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Composition and cycling of dissolved organic matter from tropical peatlands of coastal Sarawak, Borneo, revealed by fluorescence spectroscopy and PARAFAC analysis

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Abstract. Southeast Asian peatlands supply ~10% of the global flux of dissolved organic carbon (DOC) from land to the ocean, but the biogeochemical cycling of this peat-derived DOC in coastal environments is still poorly understood. Here, we use fluorescence spectroscopy and parallel factor (PARAFAC) analysis to distinguish different fractions of dissolved organic matter (DOM) in peat-draining rivers, estuaries, and coastal waters of Sarawak, Borneo. The terrigenous fractions showed high concentrations at freshwater stations within the rivers, and conservative mixing with seawater across the estuaries. The autochthonous DOM fraction, in contrast, showed low concentrations throughout our study area at all salinities. The DOM pool was also characterized by a high degree of humification in all rivers and estuaries up to salinity 25. These results indicate a predominantly terrestrial origin of the riverine DOM pool. Only at salinities >25 did we observe an increase in the proportion of autochthonous relative to terrestrial DOM. Natural sunlight exposure experiments with river water and seawater showed high photolability of the terrigenous DOM fractions, suggesting that photodegradation may account for the observed changes in DOM composition in coastal waters. Nevertheless, we estimate based on our fluorescence data that at least 20%–25% of the DOC at even our most marine stations (salinity >31) was terrestrial in origin, indicating that peatlands likely play an important role in the carbon biogeochemistry of Southeast Asian shelf seas.

1 Introduction

Tropical peatlands store around 100 Pg of carbon, of which 55% is found in Southeast Asia (Page et al., 2011; Dargie et al., 2017), mostly on the islands of Sumatra and Borneo (Dommain et al., 2014). The rivers draining Southeast Asia's peatlands export large quantities of terrigenous dissolved organic carbon (tDOC), accounting for ~10% of the global land-to-ocean DOC flux of 0.2-0.25 Pg C yr^{-1} (Meybeck, 1982; Baum et al., 2007; Moore et al., 2011; Dai et al., 2012). Terrigenous dissolved organic matter (tDOM) can play significant roles in aquatic environments: tDOM is susceptible to decomposition processes that can remineralize a considerable proportion (40% - 50%) of it in estuaries and shelf seas (Fichot and Benner, 2014; Kaiser et al., 2017). Remineralization of tDOM contributes to maintaining net heterotrophy and CO_2 outgassing in some inner estuaries and ocean margins (Borges et al., 2006; Cai, 2011; Chen and Borges, 2009), potentially causing significant seawater acidification (Alling et al., 2012; Semiletov et al., 2016). tDOM remineralization can also supply inorganic nutrients (Vähätalo and Zepp, 2005; Stedmon et al., 2007; Aarnos et al., 2012).

tDOM is increasingly recognized as labile to both photodegradation (Aarnos et al., 2018; Helms et al., 2014; Hernes, 2003) and biodegradation (Moran et al., 2000; Wickland et al., 2007; Carlson and Hansell, 2014). For example, photodegradation was estimated to account for 70%–95% of total DOM processing in the arctic lakes and rivers (Cory et al., 2014). In the Congo River, which drains extensive tropical peatlands, >95% of the lignin phenols and 45% of the total DOC pool are labile to photodegradation, which thus reduces average molecular weight and aromatic structures (Spencer et al., 2009; Stubbins et al., 2010). Microbial processing can be responsible for a major carbon loss as well, but typically results in shifts of DOM optical properties in the opposite direction to those caused by photodegradation (Moran et al., 2000). Moreover, biodegradation shows a preference for hydrophilic compounds, especially amino acid-like fractions (Wickland et al., 2007; Benner and Kaiser, 2011). On the Louisiana Shelf, the remineralization of tDOM from the Mississippi River was found to be dominated by biodegradation rather than photodegradation (Fichot and Benner, 2014). The fate of tDOM in aquatic environments also depends on the interaction between these two processes, exemplified by the elevated biodegradability of tDOM after partial photodegradation, which decomposes the bio-resistant compounds beforehand (Miller and Moran, 1997; Moran and Zepp, 1997; Moran et al., 2000; Smith and Benner, 2005).

However, our knowledge of the biogeochemical cycling of peat-derived DOM in Southeast Asia is still limited. Although several studies have shown that peatland-draining blackwater rivers in Sumatra and Borneo carry extremely high DOC concentrations with a predominantly terrestrial origin (Alkhatib et al., 2007; Baum et al., 2007; Rixen et al., 2008; Harun et al., 2015, 2016; Müller et al., 2015, 2016; Cook et al., 2017), more detailed analysis of the chemical composition of peat-derived DOM, and determination of its lability to different degradation processes, are mostly lacking. Moreover, most of these studies did not sample beyond the upper estuaries. Notably, however, Southeast Asian peat-draining rivers have low pCO_2 relative to the high DOC concentrations (Müller-Dum et al., 2018; Müller et al., 2015, 2016; Wit et al., 2015), which implies that there is little biogeochemical processing of tDOM within the rivers. However, given that tDOM is increasingly recognized as potentially labile in aquatic environments, more studies are needed to characterize Southeast Asian tDOM and its biogeochemical cycling across the full continuum from freshwater through estuaries to the coastal sea. This is particularly urgent in light of the extensive land-use changes in Southeast Asia over the past three decades, especially the conversion of peatlands to industrial plantations (Miettinen et al., 2016), which appear likely to have increased the riverine flux of peat-derived DOC (Moore et al., 2013).

In this study, we used fluorescence spectroscopy and PARAFAC analysis to investigate the composition and cycling of DOM across the continuum from peat-draining rivers to coastal waters in Sarawak, northwestern Borneo. We aimed to: (1) resolve the chemical composition of DOM and the biogeochemical fate of individual DOM fractions during riverine transport; (2) infer spatial patterns of tDOM degradation; and (3) estimate the potential contribution of photodegradation to the removal and modification of tDOM.

2 Methods

2.1 Sampling

The study region, sampling methods, and the photodegradation experiments have already been described in detail by Martin et al. (2018). Briefly, we sampled six rivers (the Rajang, Sematan, Samunsam, Maludam, Sebuyau, and Simunjan rivers), their estuaries, and open coastal waters in early March, June and September 2017 (Figure 1). These months correspond to the end of the wet northeast monsoon, during the drier southwest monsoon, and the end of the southwest monsoon, respectively. One additional sample was collected from the Lundu River estuary in September. All samples were collected within the upper 1 m and filtered on the same day through 0.2-µm pore-size Anodisc filters (47-mm diameter). The all-glass filtration system was cleaned with 1 M HCl and deionized water (18.2 MΩ cm^{-1}, referred to as “DI water” below), and filters were pre-rinsed with both DI water and sample water. Filtered samples (30 mL each) for fluorescence and absorbance spectroscopy were then preserved with 150 µL of 10 g L^{-1} NaN_3, following Tilstone et al. (2002), stored in amber borosilicate vials with PTFE-lined septa at +4° C and analyzed within 1.5 months of collection.

