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The Effects of Hurricanes and Storms on the Composition of Dissolved Organic Matter in a Southeastern U.S. Estuary

*Patricia M. Medeiros**

Department of Marine Sciences, University of Georgia, Athens, GA, United States

Extreme events such as hurricanes and tropical storms often result in large fluxes of dissolved organic carbon (DOC) to estuaries. Precipitation associated with tropical storms may be increasing in the southeastern U.S., which can potentially impact dissolved organic matter (DOM) dynamics and cycling in coastal systems. Here, DOM composition at the Altamaha River and Estuary (Georgia, U.S.A.) was investigated over multiple years capturing seasonal variations in river discharge, high precipitation events, and the passage of two hurricanes which resulted in substantial storm surges. Optical measurements of DOM indicate that the terrigenous signature in the estuary is linearly related to freshwater content and is similar after extreme events with or without a storm surge and during peak river flow. Molecular level analysis revealed significant differences, however, with a large increase of highly aromatic compounds after extreme events exceeding what would be expected by freshwater content alone. Although extreme events are often followed by increased DOC biodegradation, the terrigenous material added during those events does not appear to be more labile than the remainder of the DOM pool that was captured by ultrahigh-resolution mass spectrometry analysis. This suggests that the added terrigenous organic matter may be exported to the coastal ocean, while a fraction of the organic matter that co-varied with the terrigenous DOM may contribute to the increased biomineralization in the estuary, with implications to carbon processing in coastal areas.

Keywords: dissolved organic matter, hurricanes, DOM composition, microbial degradation, FT-ICR MS, marsh-dominated estuary, Southeastern U.S.

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***Correspondence:**
Patricia M. Medeiros
medeiros@uga.edu

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INTRODUCTION

Estuaries and coastal systems play an important role on the cycling of dissolved organic matter (DOM), serving as a link between terrestrial and oceanic ecosystems. Studies over the last decade or so have shown that a large fraction of the dissolved organic carbon (DOC) flux to estuaries and coastal regions are often associated with extreme events (Yoon and Raymond, 2012; Bianchi et al., 2013; Raymond et al., 2016). Hurricanes and tropical storms, in particular, can result in the delivery of substantial amounts of DOC to coastal systems (e.g., Letourneau and Medeiros, 2019;

Liu et al., 2019), sometimes representing 25-70% of the entire annual flux (Avery et al., 2004; Osburn et al., 2019a; Yan et al., 2020). This large addition of organic matter can impact the overall bioavailability of estuarine DOM, often resulting in increased biodegradation rates (Avery et al., 2004; Yan et al., 2020; Letourneau et al., 2021) and increased CO_2 fluxes to the atmosphere (Bianchi et al., 2013).

Recent studies have suggested that the frequency of occurrence of extreme weather events has increased over the last few decades in the southeastern U.S. (Paerl et al., 2018). Furthermore, analysis of rainfall records for North Carolina, along the U.S. southeast coast, has revealed a trend toward increasingly high precipitation associated with tropical cyclones, possibly representing a recent regime shift that could have large implications for hydrology (Paerl et al., 2019). This increased precipitation may result in an increase in the lateral transfer of DOM to the ocean compared to current conditions, with potential implications for coastal carbon cycling (Rudolph et al., 2020).

The Altamaha River and Estuary around Sapelo Island, off the Georgia coast in the southeastern U.S. (**Figure 1**), was successively impacted by Hurricanes Matthew in 2016 and Irma in 2017. Both hurricanes were characterized by intense precipitation and large storm surges, resulting in substantial flooding throughout the region (Thomas et al., 2019; Kowaleski et al., 2020). There were two other recent near misses, Hurricane Michael in 2018 (whose path from the Gulf of Mexico passed through central Georgia) and Hurricane Dorian in 2019 (track centered ~ 150 km offshore of the Georgia coast). The passage of Hurricane Matthew in fall 2016 significantly impacted DOM dynamics in Sapelo Sound, with the DOC content soon after the passage of the storm being ~ 2 times higher and DOM composition having a stronger terrigenous content than during peak river discharge conditions observed in spring (Letourneau and Medeiros, 2019). Increased terrigenous signatures in the region were also observed after the passage of Hurricane Irma in fall 2017, resulting in a 27% ± 7% increase in DOC content throughout the estuarine area (Letourneau et al., 2021).

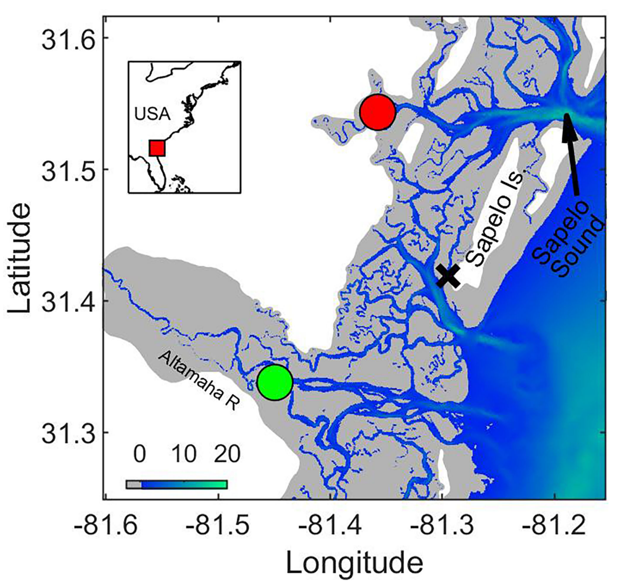

FIGURE 1 | Sampling location at the Altamaha River (green circle) and at the head of Sapelo Sound (red circle) off coastal Georgia (U.S.A.). Salt marshes and uplands are shown in gray and white, respectively. Colors indicate bottom topography in meters. Black cross shows the location of precipitation measurements at Marsh Landing.

Changes in DOM composition in the Altamaha River and Estuary in association with Hurricanes Matthew and Irma have recently been investigated using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS; Letourneau and Medeiros, 2019; Letourneau et al., 2021). The samples collected after Hurricanes Matthew and Irma used in these two studies were analyzed in the FT-ICR mass spectrometer in different years, however, which precluded direct comparisons of DOM composition between the two extreme events due to instrument variability. Letourneau et al. (2021) also noted that their sampling did not capture the peak river flow conditions and associated peak in DOC flux to the estuary that is generally observed during spring (Medeiros et al., 2017), and as such they could not compare the composition of the terrigenous DOM introduced into the estuarine area after Hurricane Irma and the terrigenous DOM introduced every spring in association with seasonality in river flow. Here, those samples were re-analyzed simultaneously, and additional samples collected soon after a high precipitation event that occurred in fall 2018 and were not associated with a tropical storm and/or storm surge were added to the analyses. This allowed for directly comparing the impact of different events on DOM composition in the river and estuary, as well as to characterize possible differences in the terrigenous DOM introduced into the system seasonally with river input and in association with extreme events such as hurricanes.

