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Hurricane pulses: Small watershed exports of dissolved nutrients and organic matter during large storms in the Southeastern USA



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Hurricane-mediated solute transport was assessed in streams in the Southeast U.S.
- Proportion and flux of soil-derived, humic, biorefractory DOM increased.
- Percentages of bioreactive DOC decreased but the total flux increased at high flows.
- Urban watersheds simultaneously exported bioreactive DOC and inorganic nutrients.
- Wetland acted as a buffer for rapid hydrological and chemical disturbances.

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ABSTRACT

Extreme weather events, such as hurricanes, can cause ecological disturbances that alter energy and nutrients across terrestrial-aquatic boundaries. Yet, relatively few studies have considered the impacts of extreme weather events on biogeochemical dynamics in watersheds at larger spatial scales. Here, we assessed the effects of Hurricanes Harvey and Irma on the export of dissolved organic matter (DOM) and nutrients in ten watersheds from five southeastern states of the United States. We quantified the magnitude of dissolved organic carbon (DOC) and nutrients exported during the storms and assessed the changes in DOM sources and bioreactivity after storms. Our results show that the storm-mobilized DOC and nutrients fluxes were primarily driven by water discharge. The proportions of terrestrial, humic-like DOM compounds increased, and percent autochthonous, protein-like DOM decreased during high flows. Percent bioreactive DOC decreased with increasing discharge. Bioreactivity increased with increasing nitrate concentration, but decreased as percent terrestrial humic-like DOM, aromaticity, and molecular weight increased. These observations suggest that storms may have shifted flow paths to shallower depths that promoted the addition of biorefractory organic matter from topsoils into the water column. Notably, the total flux of bioreactive DOC was at least nearly twice as high at peak discharge, indicating materials transported by large storm flows could strongly enhance microbial activity in

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streams, although the position of storm-mediated microbial hotspots would depend on the flow rate and other instream parameters. Additionally, compared to forest-dominated watersheds, urban watersheds exported high loads of nutrients and bioreactive DOC, and a wetland-dominated watershed had a prolonged, but relatively subdued export of DOC and nutrients. Together, our findings highlight the ecological significance of extreme weather and climate events in leading to rapid, large-magnitude changes in energy and nutrient availability within drainage networks, and the potential interactions between land use and climate change on watershed biogeochemistry.

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1. Introduction

The frequency and intensity of Atlantic hurricane activities have been increasing over recent decades, due to the tropical Atlantic Ocean warming caused by anthropogenic greenhouse gas emissions (Hayashi et al., 2004; Knutson et al., 2010; Mann et al., 2012). Most climate models predict that the intensity of tropical cyclones would increase by 2 to 11% by the year 2100 (Knutson et al., 2010). The 2017 Atlantic hurricane season, which resulted in more than \$250 billion in damage, was one of the most active and catastrophic hurricane seasons ever recorded in the US (Blake, 2018). Two storms, Hurricane Harvey (Category 4) and Hurricane Irma (Category 5), which made landfall on Gulf Coast states within two weeks of one another (Fig. 1), were responsible for 60% of the economic loss for the entire season. Harvey struck Texas on August 26, bringing a historically high amount of rainfall to southeastern Texas and causing heavy rainfalls in several southern states including Louisiana, Mississippi, Alabama, Tennessee, and Kentucky (Blake and Zelinsky, 2018). Irma demolished Caribbean islands on September 6 and subsequently made landfall in Florida, Georgia, South Carolina, and Alabama (Cangialosi et al., 2018).

Extreme weather and climate events can trigger ecosystem-level disturbances that lead to profound and widespread changes in

ecosystem structure and function. Large storms are the main drivers of exporting materials and elements from watersheds to aquatic systems (Brion et al., 2011; Buffam et al., 2001). For instance, Raymond and Saiers (2010) found that storm events were responsible for, on average, 86% of annual export of dissolved organic carbon (DOC) from 30 small forested watersheds in the eastern United States. Similarly, Wilson et al. (2013) estimated that >60% of the annual export of dissolved organic carbon and nitrogen and bioreactive DOC (BDOC) occurred during hydrological events in a forested New England stream. These findings demonstrate that storms can generate nutrient and organic matter pulses that significantly alter substrate and energy subsidies to aquatic food webs, potentially influencing water quality and ecosystem metabolism.

In recognition of the potential ecological consequences to extreme weather events, researchers have developed conceptual frameworks integrating hydrological controls (e.g., storm events) on the transport and transformation of nutrient and organic matter. For instance, Raymond et al. (2016) proposed the "Pulse and Shunt" hypothesis arguing that storm flows create pulses of bioreactive dissolved organic matter (DOM) that could be quickly shunted to downstream systems and stimulate microbial activity therein. Along a similar vein, Creed et al. (2015) and Wollheim et al. (2018) recognized the potentially important role of



Fig. 1. Map of the study area, the sample sites, and the track of Hurricane Harvey and Hurricane Irma. Red circles indicate the locations where water samples were collected. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the position of a stream within a drainage network may play in responding to intense storms and formulated "The River as a Chemostat" and the "River Network Saturation Concept", respectively. These concepts suggest that the influence of storm flows (i.e., disturbance to the system) is most significant in low-order streams, where the terrestrial supply of solutes greatly exceeds the instream demand during high flows. The disturbance due to storms becomes more limited in high-order, large rivers where demands can counterbalance the storm pulses of solutes. Kaushal et al. (2018) highlighted the importance of simultaneously examining multiple solutes to fully understand the environmental and ecological consequences of storm flows in their "Watershed Chemical Cocktails Concept", emphasizing the varied export behaviors of solutes and elements.

Though the existing conceptual frameworks can be applied to baseline, null-hypothesis scenarios, they do not easily incorporate the heterogeneous potentially strong influence of local and regional biophysical characteristics into their predictions. Such variables can often be significant, and can produce high levels of spatiotemporal variability in the amount, source, composition, and quality of solutes during storms. For example, it remains unclear whether storms enhance or lower the bioreactivity of DOM in streams. Wilson et al. (2013) suggested that storm flow DOM was labile to microbial utilization because of a reduced soil-to-stream residence time that led to 'fresh', lessdegraded compounds. Conversely, others showed that stormmobilized DOM had a high molecular weight and structural complexity (Hu et al., 2016; Lu et al., 2013; Rosenstock and Simon, 2001) that would lower the bioreactivity of DOM. Similarly, solute concentrations during storms flows may increase (e.g., Buffam et al., 2001; Raymond and Saiers, 2010; Hu et al., 2016) or decrease (Clark et al., 2008; Williams, 1989), depending on the availability of watershed supplies and watershed-stream connectivity (e.g., "transport-limited" or "source-limited export") (Basu et al., 2011; Creed et al., 2015). The diverse characters of solute transport during storm flows demonstrate the need to assess the effects of large storms on stream biogeochemistry within the context of local to regional watershed heterogeneity.