All six rivers drain peatlands, but to very varying degrees. The Rajang River catchment is dominated by mineral soils, and peatlands are only found within the delta, downstream of the town of Sibu (Staub et al., 2000; Gastaldo, 2010). The Sematan and Lundu rivers also drain catchments with more limited peatlands and a higher proportion of mineral soil. In contrast, the Samunsam, Maludam, Sebuyau, and Simunjan rivers drain catchments that consist to a large extent of peatlands, and these four rivers are considered blackwater rivers. Mangroves are found along the estuaries of all six rivers. Following the companion study by Martin et al. (2018) of DOC and colored dissolved organic matter (CDOM), we classify our sampling stations into three groups, namely, the eastern region (Rajang River and coastal water stations east of Kuching city), the western region (Sematan and Samunsam rivers, and coastal water stations west of Kuching), and the remaining three blackwater rivers.

Photodegradation experiments were conducted in June and September by exposing filtered water from the Rajang River, the Samunsam River, and eastern region seawater to natural sunlight for 3–6 days in 150-mL quartz bottles. Dark controls were wrapped in aluminum foil and black plastic. The bottles were sub-sampled every 1-3 days and samples preserved as above.

Martin et al. (2018) showed that all experiments received approximately equal sunlight irradiance over time, so for simplicity we present our results as a function of exposure time.

2.2 Fluorescence measurement and data processing

Fluorescence excitation-emission matrices (EEM) were measured using a Jobin Yvon Horiba Fluoromax-4 fluorometer (excitation: 250–450 nm at 5-nm intervals and bandwidth 5 nm; emission: 290–550 nm at 2-nm intervals and bandwidth 5 nm). To minimize self-quenching of fluorescence intensity, blackwater river samples in March were diluted ten-fold with DI water. In September, blackwater samples were instead measured in a 3 mm-pathlength cuvette without dilution. All other samples were measured undiluted in a 1cm-pathlength cuvette. Laboratory reagent blanks were made of 30 mL of DI water with 150 μL of 10 g L^{-1} NaN_3 and measured at appropriate dilution in both cuvettes for blank subtraction. NaN_3 did not contribute any blank fluorescence. Fluorescence signals were normalized to the lamp reference intensity, with spectral corrections applied by the instrument software.

Data were further processed with the MATLAB drEEM toolbox (Murphy et al., 2013) to correct for inner filter effects following Kothawala et al. (2013), convert fluorescence intensities to Raman Units (R.U.) based on the area of the water Raman peak (Lawaetz and Stedmon 2008), subtract blanks, and where necessary correct for sample dilution. First-order Raman scattering and second-order Rayleigh scattering were completely removed, while second-order Raman scattering and first-order Rayleigh scattering were smoothed by interpolation.

Following McKnight et al. (2001), we calculated the fluorescence index, FI, as the ratio of emission intensity at 450 nm to that at 500 nm, at excitation 370 nm (Eq. 1):

$$\mathrm{FI} = \frac{\mathrm{Ex370,Em450}}{\mathrm{Ex370,Em500}} \quad (1)$$

We also calculated the humification index, HIX, following Ohno (2002) (Eq. 2):

$$\mathrm{HIX} = \frac{\mathrm{Ex255},\sum \mathrm{Em}(434\rightarrow 480)}{\mathrm{Ex255},\sum \mathrm{Em}(434\rightarrow 480)+\mathrm{Ex255},\sum \mathrm{Em}(300\rightarrow 346)} \quad (2)$$

where $\mathrm{Ex255},\sum \mathrm{Em}(x \rightarrow y)$ is the integrated area under the emission spectrum from x nm to y nm excited at 255 nm (note that Ohno (2002) originally used excitation 254 nm).

2.3 PARAFAC analysis

A total of 225 corrected EEMs from field samples and the photodegradation experiments were used for PARAFAC analysis using the MATLAB drEEM toolbox, which decomposes the variation between EEMs in a dataset into multiple mathematically independent components that can be linked to different chemical compound classes (Bro and Kiers, 2003; Stedmon, et al., 2003; Stedmon and Bro, 2008; Murphy et al., 2013). A small number of outliers with abnormal EEM spectra or unusually high leverage over the model were removed. A five-component model was generated and validated by residual examination and split-half analysis. We compared our PARAFAC components with components identified by previous studies listed in the OpenFluor online database (Murphy et al., 2014) to identify the possible source and biogeochemical properties of the DOM compounds represented by these components. PARAFAC components are quantified as the highest score value at the emission maxima, known as the fluorescence intensity at the maximum (Fmax), which is taken as a measure of the concentration of each component in a sample (Murphy et al., 2013). We report our values in Raman Units (R.U.), which can be roughly converted to Quinine Sulfate Units (QSU) by multiplying by 48.9 (Stedmon and Markager, 2005a).

3 Results

3.1 Biogeochemical setting

A detailed discussion of the DOC and CDOM distribution and characteristics in the study region can be found in Martin et al. (2018). Briefly, high DOC concentrations (1,200–4,400 µmol L^{-1}), high CDOM absorption coefficients (a_{350} of 50–200 m^{-1}), and CDOM properties with clear terrestrial signals were found in all of the four blackwater rivers. The highest DOC concentrations (3,100-4,400 µmol L^{-1}) were found in the Maludam River. The Rajang and Sematan rivers had lower DOC concentrations (120-450 µmol L^{-1}) and less CDOM (a_{350} of 3–11 m^{-1}), consistent with a greater proportion of mineral soil rather than peat in these two catchments. DOC and CDOM in all estuaries showed mostly conservative mixing with seawater, except in the Rajang River, where additional organic matter input in the estuary was inferred from the DOC distribution. DOC at the stations furthest from the coast was as low as 76 µmol L^{-1}. A predominantly terrestrial origin of DOM in the rivers was inferred from the low CDOM spectral slopes at 275–295 nm ($S_{275\text{-}295}$, 0.0102–0.0144), low CDOM slope ratios (S_R, 0.601–0.867) and high specific UV absorbance at 254 nm ($SUVA_{254}$, 3.08–6.89) (Martin et al., 2018).

Chlorophyll-*a* concentrations were low at all stations, mostly below 3 µg L^{-1}, and never exceeding 5.5 µg L^{-1} (Martin et al., 2018). In the rivers, these oligotrophic conditions are most likely a result of light limitation due to high sediment (Rajang and Sematan rivers) and high CDOM (blackwater rivers) concentrations (Martin et al., 2018); at the marine stations, this most likely reflects the low nutrient concentrations that are typical for tropical seas.

3.2 FDOM compositional indices

The fluorescence index (FI) was very low across the whole study region, mostly 0.9–1.2 (Figure 2a–e). In the Rajang River and eastern region, the FI showed no change with salinity, remaining close to 1.15 without seasonal variation. The scatter in FI at salinity 0 in the Rajang River probably reflects differences in DOM between the distributary channels. All other rivers had consistently lower FI than the Rajang, ranging from 0.85–1.1. In the western region, and the Maludam and Sebuyau estuaries, FI clearly increased with salinity, although even the most marine stations still had low values. Seasonal variation in FI was only seen in the western region, where higher salinities in September were associated with ~0.03-unit higher FI than in March.