METHODS

Sample Collection and Incubation

Surface water samples were collected at high tide conditions in multiple years at the Altamaha River and at the head of Sapelo Sound in the estuary around Sapelo Island, Georgia, U.S.A. (**Figure 1**). Samples were initially collected at monthly intervals at the two sites from September 2015 to September 2016. With the passage of Hurricane Matthew in October 2016, an additional sample was collected at the head of Sapelo Sound five days after the passage of the storm. Unfortunately, no sample was collected at the Altamaha River at that time. These samples have been previously described in Letourneau and Medeiros (2019). During early 2017 to early 2018, samples were collected at 15 stations throughout the Altamaha River and Estuary at quarterly intervals, again during high tide conditions (Letourneau et al., 2021). The region was impacted by the passage of Hurricane Irma in September 2017. The sampling from Letourneau et al. (2021) included the two stations from Letourneau and Medeiros (2019). This allowed for combining the two data sets yielding a longer time series for both the Altamaha River and the head of Sapelo Sound sites. Lastly, additional samples were collected at both sites in October 2018 at high tide following a high precipitation event. Put together, these samples spanned multiple years and seasons, capturing the influence of Hurricanes Matthew and Irma as well as variations associated with seasonality in the Altamaha River discharge and variability in precipitation (**Figure 2**).

A detailed description of the sample processing is presented in Letourneau and Medeiros (2019) and in Letourneau et al. (2021). A brief summary is presented here for completeness. After collecting surface water using acid-washed carboys, all samples were filtered through pre-washed 0.2 μm Pall Supor membrane filters into Nalgene bottles for DOC and chromophoric dissolved organic matter (CDOM) analyses. Approximately 1 L of the filtrate was acidified to pH 2 (with HCl) and DOM was extracted by solid phase extraction using PPL cartridges (Agilent Bond Elut) as in Dittmar et al. (2008) for FT-ICR MS analysis.

The additional samples collected in October 2018 underwent dark incubations to characterize changes in DOM composition associated with microbial processing. For that, replicate samples were filtered through 2.7 μm Whatman GF/D filters (pre-combusted for 5 h at 450°C) into acid-washed 2 L polycarbonate bottles (to remove photosynthetically active organisms) and incubated for 120 days at the temperature of collection. Note that 120 days is longer than the residence time in the system (Wang et al., 2017). Incubations were pursued over a relatively long-time scale to increase the chances of observing significant changes in DOM composition due to microbial activity, since over short-time scales changes in DOM composition due to biodegradation are expected to be small in comparison to changes due to other processes (Martineac et al., 2021). Following Medeiros et al. (2017) and Martineac et al. (2021), inorganic nutrients (20 μM Na_2PO_4 and 50 μM NH_4Cl) were added to the raw seawater to alleviate inorganic nutrient limitation on bacterial carbon processing. At the end of the incubation period, samples were filtered through 0.2 μm

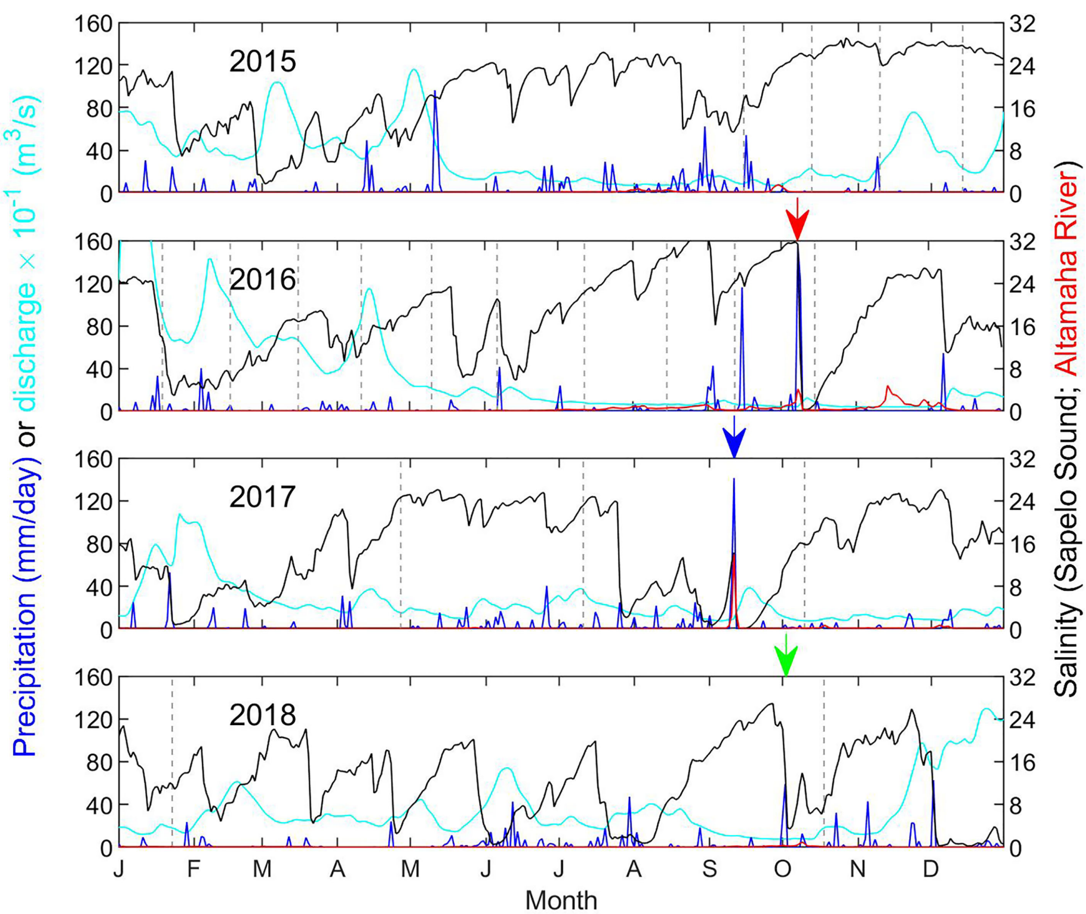

FIGURE 2 | Time series of Altamaha River discharge at Doctortown, Georgia, U.S.A. (cyan, divided by 10), precipitation at Marsh Landing (blue), salinity at the Altamaha River (red) and Sapelo Sound (black) sites. Vertical gray dashed lines indicate sampling periods. Red and blue arrows indicate timing of the passage of Hurricanes Matthew and Irma, while green arrow indicates timing of high precipitation event during fall 2018. Sampling in October 2016 was restricted to Sapelo Sound.

membrane filters and collected for DOC, CDOM and FT-ICR MS analyses as described above.