In this study, we examined the influence of Hurricanes Harvey and Irma on the export of dissolved nutrients and organic matter in a group of streams (n = 10) in the southeastern United States. The southeastern states export higher loads of land DOC than other regions of the US (Stets and Striegl, 2012) and represent a critical geographic area that has significant influences on the carbon budgets of terrestrial ecosystems and inland waters (Battin et al., 2009; Ciais et al., 2008; Yang et al., 2017). The study streams drained a diverse range of watersheds situated in five states influenced by storms related to Harvey and/or Irma. We analyzed the concentration of dissolved nutrients (nitrate, nitrite, and orthophosphate) and dissolved organic matter (DOM) and the source, composition, and bioreactivity of DOM exported during the storms. The objectives of our study were to: 1) estimate the amount of dissolved nutrients and organic matter in streams mobilized by the two hurricanes; 2) examine changes in the amount, source, and bioreactivity of DOM transported during storms as a function of stream water discharge and watershed characteristics; 3) assess the co-export of dissolved nutrients and organic matter and the consequent alterations to solute stoichiometry in streams; and, 4) discuss the relative importance of watershed heterogeneity versus storm characteristics in determining the export of dissolved nutrients and organic matter. As the frequency and intensity of extreme weather and climate events are projected to rise in the next century, this study gives insight into future variability in energy and substrate availability to aquatic food webs in southeastern streams.

2. Methodology

2.1. Study area

We sampled streams from five Gulf and South Atlantic states influenced by storms related to Hurricane Harvey and/or Hurricane Irma, including Alabama (n = 2 sites), Mississippi (n = 3), Tennessee (n = 12), Georgia (n = 2) and South Carolina (n = 1) (Fig. 1). The two states where the hurricanes made landfall, Texas and Florida, respectively, were not sampled because of logistical challenges (e.g., difficulty in site access and personnel coordination). The study areas were located in the humid subtropical climate zone, with annual temperatures ranging from 16 to 22 °C and annual precipitation from 1270 to 1626 mm. The hurricane seasons are usually from August through October, when tropical moist air masses from oceans travel northwards to the coastal states. The study sites included ten first- to sixth-order streams draining various types of land covers and landforms (Table 1). The watershed boundary of each site was delineated using the National Hydrography Dataset (NHDPlus; http://www.horizon-systems.com/NHDPlus/ NHDPlusV2_data.php), and the land use composition was calculated based on the National Land Cover Database 2011 (NLCD2011; https:// www.mrlc.gov/nlcd11_data.php). The upland drainage areas of the sampling sites ranged from 0.38 to 134.86 km². The main watershed land use was 'deciduous forest' for six sites, accounting for 69 to 96% of the drainage area, 'urban land' for three of the sampling streams (44 to 84%), and 'woody wetland' (66%) for one site (Pee Dee River, SC). Among the six forested watersheds, the major forest types were loblolly pine, white oak, red oak and hickory, and the woody wetland was surrounded by sweetgum, nuttall oak and willow oak, according to the United State Forest Service (https://databasin.org/datasets/ e874a247b7e44693ad0792fb1a252aba). The underlying geology varied from limestone, calcarenite, and gneiss bedrocks in GA and TN to alluvium consisting of gravel, sand, clay, and mud in AL, MS, and SC. Seven streams including all sites in AL and MS, Richland Creek in TN, and Pee Dee River in SC were located in floodplains with a very gentle watershed slope (<3%), whereas both sites in GA and Whites Creek in TN drained hilly terrain with a steeper watershed slope (<15%). The depth of soils was mostly between 150 and 200 cm (National Resources Conservation Service Soils (NRCSS), https://www.nrcs.usda.gov/wps/ portal/nrcs/site/soils/home/). Based on the four natural drainage classes from NRCSS, soils in the wetland-dominated watershed of the Pee Dee River were 'very poorly drained' and the two sites in GA were 'well drained'. Soils at the other sites were classified as 'somewhat well drained', 'moderately well drained', or between the two categories.

2.2. Flow characterization

The daily precipitation data of the study sites were acquired from the National Oceanic and Atmospheric Administration (NOAA) online weather data (https://w2.weather.gov/climate/). Four of the sampling streams had continuous discharge data from the United States Geological Survey (USGS) gauging stations: USGS 03431700 at the Richland Creek, TN; USGS 03431599 at the Whites Creek, TN; USGS 02135200 at the Pee Dee River, SC; and USGS 02217500 at the North Oconee River, GA. For the ungauged sites, we measured discharge during each sampling campaign following the velocity-area method from USGS (Buchanan and Somers, 1969). At each site, a uniform section of the stream was selected to measure the depth using a ruler and velocity $(m s^{-1})$ every 50 cm using a portable flowmeter (MARSH-McBIRNEY, INC., model 2000). Stream water discharge was calculated by multiplying the area by the mean velocity of each subsection and then summing across the subsections. These measurements generated daily discharge for four sites, the Mayfield Creek in AL and the upstream 1, upstream 2 and downstream of Noxubee River in MS. Two sites (Trail Creek, GA and South Sandy Creek, AL) had no available discharge data due to the difficulty in accessing to the sites during storms, and they were not included in discharge-related data analysis. Because of the high variability in baseline discharges across watersheds, and in order to compare the influences of storm-related discharge rises across the sites, we calculated relative discharge by setting the highest discharge in each site as 1 and assigning other discharge values in proportion to the highest value.

Table 1

Watershed characteristics of ten study streams in the southeastern United States.

Site name	State	GPS coordinates (°)	Sampled hurricane	Dominant land use ^a	Landform ^c	Stream order ^b	Watershed area (km ²)	Slope ^c (%)	Natural drainage class ^c
Mayfield Creek	AL	N 32.95966 W 87.40813	Harvey, Irma	Forest (95%)	Flood plains	2	22.59	0-1	Moderately well drained
South Sandy Creek	AL	N 33.012839 W	Harvey, Irma	Forest (93%)	Flood plains	4	14.28	0–2	Moderately well drained, Somewhat poorly drained
Noxubee River	MS	87.484968 N 33.26430 W 89.04510	Harvey,	Forest (96%)	Flood plains	2	2.41	0-2	Somewhat poorly drained
Noxubee River (upstream 2)	MS	N 33.27560 W 89 32000	Harvey, Irma	Forest (87%)	Flood plains	1	0.38	0–2	Somewhat poorly drained
Noxubee River	MS	N 33.27190	Harvey,	Forest (83%)	Flood plains	3	11.33	0–2	Somewhat poorly drained
Richland Creek	TN	N 36.15117	Harvey	Urban land (70%)	Flood plains	3	62.17	0–3	Moderately well drained
Whites Creek	TN	N 36.21756 W 86 82023	Harvey	Forest (69%)	Stream terraces and hillslopes	5	134.86	2–7	Moderately well drained
Trail Creek	GA	N 33.95690 W 83 36516	Irma	Forest (40%) and urban	Flood plains, hill	3	22.99	0–15	Well drained
North Oconee River	GA	N 33.94667	Irma	Urban land (84%)	Hill	4	9.47	6-10	Well drained
Pee Dee River	SC	N 33.66083 W 79.15472	Irma	Wetland (66%)	Carolina bays, depressions	6	52.04	0-2	Very poorly to poorly drained

^a Land cover data were determined based on the National Land Cover Database 2011.