The humification index (HIX) showed a hockey stick-like distribution with salinity in the Eastern and western regions, with consistently high values (~0.9) until salinities of 20–25, beyond which HIX decreased rapidly to 0.6–0.7 (Figure 2f–j). This pattern closely follows expectations from conservative mixing, especially in the western region. Highest HIX values were found in the four blackwater rivers and the Sematan River, close to 1.0, with the Rajang River having somewhat lower values of 0.8–0.9. HIX did not decrease with salinity in the Maludam and Sebuyau estuaries, but salinities here were always below 25. Some seasonal variation was observed, with HIX in the eastern region reaching lower values in September and June than in March, and HIX in the western region also reaching lower values associated with higher salinity in September than in March.

3.3 Spatial distribution and characteristics of PARAFAC components

The five-component PARAFAC model explained 99.6% of the variability between EEMs for the entire dataset. All five components (C1-C5) showed high similarity to components previously identified in various aquatic environments (Figure 3, Table 1). Specifically, C1, C2, and C3 had emission maxima in the visible wavelength range, indicating a high contribution of conjugated fluorophores to these components (Coble, 1996; Fellman et al., 2010a). C1 exhibited an emission maximum at 440 nm with two excitation maxima at 255 nm and 330 nm, which is traditionally defined as Peak C (Coble, 1996). C2 had similar spectral characteristics to C1, but both the excitation and emission maxima exhibited slight redshifts. C3 showed a narrow excitation peak with a single UVC maximum and a broad emission peak centering at 460 nm, resembling the conventionally defined Peak A. All of C1, C2, and C3 have been widely recognized as humic/fulvic acid-like components derived from terrestrial plant litter (Stedmon et al., 2003; Stedmon and Markager, 2005a; Yamashita et al., 2015), and in the present study, they primarily represented the terrestrial humic-like DOM derived from peatlands. C4 was characterized by two excitation maxima (<250 nm and 310 nm) and a relatively narrow emission peak in the UVA region, which closely matches Peak M, traditionally defined as a marine humic-like component (Coble, 1996). This component is commonly found in marine surface waters, representing a heterotrophically re-processed DOM fraction that is part of the autochthonous DOM pool and correlates with the presence of freshly produced, bio-labile compounds (Gonçalves-Araujo et al., 2015; Wagner et al., 2015; Yamashita et al., 2015; Osburn et al., 2016; Fellman et al., 2010a). C5 was a protein-like component, with its excitation/emission maxima in the traditionally defined Peak T (tryptophan-like) and Peak B (tyrosine-like) regions, and thus represents fresh DOM produced by phytoplankton (Coble, 1996; Stedmon and Markager, 2005b). The fluorescence maxima of all components and their potential sources investigated in previous literature were summarized in Table 1.

Components C1–C4 showed very similar distributions across our study region, with high values (0.1–4 RU) in the rivers, and strong decreases with salinity to values ≤0.01 RU at the most marine stations (Figure 4). Blackwater rivers had consistently 5–10-fold higher values for C1–C4 than the Rajang and Sematan rivers, reflecting the far higher DOC concentrations in blackwater samples. C5, in contrast, showed consistently low values across the study region, mostly <0.2 RU, and without a clear difference between blackwater and non-blackwater rivers. C5 also did not decrease with salinity, instead remaining at relatively constant values across the entire salinity gradient. Interestingly, neither C4 nor C5 were correlated with chlorophyll-*a* concentrations (Table 2), even though both components are often associated with autochthonous DOM (microbially re-processed and fresh DOM, respectively, for C4 and C5). This lack of correlation may at least partly be explained by the limited variation in chlorophyll-*a* concentration across our study region.

In the Samunsam, Maludam and Sematan rivers, C1, C2, and C4 showed conservative mixing with seawater (Figure 4). C3 showed evidence of non-conservative behavior in the Maludam and at some stations in the Samunsam, but behaved conservatively in the Sematan river. In the Rajang river, C1–C4 all showed positive deviations from conservative mixing, suggesting that there were additional inputs of all of these components in the Rajang estuary. A mixing model was not calculated for the Sebuyau River because it drains into the estuary of the larger Lupar River, for which we could not collect freshwater end-member samples.

Seasonal variation was not seen for any components in the eastern region. In the western region, seasonal differences were observed for components C1–C4: as for FI and HIX, the higher salinities at the most marine stations in September were associated with lower values of all four components. Moreover, C1, C2, and C4 were higher in September in the Samunsam and Sematan rivers compared to March, although C3 did not differ seasonally in these two rivers. In contrast, seasonal variation was only observed for C3 in the Maludam, Sebuyau, and Simunjan rivers, all of which had consistently lower values in September than in March. C1, C2, and C4, however, showed no seasonality in these three rivers. C5 did not vary seasonally in any of the rivers.

3.4 Behavior of FDOM fractions during photodegradation

Martin et al. (2018) already reported the losses of DOC and CDOM observed during the photodegradation experiments, with 5.6–26% of riverine DOC removed after 3–5 days of sunlight exposure (Figure 5a–d). We found even greater percentage losses of the four humic-like components (C1-C4) in the two Rajang River samples and the eastern region seawater sample (Figure 5), with C1 and C2 showing greater losses (50–68% reduction) than C3 and C4 (26–50% reduction). The reduction in all four humic-like FDOM components in the seawater experiment is particularly notable, because no loss of DOC was observed in this experiment (Martin et al., 2018). The protein-like component, C5, showed no change relative to controls in the Rajang and seawater experiments, except for possibly a minor degree of photoproduction in the September Rajang experiment. Otherwise, no photoproduction of FDOM was observed during the Rajang and seawater experiments. Sunlight exposure caused a small decrease in HIX in the two Rajang River experiments, where a slight reduction in FI was also observed, and in the seawater experiment (when comparing light versus dark bottles in this experiment, rather than relative to the initial sample).
The Samunsam River blackwater showed reductions in C1 and C2 by the end of the experiment, but the same phenomenon was also observed for the dark control samples. One of the dark-treated samples on Day 6 was considered as an outlier and omitted due to its abnormal EEM spectra. Only C2 showed clear photodegradation in excess of the dark controls. C3 and C4 of light-exposed samples were actually elevated after one day, followed by small decreases during the subsequent days, with the data overall suggesting some degree of photoproduction of C3 and C4 in this river. C5 showed a small increase relative to the initial sample in the Samunsam experiment, but dark and light samples were within error of each other. Unlike in the other experiments, HIX and FI did not change during the Samunsam River experiment.

