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Carbonate-Associated Organic Matter Is a Detectable Dissolved Organic Matter Source in a Subtropical Seagrass Meadow

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Seagrasses can enhance carbonate sediment dissolution on diel timescales through oxidation of the rhizosphere and production of acidic exudates of dissolved organic matter (DOM). Carbonates can also associate with DOM either from biogenesis or later adsorption. However, the impact of mineral dissolution on the release of carbonate-associated DOM and on surface water DOM quantity and quality is unclear. We analyzed sub-daily changes in EEMS-PARAFAC components (excitation-emission matrices with parallel factor analysis), fluorescence, and absorbance properties of surface waters over adjacent low- and high-density (LD and HD) *Thalassia testudinum* seagrass meadows in Florida Bay, United States. We compared fluorescent DOM characteristics of seagrass leaves, acidified (dissolved) sediment leachates, and surface water samples collected from the HD and LD sites with surface water from a nearby mangrove island. The HD site was higher in humic-like PARAFAC components, specific ultraviolet absorbance, and humification index. We did not observe changes in EEMs indices or PARAFAC components with cumulative photosynthetically active radiation, indicating that photodegradation was unlikely to contribute to temporal variability in DOM. Similarities among DOM optical properties from acidified sediment leachates and surface waters at both sites suggest the importance of carbonate dissolution/reprecipitation for DOM cycling, while seagrass leaf leachates were markedly dissimilar to surface waters. We observed similarities among the acidified sediment leachate, surface water, and porewater elsewhere in Florida Bay, indicating dynamic coupling between these DOM pools. From this short study, Florida Bay DOM cycling appears to be more sensitive to carbonate dissolution than to additional photodegradation or authigenic seagrass leaching.

Keywords: sediment dissolution, carbonate dissolution, organic matter, excitation-emission matrices, seagrass ecosystem

INTRODUCTION

Seagrass ecosystems are important players in the global carbon cycle, via the "blue carbon" mechanism of organic carbon storage in underlying sediments (Fourqurean et al., 2012a). Sedimentary organic carbon in seagrass meadows contains both autochthonous and allochthonous organic material from terrestrial or marine origins (Kennedy et al., 2010), and can be protected from further degradation as seagrasses can stabilize sediments, reducing resuspension and oxidative loss (Serrano et al., 2020). In carbonate sediments, however, the processes of calcium carbonate precipitation and dissolution causes the production or consumption of CO_2 in excess of net ecosystem metabolism (Mazarrasa et al., 2015; Howard et al., 2018). This carbonate dissolution can be enhanced in seagrass meadows via seagrass pumping of oxygen into the sediments during photosynthesis (Eldridge and Morse, 2000; Burdige and Zimmerman, 2002; Burdige et al., 2008, 2010), and can follow seasonal (Barrón et al., 2006; Egea et al., 2019) and diel patterns (Ziegler and Benner, 1999; Maher and Eyre, 2010), as demonstrated by lower porewater sulfide in the middle of the day (Lee and Dunton, 2000). However, the impact of this carbonate dissolution on "blue carbon" organic matter remains uncertain.

In addition to particulate organic matter, carbonate-associated organic matter contributes to the "blue carbon" stock of carbonate seagrass meadows (Howard et al., 2018). In laboratory studies, carbonates can adsorb and remove from solution aspartic acid rich fulvic acids (Carter, 1978), stearic acids, and egg albumin (Suess, 1970). In carbonate sediments, organic matter containing contain acidic functional groups can adsorb onto carbonate minerals, and autochthonous organic matter can be protected in the intracrystalline network of carbonate minerals at the point of biogenesis (Müller and Suess, 1977; Ingalls et al., 2004). It is unknown whether seagrass-mediated carbonate dissolution also results in the release of sediment-associated organic matter, or if this affects water column dissolved organic matter (DOM) quality and quantity.

Excitation-emission matrices (EEMs) with parallel factor analysis (PARAFAC) is a useful tool for assessing natural organic matter cycling and dynamics in aquatic environments (Jaffé et al., 2014), and has been implemented in an adsorption study of terrestrial DOM to Florida carbonate aquifer samples (Jin and Zimmerman, 2010). In Florida Bay, the site for this study, EEMs has been implemented to explore seasonal and episodic drivers of variations in DOM (Maie et al., 2006, 2012; Ya et al., 2015). However, the contributions of diel forcing, benthic fluxes, seagrass density, or associations with carbonate sediments to the fluorescent DOM (FDOM) signal remains uncertain. We hypothesized that surface water FDOM in seagrass meadows would vary on diel timescales because of the combined processes of sediment dissolution, seagrass exudation, and photodegradation. To test this, we used a diel sampling framework to quantify dissolved organic carbon (DOC) concentrations and FDOM at two sites of high- and low-density *Thalassia testudinum* seagrass meadows in Florida Bay. In a related experiment, we investigated the optical properties of FDOM released from acidified sediment leachates and porewater, in order to understand the contribution of sediment-associated organic matter and sediment dissolution to FDOM variability.