^b Stream order and watershed area were determined based on the National Hydrography Database.

^c Landform, watershed slope, and natural drainage class were determined based on the datasets of National Resources Conservation Service Soils.

2.3. Water sampling

Stream water samples were collected daily during and after the storm events. Harvey sampling started on August 31, 2017 and ended on September 4, 2017, and Irma sampling was from September 8 through September 16, 2017. The sites in AL and MS were influenced by both Harvey and Irma, whereas the other sites were influenced only by Harvey (streams in TN) or Irma (streams in GA and SC; Fig. 1). Surface water samples were collected in pre-cleaned glass or HPDE bottles and filtered. All samples were filtered through 0.2 µm filters (VWR syringe polyethersulfone filter) and the filtrates were divided into three fractions for the analyses of DOC, DOM, and dissolved nutrients, respectively. The fraction for dissolved nutrients was stored frozen at -20 °C until the analysis. Selecting the optimal storage method for generating accurate DOC and DOM results remains a challenge for biogeochemists. While immediate analysis after sample collection yields the most realistic results, it is often not logistically possible, and freezing and acidification are the most commonly used methods to prevent biodegradation, yet several studies that have assessed these storage methods reported varied, site-dependent results (Heinz and Zak, 2018; Peacock et al., 2015; Spencer et al., 2007; Walker et al., 2016). As such, we did not freeze or acidify samples but stored them at 4 °C in the dark and performed the measurements within two weeks.

2.4. Dissolved organic carbon and nutrient concentration

All measurements were done in duplicate. DOC and TDN (total dissolved nitrogen) concentrations were measured on a Shimadzu TOC-V total organic carbon analyzer interfaced with a TNM-1 total nitrogen measuring unit, following the method described by Shang et al. (2018). The concentrations of dissolved nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium (NH₄⁺) and phosphate (PO₄³⁻) were analyzed on a Skalar San⁺⁺ Automated Wet Chemistry Analyzer at the Dauphin Island Sea Laboratory, Alabama, following EPA methods (EPA method 353.2, 350.1, and 365.1). The flux of each solute (e.g., DOC, dissolved inorganic nutrients) was calculated as the product of water discharge and the concentration of the corresponding solute.

2.5. DOM optical properties

The optical properties of DOM can provide information about the source and composition of DOM (Lu et al., 2014, 2015a; Ohno and Bro, 2006; Wilson and Xenopoulos, 2008). The absorbance of DOM was collected on a UV-1800 Shimadzu spectrophotometer. The sample was warmed to room temperature, decanted to a quartz cuvette with a 1-cm path length, and scanned from the wavelength of 190 to 670 nm at a 1 nm interval. Three-dimensional fluorescence excitation-emission matrices (EEMs) were collected on a Horiba Jobin-Yvon Fluoromax-3 spectrofluorometer. The reading was collected at excitation wavelengths from 250 to 500 nm at 5 nm intervals and emission wavelengths from 280 to 520 nm at 3 nm intervals. The spectra were corrected for blanks, the inner filter effect, and the manufacturer's correction factors. The data were subsequently normalized relative to the area under the water Raman peak at the excitation wavelength of 350 nm (Cory and McKnight, 2005). A series of DOM source-composition indices were calculated from the absorbance and fluorescence spectra, including SUVA₂₅₄, spectral slope ratio (S_R), E₂:E₃, fluorescence index (FI), humification index (HIX), freshness index (β : α), and their calculation and interpretations are described in detail in Supplementary materials. The parallel factor analysis (PARAFAC) was conducted in MATLAB using the DOMFluor toolbox to resolve the complex fluorescence spectra into main identifiable components according to the location of excitation and emission peaks (Stedmon and Bro, 2008). The final model was validated using the split-half analysis (Murphy et al., 2013) (Supplementary Figs. S1–S3).

2.6. Experimental incubations and bioreactive DOC estimates

All samples were evaluated for bioreactive DOC, following the procedure for laboratory incubations that has been previously described in detail by Lu et al. (2013) and Shang et al. (2018). Briefly, water samples and carbon-free ultrapure water (as a blank control) were filtered through 0.2 μ m filters (VWR syringe polyethersulfone filter) and distributed to two incubation vials that represented incubation replicates. In order to start all microcosms with a similar amount and type of bacterial biomass for the incubation, all vials were inoculated with 1% (by volume) in situ raw stream water from the Mayfield Creek, AL. The incubations lasted 15 days in the dark in an incubator with the temperature maintained at 20 °C. Subsamples were collected at the start and end time points of the incubations (day 0 and 14 respectively) and refiltered through 0.2 µm prior to the analyses for DOC concentrations and DOM optical properties. Throughout the incubations, the water samples were left standing in incubations bottles in an incubator, and the lids of the bottles were removed every day to ensure oxygen availability in the headspace. BDOC was calculated as percentage decreases in DOC from day 0 to day 14, and mean BDOC values calculated from incubating carbon-free ultrapure waters were subtracted from BDOC of each sample as a blank correction. Percent BDOC was calculated as dividing DOC loss from day 0 to day 14 over the DOC concentration at day 0.

Subsamples at day 0 and 14 were also analyzed for bacteria counting assays, following the method described in detail by Nollet and De Gelder (2000). Briefly, pour plates were prepared using a non-selective Tryptic Soy Agar (TSA) to measure the total consortia of viable and culturable microbes. 100 μ L of water samples were placed aseptically on the center of 100 \times 15 mm sterile Petri plates, and 15 mL of agar was poured immediately on the sample, swished well, to create a homogenous mixture of agar and sample. The Petri plates were immediately inverted and incubated at 37 °C for 24 h, prior to the counting of microbial colonies on a magnifying colony counter. The colony forming unit (CFU) per 100 mL was used to report the growth of the culturable microbial population present in the water samples. All samples were analyzed in duplicate.

