Hurricane Harvey Links to

Ocean Heat Content and Climate Change Adaptation. Earth's Futur. 6, 730–744. https://doi.org/10.1029/2018EF000825

Warneck, P., 2000. Chemistry of the Natural Atmosphere, Second. ed. Academic Press, New York.

Willey, J.D., Kieber, R.J., Eyman, M.S., Avery, G.B., 2000. Rainwater dissolved organic carbon: Concentrations and global flux. Global Biogeochem. Cycles 14, 139–148. https://doi.org/10.1029/1999GB900036

Williams, J., 2004. Organic trace gases in the atmosphere: An overview. Environ. Chem. 1, 125–136. https://doi.org/10.1071/EN04057

VII. Appendices

Appendix A. Preliminary Analyses

A1. Harvey Preliminary Analysis

On April 27, 2018, two rainwater samples from Hurricane Harvey were analyzed. This initial analysis was executed to estimate rainwater DOC and EDOC concentrations so that further method development could occur. Campos et al. (2007) was used as the main reference by which analysis was carried out. Two sample aliquots each were taken from H3 and H24. The water was filtered with 0.7 µM GF/F filters to remove particulates. The two subsamples were analyzed individually by two different methods using a Shimadzu TOC-Vcph/cpn analyzer. A regular sensitivity catalyst was used in both methods. The first analysis was for total dissolved organic carbon (TDOC). The samples were acidified, but they were not sparged. Next, an NPOC analysis was performed. The samples were acidified and sparged.

The results for these initial trial analyses were seemingly reasonable. The carbon concentrations were low, as expected for rainwater with a marine origin (Kieber et al., 2002). The TDOC concentrations for H3 and H24 were 2.664 mg L^{-1} and 1.886 mg L^{-1}, respectively. The NPOC concentrations for H3 and H24 were 2.232 mg L^{-1} and 1.464 mg L^{-1}, respectively. If we entertain the idea that the analysis was accurate, preliminary results from Hurricane Harvey rainwater (n=2) suggested EDOC (0.427 ± 0.005 mg L^{-1}) comprised approximately 19% of total rainwater DOC (2.28 ± 0.389 mg L^{-1}).

The calibration curve used for the analyses, however, leads one to suspect the carbon concentrations may not be accurate. There are two reasons to be skeptical: (1) the instrument was calibrated with potassium hydrogen phthalate (KHP) ranging from 0 to 141.564 mg C L^{-1} and (2) a normal sensitivity platinum catalyst was used.

The limit of detection of the calibration curve was ~3.81 mg C L^{-1}. The detection limit was calculated using the LINEST function in Excel. The concentrations of both H3 and H24 are below the detection limit of the calibration curve.

As mentioned previously, the purpose of the preliminary analysis was to gain insight regarding the DOC and EDOC concentrations in the rainwater samples. By completing this analysis, it was apparent that a calibration curve with a lower range of concentrations would be better suited for future analyses.

A2. First Proposed Method

Initially, I attempted to quantify EDOC using the following procedure: (1) Quantify total dissolved carbon, (2) quantify NPOC + DIC, and (3) quantify non-purgeable organic carbon. These three analyses yield an EDOC concentration of hurricane rainwater by the following equation: EDOC = TDC – DIC – NPOC

Stock Solutions

Three sets of standard stock solutions were made: 1) methanol solution, 2) sodium bicarbonate solution, and 3) methanol plus sodium bicarbonate mixture solution. Methanol is organic carbon and sodium bicarbonate is inorganic carbon. Four aliquots were taken from each stock solution and then diluted to varying concentrations, ranging from approximately 50 mg C L^{-1} to 5 mg C L^{-1}. Each aliquot was then further divided into three groups, so a three-tiered analysis could be performed.

All glassware was decontaminated before use. Glassware was soaked in an Alconox bath for 24 hours and then rinsed with DI water. After it was dry, the glassware was muffled at 450°C for 5 hours.