METHODS

Study Site

Florida Bay (FB) is a carbonate rich, seagrass-dominated, shallow estuary in southern Florida. Primary productivity in this oligotrophic ecosystem is supported in part by the release of nutrients (Nitrogen, N, and Phosphorus, P) stored in sediments (Fourqurean et al., 2012b). The primary source of P is from the Gulf of Mexico, where seagrass productivity is higher, while the main freshwater source is through Taylor Slough from the Everglades in the northeastern bay, and a network of numerous mudbanks restrict the flow of water between basins (Fourqurean and Robblee, 1999). The sediments range from 70 to 95% calcium carbonate (Caccia et al., 2003), and associations between inorganic P and carbonates contribute to the P limitation of the ecosystem (Koch et al., 2001). While carbonate dissolution is variable, it tends to be higher in regions of increased P limitation and during periods of hyper salinity (Yates and Halley, 2006) which is likely related to the strategies employed by seagrasses to release limited carbonate-associated P through organic acid exudates (Long et al., 2008) or enhanced sulfide oxidation through oxygen pumping in the rhizosphere (Ku et al., 1999; Jensen et al., 2009) or bioturbation (Walter et al., 1993). Diurnal variations in carbonate dissolution and precipitation processes can lead to strong variations in water column alkalinity, dissolved CO_2, and pH in Florida Bay (Yates and Halley, 2006; Yates et al., 2007).

We visited the same high- and low-density seagrass sites (HD and LD, respectively) as a concurrent study into net ecosystem productivity of Florida Bay seagrasses, which were both found to be net dissolving during the study period (Van Dam et al., 2019), and are separated from each other by mudbanks and a mangrove island (M, **Figure 1**). Both HD and LD sites are located in northeastern FB, and share similar sedimentary organic matter sources (Xu et al., 2006), surface water organic matter characteristics (Maie et al., 2012), and sedimentary $CaCO_3$ content (Caccia et al., 2003). The five additional sites throughout FB have variable seagrass presence and span the productivity gradient (TC, DK, LM, BA, and SB, **Figure 1**).

Sampling Campaigns

Two multi-day diel sampling campaigns (8 days total) were conducted at HD and LD in late 2018 (**Figure 1**). Surface water (SW) samples were collected on a dawn-noon-dusk cycle during the first campaign (Oct. 28 through Nov. 01, 2018), and 4 times per day during the second campaign (November 25 through November 29, 2018). At each time point, 60 mL SW was filtered (0.45 μm) and stored in dark, acid washed, 60-mL HDPE dark bottles triple rinsed with site water. These samples were placed immediately on ice, then refrigerated at 4°C until further analysis. Excitation emission matrices (EEMs) and absorbance spectra were collected within 2 weeks, and all remaining sample water was acidified to Ph < 2 with HCl and stored at 4°C until dissolved