Chemical Analyses

As described in Letourneau and Medeiros (2019) and Letourneau et al. (2021), DOC concentrations were measured using a Shimadzu TOC-L_{CPH} analyzer with potassium hydrogen phthalate as a standard. Tests against deep-sea reference material (Hansell, 2005) revealed accuracy and precision better than 5%. DOC concentrations in samples collected in October 2018, before and after the incubations, were measured using the same procedure. Absorbance measurements of water samples for CDOM were obtained using an Agilent 8453 UV-visible spectrophotometer, for wavelengths ranging from 190 to 1100 nm, and absorption coefficients were computed as in D'Sa et al. (1999). For each sample, including those collected in October 2018, the spectral slope ($S_{275\text{-}295}$) was computed from the spectra between 275-295 nm as described in Letourneau and Medeiros (2019) and Letourneau et al. (2021). The spectral slope has been previously shown to be negatively correlated with terrigenous DOM (Fichot and Benner, 2012).

The composition of the DOM extracts (200 mg C L^{-1} in methanol) was also analyzed at the molecular level using a 9.4 T Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) at the National High Magnetic Field Laboratory (NHMFL, Florida State University, Tallahassee, FL, U.S.A.) with electrospray ionization (ESI; negative mode). These samples have been previously analyzed using the same instrumentation. However, samples from 2015-2016 (Letourneau and Medeiros, 2019) and from 2017 to early 2018 (Letourneau et al., 2021) were analyzed in different years, which makes it difficult to compare them because of instrument variability. To address this, all samples were re-run sequentially using the same instrumentation settings. Samples collected in October 2018 before and after the long-term dark incubations were included in the instrument runs, expanding the time series. In all cases, each mass spectrum was internally calibrated based on a walking calibration of abundant homologous alkylation series whose members differ in mass by multiples of 14.01565 Da (mass of a CH_2 unit) confirmed by isotopic fine structure (Savory et al., 2011), yielding mass errors < 0.5 ppm. Assignment of molecular formulae for the range of 150 and 750 Da ($^{12}C_{1\text{-}100}$ $^{1}H_{1\text{-}200}$ $^{16}O_{1\text{-}25}$ $^{14}N_{0\text{-}4}$ $S_{0\text{-}2}$ $P_{0\text{-}1}$) was performed by Kendrick mass defect analysis (Wu et al., 2004) using PetroOrg software (Corilo, 2014). Only formulae with a signal-to-noise ratio larger than 6 were considered in the analysis. Comparisons between the original analysis of the samples (e.g., Letourneau and Medeiros, 2019) and the re-analysis described here indicate that they are highly consistent to each other, suggesting that no storage effects occurred that could have changed the composition of the samples.

Statistical Analyses

Changes in DOM composition between samples were decomposed into principal components (PC) based on the relative intensity of each molecular formula after normalization by the standard deviation between samples and mean centering (Bro and Smilde, 2014). All peaks with molecular formulae assigned were used in the PC analysis. Only modes that were statistically significant (95% confidence level) are shown, so that the signals in the modes described here are significantly greater than the level of noise (Overland and Preisendorfer, 1982). Plots of PC scores are related to van Krevelen diagrams of the loadings; for a given sample, where the score of a PC is positive, DOM is relatively enriched with compounds associated with molecular formulae whose loadings for that PC are positive and relatively depleted with those whose loadings are negative.

Ancillary Data

The Altamaha River discharge is routinely measured at the Doctortown station (~ 40 km upstream from the river sampling site) by the U.S. Geological Survey (USGS) (available at http://waterdata.usgs.gov). The Georgia Coastal Ecosystem Long Term Ecological Research (GCE-LTER) program (https://gce-lter.marsci.uga.edu) measures local precipitation at Marsh Landing (see **Figure 1** for location). Spatially variable precipitation data during the passage of Hurricanes Matthew and Irma were obtained by the Integrated Multi-satellitE Retrievals for Global Precipitation Measurements (IMERG) algorithm that combines information from the Global Precipitation Measurement (GPM) satellite constellation to estimate precipitation over the majority of the Earth's surface (Huffman et al., 2019). Version 06 of the dataset was used here, which is available at 0.1° x 0.1° resolution. Sea level is measured by the National Oceanic and Atmospheric Administration at Fort Pulaski, Georgia (https://tidesandcurrents.noaa.gov/map/index.html?id=8670870) about 80 km north of the Altamaha River Estuary. A measure of sea level variability associated with the passage of Hurricanes Matthew and Irma, including the induced storm surge, was obtained by removing the predicted sea level due to tides from the measured sea level. Lastly, salinity at the head of Sapelo Sound (station GCE 1) and at the Altamaha River (station GCE 7) is also measured by the GCE-LTER program (see **Figure 1** for locations).

RESULTS

Seasonal Forcing and Extreme Events

Sapelo Sound, located about 20-25 km to the north of the Altamaha River off the Georgia coast (**Figure 1**), is characterized by high variability in freshwater content with salinity varying from 0 to 32 (**Figure 2**). During the study period, low salinity was generally observed in winter and spring, when the Altamaha River discharge was high (correlation coefficient between river discharge and salinity is -0.31, p < 0.01, with a lag of 16 days), and also following large precipitation events (Wang et al., 2017). In the fall of 2016 and 2017, in particular, salinity was brought to zero following the passage of Hurricanes Matthew (indicated by red arrow in **Figure 2**) and Irma (blue arrow), respectively. Those hurricanes were accompanied by heavy precipitation and by large storm surges (**Figures 3A, B**). While precipitation during Matthew was mostly restricted to offshore and to a thin band near the coast (**Figure 3C**), during Irma precipitation extended farther on land (**Figure 3D**) resulting in a small pulse in the