High-temperature catalytic oxidation by a Shimadzu TOC-Vcph/cpn with an ASI 5000 autosampler was used for analysis. The Shimadzu TOC-Vcph/cpn was calibrated with potassium hydrogen phthalate (KHP). Two calibration curves were created – one with concentrations ranging from 0 to 8.18 mg C L^{-1} (C1-1:C1-6) and another ranging from 9.630 to 120.3 mg C L^{-1} (C2-1:C2-3).

Each standard and blank were examined in triplicate per run. Three blanks were analyzed first. The blanks were followed by four standards. This pattern was repeated for the entire analysis. A normal sensitivity platinum catalyst was used. When sparging occurred, standards and blanks were purged for 1.5 minutes with compressed air (UN 1002).

First, the standards were analyzed for TDC (Analysis A). Typical DOC quantifications are performed via the NPOC method which includes acidification and sparging steps at the beginning of organic carbon analysis to remove inorganic carbon from solution (DIC). In addition to the DIC, an unknown quantity of exchangeable components of DOC is also removed. This batch of samples for Analysis A was neither acidified nor sparged, ensuring that as much of the TDC remained in solution as possible. The results of this initial analysis provided measurements of total dissolved carbon, including both inorganic and organic carbon species.

The r^2 values for all standards in Analysis A indicate that the measured solution concentration values correlate well with the actual solution concentrations for the total carbon analysis. It is evident from the graph, however, that the measured concentrations for sodium bicarbonate are the least accurate (Figure A1-A).

The second analysis included sparging and acidification (Analysis B). Standards were acidified to ~ pH 2 with 2N HCl and sparged for 1.5 minutes with compressed air (UN 1002).
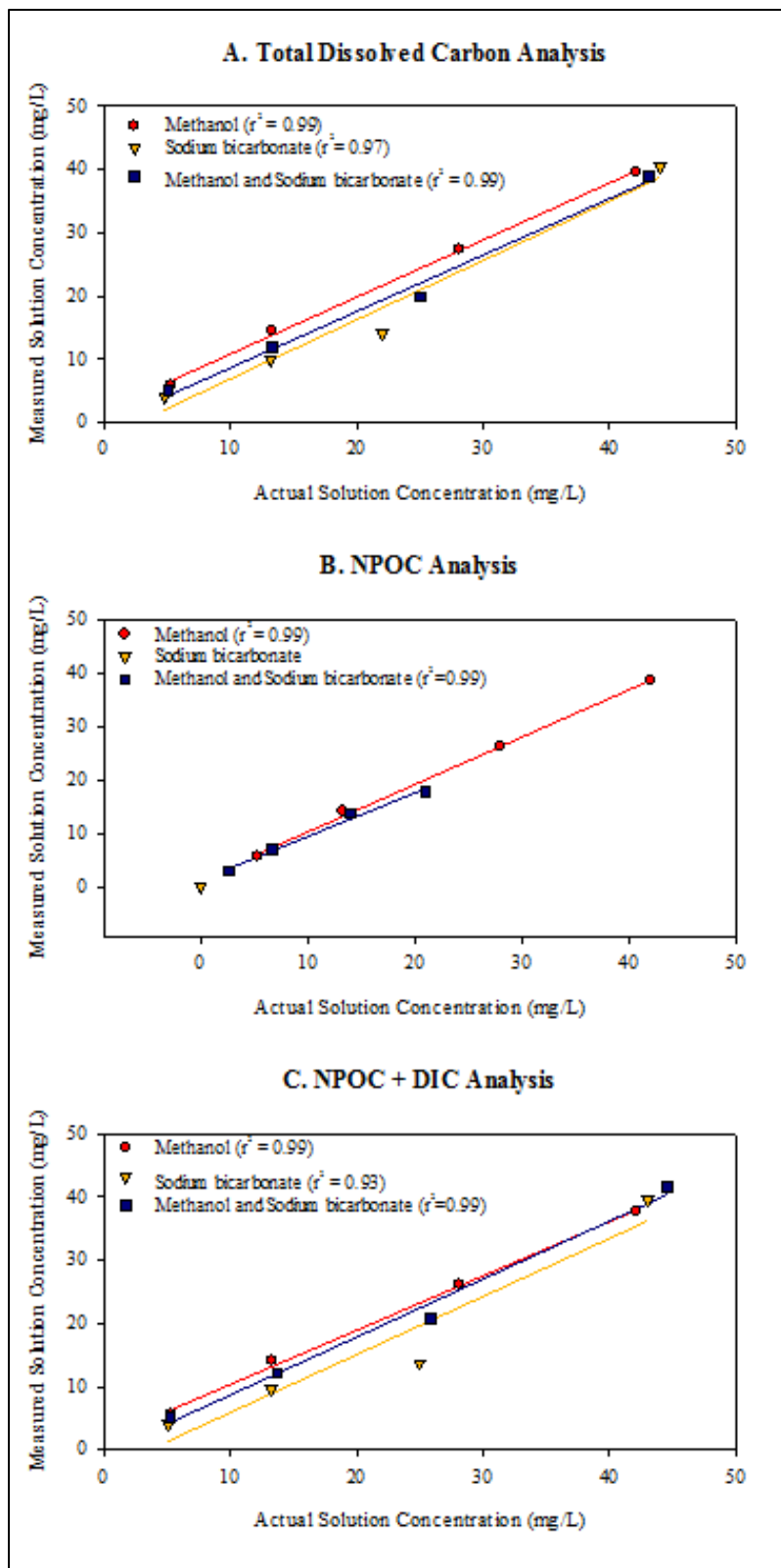
A. Total Dissolved Carbon Analysis

