

Interactive comment on “Distribution and cycling of terrigenous dissolved organic carbon in peatland-draining rivers and coastal waters of Sarawak, Borneo” by Patrick Martin et al.

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We thank Reviewer 2 for their time in reviewing our manuscript, and for providing constructive criticism. We are confident that we can revise our manuscript in a way that will address all of their questions satisfactorily. Our point-by point response is shown below, with the reviewer's comments quoted first, followed by our response.

Reviewer 2: Martin et al. explore the spatiotemporal variations of dissolved organic carbon (DOC) and colored dissolved organic matter (CDOM) using in-situ data obtained from a total of six peatland draining rivers and coastal zones in Sarawak. The photo-liability and the cycling of these riverine DOM are also further investigated and

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discussed by conducting field photo-degradation experiments. Although some of phenomena and conclusions presented in this work are not new in this region or elsewhere, it's valuable to have seasonally-resolved DOC measurements in this important tropical marine biodiversity hotspot area. Overall, the data obtained in “black waters” are very interesting and the overall quality of the study is positive and contributes to a better understanding of the DOM properties in a region that accounts for a large fraction of DOC export to the global ocean while also facing strong anthropogenic influences; however, the manuscript needs some improvements in the text and figures. Specific comments and suggestions for further improvements: The authors spent 5- pages to describe the Materials and Methods part, which is much longer than the results. Some of the methods described are not new (e.g., section 2.2.1 and 2.2.2 for measuring DOC concentration and CDOM absorbance), and can be properly shortened. Regarding the precipitation data in Fig. 1a, you may consider to highlight the locations of meteorological stations using corresponding colors in Fig. 1b-1d.

Response: We agree that the methods were quite long. We will shorten the relevant sections, although because we need to describe numerous different analyses and the photo-degradation experiment, the Methods section will inevitably remain somewhat long. The meteorological stations were previously highlighted with pink arrows in each of the panels. We plan to change the arrow colour to match the colour of the bars in panel (e).

Reviewer 2: Regarding the section 2.2.3 of conservative mixing model, you may consider giving more details about the procedures using a table or other means.

Response: It's not clear to us exactly what additional details the reviewer is requesting. We will add an additional column to our supplementary data table to indicate which stations were used as end-members for the mixing models. We will also work on the wording in this section to make it clearer. We had already referenced the Stedmon & Markager paper that explains how CDOM mixing models should be calculated, and we plan to emphasise this further as a methods paper more clearly. The actual calculation

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of two-endmember conservative mixing models is simple and is done very commonly in studies of estuarine gradients, so we do not want to expand the methods section even further by explaining this in detail. Basically, it is just calculating a weighted average concentration according to the proportion of each end-member in the mixture, so if freshwater and salinity 30 water are mixed to yield salinity 15, then the expected DOC concentration would be the average of the two end-member samples.

Reviewer 2: Page 6, line 30, can you add a reference here and describe a bit the advantages of adding NaN3 to DI water as blank?

Response: There is no specific reference for this, but maybe the reviewer misunderstood this slightly: we did not add NaN3 to the DI water in the reference cuvette of the spectrophotometer, we made proper reagent blanks with the NaN3 that were measured against the DI reference and then subtracted from the samples. We necessarily had to do this, because NaN3 does have some absorbance at wavelengths >250 nm, so we needed to correct for this. We will clarify this further in Section 2.2.2, and we also plan to add a supplementary figure to show a sodium azide blank spectrum.

Reviewer 2: Page 7, line14, absorbance should have no unit. Also, page 7, line 1 – NaN3 absorbances around 26 m-1 at 230 nm, 4 m-1 at 254 nm: shouldn't these be absorption coefficients? These are very large values and likely to influence SUVA values.

Response: We apologise for this oversight, these values are decadic absorption coefficients, not absorbances. We will correct the text. We report these numbers as decadic rather than Napierian absorption coefficients, because the sodium azide blank is most relevant for calculating SUVA254, which is done using decadic instead of Napierian coefficients. For the most part, the blanks at 254 nm were still small relative to the CDOM absorbance, given the high CDOM concentrations in most of our samples. Because the NaN3 concentration was also identical across all samples, this blank could be subtracted very accurately. On Page 11, we show that SUVA254 is extremely closely

