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 0.2–0.250.2–0.25 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 of(~3000–5500 µmol L^{-1}, or 36–66 mg L^{-1}), 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., 2019; 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~~t-DOC (Moore et al., 2013).

A companion study ~~in coastal waters in Sarawak, northwestern Borneo~~ by Martin et al. (2018) revealed high DOC and CDOM concentrations, ~~high absorbance~~ and low CDOM spectral slopes, in ~~the~~ peat-draining rivers in Sarawak, indicating large ~~terrestrial organic matter~~tDOM input, and conservative mixing of DOC with seawater. However, the composition of the organic matter and the cycling processes of different fractions after export from peatlands still remain unknown. In this study, ~~we used~~using fluorescence spectroscopy and PARAFAC analysis ~~to investigate the composition and cycling of DOM across the continuum from peat-draining rivers to coastal waters~~ in the same region, ~~Sarawak, northwestern Borneo.~~we ~~We~~ aimed to: (1) further 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. ~~but~~ ~~i~~However,~~n~~ this equatorial climate does not have ~~the~~distinct wet~~/~~ and dry seasons ~~are not distinct:~~, ~~with high~~ monthly rainfall ~~recorded~~is quite high year-round (200–400 mm,~~(~~Sa'adi et al.~~,~~ (2017)). One additional sample was collected from the Lundu River estuary in September. During each expedition, weather conditions on most ~~sampling~~ days were ~~similarly accompanied by~~ part cloudy / part sunny ~~weather conditions~~, with heavy rain showers of a few hours' duration occurring across small spatial scales on many days~~.~~. ~~and n~~No extreme weather ~~events were~~was encountered. ~~The day-to-day changes in weather conditions within each season were therefore unlikely to affect the DOM concentration and composition in a significant way.~~ 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~~distinguish between sampling stations ~~into three groups, namely,~~in 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.

2.2 Photodegradation

Photodegradation experiments were conducted in June and September by exposing filtered (0.2 µm, Anodisc) ~~filtered~~ water samples 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 repetitively sub-sampled every 1–3~~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~~3 Absorbance and f~~F~~luorescence measurement and data processing

The absorbance ~~data of colored dissolved organic matter (CDOM) from a companion study in coastal Sarawak~~measurement methods are described in detail by Martin et al. (2018) ~~was summarized and used for the fluorescence data processing in this study~~. Briefly, absorbance spectra were measured using a dual-beam Thermo Evolution 300 spectrophotometer with 10-cm, 1-cm, or 0.2-cm pathlength quartz cuvettes ~~with appropriate pathlength of either 10 cm, 1 cm or 2 mm according to the sample absorbance~~. ~~Specifically, i~~In March, when the 2-mm cuvette was unavailable, high-absorbance samples were diluted ten-fold ~~by~~with DI water and measured in a 1 ~~–~~cm cuvette. Laboratory reagent blanks of 30 mL DI water + 150 µL of 10 g L^{-1} NaN_3 were measured and subtracted from all spectra, because NaN_3 absorbs strongly at wavelengths shorter than 300 nm (McDonald et al.). Because the NaN_3 concentration was identical between samples with very little variation, the subtraction of this blank did not introduce large uncertainties even for low-CDOM samples, as we show in the Supplementary Information 1. ~~–~~Martin et al. (2018) calculated Napierian absorption coefficients at 350 nm (a_{350}~~)~~, a measure of CDOM concentration), ~~and~~the spectral slope between 275 nm and 295 nm ($S_{275–295}$~~,)~~ ~~and slope ratio of $S_{275–295}$ to $S_{350–400}$ (S_R), both of which are~~which is established as a ~~proxies~~tracer for terrestrial origin and is related to ~~for the~~average DOM molecular weight~~-)and material source~~, and specific UV absorbance at 254 nm ($SUVA_{254}$~~, the DOC-normalized decadic absorption coefficient at 254 nm)~~, a measure of the proportion of aromatic compounds in the DOM pool, and also a tracer of tDOM).

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~~ both bandwidths

5 nm). To minimize self-quenching of fluorescence ~~intensity~~, ~~blackwater river~~ samples with high absorbance in March were diluted ten-fold with DI water. In September, ~~blackwater~~ samples with high absorbance were ~~instead~~ measured undiluted in a 3 mm-pathlength cuvette ~~without dilution~~. All other samples were measured undiluted in a 1 cm-pathlength cuvette. Laboratory reagent blanks ~~were made of 30 mL~~ of DI water with ~~150 µL of 10 g L^{-1}~~ NaN_3 ~~and~~ were 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 (1) correct for inner filter effects (IFE) following Kothawala et al. (2013) using the total absorbance of each sample, ~~(*i.e.* DI water + NaN_3)~~ ~~to~~thus accounting for the presence of NaN_3 ~~and any variation in NaN_3 concentration between~~in each sample~~s~~, (2) convert fluorescence intensities to Raman Units (R.U.) based on the area of the water Raman peak (Lawaetz and Stedmon 2008), (3) subtract blanks, and (4) 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. Caution is needed for three samples, Samunsam station 4 and 5 (March) and Sebuyau station 4 (March), due to the A_{total} (sum of absorbance at each pair of excitation and emission wavelength) exceeding 1.5 ~~at~~in the short wavelength region of the EEMs (Figure S3), which resulted in invalid IFE correction (Kothawala et al., 2013) but this only potentially affected the PARAFAC results of C5 and C3 (see below) for these three samples. ~~while t~~The IFE correction is fully valid for all other samples.

Because our EEM data were corrected using instrument-specific correction factors~~Following (Cory et al., 2010)McKnight et al. (2001)~~, we calculated the fluorescence index, FI, as the ratio of emission intensity at ~~450~~ 470 nm to that at 520~~500~~ nm, at excitation 370 nm, following (Cory et al., 2010) (Eq. 1):

$$FI = \frac{Ex370,Em470}{Ex370,Em520} \quad (1)$$

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

$$HIX = \frac{Ex255,\sum Em(434\rightarrow480)}{Ex255,\sum Em(434\rightarrow480)+Ex255,\sum Em(300\rightarrow346)} \quad (2)$$

where $Ex255,\sum Em(x \rightarrow y)$ 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~~ 4 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 ~~-~~representing different organic compound classes, with different sources, biogeochemical properties and behaviors ~~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~~Four 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~~from 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~~our 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 relative concentration of each component ~~in differenta samples of~~within a dataset (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~~ was~~(3,100-4,400 µmol L^{-1})~~ ~~were~~ found in the Maludam River (3,100-4,400 µmol L^{-1})~~.~~. 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 (~~$S_{275-295}$~~,~~ (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, ranging from ~1.1 in the freshwater region of Maludam River to ~1.5 for the coastal waters of the eastern region ~~mostly 0.9–1.2~~ (Figure 2a–e). In the Rajang River and eastern region, the FI showed no ~~change~~ seasonal variation or change with salinity, remaining close to ~~1.15~~ 1.5 ~~without seasonal variation~~for the mid-salinities and varying between 1.4 and 1.6 in the coastal waters. 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 1.1–1.5.~~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 ~0.05~~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~~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 a~~w~~re 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~~ both C4 and ~~nor~~ C5 showed low or no correlation ~~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 R~~r~~iver, 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 (end of the southwest monsoon) in the Samunsam and Sematan rivers compared to March (end of ~~wet~~ northeast monsoon), 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~~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)~~(Martin et al., 2018a)~~. 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.

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~~low FI values (~~0.8–1.2~~ 1.1–1.6), ~~than~~ which overlapped the canonical terrestrial end-member range of 1.3–1.4 proposed by McKnight et al. (2001), suggesting ~~the~~ high concentrations of terrigenous fulvic acids.~~.~~ Lowest FI values were observed in the blackwater rivers (*e.g.* 1.1–1.2 in the Maludam River ~~freshwater~~), consistent with the large inputs of peatland-derived DOM. 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). The increase in FI with salinity in the western region, Maludam River and Sebuyau River, reflected ~~reduction of the contribution~~the dilution of t~~errigenous~~ DOM during estuarine mixing, but FI at even the most marine stations still indicates ~~predominant terrestrial source~~the presence of terrestrial fulvic acids. ~~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).~~ However, we note that the ranges in FI of terrestrial *versus* microbial DOM endmembers are reported as quite variable in the literature (Cory et al., 2010; McKnight et al., 2001) and the appropriate wavelength range to use for FI calculations is also still debated, given that using the emission wavelengths of 470nm/520nm proposed by Cory et al. (2010) can yield unreasonably high values (Kida et al., 2018). 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 shows that both FI and HIX appear to be robust tracers of tDOM in our study region. ~~-~~This conclusion is supported by the low CDOM spectral slope ($S_{275-295}$) 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 $S_{275-295}$ 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 $S_{275-295}$ (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). While we can rule out significant errors in $SUVA_{254}$ and $S_{275-295}$ due to the NaN_3 blanks (Supplementary Information 1), the presence of Fe(III) can lead to over-estimates in $SUVA_{254}$ (Poulin et al., 2014). Although we do not have Fe(III) measurements to quantify this potential error, nearly all of our freshwater samples have $SUVA_{254}$ of less than 5.5 with decadic absorption coefficients often exceeding 100 m^{-1}, suggesting that Fe(III) probably did not bias our estimates to a very great degree.

The strong similarity ~~between the~~in spatial distribution~~s of~~ between our components C1–C4 suggests 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 that multiple terrestrial humic-like components ~~in the same region, showing~~can show similar biogeochemical behavior along the aquatic continuum within a region (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~~clearly 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~~ after 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 (Spearman's $\rho>0.898$, $p<0.01$, Table 2) ~~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~~In addition, our photodegradation experiment with the Samunsam water suggested that there ~~could even~~might be ~~a degree of~~some 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 the DOC-normalized protein-like component Fmax value was indicative of the amino acid content in DOM and thus the bioavailability of DOM. ~~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), but the fact that our C5 did not consistently decrease with salinity ruled out a primarily terrestrial source for this component.~~ 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~~C1–C4~~) in the Rajang River and seawater ~~experiments~~samples, 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~~the Samunsam water 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%~~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 both FDOM and the bulk DOC pool mix~~es~~ conservatively with at most minor biogeochemical modifications. 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 aC1 correlates particularly strongly particularly strong correlation with lignin phenols (Yamashita et al., 2015)., and is detected in only in trace amount in the open oceans, *e.g.* ~0.006 R.U. in the tropical Atlantic Ocean (Murphy et al., 2008). , which indicated the pure terrestrial origin of C1 and ruled out its marine source. HenceThis suggests that C1 can potentially be used as a terrestrial materialtDOM tracer, byif we assumeing that itC1 behaves biogeochemically in approximately the same way as all terrigenous DOM fractionsthe total (fluorescent and non-fluorescent) tDOM pool while the marine endmember contributes no C1 , provided that fluorescence measurement and PARAFAC analysis can serve as appropriate proxies even for non-fluorescent DOM fractions. We therefore attempted to estimate tDOC in our marine coastal samples from the ratio of DOC and C1, using (Eeq.uation (3):

$$\%tDOC_{sample} = 100 \times (C1\ Fmax/DOC)_{sample} / (C1\ Fmax/DOC)_{river} \quad (3)$$

$$\%tDOC = 100 \times \frac{(C1\ Fmax/DOC)sample}{(C1\ Fmax/DOC)river} \quad (3)$$

where $(C1\ Fmax/DOC)_{river}$ is the highest value of DOC-normalized C1 Fmax at salinity 0 within the appropriate river, and$(C1\ Fmax/DOC)_{sample}$ is the DOC-normalized C1 in the sample for which %tDOC is to be estimated, and $(C1\ Fmax/DOC)_{river}$ is the highest value of DOC-normalized C1 Fmax at salinity 0 within the appropriate river. This is the most conservative way of selecting the riverine endmember values to avoid over-estimationng of %tDOC in marine samples, but the difference between using the highest C1/DOC value andif we use the mean freshwater C1/DOC value for each river, is tiny, our final %tDOC estimates are onlywhich ≤is up to 4 percentage points higher. 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. AnTo calculate the uncertainty analysis for our estimate, was conducted bywe propagateding the uncertainty ofin DOC measurement (±4.23%, Martin et al. (2018)) and that ofin Fmax values calculation (±1%, Korak et al. (2014)), which yielded an uncertainty of around ±6% ofin the final %tDOC estimate. Our analytical uncertainties are thus very minor.

