Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2018-389-AC1, 2018

Biogeosciences Discussions

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.

Patrick Martin et al.

pmartin@ntu.edu.sg

Received and published: 25 October 2018

We thank Reviewer 1 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 are quoted first, followed by our response.

Reviewer 1: Martin et al. present a concise empirical study on the spatial and temporal cycling of DOC in peatland draining rivers, Sarawak. Of particular interest are the results of the photo-degradation experiments and the fate of the riverine DOC component. The manuscript is well written and the study makes a valuable contribution to

the scientific knowledge database. I have a few minor comments: Page 5 Ln 30: acidification was chosen to preserve the DOC samples, however, this has been shown to reduce DOC concentrations (Kaplan.1994: https://doi.org/10.4319/lo.1994.39.6.1470) as well as alter spectral properties (Tfaily et al. 2011: doi:10.1016/j.aca.2011.08.037). I just wondered why cold storage was not considered?

Response: Appropriate sample storage is a problematic subject, to say the least, and neither for DOC nor for CDOM has any one protocol really become established above all others. In acidifying our DOC samples immediately upon collection and then storing them cold, we followed a method that is very commonly used in the oceanographic community, with acidification inhibiting microbial DOC metabolism. The Kaplan paper shows interesting results, although we note that it does not show a decrease in DOC upon acidification in all samples. Their analysis was also done with persulfate oxidation, which is typically less efficient than high-temperature combustion systems, so some of this apparent DOC loss could involve modification of DOC, not necessarily only mineralisation to CO2. Given that we needed to store our samples for up to 1.5 months before they could be analysed, we decided that acid-preservation seemed like a safer approach than simple cold-storage; unfortunately, we didn't have the capacity to collect and store extra samples to test this. We certainly agree that spectral properties of DOM would be altered upon acidification. All of our CDOM samples were therefore not acidified, but preserved with sodium azide to inhibit microbial activity, and stored cold alongside our DOC samples. As also explained in our response to Reviewer 2, we collected our CDOM data in part also to develop a remote sensing algorithm, and this preservation method is the recommended protocol in the ocean colour community (the appropriate citation to Tilstone et al. 2001 is given in the text on Page 5) – although measurements are then generally made at wavelengths >300 nm. Given our experience with the absorbance blanks from NaN3 up to around 270 nm, we agree with the reviewer than simple unpreserved cold storage is perhaps preferable if CDOM analysis in the UV range is planned (that said, as explained in the manuscript text and also in response to Reviewer 2, we are very confident that our blank correction was sufficiently

accurate that this did not compromise our data). We plan to add a new supplementary figure to show the absorption spectrum of sodium azide blanks.

Reviewer 1: Page 6 Ln 2: Mentions that freezing did not affect the DOC results, how as this assessed? Is there any evidence that could be added (maybe to supplementary material to support?)

Response: This was based on comparing the unfrozen samples to frozen samples from adjacent stations in the Maludam. Since all of the September Maludam samples follow very clear conservative estuarine mixing, with only a narrow range of DOC and CDOM parameters in freshwaters, frozen and unfrozen samples clearly had very similar results. Some protocols for DOC and for CDOM or FDOM samples in fact even recommend preservation by freezing, and while we think it is better not to alter samples in such a drastic way, major impacts from sample freezing are probably not common. We will a brief explanation to this section to explain why we think that freezing did not impact these results.

Reviewer 1: Page 8 Ln 9: were the quartz bottles overfilled with the water and then capped to eliminate headspace and therefore eliminate atmospheric exchange during the photo- degradation experiment? If so it would be good to include this information in the meth- ods and also how the quartz bottles were prepared e.g. combusted? I wondered if there was any sign of bacterial growth in the water samples during the experiment (just out of curiosity).