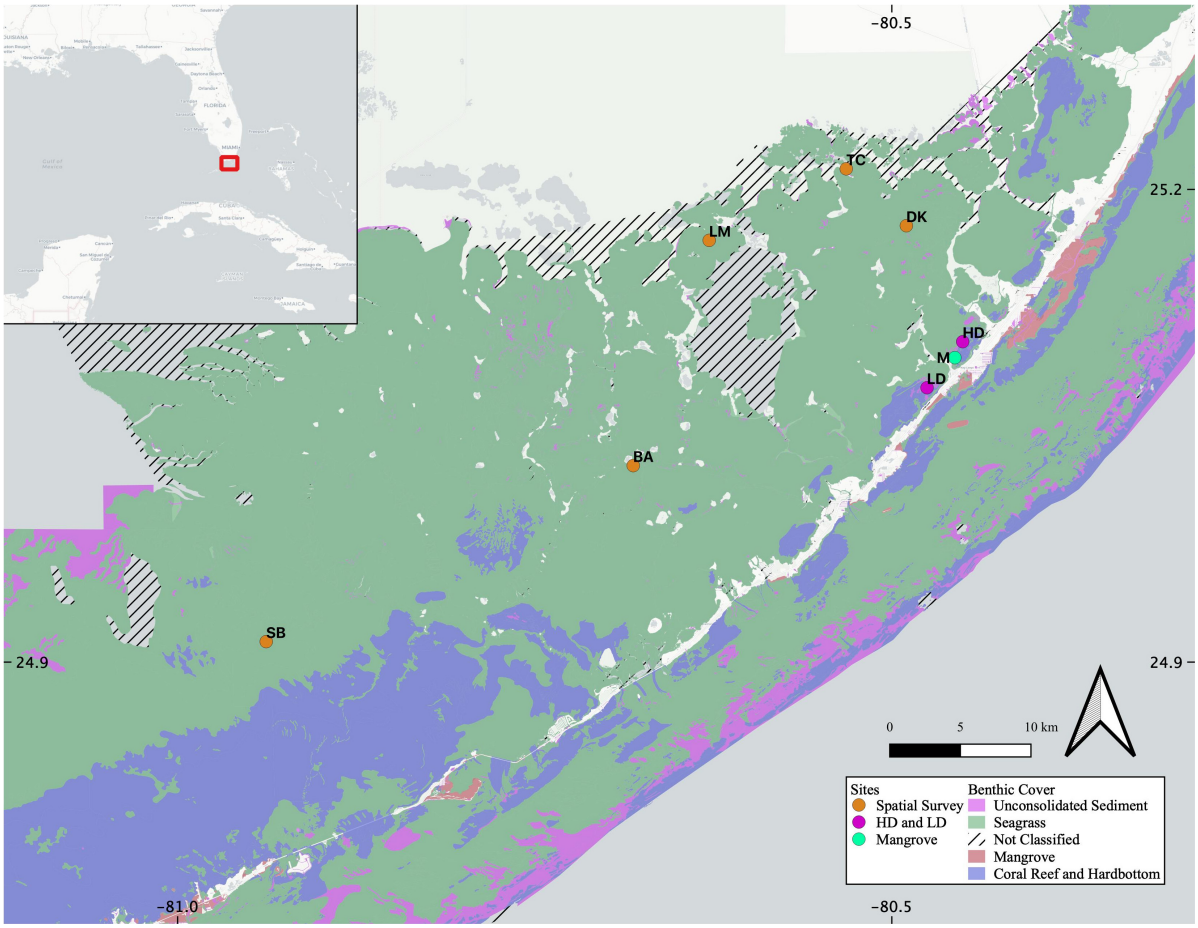

FIGURE 1 | Site map, including the location of the study area within the broader southeastern United States (inset, red box). High density (HD) and low density (LD) seagrass sites were sampled for the diel portion of the study, as well as sediment and seagrass leaching. The Mangrove site (M) was sampled for surface water comparison. The five additional sites sampled for porewater, surface water, and sediment leaching comparisons cover the entire range of Florida Bay (DK, TC, LM, BA, and SB). Benthic coverage data was acquired from the Florida Fish and Wildlife Conservation Commission- Fish and Wildlife Research Institute (FWRI FWC), Unified Reef Map.

organic carbon (DOC) analysis within 4 months of collection. Sediment grab samples and seagrass leaf clippings were collected at the HD and LD sites. Three SW samples were also collected from M (**Figure 1**) during the first campaign. Photosynthetically active radiation (PAR) was measured in the water column at both sites using a submerged Sea-bird ECO-PAR sensor (Van Dam et al., 2019), and was integrated over the day to obtain cumulative PAR (E/m^2) for our analyses.

A third sampling campaign was conducted in April 2019, in which filtered (0.45 μm) pore water (PW), filtered SW, and sediment grab samples were collected in a spatial survey of five additional sites (TC, DK, LM, BA, and SB, **Figure 1**). PW was collected using a porewater sipper with a surface shield from 10 cm sediment depth.

Sediment and Seagrass Leaf Leachates

Wet carbonate sediments were divided into two equal portions of 5–10 grams each, then diluted with ∼60 mL deionized water (DI). One portion was acidified with enough 12N HCl (about 20 drops) to give appreciable but incomplete dissolution, so as to maintain buffering and not significantly alter the supernatant pH. The sediment and supernatant solution were allowed to leach at 4°C for 48 h, upon which time the sample was filtered (0.45 μm) prior to EEMS and DOC analysis. This material constitutes the "SED_{HCl}" and "SED_{DI}" described in the results. Due to the cold leaching temperature and the pH of deionized water, a small fraction of the carbonate sediment would also be dissolved in the SED_{DI} treatment, however, SED_{HCl} represents substantially higher sediment dissolution. Seagrass leaves from both the HD and LD sites (150–500 mg) were leached with 60 mL DI water at 4°C for 48 h; we term this leachate "SG." EEMs and Absorbance data were collected on all leachates, however, DOC was analyzed for the SED_{HCl} and SED_{DI} leachates from the third campaign only. Sedimentary metals have been shown to quench the fluorescence of humic substances (Haider and Guggenberger, 2004), however, the low amount of metals such as Fe, Al, and Mn in our sediments (Caccia et al., 2003), and the incomplete dissolution of the SED_{HCl} method

suggests that the metal concentrations of the leachates would not have a large effect on FDOM signal (Poulin et al., 2014; Liu et al., 2018).

DOC, EEMs, and Absorbance Acquisition

Dissolved organic carbon was determined on acidified and filtered (0.45 μm) samples using a Shimadzu TOC-V total organic carbon analyzer. Absorbance spectra were collected (240–621 nm, 3 nm interval) concurrently with the EEMs using an Aqualog spectrofluorometer (HORIBA Scientific, HORIBA New Jersey Optical Spectroscopy Center, United States) equipped with a 150 W continuous output Xenon arc lamp and a 1 cm quartz cuvette. The emission scans were collected from 250 to 621 nm, with intervals of ∼1.5 nm, and were acquired at excitation wavelengths of 240–621 nm at intervals of 3 nm. Post-acquisition data were blank-subtracted with Milli-Q water, and corrected for inner filter effects (McKnight et al., 2001). EEMs are provided in Raman units (RU).

Specific UV absorbance at 254 ($SUVA_{254}$) is defined as the absorbance at 254 nm (m^{-1}) normalized to DOC in mg-C L^{-1} (Weishaar et al., 2003). A_{254} was estimated by linear interpolation between A_{255} and A_{252}. Absorbance at 351 (A_{351}) was used instead of A_{350}, and scaled to DOC. The slope ratio (S_R) is the ratio of the spectral slopes $S_{275-295}$ to $S_{350-400}$, which in turn were calculated by fitting a linear regression to the natural log-transformed absorbance between 275–295 and 350–400 nm (Helms et al., 2008). The fluorescence-derived indices of humification index (HIX), fluorescence index (FI) and biological (freshness) index (BIX) were calculated directly from the EEM spectra (Wagner et al., 2015). HIX tends to increase with humification and microbial processing of DOM (Wickland et al., 2007), FI has been used to assess microbial vs. terrestrial contributions to DOM (Cory et al., 2005), and BIX has been correlated with recently produced DOM (Parlanti et al., 2000). Statistical analyses were carried out in MatLab R2017a and R Studio. The relationship between each index and cumulative PAR were quantified with a linear model in R, and the slopes are provided in **Supplementary Table S1**. Differences between sites and campaigns for each index were calculated from one-way analysis of variance (one-way ANOVA), and are represented graphically in **Supplementary Figure S5**.