Methanol ($r^2 = 0.99$)
Sodium bicarbonate ($r^2 = 0.97$)
Methanol and Sodium bicarbonate ($r^2 = 0.99$)

B. NPOC Analysis

Methanol ($r^2 = 0.99$)
Sodium bicarbonate
Methanol and Sodium bicarbonate ($r^2 = 0.99$)

C. NPOC + DIC Analysis

Methanol ($r^2 = 0.99$)
Sodium bicarbonate ($r^2 = 0.93$)
Methanol and Sodium bicarbonate ($r^2 = 0.99$)

Figure A1.

This removed both DIC and EDOC from solution, leaving only the NPOC to be measured. The r^2 values for the methanol solution suggest that the actual concentrations correlate well with the measured concentrations (Figure A1-B). Sodium bicarbonate NPOC concentrations for all four aliquots were approximately zero, as expected; acidification and sparging removed the inorganic carbon from solution.

During the third analysis, sparging occurred but the standards were not acidified (Analysis C). Without acidification, the DIC remained in solution. Sparging caused exchangeable dissolved organic carbon to volatilize. The results

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of the third analysis measured total NPOC plus DIC.

The r^2 value for methanol in the third analysis suggests that the measured solution concentration values again correlate well with the actual solution concentrations, but the sodium bicarbonate r^2 value does not indicate the same amount of accuracy for measured concentrations compared to actual concentrations (Figure A1-C).

Rainwater

Four Hurricane Florence rainwater samples were filtered with pre-washed 0.7 μm pore-size GF/F filters to remove any particulates. Each sample was then divided into three subsamples so that the three different carbon analyses using a Shimadzu TOC-Vcph/cpn analyzer could be performed on each sample. The procedure outlined above was used.

Samples analyzed from Hurricane Florence (n=4) had a mean EDOC concentration of 0.315 ± 0.054 mg L^{-1} and made up about 32% of the total rainwater DOC (0.98 mg L-1). These first results from Hurricane Florence, like Hurricane Harvey discussed above, may also be flawed.

Issues with First Proposed Method

There is one major flaw in the initial method. As stated previously, DIC is removed from a water solution by acidification and sparging. This is supported by the NPOC results for sodium bicarbonate. However, the sodium bicarbonate solutions yielded erroneous results for the TDC and NPOC + DIC analyses. The solutions were not acidified. The DIC was not converted to CO_2. The solutions were sparged. What if some of the DIC remained in solution as another DIC species?