2.7. Data analysis

Our goal was to determine how hydrologic condition and watershed characteristics influenced the concentration of dissolved nutrients and DOC, the source and composition of DOM, and the bioreactivity of DOM. Because our data were not all normally distributed, we used nonparametric tests for all statistical analyses, and the level of significance, α , was set at 0.05 (two-tailed). We used Spearman's rank-order correlation to measure the strength and direction of correlation of two variables, and we used twosample Wilcoxon test to assess if significant differences existed in a given dependent parameter between two groups of watershed land cover. We further performed the redundancy analysis (RDA) using CANOCO 4.5, following the method described by Lepš and Šmilauer (2003), to assess and compare the influences of hydrological and watershed variables as predictors on the amount, source, and quality of DOM and the amount of nutrients. Prior to the RDA analysis, the variance inflation factors (VIF) of each hydrological and watershed predictor were calculated, and predictors with VIF greater than 10 were dropped to avoid multicollinearity. The hydrological and watershed predictors included were percent urban land (%urban land), percent wetland (%wetland), stream order, watershed slope, watershed area, and relative discharge. Additionally, detrended correspondence analysis (DCA) was conducted before performing RDA to determine if the linear ordination methods (e.g., RDA) is applicable, based on a model of linear response of species to the underlying environmental gradient described in Lepš and Smilauer (2003). For our data, we estimated the heterogeneity of DOM and nutrient variables along the ordination axes based on the gradient length, and we found it was feasible to perform RDA, since the gradient length for the first four axes was all shorter than 3. Monte-Carlo permutation test (999 permutations without restriction) was used to evaluate the significance of the first canonical axis and all canonical axes under a reduced model, from which the resulting *p* values were <0.01.

3. Results

3.1. Hydrology

The accumulated precipitation of the study region was 265 mm during Hurricane Harvey (August 31 to September 4, 2017) and 197 mm during Hurricane Irma (September 8 to 16). All sites showed increases in water discharge following the precipitation (Fig. 2); however, there was a large fluctuation in the magnitude of increases among sites. The four study sites with continuous discharge measurements from USGS gauging stations had well-established baseline conditions prior to and after the storms. During the storm, the peak discharges of the four sites varied in the range of 21.52 to 345.47 m³ s⁻¹, and the magnitude of increase relative to prior-storm discharges ranged from 1.20 times in the Pee Dee River to 67.20 times in the Whites Creek. According to the hydrographs (Fig. 2), storm flows lasted 3 to 6 days except for the Pee Dee River where high flows were maintained over 10 days. The Pee Dee River was also the only site draining a watershed dominated by wetlands that likely acted as temporary floodwater storage and buffered the impacts from storm events. The ungauged study streams with discharge data collected via velocity-area method had smaller drainage areas and exhibited overall low discharge, with the peak discharge varying from 0.05 to $1.94 \text{ m}^3 \text{ s}^{-1}$ and being two to four times higher than the lowest discharge measured.

3.2. Dissolved organic carbon and nutrients

Stream water DOC concentration varied in a large range, from 1.54 to 19.01 mg L^{-1} (Supplementary Table S1). Although DOC concentration did not vary as a function of relative discharge (Fig. 3a), the highest DOC concentration was observed at the peak discharge in most of the sites. DOC concentrations varied due to watershed land use, with the highest values observed in the stream draining wetlands, which were around five times higher than those from forested and urban watersheds (Table 2).

Nitrate had the highest concentration among the four inorganic N and P nutrients species analyzed (Table 2; Supplementary Table S1). None of the four species correlated with the relative discharge (Fig. 3b–e), but the concentration of inorganic N species varied due to land cover (Table 2). For all three species of N nutrients, the forested streams had significantly lower values than the streams draining urban watersheds. The values for the wetland-dominated watershed tended to fall between those for the forested and urban watersheds, yet the lowest nitrate appeared in the wetland-dominated watershed (Table 2).

3.3. Source and composition indices of dissolved organic matter

Three fluorescence components (C1 to C3) were identified by the PARAFAC analyses (Supplementary Fig. S4). C1 showed excitation and emission characteristics similar to terrestrial humic-like DOM originating from the soil and terrestrial plants, whereas C2 and C3 were spectrally similar to microbial humic-like DOM and protein-like DOM, respectively (Table 3). Among ten study sites, DOM was dominated by microbial humic-like DOM ($%C2 = 43.16 \pm 2.59\%$, mean \pm standard deviation), followed by terrestrial humic-like DOM ($%C1 = 31.30 \pm 6.12\%$) and then protein-like DOM ($%C3 = 25.55 \pm 7.03\%$).

In order to confirm the source-compositional interpretations of the fluorescence components and optical properties, we evaluated the correlations among different proxies (Table 4). Percent C1 was negatively correlated with FI and β : α and positively correlated with HIX, and percent C3 was also significantly correlated with these indices but with opposite signs. Percent C2 was positively correlated with HIX and E₂:E₃ but negatively with SUVA₂₅₄. These correlations show that soil-derived C1 was more structurally complex and diagenetically altered than protein-like C3 that was sourced mostly from instream organisms.

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Fig. 2. Precipitation and discharge of the study sites in the southeastern United States. The discharge data in the top four panels were retried from USGS gauging stations and the discharge in the panels below were collected using the velocity-area method. The letters 'H' and 'I' indicate the days of sampling during the Hurricane Harvey and Irma, respectively.

Microbial humic-like DOM C2 was humic in nature but had low aromaticity and small molecular weights.

We further evaluated the effects of flow conditions and watershed land use on DOM source-composition proxies. We found that percent contributions of C1 and C3 varied as a function of relative discharge. As relative discharge increased, %C1 increased but %C3 decreased (Fig. 4; Table 4). Percentage contributions of C1 and C3 also varied due to watershed land use types (Table 2). The wetland-influenced stream (Pee Dee River), relative to those draining urban and forested watersheds, showed significantly higher percentages of terrestrially-derived



Fig. 3. Variation in the concentrations of dissolved organic carbon and nutrients and dissolved stoichiometric ratios relative to relative discharge in the ten study streams in the southeastern United States. The *ρ* and *p* values were calculated from Spearman's rank-order correlations.

Table 2

Results of two-sample Wilcoxon tests to assess differences in dissolved organic matter and nutrients (mean \pm standard deviation^a) among different land cover. Non-overlapping super-script letters within a column indicate that significant differences between the watershed attributes were detected at the 95% confidence level.