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4 Discussion

4.1 FDOM markers as tracers of DOM sources in Sarawak

The fluorescence and humification indices (FI and HIX) are easily quantifiable markers that are commonly used to trace tDOM. In particular, FI is thought to distinguish terrestrially derived fulvic acids (FI = ~1.4) from microbially derived fulvic acids (FI = ~1.9), and to be related to percentage aromaticity of a sample (McKnight et al., 2001). In our region, all stations were characterized by considerably lower FI values (0.8–1.2) than the canonical terrestrial end-member range of 1.3–1.4 proposed by McKnight et al. (2001). Similarly low FI values (1.2–1.3) were reported recently in various temperate and Arctic rivers and swamps with large terrestrial DOM input (Cory et al., 2010; Cory and McKnight, 2005; Helms et al., 2014; Mann et al., 2016). This suggests that the very low FI values in our river samples could in principle reflect high concentrations of terrigenous fulvic acids. However, the very low FI values at even our marine stations, where other FDOM markers (see below) and CDOM properties (Martin et al., 2018) indicated lower tDOM contributions, suggests that FI does not accurately trace tDOM in our study region. In fact, Murphy et al. (2008) reported FI values of ~1.2 from the open Pacific Ocean far from terrestrial DOM inputs, and concluded that FI is unreliable at extremely low FDOM concentrations due to instrumental noise. Given that fluorescence values at our marine stations were as low as ~0.01 RU, this problem could have impacted our measurements too. However, we note that FI, as the ratio of fluorescence at 450 nm to 500 nm, in our case is essentially the ratio between our components C1 and C2, which showed a very similar distribution pattern and a strong terrigenous source (see below). This shows that caution is warranted when relying on simple fluorescence indices to trace tDOM.

The high HIX values in all rivers suggest a very high degree of humification of the DOM. The values in all rivers except the Rajang River were >0.9, overlapping with the range of HIX of fulvic acid extracted from agricultural soils (0.90 – 0.96) (Ohno, 2002). HIX declined in coastal waters, indicating a change towards less humified DOM in coastal waters. Given the wavelength ranges used to calculate HIX, we note that HIX should be very similar to the ratio of our C5 Fmax to C1 Fmax, thus indicating the relative proportions of allochthonous versus autochthonous DOM. Indeed, we found a significant and very strong correlation between HIX and C5/C1 Fmax ratio ($r^2 = 0.92$, $p < 0.01$, Figure S1). HIX therefore appears to be a more robust tracer of tDOM than FI in our study region. This conclusion is supported by the low CDOM spectral slope ($S_{275\text{-}295}$) and high $SUVA_{254}$ reported for these rivers by Martin et al. (2018). The humification process produces high-molecular weight aromatic compounds (Zech et al., 1997), and $S_{275\text{-}295}$ and $SUVA_{254}$ are correlated with mean molecular weight (Helms et al., 2008) and with aromaticity (Weishaar et al., 2003), respectively. One might therefore expect these CDOM parameters to be closely related to HIX. Interestingly, however, HIX only showed relatively weak correlations with $SUVA_{254}$ ($r^2 = 0.58$, $p < 0.01$) and with $S_{275\text{-}295}$ ($r^2 = 0.65$, $p < 0.01$), suggesting that the HIX does not trace identical chemical properties of the organic matter as the two CDOM parameters (Figure S1).

The strong similarity between the distributions of our components C1–C4 suggest that they were most likely all of terrestrial origin. This is further supported by the fact that the differences in C1–C4 values between the rivers broadly reflected their DOC concentrations, with lowest values in the Rajang and Sematan, and higher values in the blackwater rivers. Previous studies have also found multiple terrestrial humic-like components in the same region, showing similar biogeochemical behavior along the aquatic continuum (Stedmon et al., 2003; Murphy et al., 2008; Yamashita et al., 2011; Gonçalves-Araujo et al., 2015). Nevertheless, our C1–C4 do very likely correspond to chemically distinct tDOM fractions. C1 and C2 shared spectral characteristics that are conventionally assigned as humic compounds leached directly from soils, and typically show high photolability (McKnight et al. 2001; Stedmon et al. 2003; Lapierre and del Giorgio 2014; Yamashita et al. 2015). Our C3 has spectral characteristics that are also associated with terrestrial humic DOM, but often also indicative of moderate photochemical processing (Stedmon et al., 2007; Cawley et al., 2012). This is consistent with our experimental results that show lower photolability, and possibly even some photoproduction, of C3 compared to C1 and C2. Moderate photoproduction of C3 might explain why some samples in the western region deviated so strongly from conservative mixing (Figure 4l). Stubbins et al. (2014) further showed that C3 may represent highly aromatic and black carbon compounds, characterized by higher molecular weight, higher diversity in molecular structure and depletion in nitrogen compared to C1, which matches lignin-like compounds and is less modified by reprocessing since its production from plant litter.

C4 represents another class of humic-like DOM, but C4 is conventionally assigned as a marine humic-like component, and thought to be generated by heterotrophic reprocessing of aquatic autochthonous DOM (Coble, 1996; Cory and McKnight, 2005; Fellman et al., 2010a). Higher concentrations of C4 are commonly reported in productive waters, such as coastal upwelling regions and at mid-salinities in some estuaries (Coble et al., 1998; Yamashita et al., 2008; Fellman et al., 2010b). This component can be produced by bacterial reprocessing of fresh phytoplankton-derived organic matter (Kinsey et al., 2018), but also directly by phytoplankton in the absence of bacteria (Romera-Castillo et al., 2010). However, in this study, because C4 showed such a close correlation with C1 and C2, but not with chlorophyll-*a* or C5, we inferred that C4 was unlikely to be associated with aquatic primary production. Instead, C4 almost certainly had a terrestrial source from peatlands, although it is possible that our C4 is actually microbially reprocessed tDOM, as suggested by other studies (Stedmon et al., 2003; Murphy et al., 2008; Yamashita et al., 2011). Moreover, our photodegradation experiment with the Samunsam water suggested that there could even be a degree of photoproduction of C4, although overall C4 showed a more conservative mixing pattern than C3 in the western region.

C5 has spectral characteristics that are generally associated with protein-like DOM, although our C5 falls in between the canonical tryptophan-like and tyrosine-like peaks (Yamashita et al., 2015). High concentrations of protein-like components are typically reported during algal blooms, and are generally thought to trace fresh, autochthonous DOM in fresh- and seawater (Stedmon and Markager, 2005; Murphy et al., 2008; Yamashita and Jaffé, 2008; Jørgensen et al., 2011). C5 is produced by phytoplankton cultures (Kinsey et al., 2018; Romera-Castillo et al., 2010), but production rates vary between phytoplankton species (Fukuzaki et al., 2014). Furthermore, Yamashita et al. (2015) found that a protein-like component was indicative of the bioavailability of DOM, correlating strongly with DOC-normalized amino acid yields. Interestingly, we found no correlation between C5 and chlorophyll-*a* in our study region. This could be caused by several factors: for one, chlorophyll-*a* was consistently low across our study region, so there might simply not have been enough variation in aquatic primary production to cause a correlation. For another, spatial and temporal variation in phytoplankton community composition could have obscured a correlation between C5 and chlorophyll-*a* across our entire dataset. Moreover, protein-like components are typically labile to biodegradation (Wickland et al., 2007; Lønborg et al., 2010; Kinsey et al., 2018), so their production rates are not necessarily reflected in their concentrations. Finally, it has even been suggested that protein-like components can be associated with the degradation of terrigenous organic matter (Stedmon and Markager, 2005a; Yamashita et al., 2011). Although we cannot exclude this possibility, the fact that our C5 did not consistently decrease with salinity rules out a primarily terrestrial source for this component, supporting our interpretation of C5 as reflecting fresh, autochthonous DOM.