Response: The bottles were actually filled with a headspace of around 20–40 mL air, which was done to ensure that the samples would remain oxygenated throughout the duration of the experiment. If samples are filled without a headspace, DOC degradation can in principle become oxygen-limited, depending on the degradation rate. The quartz bottles were not combusted, but were acid-rinsed instead. This information will be added to the methods. We did not enumerate microbial cells in these samples, but there was no visible evidence of growth (no cloudiness or particulate matter visible).

Reviewer 1: Page 9 Ln 14: is there any way to include some information about the total distances travelled during the different campaigns (maybe on figure 1, by including a scale bar) or the distance between sampling stations to be added into the supplementary material? How was the distance between the sampling points decided?

Response: We will add a scale bar to Figure 1a to give a quick overview of the distance. The other panels already contain a lot of information so we do not want to clutter them with further scale bars, but distances can be estimated easily from the latitude axes on these panels. Distances between river stations are partly shown in Figure 3 for those rivers where multiple freshwater samples were taken. Distances between sampling points were inevitably decided according to multiple factors: during estuarine sampling, we chose stations mostly according to salinity, but distance between stations was considered as well. Logistical considerations were naturally important, e.g. the total distance that could be covered in one day. Many of the marine sampling stations were chosen according to optical water types, because of the need to use our data for remote sensing purposes – in this case we selected stations according to distance to the coast, the presence of distinct fronts, and differences in water colour. Logistical considerations were of course again important, e.g. sea conditions and prevailing currents, the total distance that could be covered given fuel, water, and time constraints, and the location of sand banks that had to be avoided for safety reasons.

Reviewer 1: Page 9 Ln 16: Was there any seasonal variability in salinity i.e. did you see a drop during the wet season due to greater freshwater input? Did you observe any salinity induced flocculation in the DOC samples which may have complicated analysis?

Response: There was some seasonality in salinity in the Western Region, as mentioned at the end of Section 3.1 (this is also visible in Figures 2 and 4). We did not specifically test for salinity-induced flocculation of DOC owing to logistical constraints; we hope to test for this during future fieldwork in the region. However, none of the estuaries showed evidence of non-conservative removal of DOC, so we suspect that

any salinity-induced flocculation probably does not have a significant impact on DOC concentrations in this region.

Reviewer 1: Page 11 Ln 26: Was there any evidence of photo-bleaching?

Response: Yes. As also requested by Reviewer 2, we will add additional panels to Figure 6 and Table 1 to show the decrease in CDOM concentration as a350.

Reviewer 1: Page 13 Ln 14: Was any POC data taken? Would have been interesting to see if there was any change in the DOC:POC ratio during the photo-degradation experiment, but as stated POC to DOC turnover is unlikely to have been captured within the experiments time frame.

Response: We did not measure POC either in our environmental samples or in the photodegradation samples. POC data for many of the stations will be presented in another manuscript in this special issue, but unfortunately the volume of water in the photodegradation incubations was insufficient anyway to filter for POC at each time-point. However, we are planning to do more follow-up work on photo-degradation of SE Asian peatland DOC, and we will certainly attempt to measure POC as part of that. Note that the water for the photo-degradation experiments was already filtered at the start of the experiment, and the incubation bottles were then sub-sampled at each time-point. These sub-samples were not re-filtered, so any DOC that was transformed to suspended POC would still be quantified as DOC with our measurements.

Reviewer 1: Page 13 Ln 24: Do you have any information on the extent of oil palm plantation coverage in this region/ the % of land likely to be covered by disturbed peat-lands?

Response: At this point we do not have updated estimates for plantation coverage and land disturbance for the region, but these questions are being addressed by other manuscripts that are in preparation for this special issue. Unfortunately, land-use data are difficult to obtain in this region on a catchment-basis. Essentially, practically all of

the peatlands need to be considered as at least partly disturbed, in the sense that they have a history of logging, and even the Maludam National Park peat forest is classed as a secondary forest. In the Rajang delta in particular, the majority of peatlands has been converted to oil palm plantations in the past years. However, the objective of this paper is not specifically to analyse effects of land-use change on DOC and CDOM concentrations, and our sampling scheme was not designed specifically to address this question.

