

Review of Gandois et al. *From Canals to the Coast: Dissolved Organic Matter and Trace Metal Composition in Rivers Draining Degraded Tropical Peatlands in Indonesia*

The manuscript by Gandois et al. examines dissolved organic matter characteristics together with trace metal composition for a peatland-draining river system in Indonesian Borneo. These results add further to our understanding of tropical peatland river biogeochemistry, and in particular the combination with trace metals makes this an important contribution that also fits the topic of the special issue very well. The manuscript is written well, the data are presented clearly, and they are discussed appropriately. I only have a series of relatively minor comments.

We thank the reviewer for his positive and constructive comments on the manuscript. We address each of the reviewer's concerns in detail below.

1) My main comment concerns the fluorescence index, which shows surprisingly high values, but also spans a large range. The canonical interpretation is that  $FI < 1.4$  indicates terrestrial fulvic acids, while  $FI > 1.4$  indicates microbially-derived fulvic acids (Cory et al. 2010), at least if instrument-specific spectral corrections are made. Here, most data even for the blackwater river are above 1.5. If instrument-specific correction factors were not applied, then it might be better to calculate the FI with lower emission wavelengths (e.g. Kida et al. 2018). Regardless of the correction factors, I think the high and variable FI data should be discussed in a bit more detail – maybe FI is not the most useful measurement to identify terrestrial vs. microbial DOM? We also found a large range in FI in our river data in Sarawak, with some rivers having  $FI > 1.4$  despite predominantly conservative transport and no indications of strong microbial DOM processing in the rivers (Zhou et al. 2019 in this special issue). I feel therefore that the conclusion in Lines 242 ff. of extensive microbial processing in some locations is perhaps somewhat questionable. What I would recommend is that the authors use their absorbance data to calculate CDOM spectral slopes for 275–295 nm and 350–400 nm. The slope at 350–400 nm is usually found to increase with microbial processing, while the slope at 275–295 increases upon both photodegradation and microbial degradation (e.g. Helms et al. 2014; Hansen et al. 2016; Lu et al. 2016). This would provide an additional indication of whether microbial processing really is taking place, or whether perhaps the FI is a problematic measurement.

We agree with the reviewer that the FI values observed are high and we explored alternative emission wavelengths below. In summary, we find they all show similar trends. We have also updated the text to highlight potential uncertainties in interpreting these values.

The fluorescence data have been corrected by applying instrument-specific corrections. The emission spectra peak around 470 nm ( $470 \pm 4$ , Figure 1). This value is similar to that recommended by Cory et al. (2010), of a maximum between 477 and 480. The shape of the spectra clearly supports the use of the 470/520 ratio to calculate the FI index (This point has been added in the manuscript L. 164-165)

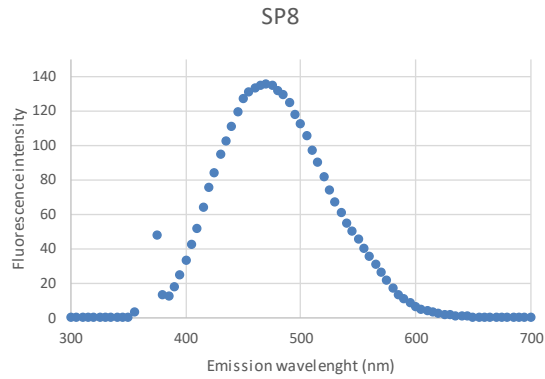


Figure 1. Example of an emission spectra for a 370 nm excitation.

We also calculated alternative FI indices using lower emission wavelengths, which lead to lower values (FI between 1 and 1.2). These values are correlated to the values presented in the manuscript ( $y=0.63x+0.11$ ,  $r^2= 0.78$ ,  $p< 4e^{-14}$ ). As stated by Cory et al. (2010), this emphasizes that trends, rather than absolute values, are most important.