Parallel factor analysis modeling and were carried out using the DrEEM 3.0 toolbox in MatLab R2017a (Murphy et al., 2013). The PARAFAC model was run on n = 97 of the 100 samples using an excitation wavelength range of 258 to 498 nm, and the zap function was used to remove anomalous peaks individually. Three samples were removed as outliers, as the high leveraging had the potential to distort the model results. A 5-component model was validated using the split-half analysis S4C4T2 and was then applied to the non-normalized full dataset. When comparisons are made between pools (PW, SW, SED_{DI}, and SED_{HCl}) PARAFAC components are expressed in percent, while temporal variations in PARAFAC components are expressed in RU. Due to the potential for matrix effects, especially the presence of halides, impacting the range of samples differently (i.e., SW vs. SED_{DI} vs. SED_{HCl}), comparisons between these sample types are made in a qualitative manner (Grebel et al., 2009).

RESULTS AND DISCUSSION

Description of PARAFAC Components

A 5-component PARAFAC model was validated for our data set (**Supplementary Figure S1**). Previously, an 8-component PARAFAC model was fit to south Florida surface water samples (Chen et al., 2010; Murphy et al., 2014), but this model could not be applied to the present dataset because of the differences in wavelength intervals between the spectrophotometer used in this study (Aqualog), and that used in Chen et al., 2010 (FluoroMax 3). A visual comparison of the PARAFAC components (**Supplementary Figure S2**) shows that our 5-component PARAFAC model captures the same general FDOM groups as the 8-component model, summarized as follows: Our C1 is similar to the reported components 3, 4, and 6, and is humic-like (Yamashita and Jaffé, 2008). Our C2 is similar to the reported component 1 and component 5, and is also humic-like. Our C3 is analogous to the reported component 2, and is humic-like. Our C4 is similar to the reported component 8 and is tryptophan protein-like. Finally, our C5 is similar to the reported component 7, and is tyrosine protein-like. The similarity between these components allows us to set our findings in the context of prior research, and the implications will be discussed in subsequent sections.

Diel Variability in Surface Water FDOM

The moderate growth in S_R and FI, and moderate reduction in HIX, observed during the second half of the second campaign (**Supplementary Figure S3**) corresponds temporally with an increase in wind speed and a drop in sea surface temperature (Van Dam et al., 2019), but otherwise temporal trends in fluorescence indices, absorbance indices, and PARAFAC components were not detected. DOC was variable at both sites throughout the study period, but was comparable with DOC values observed in central Florida Bay through a decade of monthly monitoring (Jaffé, 2018; **Supplementary Figure S4**). We hypothesized that photodegradation could be a predominant factor contributing to diel variability in surface water FDOM given that a previous study applying the 8-component model (**Supplementary Figure S2**) found that all of their components exhibited some response to light (Chen and Jaffé, 2014). Interestingly, their component 2 (similar to our C3), appeared to be a product of photodegradation, and their component 7 (similar to our C5), appeared highly photolabile (Chen and Jaffé, 2014, 2016). Despite this photo-lability and photo-production, we detected no changes in any PARAFAC component including C3 and C5 with varying cumulative PAR (**Figures 2A,B** and **Supplementary Table S1**).

Reductions in $SUVA_{254}$ are often considered as evidence for photodegradation, but we did not measure variation in $SUVA_{254}$ with PAR. However, our low $SUVA_{254}$ values of ∼1.0 (LD) to ∼1.6 (HD) suggest that this material is already highly photodegraded (**Figures 2E,F**). In fact, no measured index exhibited a significant increase or decrease with cumulative PAR ($p > 0.05$; **Supplementary Table S1**,