All our components except C2 resembled those identified recently in the Kinabatangan River in northeast Borneo, the catchment of which consists of oil palm plantations and natural forests (Harun et al., 2016), suggesting a relatively similar organic matter composition across coastal Borneo. Harun et al. (2016) showed clear seasonal variations, with higher concentration of peak A, which dominated their FDOM pool, in the wet season relative to the dry and inter-monsoonal season. This is similar to the seasonal difference in C3 in our blackwater rivers. Harun et al. (2016) also inferred an anthropogenic source of peak M from land use change and highlighted the importance of microbial and/or photochemical processing of tDOM to its production, supporting our interpretation of a terrestrial source for C4 with heterotrophic reworking.

4.2 Photochemical transformations of FDOM

We observed high photolability of the four terrestrial components (C1-C4) in the Rajang River and seawater experiments, with percentage losses of the FDOM components that substantially exceeded the loss in DOC. Moreover, as suggested by Helms et al. (2014), the decrease in HIX indicated a change to an overall less humified DOM pool with preferential losses of aromatic compounds in these three experiments. We note that although sunlight exposure can cause spectral shifts instead of complete loss of fluorescence (Helms et al., 2013), examination of our excitation and emission spectra showed large decreases in fluorescence intensity, but no shift of spectral peaks (Figure S2). Large losses of terrestrial humic components, changes to CDOM spectra, and reductions in molecular markers such as lignin phenols are commonly reported from photodegradation experiments with aquatic samples (Stedmon et al., 2007; Spencer et al., 2009; Stubbins et al., 2010). However, studies in some environments have also reported very limited tDOM photolability (Chupakova et al., 2018; Stubbins et al., 2017), highlighting the need for more experiments.

Interestingly, the Samunsam River water showed less pronounced photodegradation of FDOM components, despite experiencing the greatest photomineralization of DOC. The fact that HIX did not change in this experiment can be explained by the photoproduction of C3, which would have offset the decline in C1 and C2. It is unclear why the FDOM components in this experiment showed more limited photodegradation, given the large loss of CDOM and changes in CDOM spectral slopes (Martin et al., 2018), but these data may suggest a degree of variation between rivers in photolability and possibly in chemical composition of our FDOM components.

The protein-like component (C5) was photoresistant in all experiments, indicating low photolability of autochthonous DOM. Differences in photolability between DOM fractions are usually linked to the relative proportions of aromatic (more photolabile) versus aliphatic (less photolabile) structures (Helms et al., 2014; Stubbins et al., 2010), and phytoplankton-derived organic matter is generally dominated by more aliphatic compounds such as carbohydrates, proteins, and lipids (Lancelot, 1984).

4.3 FDOM-based estimate of terrigenous DOC fraction

Estimates of the proportion of tDOC in marine environments have been based mostly on C/N ratios, isotopic composition, and biomarkers such as lignin; such studies have shown that tDOC accounts for 0.5%-2.4% of total DOC in the open Pacific and Atlantic Oceans (Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997), 5%–22% in the Arctic shelf seas (Opsahl et al., 1999), and ≤30% on the Louisiana Shelf (Fichot and Benner, 2012). These analyses are relatively laborious and expensive. However, given that fluorescence analysis can distinguish between terrigenous and autochthonous fractions, FDOM might hold the potential to estimate tDOC in certain environments, provided that FDOM mixes conservatively. Terrestrial humic-like PARAFAC components have been shown to be strongly correlated with lignin phenol concentrations in various aquatic environments (Stedmon et al., 2003; Walker et al., 2009; Yamashita et al., 2015). In particular, C1 has been widely recognized as a component representing high molecular weight, humic-like degradation products of lignin (Coble 1996; McKnight et al., 2001; Stedmon et al., 2003; Stubbins et al., 2014), with a particularly strong correlation with lignin phenols (Yamashita et al., 2015). We therefore attempted to estimate tDOC in our marine samples from the ratio of DOC and C1, using equation (3):

$$\%\text{tDOC}_{\text{sample}} = (\text{C1 Fmax/DOC})_{\text{sample}} / (\text{C1 Fmax/DOC})_{\text{river}} \quad (3)$$

where $(\text{C1 Fmax/DOC})_{\text{river}}$ is the highest value of DOC-normalized C1 Fmax at salinity 0 within the appropriate river, and $(\text{C1 Fmax/DOC})_{\text{sample}}$ is the DOC-normalized C1 in the sample for which %tDOC is to be estimated. This approach assumes that the river endmember consists of 100% terrigenous DOC, but given the low chlorophyll-*a* concentrations in all rivers relative to the amount of DOC, this is probably a reasonable approximation. For the eastern region samples, we used the Rajang River as the riverine endmember. For the western region samples, the Samunsam River served as the riverine endmember due to its likely larger DOC export compared to the Sematan.

The %tDOC decreased with salinity (except for three mid-salinity stations in the western region) and reached minimum values of 15–25% at stations with highest salinity in both regions (Figure 6), consistent with the low HIX at these stations. Fichot and Benner (2012) previously proposed $S_{275-295}$ as a quantitative tracer of tDOM, and our %tDOC estimate is closely correlated with $S_{275-295}$ ($\rho = -0.90$, $p<0.01$, Figure S1), which never exceeded 0.025 at even our most marine stations (Martin et al., 2018). While our FDOM-based estimate needs to be viewed with caution, this relatively high tDOC contribution in coastal waters is in the same range as estimates elsewhere (Fichot and Benner, 2012; Opsahl et al., 1999), and the strong relationship with $S_{275-295}$ supports the idea that FDOM can be used as a quantitative tracer over these relatively short spatial scales. One important source of error would be the preferential loss of C1 due to photodegradation, which would actually cause us to underestimate the true %tDOC. A relatively high tDOC contribution to the coastal DOC pool is also consistent with our finding that marine waters still contained photolabile terrestrial FDOM components.

4.4 Biogeochemical fate of tDOM in Sarawak

All of our terrestrial FDOM components, C1–C4, displayed mostly conservative mixing with seawater, which suggests that tDOM does not undergo major biogeochemical processing in the rivers and estuaries. The same conclusion was also reached by Martin et al. (2018) based on the distribution of DOC and CDOM parameters. The fact that our fluorescence data independently show very similar results increases our confidence in this conclusion. The main exception to this pattern was observed in the Rajang River delta, where C1–C4 consistently showed higher values in the estuary than expected from conservative mixing. Martin et al. (2018) found that DOC showed the same pattern, and hypothesized that this reflected DOC input from surrounding peatlands, even though the concomitant increase in $S_{275\text{-}295}$ did not unambiguously support a terrigenous origin of this DOC. The fact that we see the same positive deviation from conservative mixing in all four terrestrial components, but not in our C5, strongly supports the idea that the additional DOC input into the Rajang River distributaries consists of tDOC from the peatlands, and not from autochthonous production.