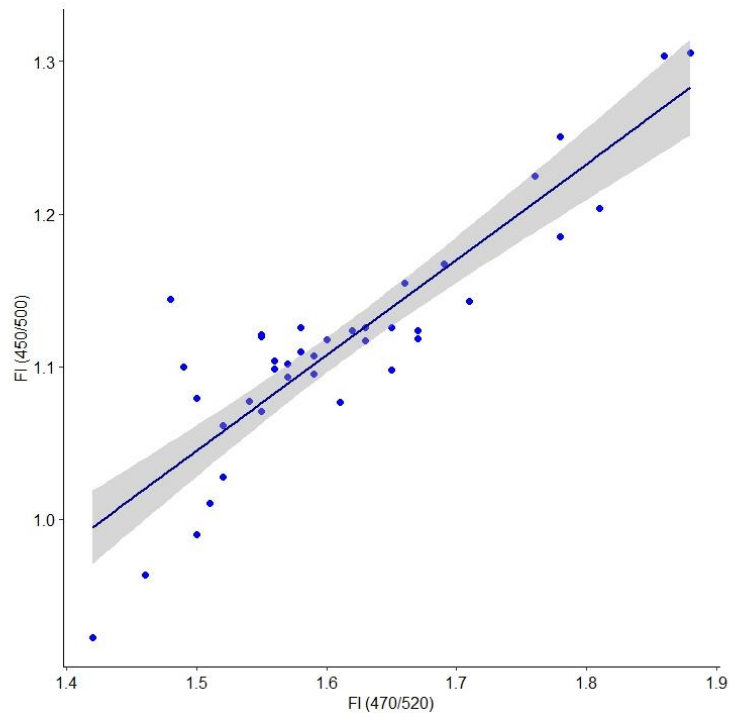


Figure 2. Relationship between the FI value calculated using ratio of emissions 450 to 500 nm and the FI value calculated with the ratio of emission of 470 to 520 nm

The ratios of spectral slopes at 275/295 and 350/400 were calculated. Higher values of these indices are also observed in sections of the river with higher FI values. This is consistent with the hypothesis of localized enhanced processing of DOM. However, we agree with the reviewer that it is difficult to conclude whether this processing is microbial or due to photodegradation. The text was modified accordingly to reflect this uncertainty (L. 199-200, 202-203, L. 263-265).

2) Line 24: “characterised the characteristics” could perhaps be phrased more elegantly

The sentence has been modified to “determined the characteristics” (L. 24).

3) Line 32: significantly higher than what? Is this compared to the whitewater river, or is this a statement in general about blackwater rivers compared to other rivers?

This statement was meant to be a comparison to the white river. This was specified at the end of the sentence (L. 33), but has now been updated for clarity.

4) Line 75: what is meant by “re-emission” as opposed to just emission? Isn’t this simply referring to emission of CO<sub>2</sub> after DOC degradation?

We agree that this word was confusing. We modified the text to “emission” (L. 79)

5) Line 82: what is meant by “with contrasted effects on optical properties”?

This part of the sentence was meant to introduce the following one, which discusses the opposite effects of microbial processing and photooxidation on aromaticity. The sentence has been modified to clarify for future readers (L. 88-89).

6) Line 118: please give the duration and temperature at which the filters were baked

The filters were baked for 5h at 450 °C. This has been added to the manuscript (L. 129).

7) Line 120: nutrient analysis is mentioned here, but the data are not shown. This is a shame, these results would be useful if they can be made available, especially since the authors mention the hypothesis that biodegradation might be nutrient-limited.

The nutrient concentrations have been included in the manuscript. In the revised version of the manuscript, Table 1 presents general water characteristics, including nutrients as well as DOM characteristics. The TM concentrations have been moved to Table 2.

8) Throughout the manuscript and figures, Cl should be changed to Cl<sup>-</sup>, since it’s referring to the chloride ion, not to chlorine.

This has been changed throughout the manuscript.

9) Lines 142–149: were the EEM data also spectrally corrected using instrument-specific correction factors?

Yes, the EEM data were spectrally corrected using instrument-specific correction factors.

This has now been clarified in the manuscript (L. 157-158).

10) Line 163: “anoxic” is the wrong word, the rivers clearly do contain measurable amounts of oxygen. Hypoxic would be a better choice.

The word “anoxic” has been replaced by “hypoxic” (L. 180).

11) Since the authors have dissolved Fe measurements at all their stations, I would recommend that they estimate how much of the absorbance at 254 nm might be due to dissolved Fe(III), using the relationship in Fig. 1 of Poulin et al. (2014). I did a quick estimate based on the mean SUVA, DOC, and Fe reported in Table 1, which suggests that the errors in SUVA are on the order of 5% or less, but it is important to have more data available about these potential interferences.