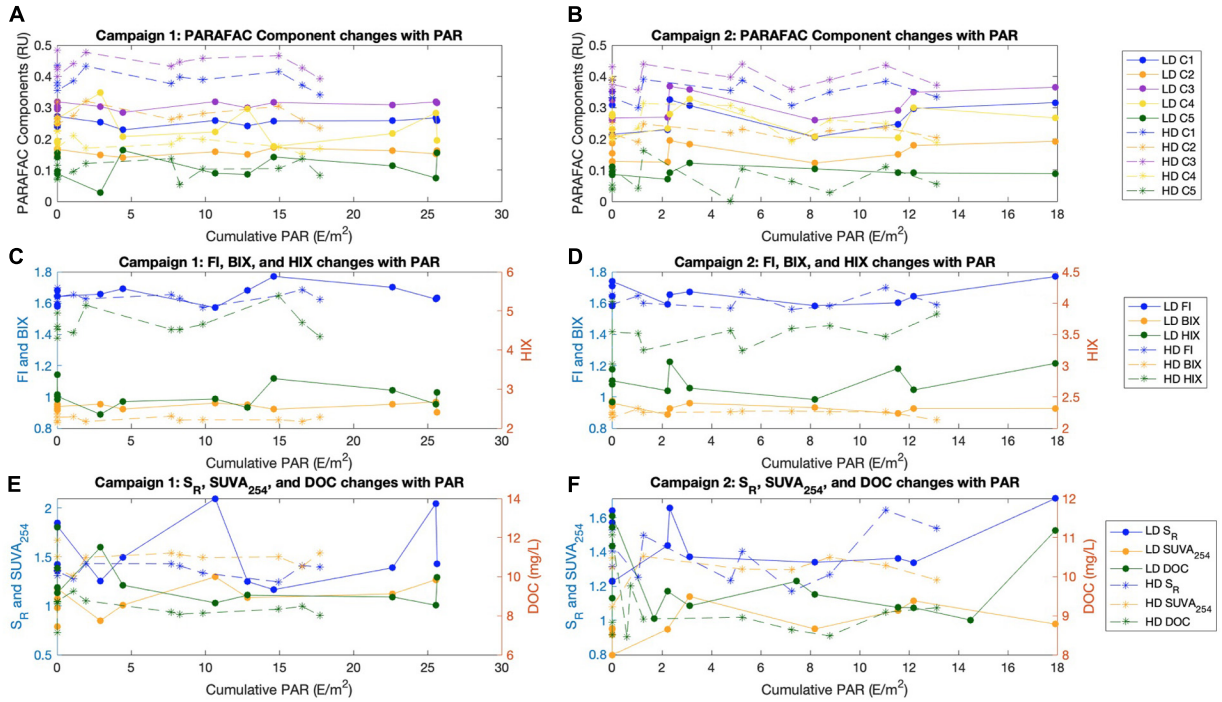

FIGURE 2 | All indices and PARAFAC components plotted against cumulative PAR (E/m^2) for the diel study, separated between Campaign 1 (Left) and Campaign 2 (Right), as well as by site (LD circles and lines, HD asterisk and dashed). **(A,B)** PARAFAC components in Raman units (RU). **(C,D)** FI and BIX on the left axis, HIX on the right axis. **(E,F)** S_R and $SUVA_{254}$ on the left axis and DOC (mg/L) on the right axis.

Figure 2). Taken together, our results suggest that DOM in FB is already significantly photodegraded, such that fluorescence and absorbance indices are temporally stable on diel timescales. This is consistent with the sequential photo- and bio- degradation of neutral sediment leachates from SB (TS/Ph11 in reference), which approached the optical signature of FB surface waters (Chen and Jaffé, 2014).

We expected that the HD site would exhibit greater variability in optical properties and DOC concentration with PAR than at the LD site, as prior studies had linked seagrass density with benthic DOC flux (Ziegler and Benner, 1999) and carbonate dissolution (Burdige and Zimmerman, 2002; Yates and Halley, 2006; Burdige et al., 2010). Instead, we did not see any such diel variability for either the HD or LD site. However, this does not mean that seagrass density and sediment dissolution do not affect surface water optical properties, for two reasons. First, estimates of net carbonate dissolution/precipitation made during the coinciding study were also not strongly related to PAR, and while the HD site was more net dissolving than the LD site, these differences were not large (Van Dam et al., 2019). So, even if a benthic flux of sediment-associated FDOM is facilitated by sediment dissolution, we would not necessarily expect to see a relationship between FDOM indices and PAR for this particular short study period. Second, it is plausible that our water column approach was not sensitive enough, and that a more dedicated experiment such as core incubations or benthic chambers would be better suited to address this question.

Spatial Variability in Surface Waters Between HD and LD Sites

Although we observed limited diel variability in FDOM and related indices, there were strong spatial differences between the HD and LD sites, as well as between sampling campaigns, which were only 1 month apart during the wet (first campaign) and late wet (second campaign) season (Ya et al., 2015). All indices were similar at the LD site for both campaigns, however, at the HD site BIX and %C4 were lower and HIX, %C1, %C2, %C3, and A_{351}/DOC were higher during the first campaign (**Supplementary Figure S5**). Between sites, the HD site was significantly higher in HIX, $SUVA_{254}$, %C1, %C2, and %C3 which are all "humic-like" (**Supplementary Figures S1**, **S5**, $p < 0.05$). Other "non-humic" indices, such as FI and S_R, were not statistically different across sites. Since the HD and LD sites were adjacent (**Figure 1**), any differences we observed could indicate fine-scale heterogeneity in DOM that was missed with broader spatial surveys (Maie et al., 2006, 2012). Furthermore, since the HD site was also higher in sedimentary organic carbon (Van Dam et al., 2019), it is plausible that variations in the "humic" DOM fraction may be related to differences in sedimentary organic matter between the two sites. This hypothesis motivated our sediment leachate assay.