We inferred in this study that C4 was terrestrial, as also shown by Harun et al. (2016) in northeastern Borneo. This suggests that in Southeast Asia, Peak M might not be part of the autochthonous marine DOM pool. Because microbial processing plays a major role in soil organic matter transformation within peatlands, we hypothesize that C4 is produced within the soil prior to the export of tDOM to rivers. The conservative mixing behavior of C4 rules out significant production by heterotrophic processing of tDOM within rivers and estuaries.

Our experimental results shed further light on the biogeochemical fate of tDOM in this region by showing the high degree of photolability of terrestrial FDOM in Sarawak. The predominantly conservative mixing of our terrestrial FDOM components thus further indicates that substantial biogeochemical processing of tDOM probably only takes place once it has mixed into marine waters with greater light penetration. This contrasts, for example, with results from the Mississippi estuary, where preferential removal of high-molecular weight compounds and oxidation of lignin were reported at the boundary from mid- to high-salinity waters, mostly as a result of photooxidation (Hernes, 2003).

Conclusions

Tropical peatlands in Sarawak, Borneo, export extremely humified DOM to coastal waters. We have identified four terrestrial humic-like PARAFAC components (C1-C4) that have high concentrations in peat-draining rivers, and mix conservatively with seawater. The rivers were dominated by terrigenous DOM, and we estimate that even our marine stations were characterized by relatively high tDOM concentrations. Of the two simple FDOM compositional indices we calculated, we found that only HIX yielded results that were consistent with our PARAFAC analysis, with the FI likely capturing only terrestrial components. Moreover, we found no evidence of genuinely marine-produced humic substances, with the canonical marine humic component also tracing terrestrial input. Although our experimental evidence shows high photolability of terrestrial FDOM, our observational data suggest that tDOM in Sarawak experiences little biogeochemical processing until it reaches fully marine waters.

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Tables and Figures

Table 1. The excitation and emission maxima of our PARAFAC components, and their possible sources and corresponding chemical compounds (wavelengths in brackets are secondary maxima).

Component	Excitation maxima	Emission maxima	Possible source/ classes of compound
C1	330 (255)	440	terrestrially derived humic matter[1,2] with high molecular weight[3] degraded from lignin[4,11]
C2	275 (385)	506	soil fulvic acid[5,6,7], reduced semi-quinone fluorophore derived from terrestrial higher plants and associated with microbial reduction reactions[8]
C3	<250	460	Terrestrially derived humic matter[1,2,3,5], photo-product[12], aromatic and black carbon compounds with high molecular weight and depleted of N[11]
C4	<250 (310)	390	marine humic-like, microbially processed autochthonous compound[1,7,8,9]
C5	275	328	protein, mixture of tryptophan-type and tyrosine-type compounds, autochthonous DOM[1,2,10]

([1]Coble, 1996; [2]Yamashita et al., 2015; [3]Stedmon et al., 2003; [4]McKnight et al., 2001; [5]Stedmon and Markager, 2005a; [6]Lochmüller and Saavedra, 1986; [7]Yamashita and Jaffé 2008; [8]Cory and McKnight, 2005; [9]Fellman et al., 2010a; [10]Yamashita et al., 2010; [11]Stubbins et al., 2014; [12]Stedmon et al., 2007)

Table 2. Pearson's correlations between PARAFAC components (C1, C4 and C5) and chlorophyll-a concentrations in different regions.

	region	chlorophyll-*a* (mg/L)		C1 Fmax (R.U.)	
		r^2	p	r^2	p
C4 Fmax (R.U.)	Eastern	0.069	0.064	**0.929**	**<0.01**
	Western	0.014	0.436	**0.880**	**<0.01**
	Blackwater	0.055	0.136	**0.872**	**<0.01**
C5 Fmax (R.U.)	Eastern	0.008	0.531		
	Western	0.014	0.446		
	Blackwater	0.026	0.307		

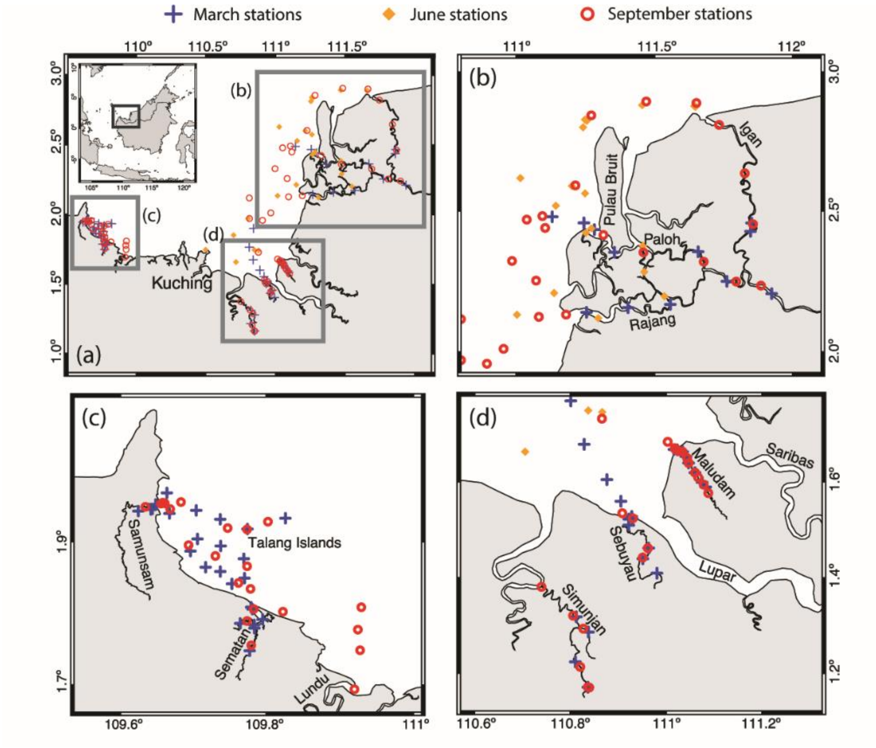

Figure 1. (a) Map of the study region and sampling sites (Martin et al., 2018). Zooming in of the three regions is shown in panels (b) – (d).