Land cover ^b	DOC (mg L ⁻¹)	BDOC (%)	%C1	%C2	%С3	FI	HIX	α:β	$\begin{array}{c} {\rm SUVA}_{254} \\ ({\rm Lmg}^{-1} \\ {\rm m}^{-1}) \end{array}$	E ₂ :E ₃	S _R	NO_3^- (mg L^{-1})	$NO_2^- \ (\mu g \ L^{-1})$	$\begin{array}{c} \text{NH}_4^+ \\ (\mu g \ L^{-1}) \end{array}$	PO ₄ ³⁻ (μg L ⁻¹)
Forest	$3.52~\pm$	24.70 \pm	31.64 \pm	42.98 \pm	$25.39~\pm$	1.72 \pm	0.64 \pm	1.00 \pm	4.53 \pm	5.05 \pm	0.76 \pm	1.10 \pm	$3.11 \pm$	$5.17 \pm$	153.09 ±
	2.21 ^a	16.20 ^a	4.52 ^a	2.19 ^a	5.65 ^a	0.06 ^a	0.05 ^a	0.11 ^a	2.58 ^a	1.59 ^a	0.07 ^a	2.00 ^a	4.52 ^a	5.69 ^a	235.51 ^{a,b}
Urban	$3.62 \pm$	39.33 \pm	26.19 \pm	43.34 \pm	30.47 \pm	1.85 \pm	$0.60 \pm$	$1.18 \pm$	$2.16 \pm$	$5.52 \pm$	$0.81 \pm$	$4.89 \pm$	12.04 \pm	$62.11 \pm$	121.84 \pm
land	1.13 ^a	15.97 ^b	2.86 ^b	3.78 ^a	4.23 ^b	0.07 ^b	0.04 ^b	0.13 ^b	0.62 ^b	1.54 ^a	0.04 ^b	5.25 ^b	5.50 ^b	39.88 ^b	165.48 ^a
Wetland	17.68 \pm	$9.22 \pm$	$45.82~\pm$	44.32 \pm	$9.86 \pm$	1.48 \pm	0.87 \pm	$0.79 \pm$	$4.97 \pm$	$4.45~\pm$	$0.80 \pm$	$0.59 \pm$	10.56 \pm	$37.06~\pm$	61.87 \pm
	1.74 ^b	4.39 ^c	0.85 ^c	0.37 ^a	0.52 ^c	0.01 ^c	0.01 ^c	0.02 ^c	0.08 ^a	0.05 ^a	0.00 ^{a,b}	0.23 ^a	1.03 ^b	7.23 ^b	22.08 ^a

^a Standard deviation was calculated from samples collected from each site at different sampling days.

^b Land cover of ten watersheds included forest (Mayfield Creek, South Sandy Creek, three streams of Noxubee River and Whites Creek), urban land (Richland Creek, Trail Creek and North Oconee Creek) and wetland (Pee Dee River).

humic-like DOM but lower percentages of microbially-derived proteinlike DOM. Except for S_R indicative of molecular weight, the DOM indices all showed significant correlations with relative discharge (Table 4), with higher aromaticity (higher SUVA₂₅₄ and lower $E_2:E_3$) and greater contribution of terrestrial, humic, diagenetically-altered DOM (lower FI and β : α but higher HIX) observed during high flows. The fluorescence index varied from 1.46 to 1.95, and the humification index varied from 0.52 to 0.87, suggesting that the stream water DOM was derived from a mixture of terrestrial and microbial sources. DOM indices also varied due to watershed land use (Table 2). Specifically, DOM from the stream draining wetlands showed the highest degree of humification but the least contributions from microbial, freshly-produced DOM (significantly lower FI and β : α but higher HIX), and the developed watersheds displayed an opposite pattern (higher FI and β : α but lower HIX). The aromaticity and molecular weight of DOM were lower (significantly lower SUVA₂₅₄ and higher S_R) from urban watersheds than those from forested and wetland watersheds.

3.4. Bioreactivity of dissolved organic matter

Percent BDOC ranged between 0.12% and 70.64% and averaged 27.40 \pm 17.55%. Based on the correlations between %BDOC and sourcecompositional indices (Table 4), DOC bioreactivity was lower in samples with higher aromaticity (SUVA₂₅₄) and terrestrial humic-like DOM (% C1) and higher when there was a larger proportion of microbial (FI), freshly-produced (β : α), low-molecular-weight DOM (E_2 : E_3 ; S_R). In addition, %BDOC was negatively correlated with the ratio of DOC:TDN and DOC:PO₄³⁻ (Table 4).

We found that %BDOC decreased as relative discharge increased (Fig. 4d), with %BDOC at the peak discharge being two to eight times lower than the value at the lowest discharge. Percent BDOC also varied due to watershed land use, being lowest for the wetland-dominated watershed and highest for the urban watersheds (Table 2). The number of culturable heterotrophic bacteria had increased during 14-day

incubation, and the increases ranged from 8 to 80 CFU averaging 28 \pm 19 CFU. However, these increases did not have a significant correlation with %BDOC (Table 4).

3.5. Fluxes of nutrients and DOM

Although the concentrations of dissolved nutrients and DOC did not vary as a function of relative discharge, the increases in discharge during storms led to higher fluxes for all the sites, with the total fluxes of NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , and DOC at the peak discharge being 1.70–4.76, 1.23-20.75, 1.45-44.00, 1.85-4.76 and 1.57-159.96 times higher than those at the lowest discharge, respectively. The percent terrestrial humic-like DOM (%C1) also increased as a function of relative discharge (Fig. 4a) whereas the percent protein-like DOM (%C3) showed opposite pattern (Fig. 4c), but the corresponding fluxes of three DOM fluorescence increased from 1.53 to 162.91, 1.45 to 131.79 and 1.38 to 94.08 fold higher at peak discharge than that at the lowest discharge for terrestrial humic-like DOM, microbial humic-like DOM and protein-like DOM, respectively. Although the proportion of BDOC declined with increasing discharge (Fig. 4d), the BDOC flux at the peak discharge increased from 1.65 to 21.80 fold relative to that at the lowest discharge. The fluxes of nutrients, DOC, DOM fluorescence and BDOC increased fitting into a power function of discharge (Fig. 5). DOC, DOM fluorescence and dissolved inorganic nitrogen (DIN) indicate a flushing mechanism (slope > 1) with increasing discharge, in opposition to PO_4^{3-} that was diluted (slope 1, and BDOC concentration remained constant relative to discharge (slope = 1, Fig. 5). Notably, the Pee Dee River, the only site draining a wetland-dominated watershed, displayed the lowest magnitude of increase in the flux of all materials, including nutrients, DOC, and BDOC, compared to urban and forested streams.

At the four sites with daily discharge available, the discharge was a strong predictor for the fluxes of DOC ($R^2 > 0.95$, p < 0.01). Discharge was also a good predictor for the fluxes of all four inorganic nutrient species in the Whites Creek ($R^2 > 0.95$, p < 0.05), as well as for the fluxes

Table 3

Excitation-emission spectra of three fluorescence components (C1–C3) identified by the PARAFAC modeling from the ten study streams in the southeastern United States, compared to previously published similar PARAFAC components against the OpenFluor database (Murphy et al., 2014).