This is a very useful suggestion. We checked the potential additional absorbance related to Fe(III) in our samples using Poulin's procedure and the total Fe concentration we measured with ICPMS. The additional contributions to absorbance from Fe (AFe(III)) are low (AFe(III)=0.04±0.02) and represent less than 5% of the measured absorbance ( $3.6 \pm 1.4\%$  across all samples). As a result, we have decided not to correct the SUVA values presented in the first version of the manuscript. We have added a brief summary of this issue in the text as clarification for future readers (L. 154-156).

12) Lines 230 ff.: the increase in C1/C2 ratio is interesting, and in fact our photodegradation experiments with peatland river water in Sarawak provide direct experimental support for this interpretation (Zhou et al. 2019). The components 1 and 2 in the present study are quite similar to C1 and C2 in Zhou et al., and in all of the experiments the ratio of C1/C2 increases upon photodegradation, especially in the blackwater river.

This is a really interesting point. We have added a comment and a reference to Zhou et al. 2019 in the text (L. 252-254).

13) Line 250: The reference to Wickland et al. has the wrong year, it should be 2012.

This has been corrected.

14) Line 250: since nutrients were measured, it would be really interesting to have these data discussed in this context. I'm actually doubtful that microbial DOM degradation is nutrient-limited, since blackwater rivers in SE Asia do tend to have a few micromolar DIN and DIP (e.g. data table in Alkhatib et al. 2007; Bange et al. 2019).

The nutrient concentration ranges have been added to the manuscript. The measured concentrations of DIN and DP are low, and fall within the range of previously reported values from black rivers of Borneo (Alkhatib et al. 2007). Higher concentrations are measured during the dry season in the black river samples. We agree with the reviewer that nutrient concentrations are unlikely to be the primary limitation on microbial activity. The general conditions in the Black river (low pH, low DO) are unfavorable to microbial activity. However, it is possible that the low nutrient concentrations present may further reduce rates of microbial activity. The sentence has been rephrased for clarity (L 269-271).

15) Section 6.4: the authors argue that the large change in DOC/Cl- ratio after the confluence of the rivers cannot be due to dilution alone, and must involve degradation of DOC. This doesn't necessarily follow: the two river systems both have similar, and low, concentrations of Cl-, but a large difference in DOC concentration. Cl- is therefore not a good tracer of the mixing behaviour. It seems more likely that the blackwater river makes a quantitatively relatively small contribution to the whitewater river, so that after mixing there is not much of an impact on the river chemistry. If the change in the ratio really was partly due to degradation, I think this would imply that the DOC from the blackwater does not degrade much in the blackwater river, then suddenly undergoes significant degradation between the confluence and the first whitewater sampling station less than 5 km downstream, but thereafter doesn't show much further degradation (since the DOC/Cl- is quite similar in all the whitewater stations). So, I think that the relevant parts of Section 6.4 need to be re-written.

We agree with the reviewer that differentiating the relative contributions of dilution vs. enhanced microbial degradation of DOM after mixing is beyond this scope of this dataset. Distinguishing the relative contributions of dilution and potentially enhanced microbial degradation of DOM after mixing is difficult with our data. Based on the reviewer's comments, we have rephrased this interpretation in the manuscript. It was intended to be presented as a possible hypothesis, but the text has now been modified to temper it, following the reviewer's suggestion (L. 323-326).

We now more clearly acknowledge that our data does not enable the determination of the relative importance of photooxidation, microbial degradation and dilution at the confluence or along the continuum. However, we do believe our data, in particular the consistent increases in  $\delta^{13}\text{C}$ -DOC and C1/C2 along the continuum, both before and after the confluence, support the important role of photo-oxidation of DOM. This possible interpretation is still discussed in the manuscript.

16) The data tables have a mixture of points and commas as the decimal marker  
This has been corrected.

17) In the figure legends, "WRu" is sometimes given as "WRt"  
This has been corrected.

18) The fonts in Figure 5 might need to be increased somewhat, it's very hard to read in a print-out.  
The fonts have been increased in Figure 5.

19) In Figure 6b, there are a few light-coloured triangles at the top left of the graph, but this symbol is not explained in the legend.  
This has been corrected. They correspond to the signature of Borneo soils.

20) The authors switch between the terms "black river" and "blackwater river". Would it be better to pick one and stick with it?  
The term backwater river was replaced by black river throughout the manuscript.

## References

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