The %tDOC generally decreased with salinity (except for three mid-salinity stations in the western region) and reached minimum values of 15±0.9% –25±1.5% at stations with highest salinity in both regions (Figure 6), consistent with the low HIX at these stations. TheInterestingly, %tDOC that exceededed 100% for theat a few mid-salinity stations in the western region. isThis could indicate possibly due to the underestimation ofthat the freshwater endmember for the C1/DOC ratio for the Samunsam River was underestimated.; Because only a single freshwater sample wascould be collected in each season from this river, the freshwater endmember might not be constrained sufficiently well. Alternatively, there could be additional sources of C1-rich DOM within the Samunsam estuary, Small channelsperhaps either from the surrounding mangroves that drain into the Samunsam estuary andor as a result of resuspension of sediments on whichthat might sorb and de-sorb the organic matter can flocculate and /or sorbed and desorbed can also contribute additional C1-rich DOM at the mid-salinities, which might

~~result in higher C1/DOC ratio compared to the freshwater region~~tDOM. The Samunsam estuary was sampled as strong tidal currents were visibly causing strong resuspension. This issue calls for further work to investigate the use of FDOM as a quantitative tracer of tDOC. ~~Fichot and Benner (2012) previously proposed $S_{275-295}$ as a quantitative tracer of tDOM, and our %tDOC estimate is closely correlated with $S_{275-295}$ (ρ =−0.90 , p<0.01, Figure S1), which never exceeded 0.025 at even our most marine stations (Martin et al., 2018).~~

~~O~~While our FDOM-based estimate needs to be viewed with caution, since we could not properly test the necessary assumption that C1 behaves like total tDOC over the spatial scale of our study. ~~However, this relatively high tDOC contribution~~ that we estimate for our ~~in coastal waters stations~~ is in the same range as estimates elsewhere ~~in other tDOM-influenced regions (Fichot and Benner, 2012; Opsahl et al., 1999).~~ Moreover ~~and the~~we found a ~~strong relationship with~~ between %tDOC and $S_{275-295}$ ~~similar to the exponential relationship between %tDOC as estimated from lignin phenols and$S_{275-295}$ shown . This~~ supports the idea that FDOM can be used as a quantitative tDOC tracer over these relatively short spatial scales~~, over which the residence time of tDOM is probably short relative to the rates of biogeochemical tDOM processing~~. ~~One important~~ likely source of error ~~would be the preferential loss of C1 due to photodegradation, which would actually cause us to underestimate the true %tDOC in marine samples, depending on the amount of solar irradiation~~. ~~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.~~

Our FDOM-based estimate needs to be viewed with caution, since we cannot fully test the underlying assumptions. Our approach assumes firstly that C1 is exclusively terrestrially derived, and has no non-terrestrial sources in estuaries and marine waters. Secondly, the approach assumes that C1 behaves biogeochemically in approximately the same way as the total (fluorescent and non-fluorescent) tDOM pool (Wagner et al., 2015). The first assumption is probably broadly valid: as discussed above, Fmax values of C1-like components in open-ocean waters are very low relative to the values across our study area. The second assumption is probably not seriously violated in our study, since we observed close to conservative mixing of both DOC and C1 in our region. In fact, the most likely degradation process we have identified, i.e. photodegradation, potentially causes preferential loss of C1 relative to total DOC, which would actually cause us to underestimate the true %tDOC in marine samples. However, over the relatively short spatial scales over which we sampled, the residence time of tDOM is probably short relative to the rates of biogeochemical tDOM processing, such that our estimates of %tDOC are perhaps not impacted strongly by any differences in degradation rates of C1 *versus* bulk tDOC. The relatively high tDOC contribution that we estimate for our coastal stations is also in the same range as estimates in other tDOM-influenced regions (Fichot and Benner, 2012; Opsahl et al., 1999), suggesting that our estimates are plausible. Moreover, we found a close exponential relationship between %tDOC and $S_{275-295}$ (%tDOC = exp (α +β $S_{275-295}$), where α=1.48, β=−126.23, Figure S1b), similar to the exponential relationship between %tDOC as estimated from lignin phenols and $S_{275-295}$ shown by Fichot and Benner (2012). 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, and showed increases in CDOM spectral slope (Martin et al., 2018).

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. Based on the DOC distribution in the delta, 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~~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.~~ The two FDOM compositional indices, FI and HIX, yielded results consistent with our PARAFAC analysis and thus can serve as robust tracers of tDOM in the coastal Sarawak. 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). The Tucker congruence coefficients (TCC) are always above 0.95, indicating strong correlations. The respective TCC values can be found in the Supplementary Data Table 2.

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~~Spearman's rank correlation -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} ρ	Sig. ~~p~~	~~r~~^{2} ρ	~~p~~Sig.
C4 Fmax (R.U.)	Eastern	~~0.069~~ **~~0.370~~**	~~0.064~~**<0.01**	**~~0.929~~0.988**	**<0.01**
	Western	~~0.014~~0.019	~~0.436~~0.897	**~~0.880~~0.972**	**<0.01**
	Blackwater	~~0.055~~ 0.304	~~0.136~~0.053	**~~0.872~~0.898**	**<0.01**
C5 Fmax (R.U.)	Eastern	**~~0.008~~ ~~0.363~~**	**~~0.531~~<0.01**		
	Western	~~0.014~~ 0.028	~~0.446~~0.850		
	Blackwater	~~0.026~~ 0.178	~~0.307~~0.266		

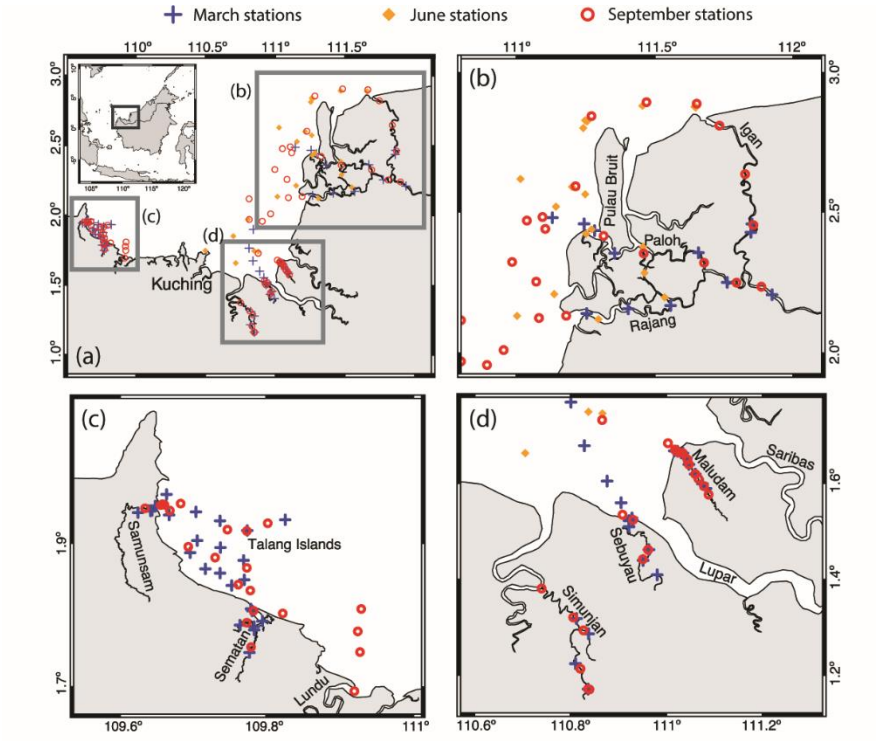

Figure 1. (a) Map of the study region and sampling sites (Martin et al., 2018). Zooming in of the three regions is shown in panels (b) – (d).

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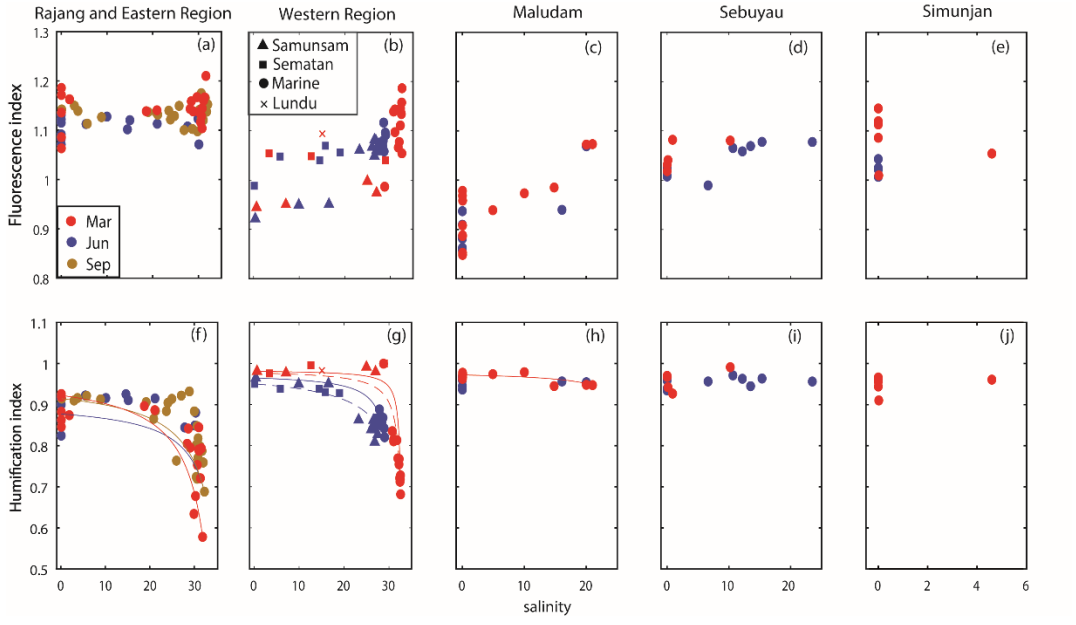


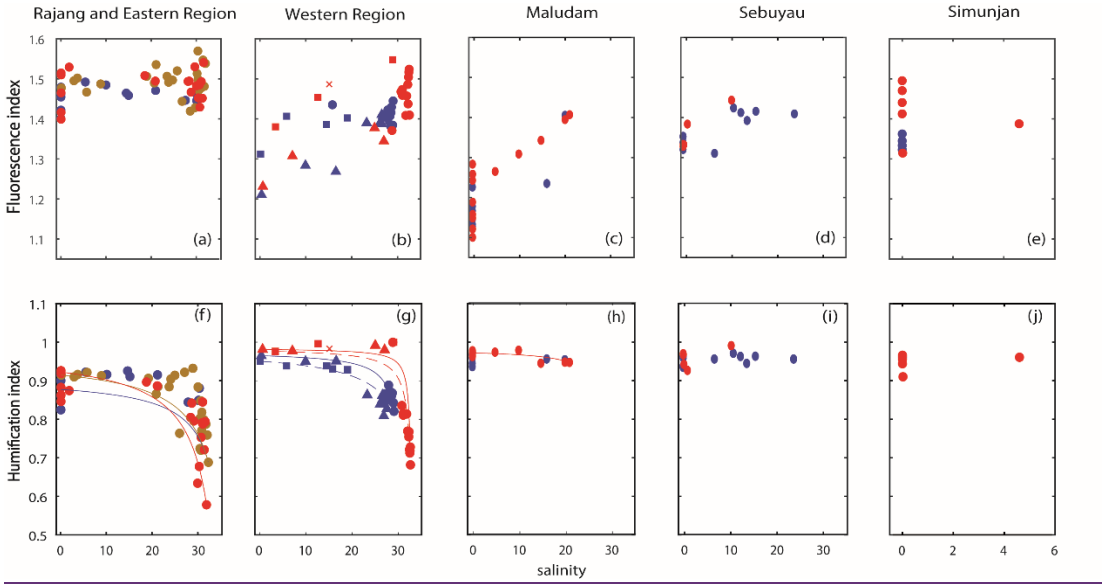


Figure 2. Spatial distribution of fluorescence index (FI) (a–ea–e) and humification index (HIX) (h–lh–l). Samples from different seasons are distinguished by colors. Samples from different regions are shown in individual panels, specified by the titles of each panel. The conservative mixing models of 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).