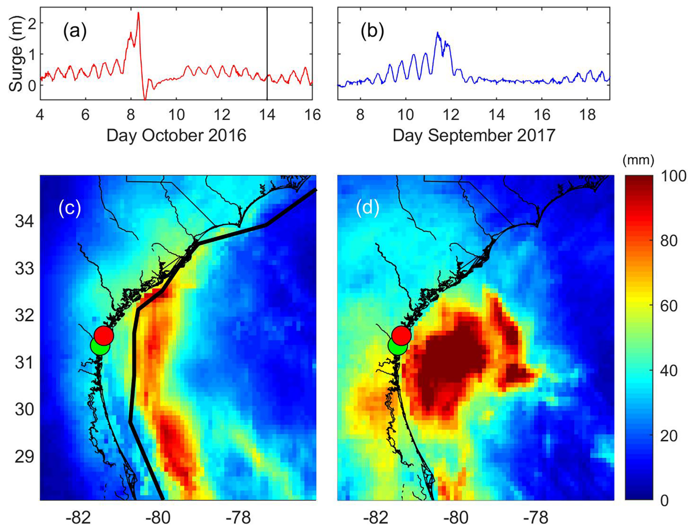

FIGURE 3 | Time series of sea level anomaly (i.e., removing predicted tides) during the passage of Hurricanes **(A)** Matthew and **(B)** Irma. Black vertical line in **(A)** indicates sampling period. Bottom panels show time-averaged maps of daily accumulated precipitation (mm) for **(C)** 6-9 October 2016 (Hurricane Matthew) and **(D)** 10-12 September 2017 (Hurricane Irma). Thick black contour in **(C)** shows Hurricane Matthew track.

Altamaha River discharge a few days after the passage of the storm (**Figure 2**). In early October 2018, an abrupt freshening was observed at the head of Sapelo Sound associated with a high precipitation event (indicated by green arrow in **Figure 2**). At the Altamaha River, salinity was essentially zero over the entire period, except for a few days during the passage of Hurricane Irma in 2017 when salinity reached 14 psu. Sampling to characterize dissolved organic matter composition captured the large freshening observed at Sapelo Sound after the passage of Hurricane Matthew in 2016 and after the high precipitation event in October 2018 (vertical gray dashed lines in **Figure 2**). In fall 2017, samples were collected approximately one month after the passage of Hurricane Irma, at which point salinity at Sapelo Sound had already increased to about 16 psu, indicating that much of the freshwater introduced into the system had already been mixed and/or transported downstream.

Patterns of DOC Content and DOM Composition Variability

Time series of DOC concentrations and of the spectral slope of absorption coefficients from 2015-2016 have been previously used to show that the terrigenous content of the DOM at both locations is characterized by large seasonal variability (Letourneau and Medeiros, 2019). Here, those analyses were expanded by adding samples collected in 2017 and 2018, capturing the influence of Hurricane Irma and of the high precipitation event in the fall of 2018. Results indicated that local salinity at Sapelo Sound is highly correlated with DOC concentration (r = -0.85; $p < 0.01$) and especially the terrigenous content of the DOM ($S_{275-295}$; r = 0.91; $p < 0.01$; **Figure 4**). They also indicated that both the passage of Hurricane Matthew (strong precipitation and storm surge, **Figures 3A, C**) and the high precipitation event in October 2018 (precipitation only, no storm surge) resulted in large inputs of DOC to the system (**Figures 4A, B**). Furthermore, the terrigenous signature after the passage of Hurricane Matthew, as revealed by $S_{275-295}$, was similar to the terrigenous content observed after the large freshening event in fall 2018 (**Figure 4C**). Large seasonal variability was also observed at the Altamaha River, correlated with river discharge (r = 0.68 for correlation with DOC and r = -0.74 for $S_{275-295}$; $p < 0.01$; **Figure 5**). The signature during fall 2018 was substantially different between the two sites, with much higher DOC content with a stronger terrigenous signature at Sapelo Sound (**Figures 4A, C**) compared to the Altamaha River site (**Figures 5A, C**).

Analysis of DOM composition at the molecular level revealed a consistent picture (**Figure 6**). Seasonal variability in DOM composition in 2015-2016 at Sapelo Sound has been shown to be explained by variations in the terrigenous content of DOM (Letourneau and Medeiros, 2019). During high river discharge conditions observed in late winter/early spring 2016 and following the passage of Hurricane Matthew in October 2016, the DOM in the system was relatively enriched with compounds with low H/C ratios and depleted with those with high H/C ratios (Letourneau and Medeiros, 2019), which is typical of gradients in terrigenous vs marine DOM inputs (e.g., Sleighter and Hatcher, 2008; Medeiros et al., 2015a). Adding the more recent observations to the principal component analysis, including from after the passage of Hurricane Irma in 2017 and from the high precipitation event in 2018, yields consistent results with DOM after those two events being enriched with terrigenous compounds characterized by low H/C ratios (**Figures 6A, B**). The overall terrigenous signature of the DOM was highly correlated with salinity (r = -0.92; $p < 0.01$; **Figure 6C**), which is consistent with results from the optical analysis (**Figure 4**).

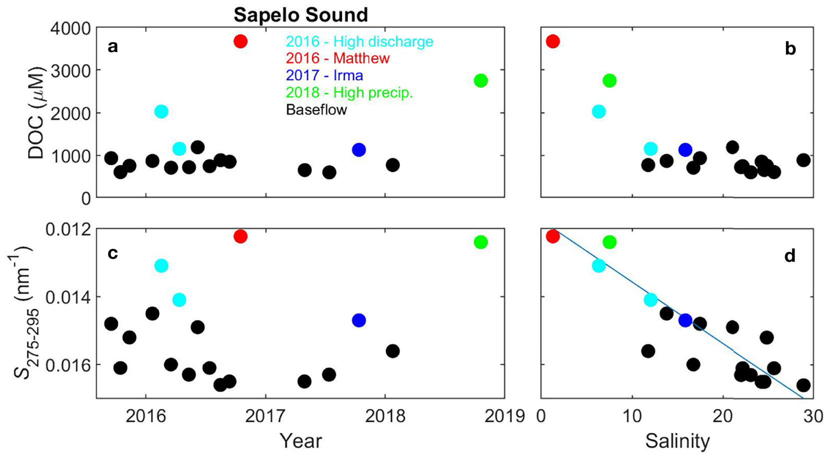

FIGURE 4 | Time series of **(A)** DOC concentration and **(C)** spectral slope coefficients ($S_{275\text{-}295}$) at Sapelo Sound. **(B)** DOC concentration and **(D)** spectral slope coefficients are also plotted versus salinity. Blue line in **(D)** shows linear fit to observations. Small spectral slope coefficients indicate a stronger terrigenous signature.