Component	Excitation maximum	Emission maximum	Present study	Similar fluores studies	scence compoi	nents in previous	Similar fluorescence components compared in OpenFluor database
	wavelength	wavelength		(Yamashita et al., 2010)	(Cory and McKnight, 2005)	(Stedmon and Markager, 2005)	(similarity score of excitation/emission ≥ 0.99)
C1	250	466	Terrestrial humic-like DOM	C2	C2	1	C1 (Osburn et al., 2016) C1 (Shutova et al., 2014) C1 (Tanaka et al., 2015) C1 (Kulkarni et al., 2018) C1 (Kowalczuk et al., 2009) C3 (Stedmon et al., 2003)
C2	250 (310)	388	Microbial humic-like DOM	C4	C3	6	C2 (Gonçalves-Araujo et al., 2016) C2 (Tanaka et al., 2015)
C3	250 (280)	322	Autochthonous, protein-like DOM	C7	C13	8	C5 (Cawley et al., 2012)

Fable 4 Spearman correlatio	n coefficients ((p) among va	rrious DOM	indices, nutri	ents and relati	ve discharge.									
	BDOC (%)	%C1	%C2	%C3	FI	HIX	β:α	$SUVA_{254}$ (L mg ⁻¹ m ⁻¹)	E2:E3	S _R	Bacteria growth (CFU)	NO_3^- (mg L ⁻¹)	DOC:TDN	D0C:P044	Relative discharge
DOC (mg I -1)	-0.623**	0.071	0.051	-0.052	-0.353**	0.158	-0.068	0.174	-0.182	0.209	-0.006	0.011	0.142	0.396*	0.251
BDOC		-0.463	0.150	0.246	0.786**	-0.297	0.553**	-0.654^{**}	0.583**	0.317*	0.104	0.558*	-0.583**	-0.554^{**}	-0.813**
%C1 %C2			0.293*	-0.908^{**} -0.615^{**}	-0.618^{**} 0.082	0.866** 0.636**	-0.950^{**} -0.169	$0.246 - 0.326^*$	0.115 0.623**	-0.239 0.117	0.229 —0.022	-0.676^{**} 0.110	0.808^{**} 0.021	0.385* —0.336*	0.447^{*} -0.142
%C3 FI					0.424**	-0.975^{**}	0.815** 0 721**	-0.071 -0.675^{**}	-0.351 0.405**	-0.183 0 345**	-0.128	— 0.576* 0.695**	-0.649** 0.733**	-0.240 0.576**	0.390* 0.487**
HIX						011-00	-0.746^{**}	0.085	0.287*	-0.187	0.124	-0.460^{**}	0.575**	0.235	0.454**
β:α								-0.339	-0.060	0.223	-0.16	0.744**	-0.897	-0.524^{**}	-0.427** 0.427**
$SUVA_{254}$ (Lmg ⁻¹ m ⁻¹)									-0./41	-0.659.0	-0.150	-0.417	0.361	0.239	0.433
E2:E3										0.443**	0.115	-0.230	0.031	-0.392^{*}	-0.454^{**}
S _R Bactoria growth											0.146	0.335*	-0.179	-0.047	-0.302 0.145
(CFU)												HH7.0-	0110	CC7.0	0.11.0
NO ²													-0.857**	-0.416^{**}	-0.342
$(mg L^{-1})$														***	****
DOC:TDN DOC:P0 ³ -														0.548	0.430
* $p < 0.05$ (the co. ** $p < 0.01$ (the co.	rrelation is sign rrelation is sign	nificant at the nificant at the	e level of α ; level of α	= 0.05). = 0.01).											

of all solutes but nitrate in the North Oconee River ($R^2 > 0.85$, p < 0.05), and except ammonium in the Richland Creek ($R^2 > 0.95$, p < 0.05), but it could only well explain the fluxes of ammonium in the Pee Dee River ($R^2 = 0.90$, p = 0.05) (Supplementary Table S2). Using the long-term gauge data during September and the flux vs. discharge curve developed from our collected samples for each site, we estimated the total September flux of dissolved organic carbon and nutrients. We found that, relative to the total flux over the entire month, the flux during Harvey or Irma related storms over four to five days accounted for disproportionally large percentages across sites and solutes. They were 24 to 99% for DOC, 70 to 85% for nitrate, 41 to 87% for nitrite, 28 to 91% for ammonium, and 54 to 94% for orthophosphate (Supplementary Table S3).

3.6. RDA analysis

Axis 1 and axis 2 of the ordination diagram together explained 45.9% of the total variance in DOM and dissolved nutrients (Fig. 6). The first canonical axis explained 35.8% of the variance and showed that nitrate, nitrite, phosphate, DOM molecular weight (S_R and E_2 : E_3), %BDOC, the proportion of microbially-derived humic DOM (%C2), FI, and β : α can be positively predicted by %urban land, watershed slope and watershed area but negatively by relative discharge. The SUVA₂₅₄, on the contrary, was positively predicted by relative discharge but negatively by %urban land, watershed slope and area. The second axis explained 10.1% of the variance, along which DOC, the proportion of terrestrially-derived humic DOM (%C1), HIX, and ammonium were positively predicted by %C3) showed an opposite pattern.

4. Discussion

4.1. Storm mobilization of terrestrial organic matter to the aquatic environment

Inland waters receive vast quantities of organic matter and nutrients from land (Battin et al., 2009). The amount and forms of these materials mediate energy flows and substrate availability to aquatic organisms and thus are of vital importance to water quality and ecosystem metabolism (Young et al., 2008). Both modeling and empirical studies have shown that terrestrial organic matter serves as an important energy subsidy in lotic ecosystems, manifested by the prevalence of streams and rivers that are heterotrophic (Webster, 2007). Our results provide strong evidence that hurricanes can lead to hydrological and chemical disturbance to multiple streams simultaneously in a large geographical region. Though usually brief, large storms can shift the quantity and quality of terrestrial supplies of organic matter and nutrients to rivers and streams in a significant and rapid manner.

By evaluating changes in DOM and nutrients as a function of relative discharge, we were able to isolate the effects of flow variation by removing the effects of watershed heterogeneity. We found the source and composition of DOM in all streams showed consistent shifts relative to relative discharge (Fig. 4). That is, a shift from autochthonous to allochthonous sources of DOM occurred during the storms, as evidenced by an increasing contribution of high-molecular-weight, structurally complex, humic compounds relative to protein-like, less diageneticallyaltered compounds (Fig. 4). Meanwhile, the flux of DOC and soilderived humic-like compounds increased with rising discharge at all sites (Fig. 5). These changes demonstrate a shift to shallower flow paths during the storms that enabled the mobilization of plantderived organic compounds accumulating in upper soil horizons (Hu et al., 2016; Singh et al., 2014; Yoon and Raymond, 2012). Our data further demonstrate that storm flows can lead to the accumulation of aromatic, humic-like compounds in streams. Similarly, Fasching et al. (2016) found that summer storms enhanced the stream water DOC concentration with an elevated HIX and reduced S_R in a second-order



Fig. 4. Variation in the proportions of the three DOM components, the percentage contributions of bioreactive DOC, DOM source and quality proxies relative to relative discharge in the study streams in the southeastern United States. The *ρ* and *p* values were calculated from Spearman's rank-order correlations. A linear fitting line (blue line) with 95% confidence intervals (grey shade) is plotted for BDOC vs. relative discharge as the two parameters shows an apparent linear correlation pattern. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

stream located in the eastern Alps. In addition, Vidon et al. (2008) observed increased DOC concentrations and enrichment of aromatic substances and lignins in two headwater streams during storms.