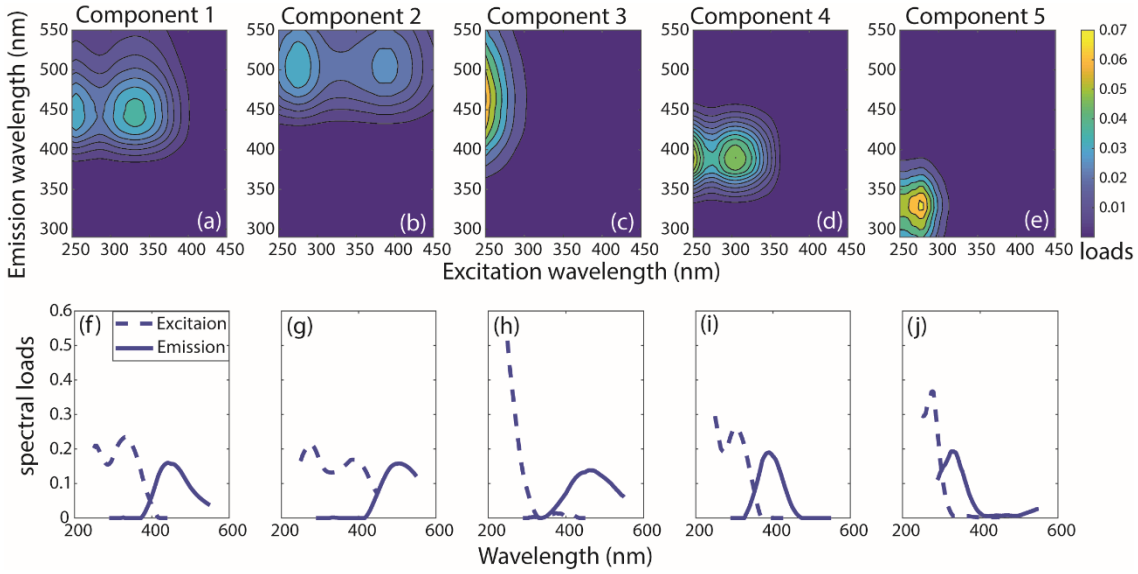
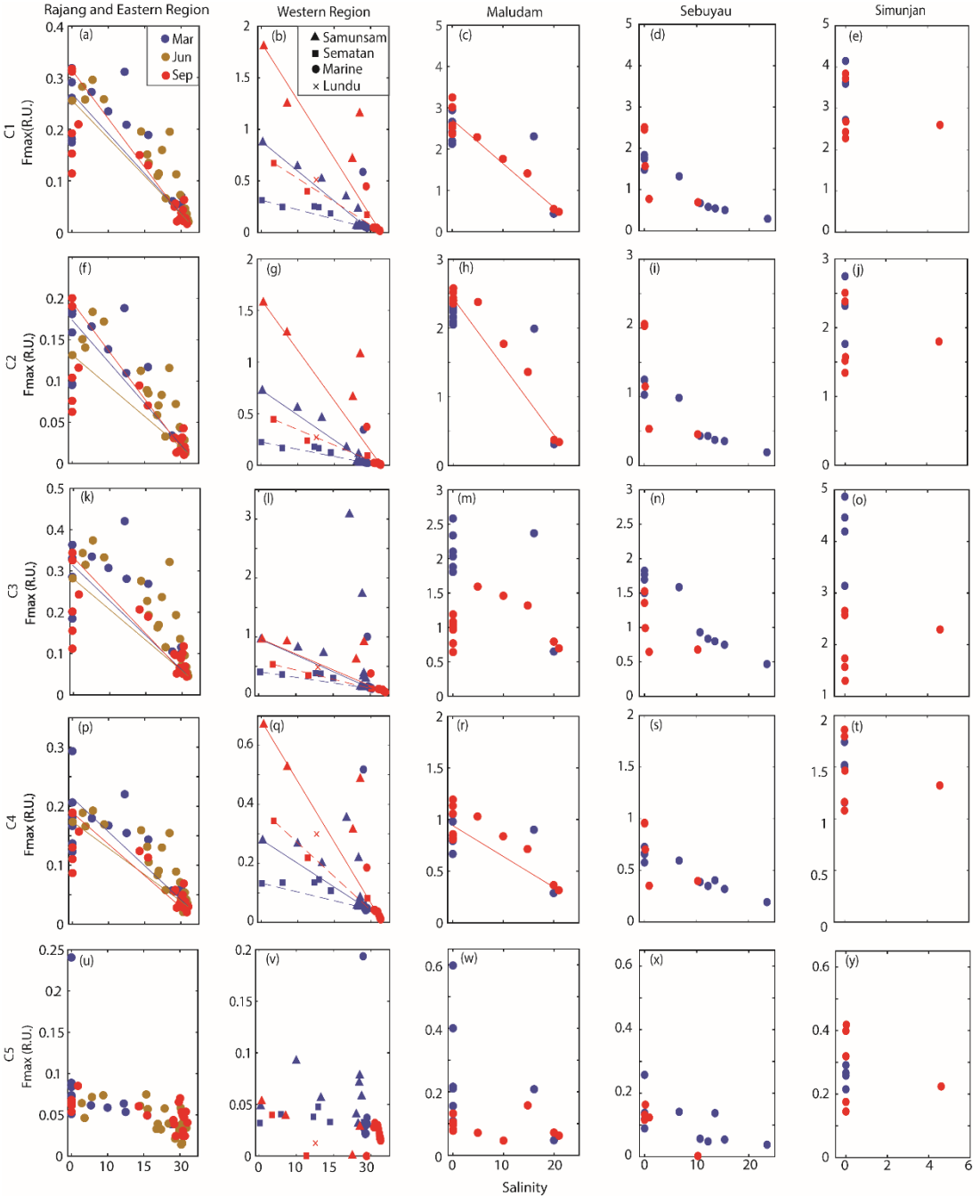


Figure 3. The 3-D fingerprint spectra (a–ea–e) and spectral loads (f–jf–j) of the five components identified by PARAFAC analysis. The overlaid excitation and emission loadings of the validated split dataset can be found in Figure S4.


Rajang and Eastern Region
Western Region
Maludam
Sebuyau
Simunjan
Mar
Jun
Sep
Samunsam
Sematan
Marine
Lundu
C1 Fmax(R.U.)
C2 Fmax (R.U.)
C3 Fmax (R.U.)
C4 Fmax (R.U.)
C5 Fmax (R.U.)
Salinity

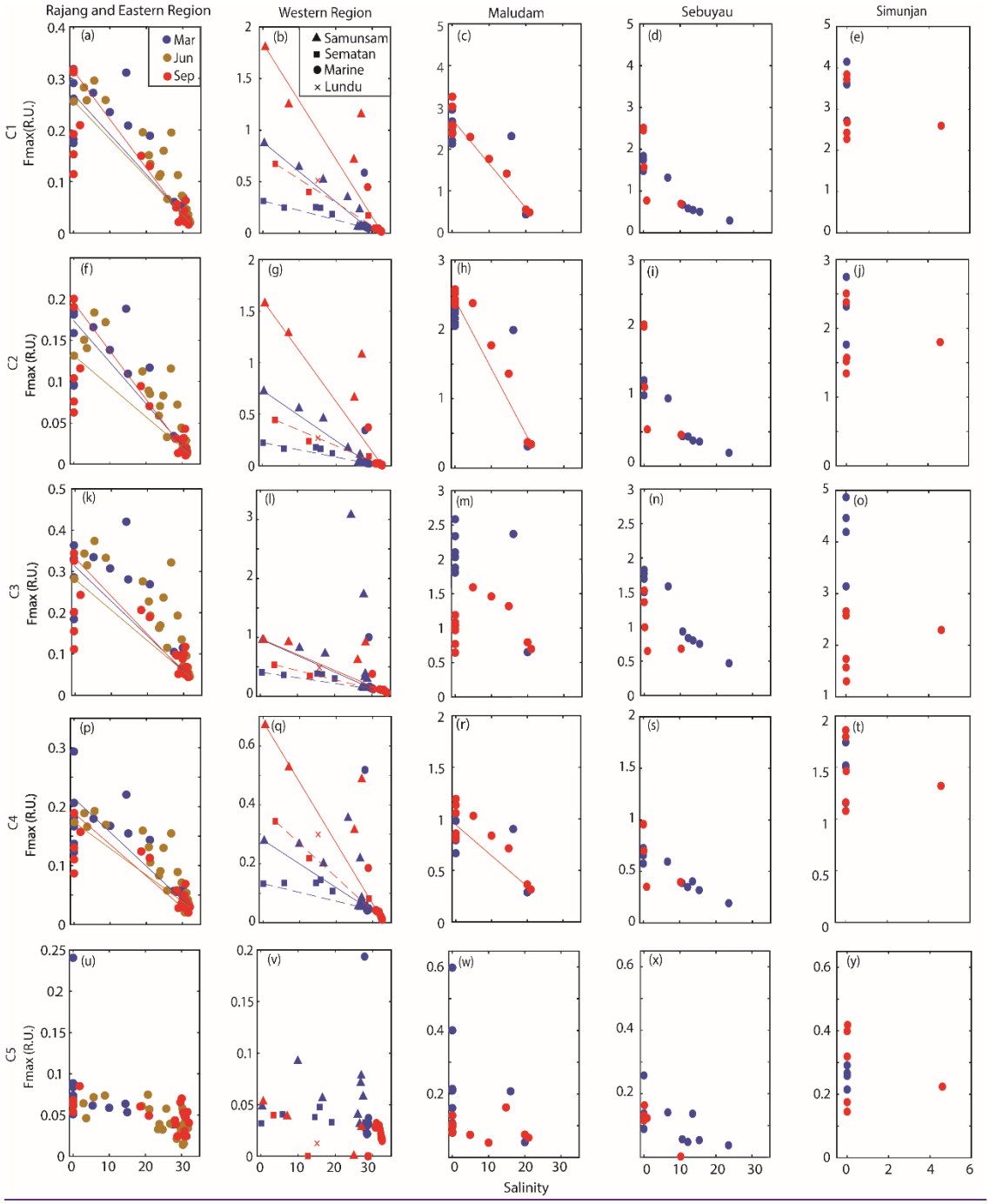


Figure 4. The spatial distribution of C1–C5~~C1—C5~~ Fmax (a–~~—~~y) for the Rajang and eastern region, the western region, Maludam River, Sebuyau River and Simunjan River. Colors distinguish samples from different seasons in panel (a) to (y)~~, while they distinguish samples from different regions in 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.