Reviewer 1: Page 13 Ln 27: Another reference that might be good to add is Materic et al. (2017) (https://doi.org/10.1038/s41598-017-16256-x) who observed differences in the composition of organic compounds between forest and disturbed peatlands (some data is from Sarawak).

Response: Thanks, we had not yet come across this paper. We will add this citation to the manuscript.

Reviewer 1: Page 14 Ln 9: I wonder if the lower DOC concentrations observed at the end of the drier season could be a reflection of the interaction between the hydrology and photo- degradation i.e. during the dry season flow conditions will be low which could lead to longer residence times leading to greater UV exposure and thus DOC degradation. Again, just a thought.

Response: We certainly cannot rule out this possibility, but we suspect that photo-degradation in the rivers is probably not so pronounced. All rivers showed significant flow in all seasons, and because of the extremely high light attenuation in all rivers (due to CDOM and sediments) a large change in water residence time would be needed to allow for significant photo-degradation within the rivers. Moreover, if photo-degradation was significant in the rivers, we would probably see more consistent seasonal variation in DOC across the rivers.

Reviewer 1: Page 14 Ln 20: considering how photo liable the DOC is could this not have produced molecular level changes complicating its identification with respect to

terrestrial sources, especially in samples collected further downstream which have been exposed to greater periods of light exposure? So maybe the terrigenous signal identified in the samples is even stronger? Just a thought.

Response: Yes, this is a good point: we agree that any estimate of terrigenous contribution in marine samples based on S275-295 would, if anything, be an under-estimate. As also mentioned above, we suspect that photo-degradation is not really at play within the rivers themselves, because of the short water residence times and the extremely high light attenuation. Instead, photo-degradation of tDOM most likely only becomes significant in coastal waters once sediments have partly settled and the euphotic depth is greater.

Reviewer 1: Page 16 Ln 16: If the majority of the landscape is oil palm plantation I guess the drainage channels/ continuous yearly peat drainage could be ensuring that there is a continuous and direct flow of water (and thus DOC) into the river system, topping up the supply. Maybe this could also explain why there are higher DOC concentrations above the mixing line?

Response: This is certainly a possibility, although given the generally high year-round precipitation, it is likely that there is also simply a high amount of natural input year-round. The peatlands in the Rajang delta are drained naturally by a network of small rivers and streams that discharge into the Rajang distributary branches. We cannot say whether conversion to oil palm plantations may have increased this DOC input, although we cite the literature from site-specific studies elsewhere on Borneo that have shown increased DOC losses due to land-use.

Reviewer 1: Page 16 Ln 19: As the majority of Rajang catchment is draining disturbed landcover (i.e. oil palm plantation) this could be contributing to an increased nutrient input from the pesticides and fertilisers and thus cause eutrophication to come degree and contribute to the DOC pool (even though I see that the chlorophyll is low). However, the sampling campaigns are designed to show us a 'snap-shot' of the spatial

variability of the stream network across different seasons, so perhaps it is hard to rule out autochthonous DOC sources completely? Maybe there could be a lag response?

Response: Trying to understand the impact of fertiliser input from the plantations would be an interesting and important study. Depending on the magnitude of this nutrient input, it certainly might contribute to eutrophication. Again, however, we strongly suspect that primary production within the rivers is too strongly light-limited for there to be a response to nutrient input within the rivers and estuaries, so most likely there would be a down-stream effect in coastal waters, once the water clarity is higher. The question of how the underwater light level is controlled in this region will be addressed in a separate manuscript that is currently in preparation for this special issue. We would point out that although our sampling is indeed a snap-shot, any nutrient input from the plantations should have been happening also well in advance of our sampling campaign, so if there really was a downstream increase in chlorophyll due to nutrient inputs we would expect to see elevated chlorophyll concentrations within the rivers and estuaries, but the chlorophyll concentrations there are mostly very low. However, a more thorough discussion of these patterns will be the subject of the bio-optical manuscript that is currently in preparation.

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