Potential FDOM Source Attribution

We hypothesized the existence of three predominant FDOM sources to the HD and LD surface waters: (1) seagrass

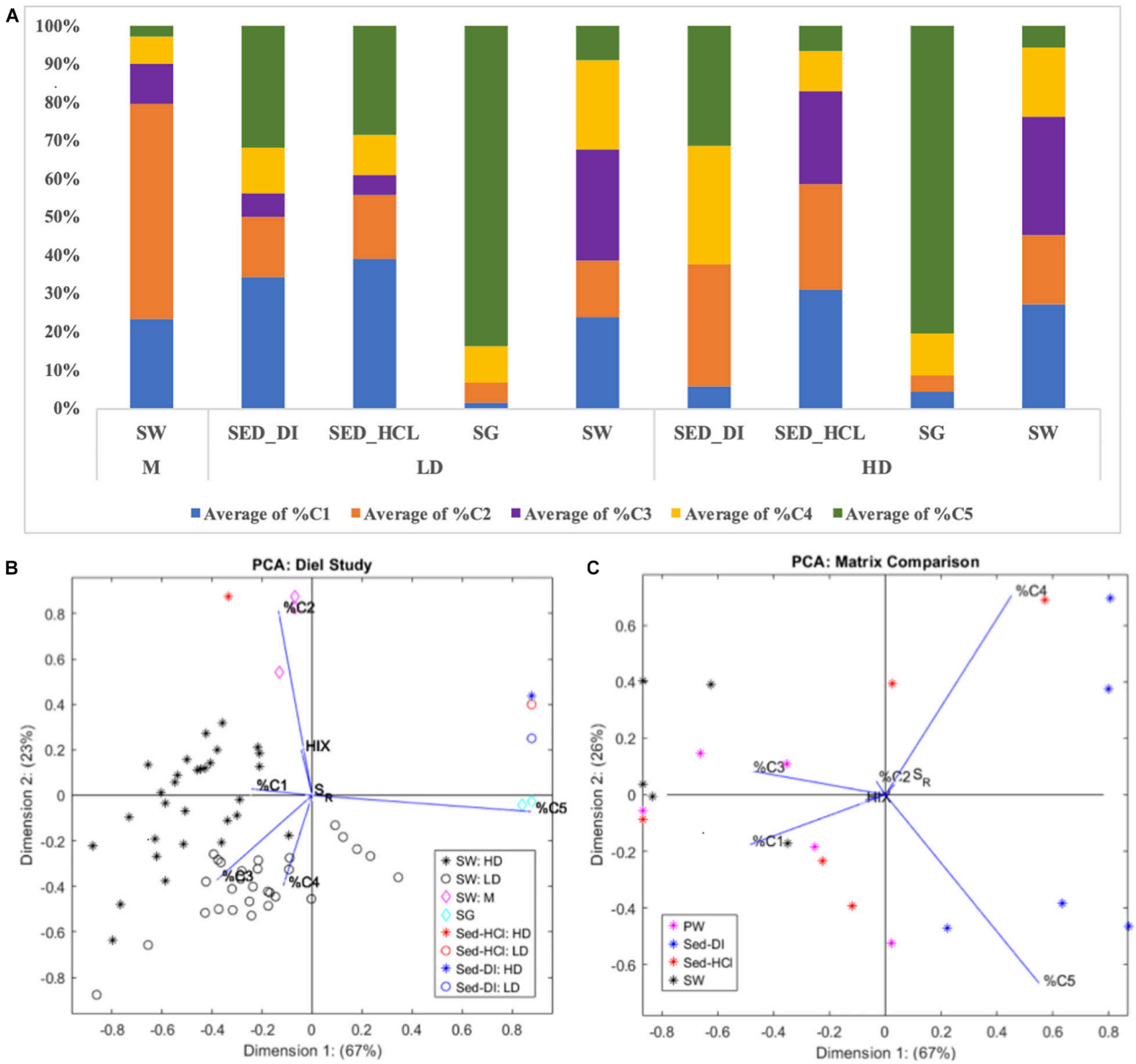

FIGURE 3 | (A) PARAFAC component makeup of the different matrixes (SW, SG, SED_{DI}, and SED_{HCl}) from the HD and LD sites, compared to the nearby Mangrove (M) site. **(B)** PCA of the data shown in the top figure, from the diel portion of this study. **(C)** PCA of the data from the five additional sites throughout FB, separated by matrix (PW, SW, SED_{DI}, and SED_{HCl}).

leachates/exudates, (2) nearby mangroves, and (3) sediment dissolution. Prior studies (Chen and Jaffé, 2014, 2016) used the 8-component FCE PARAFAC model to explore seagrass leaf leachates and explicitly non-dissolving sediment leachates from one site in western FB (SB, or TS/Ph11 in the reference). We expand on this work by comparing the surface water FDOM at both HD and LD sites with that of SG leachates, mangrove SW collected from M (**Figure 1**), and the SED_{DI} and SED_{HCl} leachates. Both HD and LD SG were dominated by C5, minimal C4, C2, and C1, and no C3, and contrasted sharply from that of HD and LD SW, which contained all components, but were dominated by C1, C3, and C4 (**Figure 3A**). Our SG leachates show similar fluorescence to SG in Chen and Jaffé (2014), who found that their seagrass leaf leachates at SB were also dominated by C5 (their component 7), and showed little or no C3 (their component 2). Although C5 was also likely highly photodegradable, these results suggest that seagrasses are not themselves predominant contributors to the surface water FDOM signal.