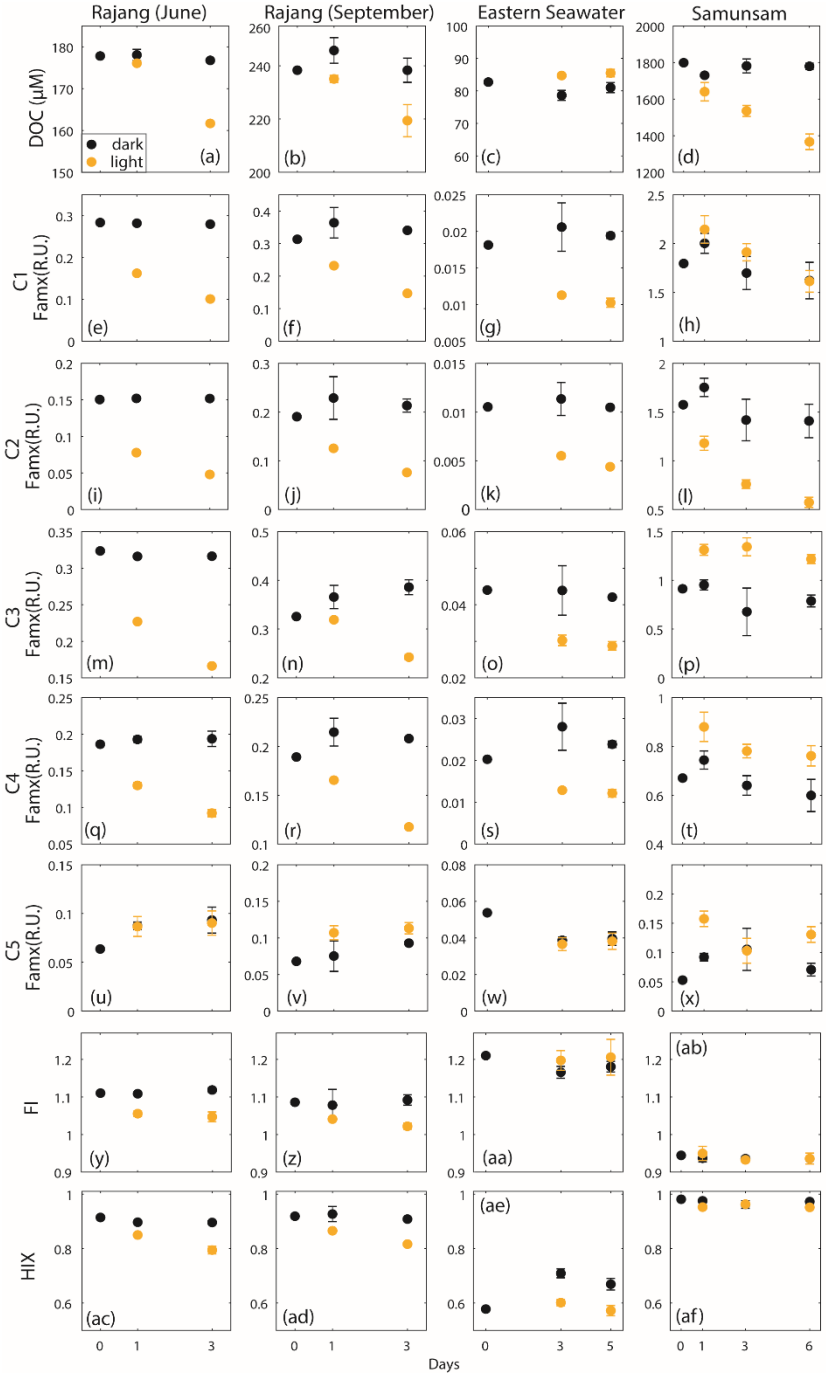


Figure 5. Changes in DOC (a–d), C1—C5 Fmax (e–x), FI (y–ab) and HIX (ac–af) of samples from Rajang River in June and September, from seawater of eastern region and from Samunsam River during the photodegradation experiment. DOC data are taken from Martin et al. (2018).

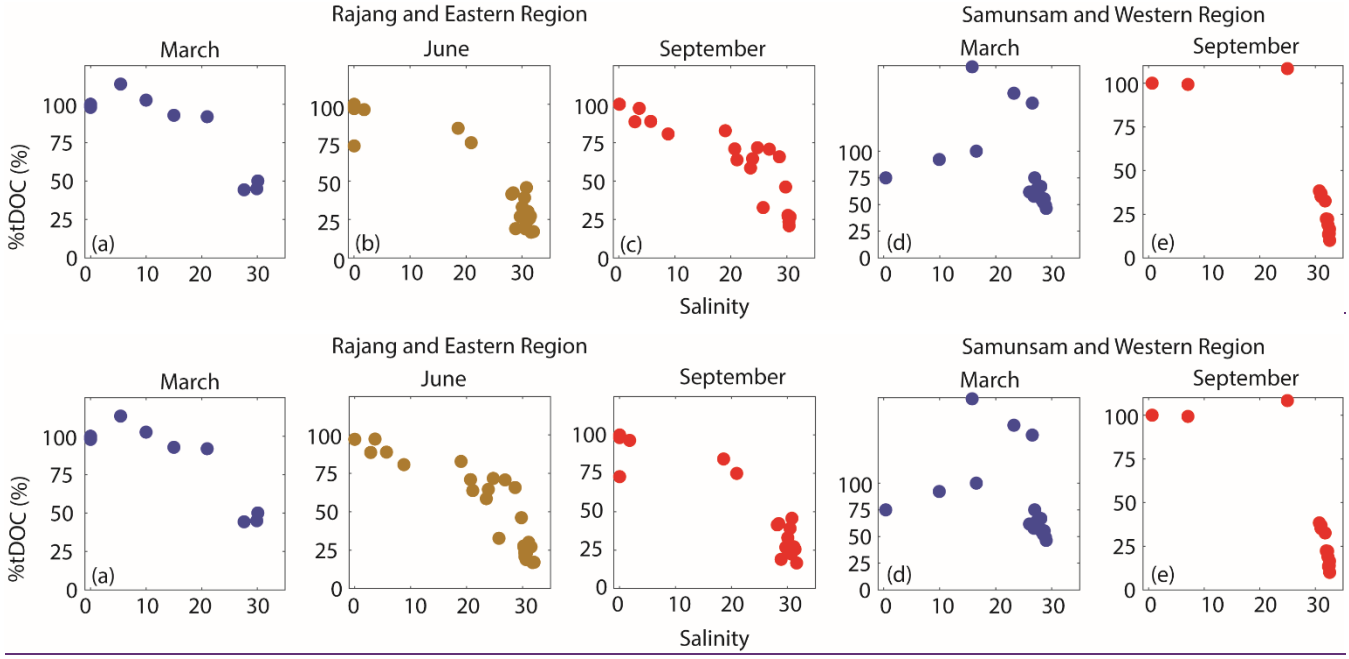


Figure 6. Estimated percentage contribution of terrigenous DOC to the total DOC pool (%tDOC) against salinity for all estuarine samples in the eastern and western regions.

Response to Associate Editor's Comment

We are grateful to the associate editor for their time in reviewing our manuscript and providing additional constructive suggestions regarding the sodium azide blank. Our detailed response is below, following the quoted associate editor's comments.

Comment:

The authors have engaged constructively with the reviewers' comments but further work is required to the Level of a Major Revision addressing the reviewers (especially Reviewer #2) concerns. There is a specific technical issue of the use of Sodium Azide as a preservative of reactive DOM in the filtered water samples. This is a general practice based on NASA and COLOURS protocols codified in the REVAMP protocols (G.H. Tilstone et al. 2002) which were developed and tested for the "Regional Validation of MERIS Chlorophyll products in North Sea coastal waters" .

The Azide ion itself has absorption in the UV and visible range. Tilstone etal. (2002) attribute 10% of the total absorption at 440 nm to the azide. This is not a fixed ratio but is determined by the relative amounts of azide and DOM and the UV absorption characteristic of the DOM at shorter wave lengths. The relative magnitude of this potential artefact will change at shorter wave lengths (in UV). Zhou et al. have addressed this potential weakness in their PARAFAC analysis by using the appropriate blanks. However, as noted by Referee #2 the problem may arise in the specific context of the determination of the spectral slope and the SUVA. While acknowledging these problems the author's response has been to assert that they may be discounted relying in part on the more detailed spectral measurements on the azide blank solutions reported in the supplement to the associated paper by Martin et al. The spectrum of sodium azide in water has been reported in the literature (McDonald et al. J. Chem.Phys. 52(1): 1332-1340 (1970)). However, their rebuttal lacks any quantitative detail. The authors are reluctant to pursue this issue further as it introduces a complicated technical /methodological discussion which is only marginally related to their main conclusions about the distribution of terrigenous DOM.

Reviewer #2 also notes the possible role of heavy metals complexed with the DOM interacting with the azide ion to produce coloured species which change the absorption spectra of the solutions. These effects will not be compensated for by the use of azide blanks.

These technical issues somewhat weaken, but do not vitiate, the main conclusions. The problem ultimately arises from the use of a protocol under circumstances which are outside its demonstrated range of validity. These problems are exacerbated by the logistic constraints of working on small boats in remote locations where the alterative sample preservation protocol by refrigeration are not to hand. My suggested resolution of this problem is to publish the paper subject to a major revision as outlined in the Authors response to the review comments but include an additional supplement where there is quantitative discussion of the likely size of perturbations due to the azide blank including the relative magnitude of the errors which arise and a demonstration that these effects may be accounted for and do not alter the conclusions.

Response:

The suggestion to conduct a thorough analysis of the effects of NaN_3 blanks on CDOM parameters in a supplement is an excellent idea. As the editor says, our initial reluctance to go into this matter in detail in this manuscript was because it is somewhat peripheral to our analysis of FDOM, but as a supplement it does not distract from the main topics of this paper.

We have therefore written a detailed supplementary text that is referred to in our Methods section (Page 4), in which we quantitatively estimate the uncertainty that the NaN_3 blank introduces in the $SUVA_{254}$ and $S_{275\text{-}295}$. This analysis shows that the NaN_3 blank introduces only relatively small uncertainties in both parameters: the estimated total uncertainty in $SUVA_{254}$ is <10% for all samples (partly from NaN_3 blank and partly from DOC analytical error), and the estimated uncertainty in $S_{275\text{-}295}$ from the NaN_3 blank is <1% for all samples.