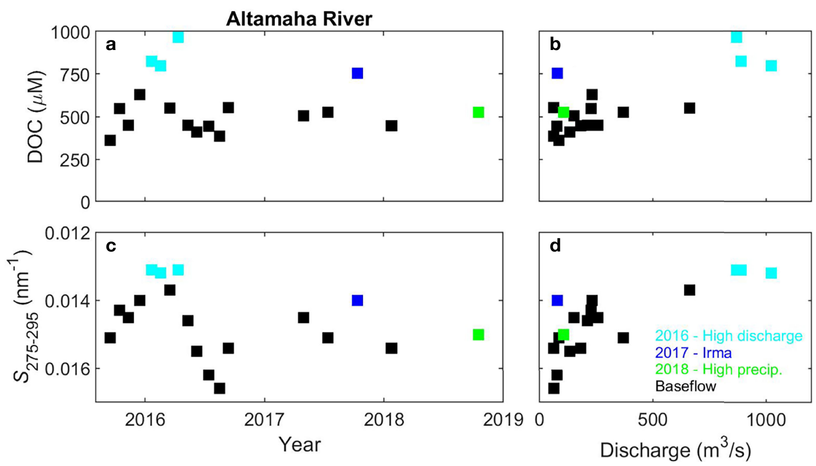

FIGURE 5 | Time series of **(A)** DOC concentration and **(C)** spectral slope coefficients ($S_{275\text{-}295}$) at the Altamaha River. **(B)** DOC concentration and **(D)** spectral slope coefficients are also plotted versus river discharge. Small spectral slope coefficients indicate a stronger terrigenous signature.

Indeed, PC 1 and $S_{275\text{-}295}$ are strongly negatively correlated to each other (r = -0.97; $p < 0.01$). Furthermore, of the compounds associated with molecular formulae enriched at Sapelo Sound during events that resulted in low salinity conditions (red dots in **Figure 6B**), around 70-80% were polycyclic aromatic or highly aromatic compounds (**Figure S1**; Šantl-Temkiv et al., 2013; Seidel et al., 2014). Terrigenous DOM has been shown previously to be enriched in aromatic compounds (Mannino and Harvey, 2004; Ziolkowski and Druffel, 2010; Medeiros et al., 2015a). Collectively, these analyses indicate that the overall terrigenous content of the DOM is linearly related to freshwater content at Sapelo Sound, regardless of the freshwater input being associated with seasonal variability in river discharge or with high precipitation events with or without storm surge. Indeed, the overall change in DOM composition after the passage of Hurricane Matthew, which resulted in strong precipitation and storm surge, was similar to the change in composition observed after a large precipitation event in 2018 which was not associated with a storm surge (**Figures 4**, **6** and **S1**).

At the mouth of the Altamaha River, the terrigenous content of the DOM has been shown to vary seasonally in relation to variations in river discharge (Letourneau and Medeiros, 2019). Once again, expanding the analysis to include observations from 2017 and 2018 produce quantitatively similar results, with DOM with a stronger terrigenous content being found during higher river discharge conditions (**Figure 7**). Thus, the terrigenous signature of the DOM increased at both locations associated

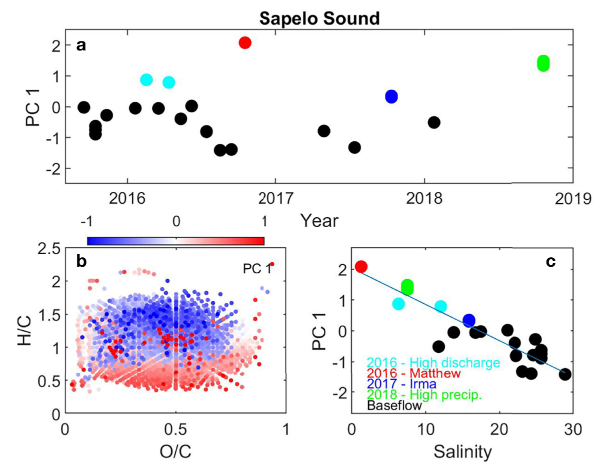

FIGURE 6 | Principal component analysis of DOM composition at the head of Sapelo Sound. **(A)** Scores of the first principal component. **(B)** van Krevelen diagram color coded with loadings of PC 1 (colorbar shown on top of panel **B**). **(C)** Scores of PC 1 plotted against salinity. Blue line is a linear fit to the data.

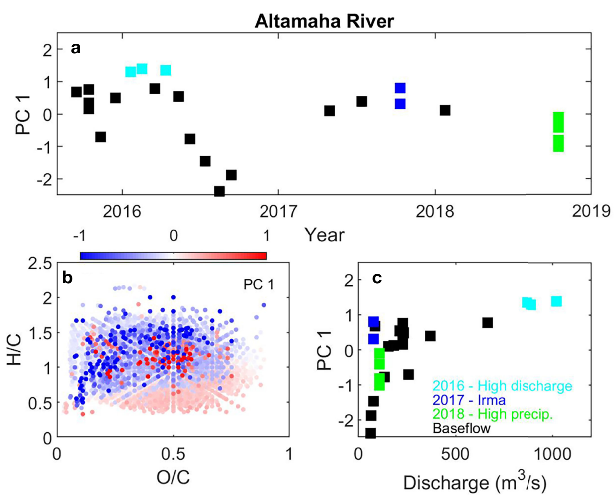

FIGURE 7 | Principal component analysis of DOM composition at the Altamaha River. **(A)** Scores of the first principal component. **(B)** van Krevelen diagram color coded with loadings of PC 1 (colorbar shown on top of panel **B**). **(C)** Scores of PC 1 plotted against Altamaha River discharge.

with the input of freshwater. However, comparing the molecular formulae that have their relative abundance increased between the two sites on an individual basis revealed differences (compare van Krevelen diagrams for Sapelo Sound, **Figure 6B**, and for Altamaha River, **Figure 7B**). While 70% of the formulae enriched at the Altamaha River following high discharge conditions (positive loading in **Figure 7B**) were also enriched at Sapelo Sound following high precipitation events (positive loading in **Figure 6B**), 60% of the formulae enriched at Sapelo Sound following a high precipitation event were also enriched at the Altamaha River following high discharge conditions. This indicates that although much of the terrigenous material introduced into the estuary when freshwater input is large can be found at both sites, some of that material introduced at Sapelo Sound after the passage of storms and/or high precipitation events have different characteristics compared to the input observed at the river during high discharge conditions.