Our flux estimates demonstrate that hurricanes are highly efficient in mobilizing allochthonous organic matter to aquatic systems. In the four study sites with a continuous discharge record, the hurricanerelated storms over 4 to 5 days corresponded to the largest stream water discharge recorded in September, and they contributed up to 98% of the total monthly flux of DOC. The disproportionally important role of hurricane-related storms in transporting organic matter has been previously reported. Hurricane Irene was responsible for 43% of the mean annual DOC flux in a second-order mountainous stream in New York, though it only lasted five days (Yoon and Raymond, 2012), and Hurricane Gustav over 9 days contributed to 24% of annual DOC flux in forest-dominated lower Pear River watershed in Mississippi (Cai et al., 2013). In the Cape Fear region of North Caroline, Hurricane Fran and Hurricane Floyd accounted for over 30% and 50% of annual DOC flux in rivers, respectively, but Hurricane Bertha and Hurricane Bonnie did not cause large increases in DOC flux due to minimal effects on flow rates (Avery Jr et al., 2004).

4.2. Controls of watershed heterogeneity on solute transport in streams

It has been well recognized that a range of watershed attributes can mediate the export of terrestrially-derived materials. Yet, the effects of watershed heterogeneity and hydrological flows are difficult to separate



In(Discharge) (m³ s⁻¹)

Fig. 5. Variation in the flux of DOC, bioreactive DOC, three fluorescence components, dissolved inorganic nitrogen, and orthophosphate relative to discharge in the study streams in the southeastern United States. Blue dashed lines represent power regression trendlines, and the associated functions, R-square, and *p* values are presented. The grey shades represent 95% confidential interval. As discharge rises, solute concentration remains constant when the slope of the fitting line is equal to 1, increases when the slope is higher than 1, and decreases when the slope is <1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Redundancy analysis of hydrological and watershed variables (red arrows) as predictors for streamwater DOM properties and nutrients (black arrows) in the study streams in the southeastern United States. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(e.g., large watershed size and steep watershed slope often contribute to large water discharge). For example, Shang et al. (2018) studied the effects of agricultural land use on DOM export in a group of regional streams during baseflow conditions, and despite the spatial proximity of the study sites, the authors suggested that the influences of watershed heterogeneity were such that watershed-specific monitoring was needed to developed management practices that directly integrate organic carbon. In the present study, study sites were selected based on the availability of continuous discharge data and the practicability of sample collection during or immediately after the storms. The studied watersheds exhibited various characters but were not encompassing a range or gradient of certain watershed attributes (Table 1). Nevertheless, the influence of watershed still emerged as an important factor in our models. First, our results demonstrated that a relatively higher steam order, or a larger watershed area, corresponded to lower molecular weights of DOM and a greater proportion of autochthonous DOM (Fig. 6). This observation fits in the conceptual understanding of a general longitudinal pattern of DOM in lotic ecosystems. That is, as stream water DOM is transported from small streams to large rivers, it is increasingly shaped by photochemical and instream microbial alterations (Vannote et al., 1980; Raymond et al., 2016). However, it needs to be acknowledged that the study streams were not from the same fluvial continuum within a particular drainage network.

Second, our results underscore the importance of watershed land use/land cover in DOM and nutrient export. In particular, the Pee Dee River, the only site draining a wetland-dominated watershed, responded differently from other sites to the storms. The DOM in the Pee Dee River was characterized by a higher DOC concentration and a greater contribution of humic compounds originating from the decay of land plants, suggesting that wetlands had a high capacity of storing and releasing allochthonous organic matter to streams. Ecologists have long recognized the importance of wetlands and floodplains on providing organic matter as food resources to stream consumers (Atkinson et al., 2019; Edwards et al., 1990; Schenk et al., 2012). In wetland soils, the low oxygen availability, in tandem with prolonged soilwater contract time, facilities accumulation and effective leaching of structurally complex compounds. Yang et al. (2017), through compiling and analyzing dissolved organic carbon data from 1402 USGS gauge stations, found that wetlands positively influenced DOC concentrations, which suggests the high organic matter storage capacity of wetlands. Furthermore, relative to other sites showing rapid responses in water discharge and material flux, the magnitude of increase in the Pee Dee River was smaller (e.g., 1.56-fold increase in DOC flux) but more longlasting (>10 days), suggesting that wetland soils retained both water and organic compounds and acted as a sponge assimilating and dampening rapid and extreme hydrological disturbance to streams. Rather than releasing large, brief pulses of materials as seen in other streams, wetlands served as a buffer against rapid mobilization of allochthonous organic matter and nutrients to streams. This finding further highlights the importance of maintaining riparian swamps that are naturally abundant in the low-relief Coastal Plains along the eastern U.S. and Gulf of Mexico (Yang et al., 2017) but have been suffering a rapid loss due to human development (Kirwan and Megonigal, 2013; Nicholls et al., 1999)

Lastly, the watersheds influenced by urban development were more efficient in exporting inorganic N and P nutrients and biologically labile organic matter (Fig. 6; Table 2). Although considerable research has shown that urban lands are an important contributor to surface water nutrient pollution, rather less attention has been paid to the cotransport of inorganic nutrients and labile organic matter. High nutrient availability, by itself, can enhance the microbial degradation and assimilation of organic matter (Newbold et al., 2006; Romaní et al., 2004), and its co-export with labile organic matter in urban streams suggests that urban storm runoff may be particularly efficient in stimulating aquatic microbial activities. Furthermore, our results agree with previous findings that urban land use enhances the contributions of structurally simple, low-molecular-weight DOM in streams (Lu et al., 2014; Petrone et al., 2009; Williams et al., 2010; Yu et al., 2015). This pattern may be attributed to stimulated instream primary production and/or loss of soils enriched with humic organic compounds due to watershed development. These studies were mostly done at baseflow conditions, and our results showed similar influences persisting during storm flows.