The reason why the NaN_3 blank introduces only little uncertainty in these parameters is because the concentration of NaN_3 was very consistent between all our samples. Thus, although the NaN_3 contributed a high proportion of the absorbance at short UV wavelengths, this blank could be quantified and

subtracted with high accuracy, as we show in the Supplementary Information 1. We are grateful to the editor for suggesting this addition, which will hopefully alleviate any concerns that any readers may have. This said, we believe that the associate editor is mistaken in saying that "*The azide ion itself has absorption in the UV and visible range*". The absorption spectrum of sodium azide is presented in McDonald et al. (1970)that the editor referenced, and was also measured by us in the many NaN_3 blanks we prepared, and sodium azide in aqueous solution does not absorb at wavelengths above about 300 nm. The recommendation in the Tilstone et al. REVAMP protocols for using sodium azide is referenced back to a paper by Ferrari et al. (1996), in which the authors also state that sodium azide does not absorb above 300 nm. In the supplementary figures to the REVAMP protocols, Tilstone et al. (2002) show higher absorbance at all wavelengths from 300 – 800 nm for the spiked replicates compared to the non-spiked replicates. However, this is not consistent with the absorption spectrum of NaN_3, and is more suggestive of changes in the baseline than genuine blank absorption from a specific molecule. Our NaN_3 blanks do not show absorption above about 300 nm, as we discussed above, which is why we focused our uncertainty analysis just on CDOM parameters that are measured at wavelengths where NaN_3 genuinely absorbs light.

We agree with the reviewer and the editor that the possibility of Fe(III) interference for $SUVA_{254}$ needed addressing, and have added some additional discussion on this issue in the revised manuscript (P10 L10 – 14 in the revised version) . Unfortunately, we do not have Fe(III) measurements, so we cannot quantify the impact on $SUVA_{254}$. However, almost all of our $SUVA_{254}$ values are actually within a reasonable range (<5.5) while having very high decadic absorption coefficients, so we believe that Fe(III) is probably not a very significant factor in our samples. However, we agree that it is important to explicitly acknowledge this as a potential source of uncertainty. We note that the reviewer does not actually refer to any interactions between Fe(III) and NaN_3, and we are not aware of specific absorbent species that would be produced through such hypothetical reactions. We have therefore restricted ourselves to just addressing the reviewer's comments that separately raise the possibility of interference from Fe(III) and of interference from NaN_3.

References

McDonald, J. R., Rabalais, J. W. and McGlynn, S. P.: Electronic Spectra of the Azide Ion, Hydrazoic Acid, and Azido Molecules, J. Chem. Phys., 52(3), 1332–1340, doi:10.1063/1.1673134, 1970.

Tilstone, G. H., Moore, G. F., Doerffer, R., Røttgers, R., Ruddick, K. G., Pasterkamp, R. and Jørgensen, P. V: REVAMP Protocols Regional Validation of MERIS Chlorophyll products in, Work. Meet. MERIS AATSR Calibration Geophys. Valid. (ENVISAT MAVT-2003), (October), 1–77, 2002.

Response to Reviewer 1

We are very grateful for the reviewer's time and efforts spent on these helpful and constructive comments. Our responses to the reviewer comments are posted below, with the reviewer's comments quoted first in italics. We believe that we can address all of the reviewer's comments, and will revise our manuscript accordingly.

2. Comments to Author

Note: I also read the companion paper 'Distribution and cycling of terrigenous dissolved organic carbon in peatland-draining rivers and coastal waters of Sarawak, Borneo' and the relevant review comments and the authors' answers to the comments.

This study (bg-2018-508) aimed to distinguish different fractions of dissolved organic matter (DOM) in peat-draining rivers, estuaries, and coastal waters of Sarawak, Borneo, using fluorescence spectroscopy and parallel factor (PARAFAC) analysis. The authors observed that the terrigenous fractions showed high concentrations at freshwater stations within the rivers, and conservative mixing with seawater across the estuaries, while the autochthonous DOM fraction showed low concentrations at all salinities. The authors claim that, based on the fluorescence data and little changes in optical properties of DOM, at least 20%–25% of the DOC at even the most marine stations (salinity >31) was terrestrial in origin. Although not all of the data provided is new to the relevant field, the content of this paper fulfills the requirements for the submission to Biogeosciences of which aims and scopes are to publish studies on all aspects of the interactions between the biological, chemical, and physical processes in terrestrial or extraterrestrial life with the geosphere, hydrosphere, and atmosphere. The title is representative of the article contents and the abstract summarize the contents clearly. Therefore, I recommend accepting this paper after the authors revise all the necessary points.

I have serious concerns about the use of sodium azide (NaN3) as a preservative for samples analyzed by UV absorption and fluorescence spectroscopy. Also, the emission wavelengths used to calculate fluorescence index (FI) seem inadequate. Finally, estimation of %tDOM by fluorescence is questionable.

Response:

We are glad that the reviewer appreciates our study. We have addressed all of the specific concerns raised by the reviewer in our responses below.

Comment 2.1.1 Estimate of terrestrial contribution

FDOM is only a small portion of the bulk DOM, and thus estimation of %tDOM by fluorescence is troublesome. PARAFAC components can be used to better understand biogeochemical processes that occur during the estuarine mixing, but PARAFAC components alone are not sufficient to estimate the tDOM contribution at given salinity. To make it possible, you must assume that all the rest of components in riverine DOM other than FDOM (PARAFAC component C1 in this case) behaves in the same way as C1 does during the estuarine mixing and that marine end-member has no C1. Please explicitly state your assumptions. It's not enough in the current form.

Response:

The reviewer correctly identifies the assumptions that underlie our estimate of %tDOC, *i.e.* that all the terrigenous DOM fractions, both fluorescent and non-fluorescent, behave in the same way during the river-coastal sea interactions as C1, and that C1 represents terrestrial humic-like fractions that only come from terrestrial sources, while the marine environment in the open ocean has no C1. We agree that these assumptions need to be made clearer than in our original submission, and we have explicitly stated all these assumptions in the revised manuscript (bottom of P13 in the marked-up version).

We believe that our assumptions are reasonable for the estimate of %tDOC within our relatively small study region because of the following three reasons.

(1) The predominantly conservative behavior of DOC concentration along the salinity gradient indicates that the distribution of DOC is mostly controlled by the mixing of freshwater and seawater, so our data do not suggest strong biogeochemical processing of the bulk DOC pool.

(2) Our C1 is very similar to terrigenous humic-like components identified in many other studies (Stedmon et al., 2003; Stubbins et al., 2014; Yamashita et al., 2015). Although we fully agree that fluorescent DOM only accounts for a small fraction of the total DOM pool, it has already been shown elsewhere that FDOM components are appropriate proxies for both fluorescent and non-fluorescent terrigenous DOM in the coastal aquatic environment, with strong correlations noted between fluorescent DOM measurements (including PARAFAC analysis) and molecular-scale measurements by mass spectrometry (Wagner et al., 2015). This indicates that our assumption that C1 behaves in the same way as non-fluorescent terrigenous DOM fractions during the freshwater-seawater mixing is in principle plausible. A more likely source of error in our study might be the preferential loss relative to non-fluorescent DOM of C1 caused by photo-degradation, given the high photo-lability of C1 found in this study. Preferential loss of C1 would lead us to under-estimate %tDOC in our marine samples, although the exact degree of C1 photo-lability needs to be better constrained in future experiments with South-East Asian peatland samples. However, because our C1 showed predominantly conservative mixing behavior across our sample set, our data do not suggest that C1 was rapidly and preferentially removed within our study region. This is perhaps also because the spatial scales across which we sampled are ultimately not that extensive, so the tDOM residence time is probably still relatively short compared to the degradation rates of bulk tDOC and our C1.

(3) Other studies have found only very low concentrations of C1-like FDOM components in the open ocean environment. For example, Murphy et al. (2008) reported only ~0.006 R.U. of a terrestrial humic-like component in the tropical Atlantic,

which is ten-times lower than the values we observed at our fully marine stations in Sarawak. Since, unfortunately, we do not have open-ocean samples as a pure marine endmember, we necessarily have to assume that our C1 is purely terrestrial in origin. While this assumption may lead us to slightly over-estimate %tDOC, existing open-ocean data do not suggest that this is a large source of error in our estimate (and, in fact, it might be counter-acted by the impacts of photo-degradation on C1).

We have added some additional discussion along these lines to justify our assumptions in the revised manuscript (bottom of P14 in the marked-up version).

Comment:

Also, how do you explain %tDOC of >100% in Samunsam and Western Region (in March) at salinity >10 under your assumption?

Response:

We agree that the few stations with %tDOC > 100% in the western region (mostly in March) are puzzling, and this clearly calls for further work to investigate the use of FDOM as a quantitative tracer of tDOC. One possible reason is that the freshwater end-member value for C1/DOC ratio was underestimated for the Samunsam River. Because we could only collect a single freshwater sample in each season in the Western Region, the freshwater endmember might not be constrained sufficiently well. While the Samunsam does not have any large tributaries along the stretches we sampled, small channels from the surrounding mangroves do drain into the Samunsam estuary, so we cannot rule out additional inputs of C1-rich DOM at mid-salinities. We note also that the Samunsam estuary is shallow, and especially in March there was a lot of resuspension of sediments at the mid-salinity stations that we sampled due to the strong tidal currents. Because terrestrial DOM can flocculate and/or be sorbed and desorbed from sediments, it is possible that resuspended sediments at these few estuarine stations acted as an additional source of C1. More FDOM and DOC data from this river system would ideally be needed to determine why the C1/DOC ratios at mid-salinities were higher than in the freshwater endmember. We have added some additional discussion of this question to the appropriate part of the manuscript (P13 L26-P14L2 in the marked-up version).

Comment:

In addition, Fmax/DOC is known to be susceptible to errors caused by the fluorescence intensity and DOC measurements (Korak et al. 2014), and the authors should include an evaluation of such an uncertainty (error propagation analysis), since %tDOM estimation is I believe the most important part of this study.

Response:

This is an important point concerning the accuracy of our estimate of %tDOC. As suggested by the reviewer, we have added an evaluation of uncertainty to the revised manuscript. For uncertainty analysis, we adopted ±4.3% uncertainty for DOC, based

on the percentage uncertainty of repeated DOC measurements of the certified deep-sea water reference material (data from Martin et al., 2018). We adopted ±1% as the estimated error of the Fmax values of C1 (peak C) based on Korak et al., (2014). Formally propagating these uncertainties yields an uncertainty of around ±6% of the final tDOC estimate, so for a sample with 30% tDOC, the analytical uncertainty would amount to ±2% tDOC (so the sample would be estimated to have 30 ± 2% tDOC). Because this analytical error is very small compared to the range of %tDOC that we estimate for our marine samples (which ranges by a factor of around 2), the analytical uncertainties are not really relevant. We have added a short explanation of this in the revised version (P13 L20-23 in the marked-up version).

Comment:

Generally, in estuarine environments, contribution from estuarine vegetation (mangrove and marsh) is done by an end-member mixing model (0.1 salinity increment) using DOC concentrations of the fresh and marine end-member (Cawley et al. 2014). Because the main subject of this study is tropical peatlands, I feel that what the authors want to investigate is not riverine (derived from upper regions) inputs but inputs from the peatlands located in the estuary. The authors may reassess contributions from the peatlands using the method reported in, for example, Cawley et al. (2014).