Because of the inability of the Shimadzu TOC-Vcph/cpn analyzer to accurately measure DIC by this method, another approach was necessary. The DIC needed to be measured separately and with a method approved for DIC analysis.

Appendix B. Covid-19

Between the preliminary analyses and March 2020 it was determined that filtering of samples was not a necessary step. Willey et al. (2000) demonstrated there was no statistical difference between filtered and unfiltered rainwater samples for DOC analysis of hurricane rainwater in Wilmington, North Carolina.

As of March 2020, a Shimadzu TOC-L was used for most organic carbon analyses. Switching to the TOC-L was recommended by Shimadzu Laboratories (Durham, NC) because it is better suited for use with a high sensitivity catalyst. A high sensitivity catalyst was necessary because many of the rainwater samples were expected to have low concentrations of carbon (<2.5 mg L^{-1}), as demonstrated from the preliminary analyses. Each standard and blank were examined in triplicate per run and when sparging occurred it lasted for 1.5 minutes with compressed air (UN 1002).

On February 28, 2020, all rainwater samples (original collection jars) were moved from a freezer to a refrigerator. Samples remained in the fridge as they thawed. Once thawed, subsamples were removed from each container. Two subsamples (one for TDC analysis and one for NPOC analysis) were put into glass scintillation vials. On March 5, 2020, all samples were transported to Shimadzu Laboratories, Durham, NC. TDC analysis on most of the rainwater samples was completed March 5-6, 2020.

Plans were made to return to Shimadzu Laboratories the following week (March 13, 2020). Because of the impending return to Durham, samples were left at Shimadzu Laboratories in a refrigerator rather than transported back to Greenville. Unfortunately, circumstances arose that prevented Shimadzu being available for analysis on March 13. The date was moved to the

following week. I was to return to Durham to finish analyzing the rainwater samples on March 18, 2020.

This plan was upended due to the COVID-19 pandemic. Shimadzu Laboratories temporarily shut down (March 16, 2020) and East Carolina University suspended university-sponsored travel (March 17, 2020). All laboratory research came to a halt for approximately one month.

Shimadzu reopened their laboratory on April 20, 2020. University travel was still restricted at this time, however. Shimadzu delivered the TOC-L to ECU the week of April 20th. The rainwater samples were returned to ECU the following week. At that time, the rainwater had been refrigerated for nearly two months. The reliability of the results gathered from samples stored in this way is questionable. Spyres et al. (2000) insists that cold storage alone is not an appropriate storage mechanism; acidification protects samples from degradation. Even so, I decided to analyze the samples for NPOC on April 27, 2020.

The results from the NPOC analysis were peculiar. Because NPOC is a fraction of total dissolved carbon, one expects NPOC concentrations to be lower than TDC concentrations. Most of the samples analyzed for NPOC on April 27th returned carbon concentrations *higher* than the TDC concentrations measured on March 5th (Figure B1).