The M site is situated between the HD and LD sites (**Figure 1**), allowing us to identify any presence of a "mangrove" source of FDOM. Surface waters at M were dominated by C2, and to a lesser extent C1 and C3, with only small amounts, if any, of C4 and C5 (**Figure 3A**). Conversely, C2 was only a minor

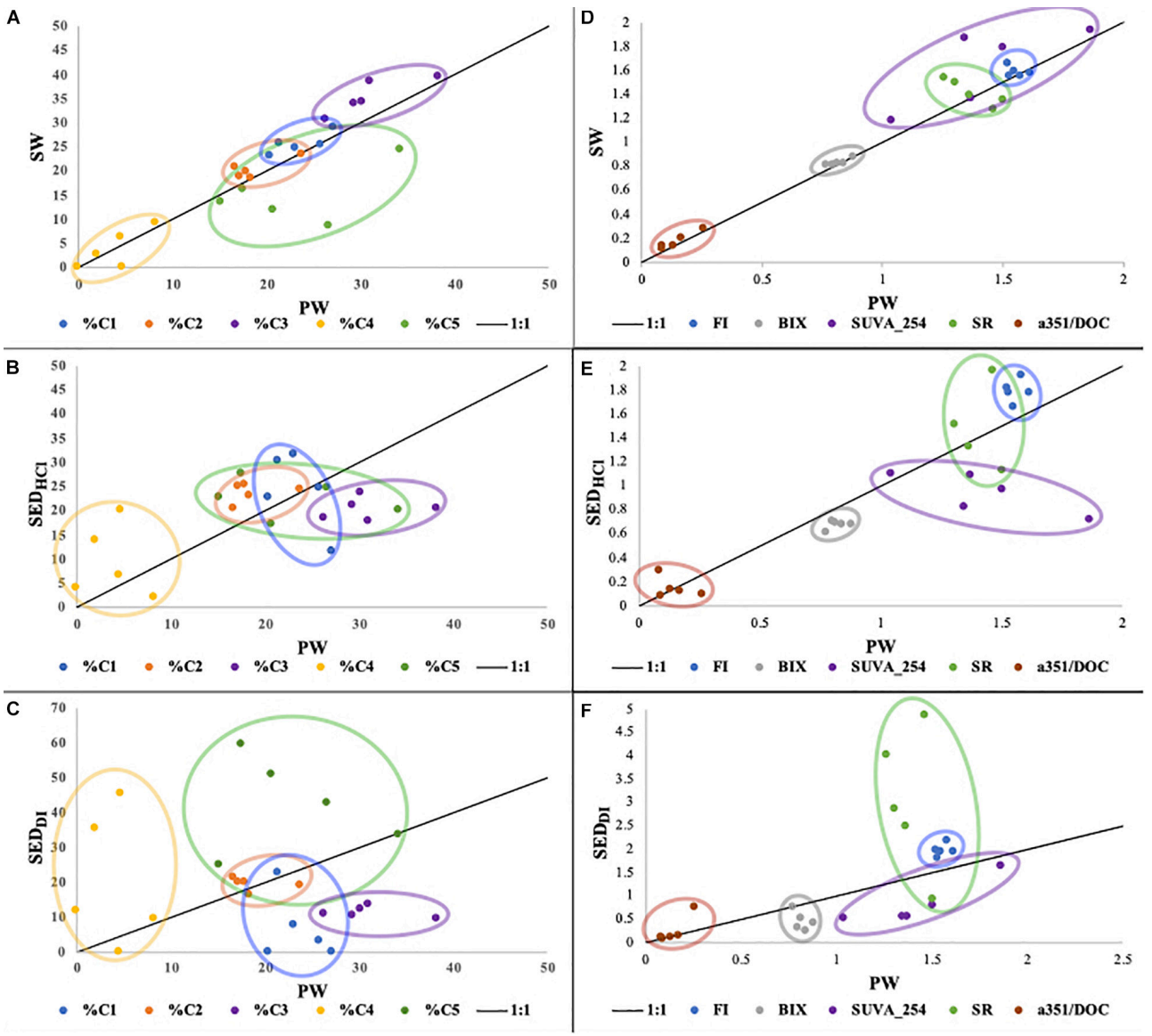

FIGURE 4 | Comparison of PARAFAC component composition **(A–C)** and other optical properties **(D–F)** for the 5 Florida Bay sites (DK, SB, LM, BA, and TC) and 4 pools (SW, PW, SED_{HCl}, and SED_{DI}). PW is on the *x*-axis, with either SW **(A,D)**, SED_{HCl} **(B,E)**, or SED_{DI} **(C,F)** on the *y*-axis. One sample was used for each site and each pool (n = 20).

component of HD and LD SW. While Chen and Jaffé (2014) did not explicitly consider mangroves in Florida Bay, they did collect surface waters from the mangrove-dominated section of Shark River Slough (SRS5 in their report), which is located north of FB on the western coast of south Florida. They found mangrove SW dominated by their components 1 and 5, and to a lesser extent, components 2, 3, 4, and 6, which are similar to our components C2, C1, and C3. Interestingly, their components 1, 3, 4, 5, and 6 were found to be much more photo-reactive than bio-reactive. Thus, the differences between SW collected from M, HD, and LD sites does not rule out mangroves as a possible source for surface water FDOM, as the optical signal could be modified due to photodegradation in clear FB waters. However, our diel study does not show a change in C1, C2, or C3 as a function of cumulative PAR (**Figure 2**).