4.3. Fate and ecological significance of storm-mediated export of DOM and nutrients

Although storm pulses of organic matter and nutrients have been recorded across systems and studies (Buffam et al., 2001; Inamdar et al., 2006), the fate of storm-related DOM and nutrients after they enter streams remains poorly characterized. Allochthonous organic matter constitutes a significant fraction of riverine respiration, particularly in small streams and upstream river reaches where light limitation hinders instream primary production (Webster, 2007). However, this pattern can be shifted by storm flows—the 'Pulse and Shunt Concept' argues that most reactive DOM transported by storms will be consumed in downstream rivers, due to the rapid transport of DOM during high flow events. Our results support this idea by demonstrating the flux of BDOC that was co-mediated by the concentration of BDOC and the discharge increased during storms (Fig. 5), which could stimulate microbial activities downstream. Our data also provide a mechanistic explanation for the longer uptake distance of terrestrial DOM during storms, besides a higher flow rate, by showing that percent BDOC was negatively correlated with relative discharge and strongly regulated by DOM composition (Fig. 4d; Table 4). The reduced residence time of DOM has been considered to be the primary reason for the longer uptake distance of DOM at higher flows (Raymond et al., 2016; Wollheim et al., 2018), and our data show that the increased proportions of humic, refractory DOM compounds can also dictate the uptake length. Our laboratory incubations give further insights into the fate of this storm-mediated BDOC flux. The degradation of DOC was accompanied by increases in the number of culturable heterotrophic bacteria over the course of incubations, suggesting that part of this DOC supported bacteria growth, in addition to fueling bacteria respiration. These results agree with previous studies showing that terrestrial DOM is an important substrate to heterotrophic bacteria biomass through anabolic processes (Hitchcock et al., 2016; Zhang et al., 2018), and terrestrial DOM, although traditionally viewed as refractory, could be more preferentially respired by heterotrophic bacterioplankton than autochthonous DOM (Karlsson et al., 2007).

Factors modulating the bioreactivity of DOC appeared to be spatially and temporally variable. The negative influence of discharge on BDOC observed here is different from some studies reporting that percent bioreactive DOC increased during high flows. Those observations were interpreted as a result of storm mobilization of upper soil compounds that had not been extensively degraded along the soil-to-stream continuum (Fellman et al., 2009; Wilson et al., 2013). The contrasting observations may reflect geographic and temporal variability. Our samples were collected from low-gradient streams during a humid summer, where DOM exported to streams had been largely altered in soils because soil columns had been thoroughly in contact with water for extended periods of time at higher temperatures. Furthermore, our sampling captured peak flow and posterior conditions (i.e., on the falling limb of a hydrograph) but not prior conditions (i.e., on the rising limb) (Fig. 2), and it is likely that we did not capture the more bioreactive DOM pool that was transported to the streams during early periods of flushing. As with uncertainties in how stream water DOM bioreactivity responds to storms, the consensus has not been reached regarding primary factors controlling DOM bioreactivity. The strong compositional controls on DOM bioreactivity observed here has been reported in some studies (Mann et al., 2012) but not in others (Lu et al., 2013; Wilson et al., 2016). These different observations may be related to the limitation of analytical techniques and experimental methods being commonly employed. For example, many BDOC incubation experiments considered only organic compounds completely remineralized or assimilated by microbes but did not count those partially oxidized. Lu et al. (2015b), through using a high-resolution ESI-FTICR-MS (Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry) technique, found that stream water DOM compounds can be significantly altered at the molecular level even when BDOC was barely detectable. On the other hand, the decoupling of BDOC and DOM composition may indeed reflect the importance of other mediating factors. Lu et al. (2013) found that BDOC in a group of streams in Virginia could not be explained by DOM composition but it is driven by stream water temperature fluctuation. Additionally, Wilson et al. (2016) suggested that microbes in small shaded streams could have adapted to degrading humic, structurally complex compounds that are commonly viewed as bio-refractory.

In all streams we sampled, we observed that storm flows led to rapid, large alterations of ecological stoichiometry (DOC: TDN and DOC: orthophosphate) (Fig. 3), which demonstrates that hurricanes are potent drivers of stoichiometric equilibrium deviations in inland waters. While the Redfield ratio (C:N:P = 106:16:1) has been widely used in marine systems to understand the elemental balance between microorganisms and the surrounding environment, the stoichiometric ratios in inland waters are highly variable with spatial and temporal differences remaining poorly formulated. Based on over 2000 observations from lakes, the seston stoichiometry of C:N:P averaged 166:20:1 (Sterner et al., 2008). Even though stoichiometry plays a central role in mediating the chemical constituents of microorganisms and biological fate of DOM, very few studies have reported the stoichiometric ratios of dissolved fractions (McDowell et al., 2019; They et al., 2017). In our samples, the negative correlations percent BDOC displayed with DOC: TDN and DOC:PO $_4^{3-}$ possibly indicate a preferred uptake of nutrients relative to DOC by microbes (Table 4). DOC: nutrient ratios were higher as discharge increased (Fig. 3f), demonstrating that storms caused disruptions of stoichiometric equilibrium established at baseflow conditions due to the inputs of nutrient-poor, carbon-enriched terrestrial materials. However, as storm flows move downstream through the river network, we expect their terrestrial stoichiometric signatures, given sufficient time, will be processed and integrated into aquatic microbes (They et al., 2017). Under a future scenario of more frequent extreme storms, deviations to terrestrial stoichiometric ratios would occur more often, which may eventually change the average stoichiometric balance in inland waters and restructure aquatic communities and ecosystem processes.

5. Conclusion

Although hurricanes have been viewed as a potent ecosystem-level disturbance to inland waters, few studies have evaluated the effects of hurricanes on stream biogeochemistry in a large geographic region. In this study, we investigated the amount and quality of DOM and the amount of inorganic N and P nutrients in ten subtropical streams influenced by large storms related to two major Hurricanes in 2017, Hurricane Harvey and Hurricane Irma. Our study sites were located in the southeastern states, where rivers are known to export large quantities of DOC. Our results demonstrate that hurricane-related storms led to significant alterations in the quantity of dissolved nutrients and the quantity, source, composition, and quality of DOM in streams. The total amount of nutrients and DOC exported increased in all streams; yet, the magnitude of increases varied with watershed characteristics. The sources and composition of DOM were strongly governed by flow variability, showing a reduction in the contribution of protein-like compounds but an increase in the contribution of terrestrial humic-like compounds at high flows. The bioreactivity of DOC declined during high flows; however, the total yield of bioreactive DOC exported increased with increasing discharge. Watershed characteristics also regulated how streams responded to storms, as evidenced by the varied patterns of DOM and nutrient export among the study streams. In particular, wetlands seemed to be efficient buffers for hydrological and chemical disturbances. The response of streams to Hurricane Harvey and Irma observed here, including changes in the yield, source and composition of DOM, nutrient availability, and ecological stoichiometry of elemental fluxes, highlights the ecological significance of large storms. As extreme weather and climate events are projected to rise in many regions of the world, rivers and streams may experience structural and functional changes associated with alterations in the flow of energy and nutrients across terrestrial-aquatic boundaries. Future research should focus on characterizing the biological and ecological fate (e.g., downstream transport vs. photochemical degradation vs. microbial degradation) of land materials transported to streams by large storms.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2019.06.351.

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