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related with SUVA at 280 nm, a wavelength at which NaN3 has no significant absorbance, across our dataset ($r^2 = 0.990$). This indicates that our SUVA254 estimates were not affected by the NaN3 blank. We plan to show the spectrum of a sodium azide blank as a supplementary figure, which will help to illustrate this more clearly. We used NaN3 because this is the recommended preservation protocol for CDOM samples in the ocean colour / remote sensing community (as in Tilstone et al. 2001, cited on Page 5), and we are currently using our CDOM data for a satellite remote sensing analysis. However, because CDOM measurements for remote sensing purposes are usually made at wavelengths above 300 nm, we were unaware of this blank issue in advance. We then continued with this protocol for the sake of consistency across our dataset. With hindsight, it is maybe better not to use NaN3 for CDOM analysis at wavelengths below 300 nm, but we were clearly able to correct for this blank without significantly compromising our data.

Reviewer 2: Page 11, line 21-25, can you describe more about the highly scattered data in range of 2.5-3.5 of log DOC (Fig. 5b) and 1.0-2.0 of log S275-295 (Fig 5c) (e.g., geolocation of the scattered data) since you mentioned that no strong seasonal changes in DOM composition within your study region in discussions; Page 16, line 17-18), which contradict a bit with the results here. In addition, you may consider to keep same scale of these parameters in Fig. 5 instead of using log scale for some parameters.

Response: The scatter in these relationships at the high DOC concentrations (>2.5 log(DOC)) is largely due to inherent variability between the rivers: the Rajang, Se-matan, and Simunjan have somewhat higher S275–295 at a given DOC or CDOM concentration than the Maludam or Samunsam. The lack of seasonal variation in these relationships is most obvious when comparing the March and September data: both datasets cover nearly the full range of data and both follow the same trajectory (including the scatter at higher DOC concentrations). The reason why it looks like there is some seasonality is two-fold: first, because we were unable to sample all sites in

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all seasons, and thus the June data (only Rajang and marine samples) only cover a smaller range of values than the other seasons. Secondly, in June and September, we were able to sample marine waters with lower DOC concentrations, which could not be sampled because of weather conditions in March. Therefore, the March data do not extend to such low DOC / high S275–295 values as the other two seasons. However, our point here is that all of the data essentially follow the same trajectory on these plots, rather than clustering into two parallel relationships by season (as found in some studies of other regions). We plan to expand this section slightly to explain some of this in more detail, and hopefully this is enough to clarify our point sufficiently. We did try plotting these data using linear scales instead of log scales. Unfortunately, because our data span such a large range in DOC and in CDOM concentration, plotting on a linear scale makes it very hard to properly see most of the data, because it is not possible to distinguish properly any samples with less than about 250 μM DOC. We agree that log-scales make it harder to directly compare these data to our other figures, but otherwise the relationships we are trying to visualise are simply impossible to see across the full dataset.

Reviewer 2: Regarding Fig. 6, can you specify the black and yellow symbols in figure caption? Also, page 11, line 27, it is written that both “. . .DOC and CDOM decreasing after sunlight exposure” however, Figure 6 and Table 1 do not show CDOM absorption values. It would be important to also show the relative decrease in CDOM at 350 nm with light exposure. Figure 6 is also repeated in supplementary S3.

Response: We will specify the symbol colours in the figure caption. CDOM did indeed decrease, and we plan to add one more row of panels to Figure 6 to show the decrease in CDOM, as a₃₅₀. We agree with the reviewer that showing the a₃₅₀ data for the photodegradation experiments is important, and we therefore also plan to show the a₃₅₀ data in Table 1 instead of showing the S_{350–400} data, given than S_{350–400} mostly showed little change relative to the controls, as is obvious in Figure 6. Unfortunately, the table is too small to show all these parameters. Figure 6 is not exactly repeated in

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the supplementary information: our SI Fig. 3 shows the photo-degradation data plotted against the number of days of sunlight exposure, while Figure 6 shows the data plotted against our estimated cumulative irradiance. We think it is important to show both, because the different days do have differences in irradiance. Conversely, because we could not measure the cumulative irradiance exactly, we think it is important to also show the data plotted against time for comparison.

Reviewer 2: Page 13, line 10-15, it might not accurate to rule out a major autochthonous source of DOC just according to low surface Chl a concentration since the DOC fluxes from benthic flora to the overlying water column might also be another possible reason for high DOC in shallow estuary.