Input of Terrigenous DOM During Extreme Events: Characteristics and Biodegradation

To characterize the input of DOM after extreme events, 481 molecular formulae that had their relative abundance strongly increased (anomaly larger than one standard deviation) at Sapelo Sound after the passage of Hurricane Matthew were identified. Their relative contribution to the total intensity of all peaks in the spectra of all samples analyzed were quantified both at Sapelo Sound and at the Altamaha River. For the sample collected after Hurricane Matthew and after the high precipitation event in 2018, those formulae accounted for ~ 24% and ~ 15% of the total intensity in the spectrum at Sapelo Sound, respectively (red and green circles in **Figure 8**). For other samples from Sapelo Sound, their contribution varied linearly with salinity (r = -0.75, p < 0.01), ranging from 4 to 10%. Note that when computing the linear fit to observations (solid red line in **Figure 8**), the samples from Hurricane Matthew and from the high precipitation event in 2018 were not included, and thus salinity ranged from 6 to 29 psu. If the fit is extended to zero salinity, the predicted contribution of those formulae to the total intensity agrees well with the contributions actually observed in the samples from the Altamaha River (zero salinity; squares in **Figure 8**; note that samples from the Altamaha River were not used in the linear fit). This supports the interpretation that some of the formulae significantly enriched at Sapelo Sound after extreme events are associated with terrigenous material commonly present in the system and their abundance is related to freshwater content. Following high precipitation events (associated or not with hurricanes and storm surges), however, the abundance of those formulae increased substantially, accounting for an unexpectedly large fraction of the DOM in the estuary, more than expected by changes in freshwater content alone (red and green circles in **Figure 8**).

Results from the dark incubations for samples collected after the high precipitation event in October 2018 were used to characterize microbial degradation of dissolved organic matter, especially focusing on the terrigenous material introduced into the system. The analysis was focused on samples collected at the head of Sapelo Sound, since the input of terrigenous material following the high precipitation event in fall 2018 was more evident there than at the Altamaha River (**Figure 8**; compare also **Figures 4**, **5**). DOC concentration decreased by 14.7% during the incubation, from 2,751 ± 40 to 2,345 ± 23 µM. Repeating the characterization of the DOM composition including the samples from the end of the incubation yields results nearly identical to those shown before (compare **Figures S2** and **6**), indicating that the long-term incubation did not result in comparatively large transformations in DOM composition (this remains true when analyzing principal

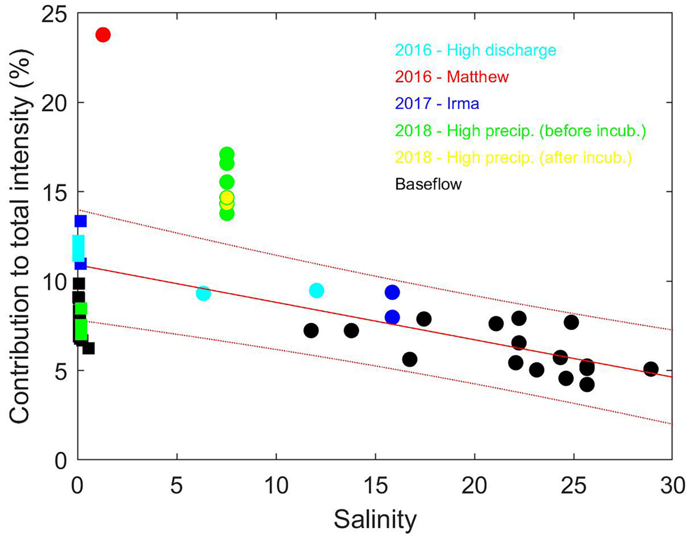

FIGURE 8 | Input of terrigenous DOM during extreme events. Percentage contribution of 481 molecular formulae that had their relative abundance strongly increased at Sapelo Sound after the passage of Hurricane Matthew to the sum of the magnitude of all peaks with molecular formula assigned in FT-ICR MS spectra for all samples. Circles represent samples collected at Sapelo Sound, while squares are samples collected at the Altamaha River, color coded according to the legend. Red line shows linear fit to observations (only using samples from Sapelo Sound, except for those collected after the passage of Hurricane Matthew or the high precipitation event in October 2018; see text for details). Dashed red lines show predicted intervals.

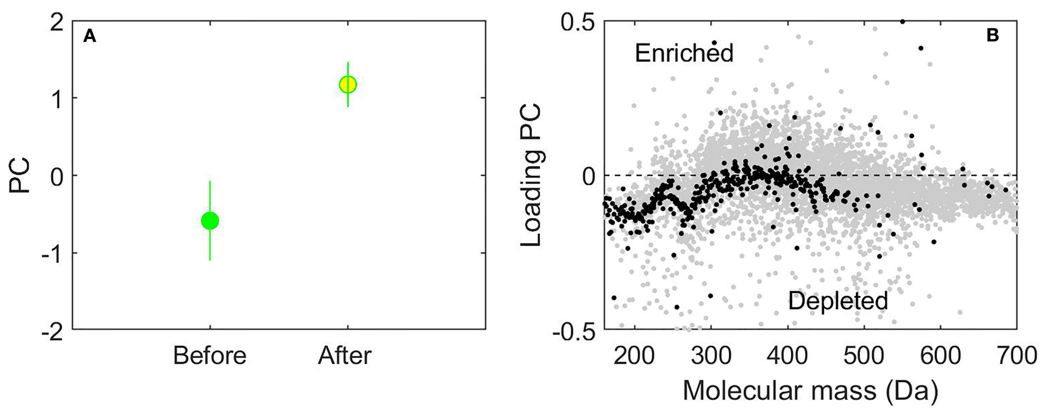

FIGURE 9 | Changes in DOM composition due to biodegradation following a strong freshening event. **(A)** Score of principal component of DOM composition for samples collected at Sapelo Sound after a high precipitation event in October 2018, before (green) and after (yellow) dark incubation. **(B)** Loading of PC versus molecular mass (Da). Gray dots indicate all molecular formulae, while the 481 molecular formulae that had their relative abundance strongly increased at Sapelo Sound after extreme events are shown in black.

components 2 to 5, indicating that large transformations in DOM composition associated with biodegradation were not captured by other PCs either). This result indicates that the terrigenous material captured by FT-ICR MS analysis that was introduced into the system during the high precipitation event was not preferentially transformed by microbes. That is consistent with the fact that the contribution of the terrigenous material introduced during high precipitation events to total intensity of all peaks in the spectrum did not change after the incubation (compare yellow and green circles in **Figure 8**). Lastly, the DOM compositions pre- and post-incubation for the samples collected at Sapelo Sound after the high precipitation event in 2018 were directly compared (**Figure 9A**). Tracking the 481 formulae found to be enriched at the head of Sapelo Sound after extreme events (shown by black dots in **Figure 9B**) revealed a distribution pattern (PC loading vs molecular mass) similar to the overall distribution pattern observed for all formulae (shown by gray dots). There is a tendency for small compounds with molecular mass < ~ 300 Da to be depleted during the incubation (loadings are mostly negative for compounds shown by black dots for molecular mass < 300 Da), but that tendency is also observed for the overall distribution for all formulae (gray dots). This indicates that the terrigenous material captured by FT-ICR MS that was introduced into the system after extreme events was not preferentially consumed during the incubation in comparison to the overall fraction of the DOM pool captured by the analysis.