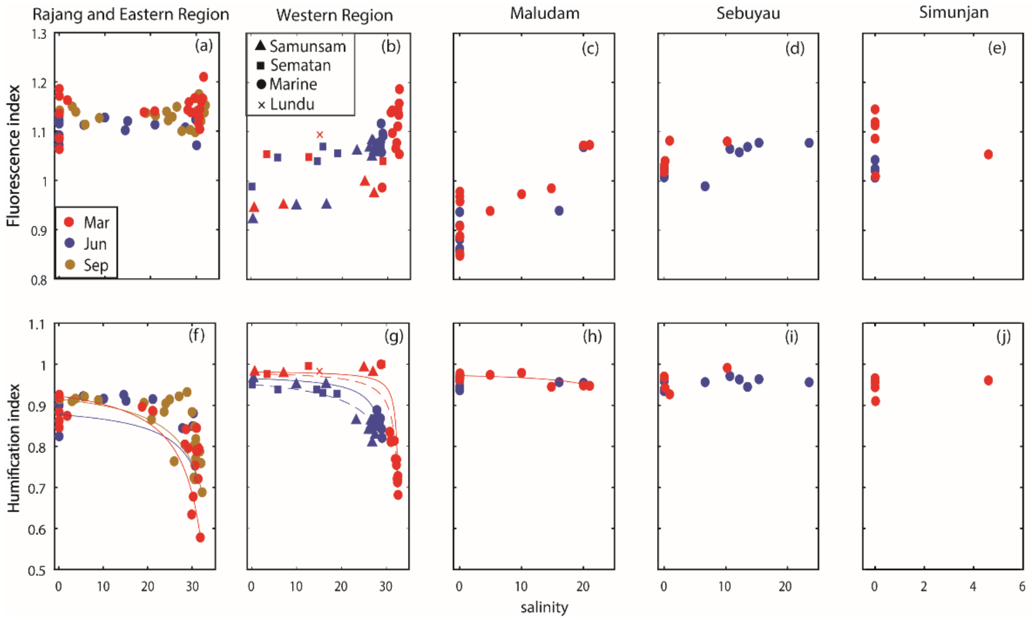

Figure 2. Spatial distribution of fluorescence index (FI) (a-e) and humification index (HIX) (h-l). Samples from different seasons are distinguished by colors. Samples from different regions are shown in individual panels, specified by the titles of each panel. The conservative mixing models of HIX are delineated for the Rajang and eastern region by solid lines in panel (f), for Samunsam river by solid lines and for Sematan river by dashed lines in panel (g), and for Maludam river by the solid line in panel (h).

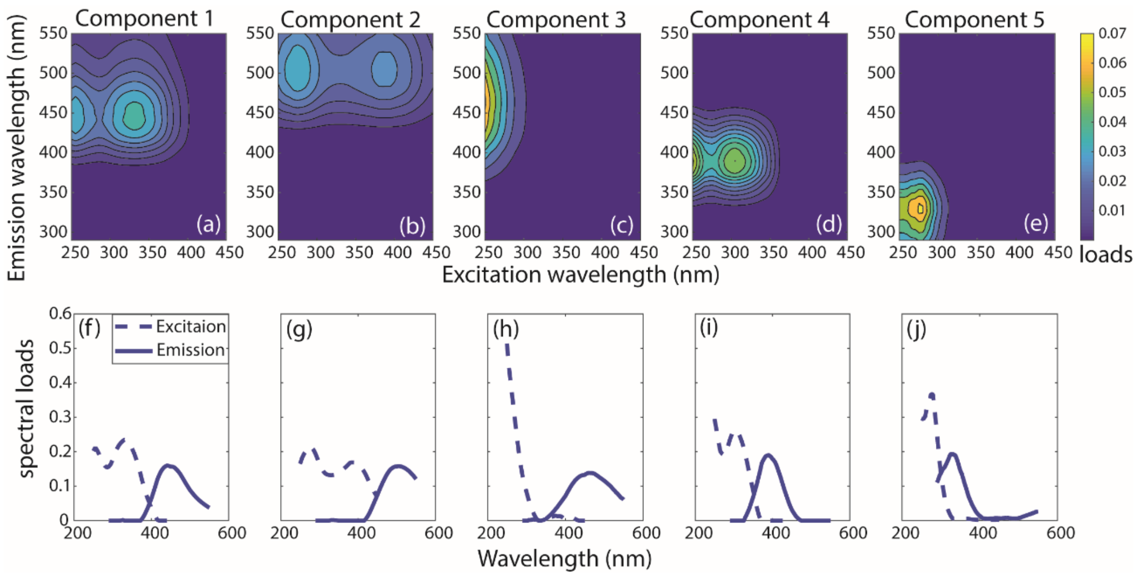

Figure 3. The 3-D fingerprint spectra (a-e) and spectral loads (f-j) of the five components identified by PARAFAC analysis.