Response: This is a good point. Essentially, this would require significant stocks of benthic macrophytes in the rivers. However, although we have no systematic data of macrophyte cover, we believe that it is very unlikely that macrophytes are present in significant quantities in any of our rivers. First, in the Rajang and Sematan rivers, the suspended sediment concentrations are very high and prevent deep light penetration; the same is true for all of the blackwater rivers due to the high CDOM concentrations. Secchi depths were measured at some stations in the Rajang and were always less than 30 cm relative to a river depth of often ≥ 10 m. Moreover, although moderate to large amounts of terrestrial plant debris (branches and leaves of trees, tree trunks, entire clusters of palm trees) were always seen floating at the surface of all rivers and out at sea, we never observed debris of aquatic macrophytes. Exposed river banks at low tide also never showed evidence of aquatic macrophytes. In the blackwater rivers we often had the opportunity to see the upper 10–30 cm of the river bank below the water line, but also never saw any macrophytes, only the sediment. We will slightly expand this passage to explain that we never saw evidence of aquatic macrophytes, and that benthic primary production is likely to be at most minimal owing to the low light penetration in all rivers.

Reviewer 2: Page 14, line 10-14 “the high precipitation in Maludam in September . . .

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.. DOC concentrations" which is not clear to me and I am wondering if there is previous study that reported this phenomenon; if yes, you may want to add a reference here. In addition, the lower DOC concentrations mentioned there could probably be associated with other environmental factors. The hydrological and meteorological conditions during wet and dry season could be different, which will change the residence time of waters and solar radiation, further affect DOC and CDOM properties there.

Response: We agree that this was not very clearly phrased. We will expand this section slightly to clarify our meaning: especially in peatlands, it has been noted that high precipitation can lower DOC concentrations in rivers by essentially creating a dilution effect, as described in the Clark et al. (2007) paper that we cited a few sentences previously. We will explain more clearly that this could be a dilution effect. Of course, the reviewer is quite correct in pointing out that numerous other environmental factors could influence the DOC seasonality in each river, and our intention was not to try and argue for one factor over another. However, because the Maludam catchment did appear to experience particularly high precipitation shortly before we sampled (as is apparent in Fig. 1), we feel that it is appropriate to point out that this might have influenced the apparent seasonality we recorded in this particular river.

Reviewer 2: The authors may consider mentioning the conservative mixing model in the abstract and conclusions since the model was used to "validate" their DOC and CDOM measurements in the result for several times. In addition, it's better to describe the advantages or reasons to include this model in this work, so far, it looks weakly linked to other parts.

Response: We already implicitly refer to the mixing models in the abstract when we state that "DOC and CDOM showed conservative mixing with seawater". Because the abstract is already quite long, it is probably better not to discuss the mixing models here in more detail. Calculating conservative mixing models is basically a standard practice when studying biogeochemical fluxes from rivers into seawater across the estuarine mixing zone. We never actually use the result of our mixing models to validate

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our results, we use them instead to show whether or not our results are consistent with DOC and CDOM mixing conservatively, or whether non-conservative addition/removal is happening in the estuaries. This can't be done properly without actually calculating the mixing models. Given that it is an important objective of our study to determine whether or not the DOC and CDOM are mixing conservatively in these estuaries, the mixing models are actually integral to our analysis, which is why we show the curves of all our mixing models in Figures 2 and 4. These models essentially show us the theoretically expected changes in DOC and CDOM with salinity if all of the DOC and CDOM are mixing fully conservatively. In most cases we find that our data are consistent with these theoretical predictions, except in the Rajang. These conclusions cannot be properly supported without showing the theoretical mixing lines from the mixing models.

Reviewer 2: Regarding Table 1, please keep the font size and typeface consistent and change "*" to "x".

Response: This will be done.

Reviewer 2: It would also be valuable to provide more information on the six rivers regarding their size, length, drainage basin, discharge, etc.

Response: We will add some additional information about the rivers to Section 2.1, especially the approximate lengths of the rivers. Other manuscripts that are currently in preparation for this special issue will present more detailed information about the catchments, including estimates of the extent of peat soils and plantations in the catchments. Unfortunately, there are no readily available datasets for the areal extent of most of the drainage basins, the exact proportion of peat soils in each basin, or river discharge. These estimates are still being put together by other groups, so the information will ultimately be available within the special issue, but the data are not yet finalised enough to be summarised here. Since the objective of our manuscript is mostly to understand the distribution of DOC and CDOM across the river-to-seawater gradients and exam-

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ine the biogeochemical processing of this DOM, this information is not critical for an understanding of our paper.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2018-389>, 2018.

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