Response:

We fully agree that a two-endmember mixing model using DOM concentrations of the freshwater and marine endmembers is an appropriate method for investigating DOM fluxes through estuaries to the sea. In coastal Sarawak, the companion paper (Martin et al., 2018) already conducted this analysis for DOC concentrations and in our study we use the same approach to study the distribution of FDOM components. We follow the same mixing model calculations as used by Cawley et al. (2014). Both in Martin et al. (2018) and the present study, we identified a conservative mixing pattern in the Western Region and additional input from the peatlands located in the delta of the Eastern Region, based on this mixing model approach. In this study, because we were able to decompose the FDOM as a mixture into multiple components representing different organic matter fractions from different sources, we could more confidently identify peatlands as the source of the additional DOC input along the Rajang Delta (as opposed to autochthonous production). However, the Rajang is the only one of our rivers in which the peatlands are exclusively located within the estuary, leading to the slightly non-conservative mixing pattern within the estuary. However, this could only be diagnosed because we used a mixing model based on a fully freshwater end-member station. Because we are already calculating mixing models as in Cawley et al. (2014) for all our rivers, we do not propose to make changes to these calculations.

Comment 2.1.2 NaN_3

Although you said 'NaN3 did not contribute any blank fluorescence', it did contribute to sample absorbance, as you mentioned in the companion paper. Indeed sample preservation is still a major challenge, and I do use NaN3 to preserve samples for DOC analysis. However, I never use NaN3 to preserve samples for optical analysis because of the strong UV absorbance by NaN3 even at a low concentration (0.005% (w/v) in this study). I agree that if your samples have high absorbance, you could correct for the NaN3 absorbance accurately. However, when measuring EEM for samples containing NaN3, it seems that you failed to correct for the inner-filter effects (IFEs) caused by NaN3, because for the IFEs correction you used the absorbance of CDOM that were obtained by subtracting the absorbance of NaN3 from that of samples containing NaN3. In that way, you underestimated fluorescence in the EEM regions where NaN3 absorbed light (Ex 250–280). This is very serious because you mentioned the protein-like component 'showed consistently low values across the study region', and this could be due to underestimation of the protein-like component. The relative degree of the underestimation will be larger with decreasing sample absorbance relative to that of NaN3.

If you will correct (or may have corrected) for IFEs including NaN3 absorbance, please explain the degree of uncertainty of the correction. Because, although you said all samples had the same NaN3 concentration, there should be some variation in the concentration caused by, for example, repetitive volumetric measurements of samples (30 mL) and NaN3 solution (150 μL).

Response:

The reviewer points out a critical aspect of EEM correction. We clearly did not explain the details of the inner filter effect corrections well enough. Indeed, we used the total absorbance of each sample (*i.e.*, absorbance of CDOM and NaN_3) for the inner filter effect correction. We then converted the fluorescence intensity to Raman Units, and then subtracted the fluorescence of our reagent blanks (DI water + NaN_3). Therefore, we do not underestimate the fluorescence intensity. This inner filter effect correction does not contribute any additional uncertainty from the presence of NaN_3, because the total absorbance of each individual sample was measured (we collected one single sample to measure both absorbance and fluorescence). Any variation in NaN_3 concentration between samples is therefore fully accounted for and included in the corrections. We have explained this important aspect more thoroughly in the methods section of the revised manuscript (P5 L8 in the marked-up version).

The issue of sample preservation with NaN_3 was already addressed in the discussion of the paper by Martin et al. (2018) in this issue: the reason we decided to try to use NaN_3 as a preservative was so we could follow the CDOM sampling protocols in use by the ocean remote sensing community, since our CDOM data are being used for remote sensing algorithm development. Given the problem with high blanks in the UV range, we would agree that this is not ideal for measurements below about 280 nm wavelength, but in our sample set we are very confident that we could correct for this blank with high accuracy, as discussed in Martin et al. (2018) and the accompanying discussion.

As also requested by the associate editor, we have added a full quantitative analysis of the uncertainty that the NaN_3 blank contributes to our estimates of CDOM parameters as Supplementary Information 1, where we analyzed the percentage contribution of NaN_3 blank to the total absorption coefficient, the uncertainty in NaN_3 blank absorption coefficients,

uncertainty in $SUVA_{254}$ and uncertainty in $S_{275-295}$. To summarize this analysis, we find that, although the NaN_3 blank contributed a significant proportion of total sample absorption at short wavelengths, the uncertainty in the NaN_3 concentration in each sample was sufficiently small that the blank subtraction actually adds only a small amount of uncertainty to the estimated CDOM parameters.

Comment 2.1.3 FI

Did you apply instrument-specific correction for EEM? If so, the emission wavelength for FI must be 470/520 nm instead of 450/500 nm (Cory et al. 2010; Kida et al. 2018), because the emission peak often lies between 450 and 500 nm when the correction applied, which makes FI meaningless (FI must be calculated on the right side of the emission peak). If not, please write so in M&M section, because in that case your results are not directly comparable with other studies. It is often observed that if not corrected for the instrument-specific bias, the variability of FI between instruments is large for a given sample.

Response:

We are grateful to the reviewer for pointing out this issue. We did indeed apply an instrument-specific correction, so we have now re-calculated the FI using fluorescence intensities at 470/520 nm following Cory et al. (2010). This results in higher FI values for all samples, but the same distribution pattern along the salinity gradient, and the re-calculated FI values still show clear terrigenous signals for the blackwater rivers. The Eastern Region exhibits more mixed signals of terrestrial and microbial fulvic acids, but more towards the terrestrial endmember. We have interpreted the new FI results accordingly in the revised manuscript (P6 L24–29, P9 L6–27 in the marked-up version). However, we also note that the ranges in FI of terrestrial *versus* microbial DOM endmembers are reported as quite variable in the literature, and the appropriate wavelength range to use for FI calculations is also still debated: even the paper mentioned by the reviewer (Kida et al. 2018) ultimately decided to calculate the FI at the traditional wavelengths of 450/500 nm because they judged the values at the longer wavelengths to be unreasonably high. We have included some extra discussion of this point in the revised manuscript (P9 L24–27 in the marked-up version).

2.2 Minor comments

Comment:

Table 2. Was the distribution of the PARAFAC components and chlorophyll-a normally distributed? If not, Spearman's rank correlation should be used instead. Note that strong parametric linear relationships between PARAFAC components are unlikely considering the theory of PARAFAC. If components have a strong linear correlation, PARAFAC cannot resolve these components and they appear as a single combined component. Correlations between PARAFAC components are generally expressed by a log-log plot or Fmax/DOC plot (Stedmon and Markager 2005).

Response:

The PARAFAC components and chlorophyll-*a* were not normally distributed, so we have changed our correlation analyses to use Spearman's rank correlation (Table 2 in the marked-up version). Because the point of our correlation analyses is to show how our PARAFAC components co-vary with each other and with chlorophyll-a concentration across the salinity gradient, we decided not to normalize FDOM to DOC, because that would cancel out much of the variation that we are trying to analyze in this case. However, we agree of course with the point that the reviewer makes that very strong parametric linear relationships between PARAFAC components are ruled out by virtue of how PARAFAC models are calculated. However, this does not mean that PARAFAC components cannot be correlated with each other at all.

Comment:

P2L26 'extremely high DOC concentrations' Please specify the DOC range, as it depends on person when a DOC concentration is 'extremely' high.

Response:

The DOC range in the blackwater rivers in Sumatra and Borneo is up to 3000–5500 µmol L^{-1} or 36–66 mg C L^{-1}, which lie on the highest DOC concentrations in the rivers reported globally. We have specified these numbers in the revised version (P2 L27 in the marked-up version).

Comment:

P3L11 Sampling

How was the weather on the sampling days? In addition to seasonal changes, daily changes in rainfall and water flow conditions would affect DOM concentrations and compositions. If you discuss seasonal changes, at least the weather should be the same.

Response:

During the sampling cruises, we did not encounter extreme weather events. Overall, during each expedition most days had part cloudy / part sunny weather conditions, and heavy rain showers of a few hours' duration occurred on many days (usually in the afternoon), as is typical for this equatorial climate. Cloud-free days were rare. Because a lot of the rainfall in this region takes place across small spatial scales, the weather conditions during any one day at any one particular location are not necessarily indicative of the weather across an entire river catchment. Hence, it is unlikely that DOM concentrations and composition were affected in a significant way by day-to-day changes in weather conditions, and indeed we do not see any evidence of this in our dataset. We have included some additional description to this effect in the methods section of the revised manuscript (P3 L21–24 in the marked-up version).

Comment:

P3L30 Was the condition of the photodegradation experiment sterile (biodegradation-free)? If not, how about the effect of biodegradation? Please add some more details about the photodegradation experiment. For example, water inside the bottles was repetitively sub-sampled or you prepared many bottles and each bottle was collected as a sub-sample?

Response:

The photo-degradation samples were filtered by 0.2-μm pore-size Anodisc filters to remove bacteria in order to rule out any effect of biodegradation or solubilization of particulate organic matter. Bottles were repetitively sub-sampled, and while this may have introduced some microbial contamination, this would have affected the dark control bottles to an equal extent. We have added these experimental details in the revised manuscript (P4 L11 – 13 in the marked-up version).

Comment:

P4L3 'To minimize self-quenching of fluorescence intensity' Please add information on the maximum absorbance value of the measured samples, since IFE correction becomes invalid if sample absorbance is too high. Also, how you measured absorbance data is completely lacking. Please explain it in this section, and reference to the companion paper alone is not sufficient.

Response:

We have included a brief summary in the M&M section revised manuscript of how the absorbance measurements were conducted (P4 L17 – 25 in the marked-up version): we used a dual-beam Thermo Evolution 300 spectrophotometer with quartz cuvettes, and selected a cuvette pathlength of either 100 mm, 10 mm, or 2 mm according to the sample absorbance (for the March data, high-absorbance samples were diluted with DI water because the 2-mm cuvette was unavailable).

For fluorescence measurements, we used a 1-cm cuvette for samples with low absorbance, while samples with high absorbance were either diluted 10-fold with DI water and then measured in a 1-cm cuvette (March samples), or measured undiluted in a 3-mm cuvette. For all samples, we used the A_{total} of the appropriate dilution and pathlength at which the fluorescence measurements were conducted.

Kothawala et al. (2013) proposed that the inner filter effect correction is invalid for EEM regions with A_{total} >1.5 because of non-linearity between absorbance and fluorescence intensity. We have three samples for which A_{total} > 1.5 in part of the EEM spectrum, as shown in Figure 1 below. Therefore, the PARAFAC results of these three samples, especially the C5, should be treated with caution. The A_{total} values of all other samples are below 1.5 across the whole EEM, so the inner filter effect correction is fully valid for them. This information has been added to the M&M section (P5 L13 – 15 in the marked-up version) and the Figure 1 below has been added to the Supplementary Information as Figure S3.

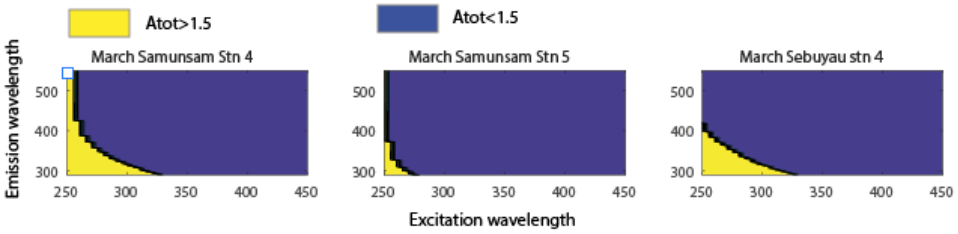


Figure 1. Samples with A_{total} above 1.5. The yellow shades indicate the regions where Atot > 1.5 in the respective EEMs.

Comment:

P4L27 'chemical compound classes' The authors need to be careful here. What PARAFAC can do is to statistically deconvolute EEMs into underlying building blocks, termed 'components', and these components are rarely related to specific chemical compounds. I think the authors understood that, but for those who are not familiar with PARAFAC, the author's statement may be misleading.