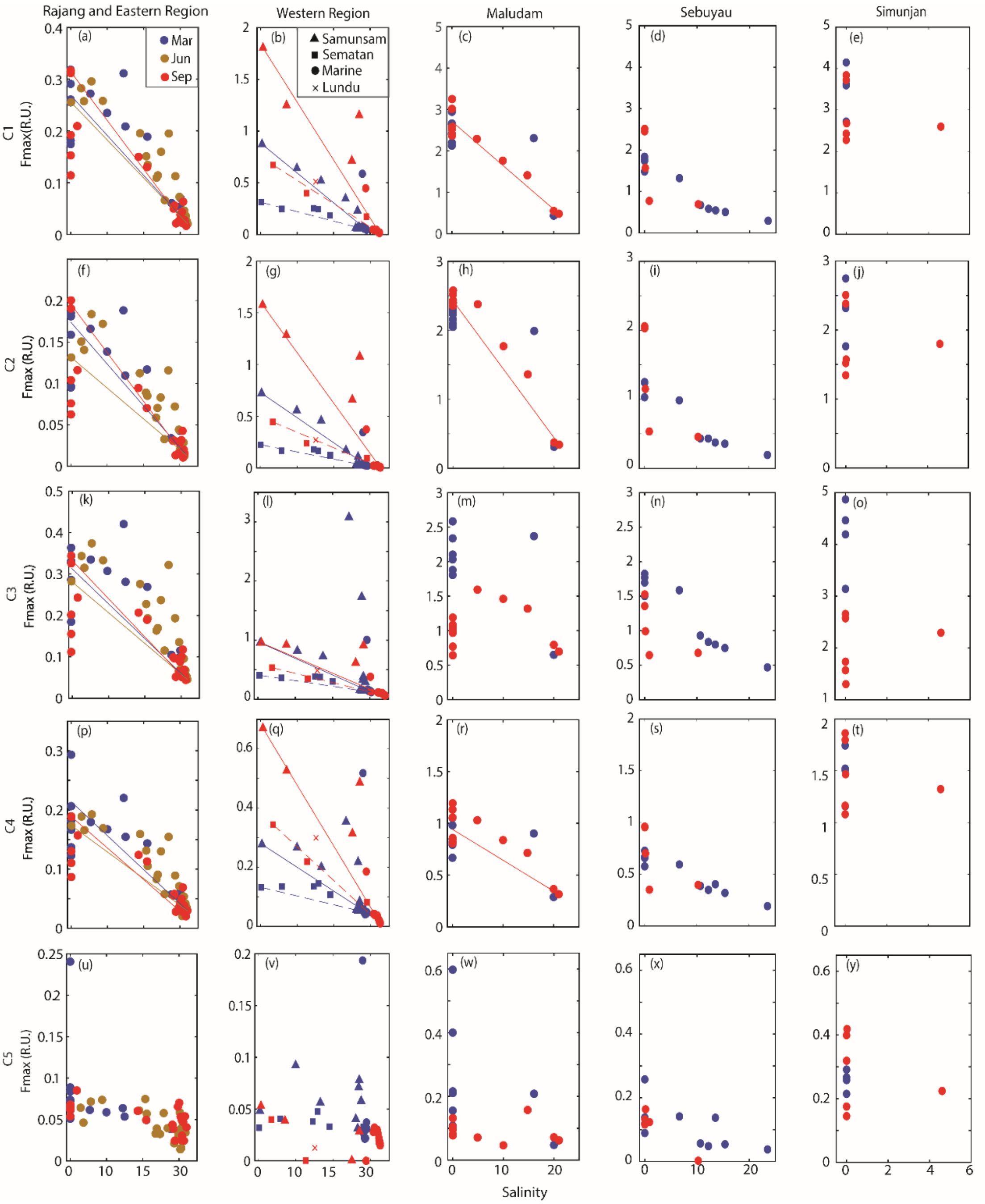

Figure 4. The spatial distribution of C1 – C5 Fmax (a – y) for the Rajang and eastern region, the western region, Maludam River, Sebuyau River and Simunjan River. Colors distinguish samples from different seasons in panel (a) to (y) while they distinguish samples from different regions in the panel (z). The conservative mixing models of C1 – C4 are delineated for the Rajang and eastern region by solid lines, for Samunsam River by solid lines, for Sematan River by dashed lines, and for Maludam River by solid lines.

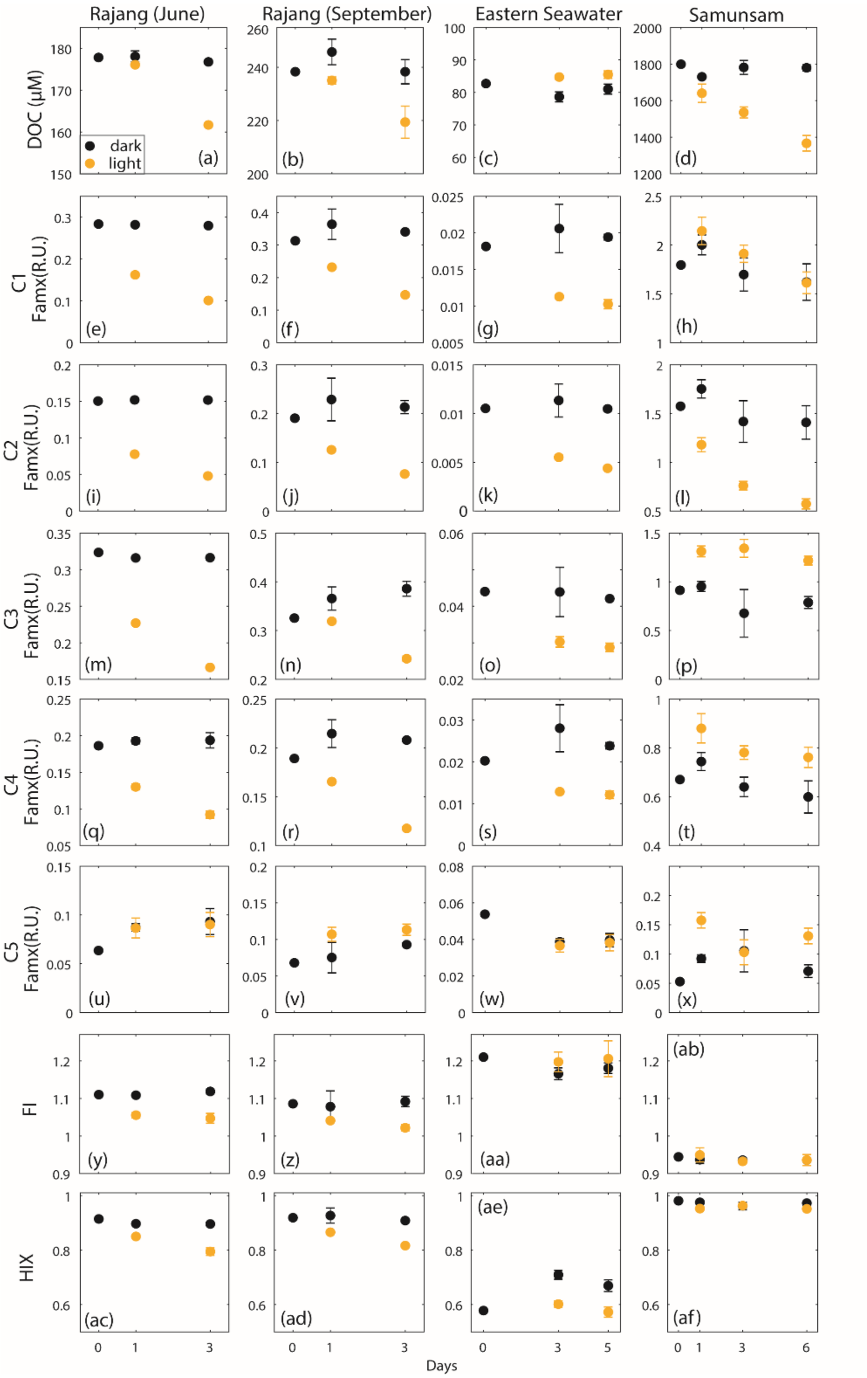

Figure 5. Changes in DOC (a–d), C1 – C5 Fmax (e–x), FI (y–ab) and HIX (ac–af) of samples from Rajang River in June and September, from seawater of eastern region and from Samunsam River during the photodegradation experiment. DOC data are taken from Martin et al. (2018).

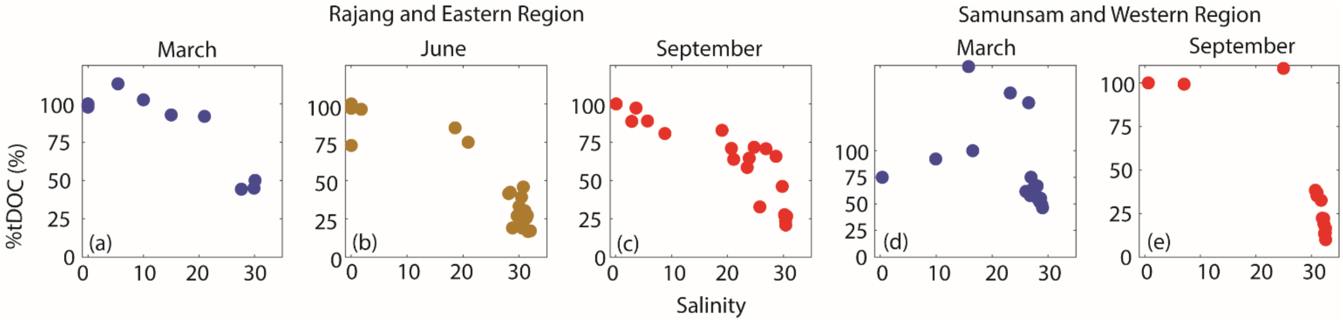

Figure 6. Estimated percentage contribution of terrigenous DOC to the total DOC pool (%tDOC) against salinity for all estuarine samples
5 in the eastern and western regions.