DISCUSSION

Many studies over the last decade have shown that the passage of tropical storms and/or hurricanes can result in large fluxes of DOC to estuaries (Cao and Tzortziou, 2021), significantly impacting DOM dynamics and cycling and CO_2 air-sea exchange in coastal systems (Avery et al., 2004; Bianchi et al., 2013; Letourneau and Medeiros, 2019; Rudolph et al., 2020; Yan et al., 2020, among others). Studies have also revealed a trend toward increasingly high precipitation associated with tropical cyclones over the last century in the southeastern U.S. (Paerl et al., 2019), indicating a potential for increased lateral transport of DOM from land to estuaries. Here, observations spanning multiple years were used to characterize changes in estuarine DOM composition associated with two hurricanes and with a high precipitation event not associated with a hurricane, and to compare it with the terrigenous material introduced seasonally in the system in association with variability in river discharge.

The channel where samples were collected at the head of Sapelo Sound is relatively narrow, about 20 m wide. Because of its small volume, the channel is heavily influenced by local precipitation, as shown previously by Wang et al. (2017), and it experiences the full range of salinity variability from zero following large rainfall events to near oceanic conditions during dry periods. Overall DOM composition at this site is linearly related to salinity, with both optical and molecular analyses indicating a stronger terrigenous signature when freshwater content is higher. Furthermore, traditional measurements of terrigenous DOM (e.g., $S_{275-295}$) were found to be similar for different events with distinct characteristics. For example, Hurricane Matthew caused extensive flooding throughout the southeastern U.S. (Musser et al., 2017; Stewart, 2017) in association with heavy precipitation and storm surge. Rudolph et al. (2020) has shown that this resulted in increased hydrologic connectivity between riparian wetlands and the Neuse River Estuary (located ~ 600 km to the north of the Altamaha River Estuary), which can allow for flushing of accumulated organic matter (Tockner et al., 1999; Wolf et al., 2013). In fall 2018, on the other hand, the freshening was associated with local precipitation (weaker than during Hurricane Matthew) and no storm surge was observed. Freshening was also observed during high Altamaha River discharge conditions in late winter/early spring 2016. Despite these differences, $S_{275-295}$ measured after Hurricane Matthew, the high precipitation event in fall 2018 and after high river discharge conditions during winter/spring 2016 (red, green and cyan circles in **Figures 4C, D**, respectively) were similar to each other and consistent with the freshwater content during the time of sampling. The same is true based on principal component analysis of DOM composition from FT-ICR MS data. Letourneau and Medeiros (2019) used the 2015-2016 data to show that DOM at Sapelo Sound was enriched with formulae with low H/C ratios after Hurricane Matthew and during high river discharge conditions observed in late winter/early spring. The analyses shown here including observations for 2017-2018, which captured the passage of Hurricane Irma and a high precipitation event in fall 2018, revealed a consistent picture, with the dominant principal component capturing the relative increase in the abundance of the same formulae with low H/C ratios (shown by red dots in **Figure 6B**) during these events. Collectively, these analyses looking at broad measures of terrigenous DOM content suggest that the terrigenous material introduced into the system following extreme events is not particularly different from the terrigenous material seasonally observed in the estuary. Analyses of terrigenous DOC in Galveston Bay in the Gulf of Mexico after the passage of Hurricane Harvey in 2017 revealed a consistent picture. Source composition of terrigenous DOC was not substantially altered after the flooding event, as revealed by relatively invariant ratios of syringyl/vanillyl and cinnamyl/vanillyl phenols (Yan et al., 2020).

Although this broad view indicated no large differences in the composition of the terrigenous DOM introduced into Sapelo Sound, focusing on compounds that were strongly enriched after the passage of Hurricane Matthew revealed significant differences. Tracking the relative abundance of 481 formulae strongly enriched after the passage the Hurricane Matthew revealed that they are present in all samples, both at Sapelo Sound and at the Altamaha River, and their abundances are generally linearly related to freshwater content, consistent with results discussed above. However, they make a significantly higher contribution to the spectra of samples collected at Sapelo Sound after Hurricane Matthew and the high precipitation event in fall 2018, by a factor of 1.5-2. These compounds are characterized by very low H/C ratios (median of 0.63; 75% had H/C < 0.8 and 95% had H/C < 1.4), and they occupy different regions in van Krevelen space compared to compounds often associated with the input of salt marsh-derived organic matter (Medeiros et al., 2015b). Given that the Altamaha River discharge was very low during these two events (**Figure 2**), and that DOC contents in rainwater is generally low (Willey et al., 2000; Avery et al., 2003), it is likely that the input is associated with remobilization of DOM stored in adjacent forested wetlands (Osburn et al., 2019b).

The remobilization of this terrigenous material with very low H/C ratios may be associated with inundation due to storm surge, as observed during Hurricanes Matthew and Irma, but results indicate that local rainfall not associated with tropical storms or hurricanes, such as that observed in fall 2018, also results in remobilization of those terrigenous compounds. In fact, it is difficult to separate the contribution from rainfall and from storm surge. Even though Hurricane Matthew caused substantial storm surge, the sampling occurred approximately five days after the passage of the storm. Salinity was 32 immediately before the passage of the storm, but it decreased to 0 over a period of 2 days, when accumulated rainfall over those 48 hours was about 278 mm. This result indicates that by the time of the sampling 5 days after the passage of the storm, most of the estuarine water (salinity > 0) that inundated the uplands during the storm surge had already been replaced by freshwater from precipitation. Thus, the increase in the relative abundance of the 481 molecular formulae reported here may have been primarily associated with precipitation, rather than storm surge. However, Letourneau et al. (2021) showed that DOM had a stronger terrigenous content throughout the estuary after the passage of Hurricane Irma in 2017 even though salinity did not change significantly (their **Figure 5**). This change in DOM composition without a change in salinity is consistent with remobilization of DOM stored in soils *via* storm surge. Thus, it is possible that inundation associated with storm surge makes a larger contribution to changes in DOM composition in wider channels with a large water volume, since in narrow channels the low water volume can more easily be replaced by freshwater from precipitation. It will be interesting to see if future samples collected soon after the passage of severe storms or hurricanes, before the water that inundated the uplands during the storm surge is completely replaced, will also reveal a large influence of the remobilized terrigenous material shown here to be associated with precipitation. It would also be interesting to re-analyze these samples by FT-ICR MS using ESI positive mode. This is because some functional groups such as carboxylic acids are easily deprotonated and may be preferentially ionized in negative mode relative to other compounds (Kim et al., 2003) due to charge competition (Tfaily et al., 2015). Given that terrestrial aromatic compounds often have a high carboxyl content (e.g., Kramer et al., 2012), this ion suppression may lead to a potential overestimation of aromatic DOM components in these samples. Indeed, Ohno et al. (2016) showed that analyses using ESI positive mode often result in a preferential increase in the number of assignments for the aliphatic and carbohydrate-like components of the DOM, since aromatic DOM molecular can suppress the ionization of these entities in negative mode.