Response:

We fully agree with the reviewer that caution is needed here, hence we referred to "compound classes", not "compounds". We have re-phrase this as "…which decomposes the variation between EEMs in a dataset into multiple mathematically independent components representing different organic compound classes, with different sources, biogeochemical properties and behaviors." (P5 L27 in the marked-up version) to make this clearer also to non-specialists and avoid misunderstanding each PARAFAC component as a specific chemical molecule.

Comment: P4L28 Specify how many samples were removed.

Response:

Four samples were removed. We have added this information to the revised manuscript. (P5 L29 in the marked-up version)

Comment:

P4L29 Please add in Fig. 3 the excitation and emission loadings of the validated split dataset.

Response:

The excitation and emission loadings of the validated split dataset were saved during PARAFAC analysis and has been shown as an additional supplementary figure (Figure S4). It can provide further information about the validity of our five-component PARAFAC model for the readers.

Comment:

P5L1 Fmax is not just a score value. "Fmax is calculated by multiplying the maximum excitation loading and maximum emission loading for each component by its score, producing intensities in the same measurement scale as the original EEMs" (Murphy et al. 2013).

Also, Fmax cannot be a major of the concentration of each component in a sample, "because different fluorophores can have very different efficiencies at absorbing and converting incident radiation to fluorescence (Murphy et al. 2013)." Rather, "Quantitative and qualitative information may however be obtained from changes in the intensity of a given component, or in the ratios of any two components, between samples in the dataset (Murphy et al. 2013)."

Response:

We have corrected our explanation of Fmax.

We fully agree that Fmax cannot indicate the absolute concentration of compounds, but instead indicates relative changes in concentration of each component between samples, which is the way we interpret our PARAFAC results throughout the manuscript. We realise that our description here was perhaps slightly misleading, so we have re-phrased the section to read "which is taken as a measure of the relative concentration of each component in different samples of a dataset" (P6 L2 in the marked-up version).

Comment:

P5L8&L15 a350, S275–295, SR, and SUVA254 appeared for the first time here without explanations what they are. This is not kind for those who are not familiar with the optical indices. This is relevant to my comment on P4L3. Now I think that you need to make another section in M&M that explains the absorbance measurement and absorbance-based indices. However, personally I think that you can completely cut the sentences with respect to SR, a350 and SUVA254 since you mentioned about SR and a350 only once or twice and did not discuss SUVA results (just correlation with HIX).

Response:

We reviewed the need for mentioning each of these measurements, and have decided to omit all mention of the spectral slope ratio. We have added a brief explanation of any CDOM terms that are used (P4 L25 – 30 in the marked-up version). We believe that it is useful to briefly summarise these CDOM results from the companion paper in order to provide the readers with additional background about the CDOM concentration, DOM molecular weight and source in these rivers so that readers can appreciate the FDOM analysis more easily.

Comment:

As for S275–295, you may want to use it to support your idea that an FDOM-based estimate of tDOM is OK. However, I am not totally convinced that being correlated with S275–295 supports the correctness of your fluorescence-based %tDOM (P11L24), because estimations of %tDOM based on S275–295 is non-linear (Fichot and Benner 2012).

Response:

We agree that a correlation between our %tDOC estimates and $S_{275-295}$ does not prove the correctness of our method of calculating the %tDOC, but we do believe that it adds additional support: as in Fichot & Benner (2012), we find that there is an exponential relationship between %tDOC and $S_{275-295}$, as shown in Figure 2 below (%tDOC = exp ($\alpha + \beta S_{275-295}$), where α=1.48, β=-126.23). We have added the exponential regression model of the relationship between %tDOC and $S_{275-295}$ to the revised manuscript (P14 L28 – 30 in the marked-up version) and replaced Figure S1(b) with Figure 2 below.

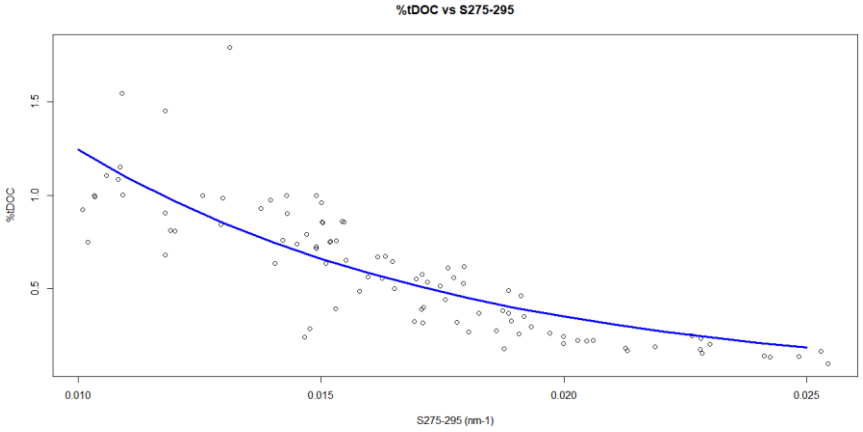


Figure 2. Relationship between estimate of %tDOC and $S_{275-295}$. The observation data is plotted using circles and the exponential regression model is presented by the blue solid line.

Comment:

P5L16 "SUVA254, 3.08–6.89" SUVA value of 6.89 is too high. Even the highest aromaticity sample (Ar >40%) in Weishaar et al. (2003) had the SUVA value of 5.3, and the possible maximum SUVA value (~5) has been recently suggested from a molecular analysis (Kellerman et al. 2018). Iron(III) is most probably interfering with SUVA determination in your sample dataset (Poulin et al., 2014). *If the authors did not measure Fe(III) and also have no stored sample for Fe(III) measurement, please state in the manuscript that some of SUVA values in this study was overestimated by interferences from Fe(III) to an unknown degree. Note that, if Fe(III) contributes to SUVA254 to a similar degree for all the samples, SUVA254 and SUVA280 would still have a high correlation.*

Another possibility is the interference by NaN3 even after the blank correction. This is possible when the sample CDOM absorbance was low. Please add the information on the NaN3 absorbance contribution to sample absorbance at 254 nm.

According to Fig S1&2 of the companion paper, decadic absorption coefficient of the NaN3 solution was about 4 m−1, which was about 10% - 30% of that of Rajang, Sematan, and Lundu samples and 50%–200% of marine samples. These values are not trivial.

Response:

Unfortunately we do not have Fe(III) measurements, so we cannot rule out that the $SUVA_{254}$ values were impacted by iron. However, we note that peat-draining blackwater rivers typically have very low dissolved mineral concentrations. Moreover, our river water samples, especially those with highest $SUVA_{254}$, often had decadic absorption coefficients greater than 100 m^{-1}, so based on the data shown in the Poulin et al. (2014) paper, a very high Fe(III) concentration would be needed to significantly bias our estimates. We have added some discussion about this possible issue in the revised manuscript (P10 L10 – 14 in the marked-up version). While the Kellerman et al. paper is a very interesting study, we note that the authors only very tentatively propose an upper boundary of around 5.5 for $SUVA_{254}$, given their limited sample set, while other recent studies still use $SUVA_{254}$ up to 6.0 (*e.g.*Massicotte et al. (2017)). All but one of our samples had $SUVA_{254}$ below 6.0, and most samples were below 5.5, so even if our highest SUVA values are impacted by the presence of iron, this is unlikely to have affected our dataset to a very serious degree. Given the very large environmental gradients we sampled across, we think it is rather unlikely that the Fe(III) concentration was proportional to CDOM *a*(254) across all of our samples, so we still suspect that the strong correlation between $SUVA_{254}$ and $SUVA_{280}$ supports the reliability of our $SUVA_{254}$ estimates.

The possibility that NaN_3 was responsible for the high $SUVA_{254}$ values was already ruled out in the paper by Martin et al. (2018), given the very strong and linear relationship between $SUVA_{254}$ and $SUVA_{280}$, because NaN_3 no longer has any significant absorbance at 280 nm (besides, while the NaN_3 absorbance at 254 nm was certainly high, the NaN_3 concentration was kept very consistent between samples and was thus corrected for accurately). We have now quantitatively analyzed the uncertainty in NaN_3 and its effect on the uncertainties in $SUVA_{254}$ and $S_{275\text{-}295}$ in the supplementary information 1, where we also show the proportional contribution of the NaN_3 blank to sample absorbance for all samples from 250–320 nm.

Comment:

P6L3 Please add seasonal climatic information (dry? rainy?) after months so that readers can easily understand climatic conditions, not only in the M&M section.

Response:

We have added this where appropriate. It is important to note that in this equatorial climate there are not very distinct wet and dry seasons, instead, there is quite high rainfall year-round, that increases further during the wettest time of the year. We have highlighted this more clearly in the Methods section (P3 L20 – 21)

Comment:

P9L31 "correlating strongly with DOC-normalized amino acid yields" This is not a correct citation.

The correlation coefficient was r = 0.62 (Fig. 8b in Yamashita et al., 2015), at best moderate correlation.

Response:

This is a valid point. This sentence has been rephrased as "Furthermore, Yamashita et al. (2015) found that the DOC normalized protein-like component Fmax value was indicative of the amino acid content in DOM and thus the bioavailability of DOM." (P11 L14 in the marked-up version)

2.3 Technical corrections

Comment:

P2L5 & L7 '0.2-0.25 Pg C yr-1' and '40% - 50%' should be 0.2–0.25 Pg C yr−1 and 40–50% (or 40%–50%). Please check the usage for minus (−), hyphen (-), en dash (–), and em dash (—). I did not correct for the rest of the manuscript.

Response:

We have checked and corrected the usage of these symbols.

Comment:

In Fig 2&4, it would be better to set the x axis to the same scale (maximum salinity of 35) except for the Simunjan River results so that comparisons between rivers become easier and more straightforward.

Response:

We have set the x axis to the same scale except the Simunjan river as suggested by the reviewer to make the figures easier for the readers.

Comment:

The caption of Fig. 4 says 'while they distinguish samples from different regions in the panel (z)', but I can't find the panel (z).

Response:

The panel (z) was removed from the manuscript before submission, but we forgot to correct the caption. We have deleted "panel (z)" from the caption. We apologize for the mistake.

Comment:

In Table 1, pleased add Tucker congruence coefficient (TCC) values so that readers can evaluate how much the comparisons are quantitative. Add the relevant explanations in M&M section as well.

Response:

The tucker congruence coefficients between our models and the models from the cited literatures were all above 0.95, which indicates strong correlations. The respective TCC values can be found in the OpenFluor report attached as the Supplementary Data Table 2. Specifically, both Coble et al. (1996) and McKnight et al. (2001) did not run PARAFAC analysis so no TCC can be provided for them. We cited these two papers because the peak positions and spectra of our components are close to theirs identified by the peak-picking technique and they have been widely acknowledged as the nomenclature of FDOM EEM peaks. We are trying to keep the table concise and highlight the most critical information of the possible source and biogeochemical properties of the compound classes represented by our PARAFAC components so we were considering not add the respective TCC values for each pair of the models but this OpenFluor report has been uploaded as part of the Supplementary Information 3 and we have added the relevant explanations of TCC in the Table 1.

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Response to Reviewer 2

We thank the reviewer for their time and their constructive and helpful comments. Our point-by-point responses are posted below, with the reviewer's comments being quoted first in italics.

Comment:

1. A major portion of the findings (high photolability of tDOM; large tDOM contribution to the shelf DOM pool) echo findings in the companion paper (Martin et al. 2018). I suggest reframing the introduction and adding a paragraph briefly summarizing the findings of the companion manuscript and describing how the present study will build on this work. In particular, what you can learn from EEMs that hasn't been revealed with bulk DOC and CDOM analysis.