Initially, I thought this erroneous result could be due to either the degradation of the sample while it was in storage or the contamination of acid used for DIC removal. I decided to thaw out some archived samples to determine whether the high NPOC results were simply a
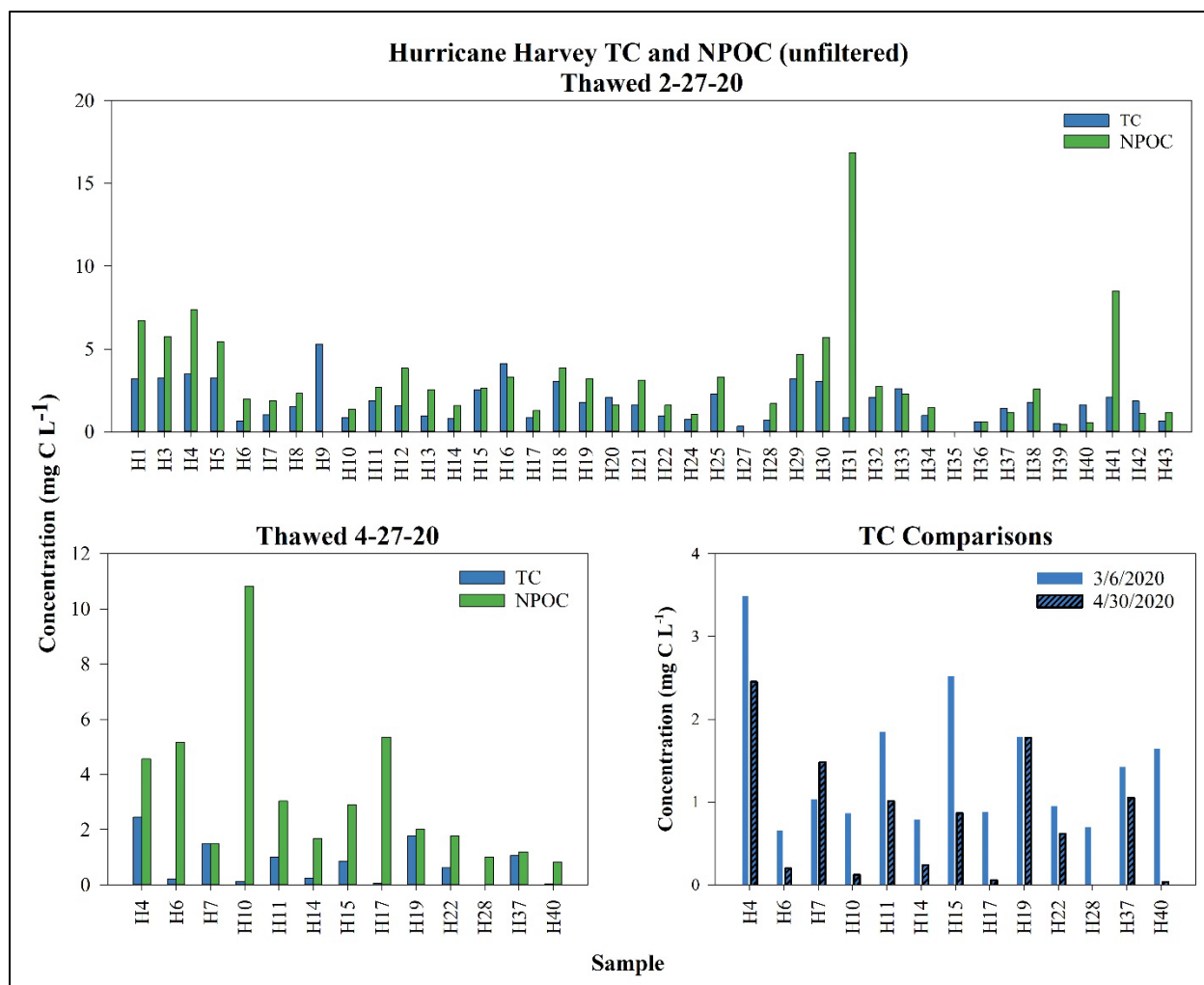
Figure B1.

function of storage or if there was another reason for the strange results. I also made a new batch

of 2N HCl for acidification. Again, the NPOC concentrations were higher than the TDC

concentrations (Figure B1). Furthermore, the TC values from the samples newly thawed on

4/27/20 did not correlate with the TC values from the analysis on 3/6/20 (Figure B1).

The higher NPOC concentrations were attributable to neither the long-refrigeration

storage time nor the contamination of acid. Perhaps the acidification step used for NPOC

analysis made some portion of the DOC pool accessible to oxidation that was not oxidizable at

the ambient pH used for TDC analysis. Recalling that the samples were not filtered, the next

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reasonable step was to filter the samples to remove this potentially pH-dependent oxidizable

portion. Therefore, all samples were filtered prior to analysis, as discussed in the main text.