Our analyses indicated that DOC concentration and DOM composition at the head of Sapelo Sound is strongly dependent on freshwater content. In narrow and shallow areas in the estuary, however, freshwater content can vary substantially on very short-time scales. As a result, DOC concentration and DOM composition in those regions will also possibly vary on short-time scales. This likely explains the large difference in the response reported here for Hurricanes Matthew and Irma (compare red and blue circles in **Figures 4**, **6** and **8**). Sampling after Hurricane Irma occurred 30 days after the passage of the storm, at which point salinity had already increased from 0 to 16. Thus, even though the terrigenous content of DOM at the head of Sapelo Sound was substantially enriched compared to other sites in the estuary at that time (Letourneau et al., 2021), it was much less terrigenous than in other instances when salinity was lower (**Figure 6C**). This highlights the importance of collecting samples as soon as possible after severe storms to investigate their impact on DOM dynamics in coastal regions, even though that can be challenging because access to these systems is often difficult and/or unsafe soon after the passage of hurricanes.

Our analyses also revealed differences in the response between the two sites. Unfortunately, it was not possible to collect samples after Hurricane Matthew at the Altamaha River site, but samples collected after the high precipitation event in fall 2018 indicated no large input of terrigenous DOM at that site (**Figures 5C**, **7**). The relative contribution of the 481 molecular formulae previously identified as being strongly enriched at Sapelo Sound after extreme events is also smaller at the Altamaha River during the high precipitation event in fall 2018 (compare green squares and green circles in **Figure 8**). This result suggested that although local precipitation plays an important role increasing the terrigenous content of DOM in some regions of the estuary (e.g., head of Sapelo Sound), it likely plays a small role in the mainstem of the river, possibly because of its comparatively large water volume and high background DOC content. The spatial structure of precipitation events will also result in different responses in different parts of the estuary. Precipitation measurements used here were collected at the Marsh Landing weather station, which is located about 18 km from the sampling station at the head of Sapelo Sound (**Figure 1**). There are several instances when salinity at the head of Sapelo Sound decreased substantially when no rainfall or increased river discharge were observed (e.g., late July 2017; **Figure 2**), which could be associated with spatial variability in rainfall patterns.

Studies over the last decade or so have revealed that the input of terrigenous DOM to coastal systems associated with extreme events is often accompanied by high biomineralization rates. A large flooding event in summer 2011 in the Mississippi River basin resulted in large DOC consumption by bacteria in floodwaters, contributing to temporarily changing shelf waters in the northern Gulf of Mexico from a net sink to a net source of CO_2 to the atmosphere (Bianchi et al., 2013). High biomineralization of terrigenous DOC has been reported in Galveston Bay in the Gulf of Mexico after the passage of Hurricane Harvey (Yan et al., 2020). Letourneau et al. (2021) also reported increased DOC consumption throughout the estuary after the passage of Hurricane Irma in 2017, including at the head of Sapelo Sound. Letourneau et al. (2021) did not analyze DOM composition by FT-ICR MS at the end of the incubations, however, so they could not characterize at the molecular level which components of the DOM were preferentially degraded. Although incubations were not pursued for the samples collected after Hurricane Matthew, samples from Sapelo Sound collected after the high precipitation event in fall 2018 were incubated in the dark resulting in DOC consumption of ~15%, which is comparable to those reported by Letourneau et al. (2021). The analysis at the molecular level suggested that the terrigenous material captured by FT-ICR MS analysis that was strongly enriched at Sapelo Sound after extreme events is not particularly biolabile, at least no more so than other compounds present in the overall DOM pool with similar molecular mass, and thus it can be potentially exported to the coastal ocean on a scale of a few days to weeks (Wang et al., 2017). Since increased DOC mineralization was observed at Sapelo Sound after storms events (Letourneau et al., 2021), this suggests that it is mainly driven by biodegradation of compounds that fall outside the analytical window used here. Indeed, Letourneau et al. (2021) using optical analysis observed that less aromatic DOM that co-varied with the terrigenous material introduced into Sapelo Sound after the passage of Hurricane Irma had been preferentially degraded. This seems to be different from what was observed at Galveston Bay after Hurricane Harvey, however, when high removal efficiency of the terrigenous DOC was observed (Yan et al., 2020). This could be related to differences in the composition of the terrigenous material (and in its lability) introduced into these two systems following extreme events, but it could also be associated with differences in microbial community compositions, which may have been more or less capable of degrading the added material (Moran et al., 2016). The incubations pursued here occurred in the dark and as such they did not capture the influence of photochemical reactions, which are known to efficiently remove aromatic compounds (e.g., Riedel et al., 2016). Thus, it is also possible that the terrigenous material strongly enriched at Sapelo Sound after extreme events is susceptible to photodegradation as it is transported to the ocean. Given that flooding events may become more frequent in the future in association with changes in climate (Paerl et al., 2019), and that the addition of DOC due to flooding events may be large enough to change the sign of the carbon exchange with the atmosphere (Bianchi et al., 2013), it is important that future studies focus on characterizing the components of the added DOM after extreme events that are bio- and/or photo-labile and how and why they may vary between different coastal systems.

DATA AVAILABILITY STATEMENT

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession number(s) can be found below: Data for this manuscript will be made available online at the Georgia Coastal Ecosystems LTER data portal (https://gce-lter.marsci.uga.edu) by the time of publication.

AUTHOR CONTRIBUTIONS

PM conceived and designed the study, analyzed the data, and wrote the manuscript. The author confirms being the sole contributor of this work and has approved it for publication.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2022.855720/full#supplementary-material

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