Response:

We have summarized the findings from the companion paper in section 3.1 but we agree with the reviewer that these findings should be briefly summarized at the end of the introduction as well. This will provide the readers with more background knowledge of the biogeochemical settings of dissolved organic carbon and colored dissolved organic matter. We have now done this, and explained how our study builds on the companion paper (P3 L5 – 10 in the marked-up version).

Comment:

2. The calculation of tDOM appears to be oversimplified.

-Why is the sample with the highest value of normalized C1 Fmax used for the river endmember? Since there appears to be a lot of variation at 0 salinity, wouldn't an average be more appropriate? Is it possible to do a formal sensitivity analysis based on different choices of endmember?

Response:

2.1 Selecting appropriate endmember values is of course an important aspect for our calculation. In our method, we used C1 as a quantitative tracer of terrigenous organic carbon, and selecting the highest C1/DOC value in the low salinity range as the terrestrial endmember makes our estimates more conservative. If we over-estimate the C1/DOC ratio of the freshwater end-member, our approach will correspondingly under-estimate the %tDOC in marine water. This is why we did not use the mean value of C1/DOC of all the freshwater samples. Using an average of the freshwater C1/DOC values would increase the final estimated %tDOC for the marine samples. We have now calculated how big this difference is, and found that our estimate increases by ~2 percentage points for March (since there is only tiny variability for the freshwater in March), and by up to 4 percentage points in September. The estimated range of %tDOC in September would then increase from 19%–45% to 20%–

49%. Only one freshwater sample was collected in June. The difference between using the highest C1/DOC ratio or the mean value to do the calculation is not so pronounced for this estimation, relative to the range of %tDOC for our marine stations. We have included a brief summary of this information in the revised manuscript (P13 L12 – 16 in the marked-up version).

We realized that in our original Figure 6, the data from June and the data from September were accidentally switched. The correct Figure 6 is as below, which has replaced the wrong one in the revised manuscript. We apologize for the mistake.

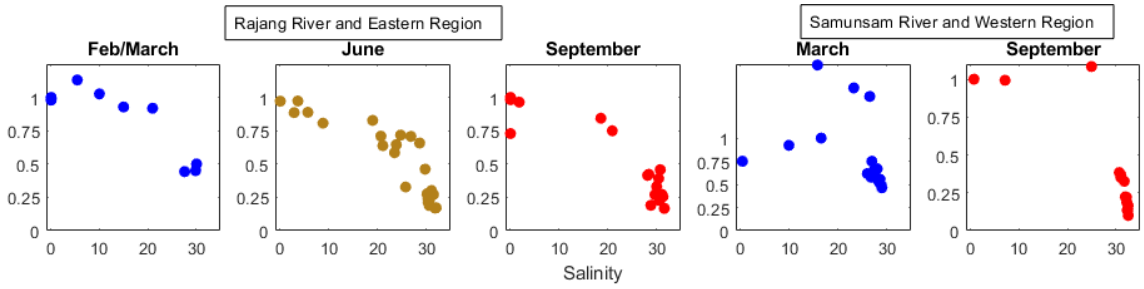

Figure 1. The correct Figure 6 in the manuscript (Estimated %tDOC).

Comment:

-Equation 3 does not include a marine endmember, which implies that (1) C1 Fmax varies linearly with tDOC, and (2) C1 would be 0 in a hypothetical pure marine DOM sample. Both assumptions should be stated and justified. It is also assumed that C1 has the same reactivity as bulk tDOM despite representing a small, compositionally distinct fraction.

Response:

A more explicit statement of these assumptions was also requested by Reviewer 1, and we have now stated the underlying assumptions clearly in the manuscript, and added some further discussion to support them (P14 L16–32 in the marked-up version). Basically, we believe that our assumptions are reasonable for the estimate of %tDOC within our relatively small study region because of the following three reasons:

(1) The predominantly conservative behavior of DOC concentration along the salinity gradient indicates that the distribution of DOC is mostly controlled by the mixing of freshwater and seawater, so our data do not suggest strong biogeochemical processing of the bulk DOC pool.

(2) Our C1 is very similar to terrigenous humic-like components identified in many other studies (Stedmon et al., 2003; Stubbins et al., 2014; Yamashita et al., 2015). Although we fully agree that fluorescent DOM only accounts for a small fraction of the total DOM pool, it has already been shown elsewhere that FDOM components are appropriate proxies for both fluorescent and non-fluorescent terrigenous DOM in the coastal aquatic environment, with strong correlations noted between fluorescent DOM measurements (including PARAFAC analysis) and molecular-scale measurements by mass spectrometry (Wagner et al., 2015). This indicates that our assumption that C1 behaves in the same way as non-fluorescent terrigenous DOM fractions during the freshwater-seawater mixing is in principle plausible. A more likely source of error in our study might be

the preferential loss relative to non-fluorescent DOM of C1 caused by photo-degradation, given the high photo-lability of C1 found in this study. Preferential loss of C1 would lead us to under-estimate %tDOC in our marine samples, although the exact degree of C1 photo-lability needs to be better constrained in future experiments with South-East Asian peatland samples. However, because our C1 showed predominantly conservative mixing behavior across our sample set, our data do not suggest that C1 was rapidly and preferentially removed within our study region. Ultimately, the spatial scales over which we sampled are not so large, and we suspect that the residence time of tDOM across this area is probably not very long relative to the degradation time-scales of tDOC and C1.

(3) Other studies have found only very low concentrations of C1-like FDOM components in the open ocean environment. For example, Murphy et al. (2008) reported only ~0.006 R.U. of a terrestrial humic-like component in the tropical Atlantic, which is ten-times lower than the values we observed at our fully marine stations in Sarawak. Since, unfortunately, we do not have open-ocean samples as a pure marine endmember, we necessarily have to assume that our C1 is purely terrestrial in origin. While this assumption may lead us to slightly over-estimate %tDOC, existing open-ocean data do not suggest that this is a large source of error in our estimate (and, in fact, it would be counter-acted by the impacts of photo-degradation on C1).

We have added some additional discussion along these lines to justify our assumptions in the revised manuscript (P13 L2 – 6 and P14 L16 – 32 in the marked-up version).

Comment:

-The identification of endmembers in Table S1 doesn't match the description in the text. There are marine end-members identified (not used in Eq 3), and some of the river endmembers are presented as an average of multiple stations instead of the station with the highest C1 Fmax as indicated in the text.

Response:

The endmember stations listed in Table S1 are the endmembers we used for the conservative mixing models of the spatial distribution of PARAFAC components and HIX (Fig. 2 of the manuscript). To estimate %tDOC, we used the highest value of C1/DOC of all freshwater stations in the Rajang and in the Samunsam so as to be more conservative, and these were not the same stations. We have described this more clearly in the revised manuscript to avoid confusion (P13 L12 in the marked-up version and Supplementary Data Table 1).

Comment:

-Calculation of the %tDOC should be included in the methods section and more information provided.

Response:

We explained the method of calculation of %tDOC in the discussion section because this is a derivative calculation based on the PARAFAC analysis that followed from our results of conservative behavior of C1 and DOC. We re-considered the

placement of this description in the revised version, and we finally decided to leave it in the discussion section. We have checked to ensure that all necessary information is included (P13 L1 – 24 in the marked-up version).

Other minor comments

Comment:

Methods: Photodegradation experiments should be in separate subsection.

Response:

We have describe the photodegradation experiment methods with more details in a separate section (P4 L10 in the marked-up version), as also requested by Reviewer 1

Comment:

Page 9, lines 13-24: paragraph mostly repeats info found elsewhere in the paper.

Response:

We think that this section is actually necessary, because we discuss further the possible source of C4. Our analysis suggests strongly that our C4 has a terrestrial source, although it is conventionally associated more commonly with organic matter of marine origin. This is an important point in the paper, and together with the FDOM data from the Haroun et al. paper that we cite later in this section, our results will help to guide future efforts in this region to trace terrestrial carbon inputs. While there is inevitably a small degree of repetition, in Section 3.2 we simply compared the spectral characteristics of C4 with previous studies, without discussing the question of sources of the components.

Comment:

Line 22: moreover is not the correct word here.

Response:

We changed to “In addition” instead.

Comment:

Page 10, lines 5-6: this sentence is contradictory.

Response:

This sentence has been rephrased to state that the primary source of C5 in this study does not appear to be terrestrial (P11 L23 in the marked-up version).

Comment:

Fig 4: legend indicates colors indicate regions in panel z.. figure appears to only go to panel y.

Response:

Fig 4. The panel (z) was removed from this figure before submission. We have removed “panel (z)” from the caption as well. We are grateful to the reviewer for pointing this out. We apologize for the mistake.

List of all relevant changes in the revised manuscript

The numbers of pages and lines below are referring to the marked-up version.

P2 L27 Typical DOC concentration in blackwater rivers in Southeast Asia added

P3 L5 – 10 Brief summary of major findings from the companion paper (Martin et al. 2018) and explanation of how this study developed based on the companion study added

P3 L20 – 21 Explanation of dry/wet season in the study region added

P3 L21 – 24 Explanation of the weather condition during sampling trips added

P4 L11 – 13 Details of photodegradation experiment added

Photodegradation experiment method written in a separate section

P4 L17 – 25 Details of absorbance measurement added

P4 L25 – 30 Explanation of CDOM terms used in this paper added

P5 L8 More thorough explanation of using total absorption coefficient to conduct inner filter effect correction for the EEMs added

P5 L13 – 15 Explanation of Atotal values of our samples added

P5 L27 Explanation of PARAFAC rephrased

P5 L29 Number of samples that were removed during PARAFAC analysis added

P6 L2 Explanation of Fmax rephrased

P6 L24 – 29 and P9 L6 – 27 Re-calculated FI and interpretation added

P9 L24 – 27 Additional discussion on the selection of wavelengths to calculate FI added.

P10 L10 – 14 Additional discussion on the potential interference of Fe(III) on $SUVA_{254}$

P11 L14 Citation of Yamashita et al. 2015 paper rephrased

P11 L24 Sentence rephrased

P13 L2 – 6 Further explanation of the assumptions of estimate of %tDOC added

P13 L12 – 16 Summary of the variability of %tDOC due to different ways of selecting riverine endmembers added

P13 L20 – 23 Explanation of uncertainty in the Fmax of C1/DOC added

P13 L26 – P14 L2 Discussion on the %tDOC > 100% in four stations in the Western Region added

P14 L16 – 32 Additional discussion on the assumptions of our estimate of %tDOC added

P14 L28 – 30 Regression model of the relationship between %tDOC and $S_{275-295}$ added

Table 2 Spearman's rank correlation used

Figure 2&4 the x axis reset

Figure 4 "panel (z)" in the caption removed

Figure 6 Panel b and c swapped

Supplementary Figure 1b (Figure S1b) replaced by the figure of exponential regression model of the relationship between %tDOC and $S_{275-295}$

Supplementary Figure 3 (Figure S3) added: Samples with Atotal > 1.5

Supplementary Figure 4 (Figure S4) added: excitation and emission loadings of the validated split dataset.

Supplementary Data Table 1 Riverine endmember of estimate of %tDOC added

Supplementary Data Table 2 added: Open-Fluor report with Tucker Congruence Coefficients.

Supplementary Information 1 added to explain the quantitative analysis of the uncertainty in NaN_3 blank and its effect on the CDOM parameters.