Our third hypothetical source of FDOM was from the sediments. We conducted two sediment leachate treatments, one intended to minimize the impact of carbonate dissolution (SED_{DI}) and one with enhanced sediment dissolution (SED_{HCl}). Our SED_{DI} protocol is most comparable to the passive leaching with DOC-reduced site water demonstrated in Chen and Jaffé (2014). When considering the percent component makeup of these leachates, the HD SED_{HCl} is much more similar to HD SW than the HD SED_{DI}, while both of the sediment leachates at the LD site are more similar to LD SW than either M or LD SG (**Figure 3A**). Our PCA analysis demonstrates that %C5, and to

a lesser extent %C2 and %C3, are most important in explaining the variability between the different pools. HD SED_{HCl} was more closely related to HD SW than HD SED_{DI}, however, due to the prevalence of the highly photolabile C5 (the main explainer variable of Dimension 1), the LD SED_{HCl} and LD SED_{DI} both clustered closer to LD SG than LD SW (**Figure 3B**). In the Chen and Jaffé (2014) study, mangrove SW was more similar to their Florida Bay SW than the neutrally leached sediment. This indicates that if sediment dissolution is not explicitly considered, the role of sediment dissolution or reprecipitation processes in contributing to DOM cycling in Florida Bay could be overlooked.

The leachate study suggests that seagrasses or mangroves are not necessarily the major direct sources of FDOM to overlying water. Instead, we highlight the process of sediment carbonate dissolution as a potential source of FDOM to surface waters. This sediment carbonate dissolution could be impacted by seagrasses, and we attempted to elucidate this connection by studying seagrass meadows of high and low density. However, rates of carbonate dissolution were similarly low between HD and LD sites during this study period (Van Dam et al., 2019), challenging our ability to distinguish its influence on DOM variability in space or time.

Sediment, Porewater, and Surface Water FDOM Throughout Florida Bay

To further investigate this apparent similarity between the FDOM of SW and SED_{HCl}, we collected samples from 5 additional sites (TC, DK, LM, BA, and SB; **Figure 1**), consisting of a single sample for each site and each pool (PW, SW, SED_{DI}, and SED_{HCl}). When considering carbonate dissolution as a potential source of organic matter, PW can be considered an intermediary pool between SED_{HCl} and SW. For this reason, it can be useful to compare SW to PW, as well as SED_{HCl} and SED_{DI} to PW. Across all sites, the FDOM and absorbance indices clustered around the 1:1 line, suggesting rapid exchange between PW and SW DOM pools. We observed deviations from the 1:1 line for %C5, which was much higher in PW than in SW for most sites, likely due to its photo-lability (Chen and Jaffé, 2014). $SUVA_{254}$ tended to be higher in SW than PW, but differences in SW and PW S_R were less clear (**Figures 4A,D**). Decreases in PW $SUVA_{254}$ were potentially related to releases of labile but not chromophoric DOC from seagrasses in the rhizosphere.

We also observed a strong relationship between SED_{HCl} leachates and PW (**Figures 4B,E**) for most components and indices, indicating a biogeochemical link between the DOM in PW and that associated with carbonate sediments. Deviations observed for %C3 and $SUVA_{254}$, which behaved similarly due to overlapping spectral properties, and were higher in PW than SED_{HCl}, imply that C3 was less strongly associated with carbonates. In contrast, the SED_{DI} leachates appeared much less related to PW (**Figures 4C,F**). This is consistent with the prior leachate study in Florida Bay, which found that FB sediment leachates using non-acidified waters were very dissimilar to surface waters (Chen and Jaffé, 2014), and clearly contrasts with our SED_{HCl} leachates. Both their study, and our SED_{DI} leachates, attempted to minimize sediment dissolution, whereas our SED_{HCl} approach attempted to highlight sediment dissolution. The relationships among these pools can also be seen in our PCA analysis, which shows 4 of the SED_{HCl} clustering near the PW or SW along with the variables %C1 and %C3, whereas the SED_{DI} is more dissimilar and clusters nearer the variables %C5 and %C4 (**Figure 3C**). The SED_{HCl} leaching released large quantities of DOC relative to SED_{DI}, enough to increase the DOC concentration in the leachates by 145 to 260% across the 5 sites, illustrating the potential contribution of this pool in *in situ* seagrass meadows (**Supplementary Table S2**).

CONCLUDING REMARKS

The results of our unique HCl-leaching procedure indicate that carbonate sediment dissolution could be an important mechanism, linking sediment-associated organic matter to the broader dissolved organic matter cycle in carbonate seagrass systems like Florida Bay. We suggest that the exchange between SED_{HCl} and PW pools are facilitated by sediment dissolution and reprecipitation, and subsequently PW and SW pools mix upon periodic sediment resuspension events, bioturbation, or slow diffusive exchange. Although our diel study was not able to elucidate this laboratory derived relationship in the field, this study lays the groundwork for future investigations to measure the sediment-water FDOM flux alongside estimates of carbonate dissolution, to address the reversibility of the process, and investigate the alteration of DOM by its association with carbonates.

DATA AVAILABILITY STATEMENT

The dataset generated for this study is available on Figshare (https://doi.org/10.6084/m9.figshare.12611897.v2). PAR data used for this article is already published and is available at Figshare (https://doi.org/10.6084/m9.figshare.7707029.v1). The PARAFAC model is available on OpenFluor (OpenFluor ID 2859).

AUTHOR CONTRIBUTIONS

MZ wrote the manuscript, developed the PARAFAC model, and was instrumental in the sediment leachate study design. BV and CL created the diel study, were instrumental in field work, and provided detailed edits to the manuscript. JK was instrumental in the study design and also provided detailed edits and comments to the manuscript. All authors contributed to the article and approved the submitted version.

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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.2020.580284/full#supplementary-material

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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