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Interactive comment on "Shift in the chemical composition of dissolved organic matter in the Congo River network" *by* Thibault Lambert et al.

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Anonymous Referee #1 Received and published: 20 July 2016

REPLY: We thank the reviewer for raising a number of issues that stimulated us to clarify text and strengthen the manuscript.

This manuscript examines the chemical composition of DOM in the Congo River basin. The data presented is predominantly optical (CDOM/FDOM) alongside 13C-DOC and DOC concentration data and I have major concerns with the optical data quality from the study that is likely unfortunately beyond the authors control. This leads to issues with data interpretation as well as clear overinterpretation of the data with respect to processing for which there is no evidence presented. The manuscript is clearly organized but there are a lot of mistakes with English language throughout that need a

careful read through before it would be suitable for publication. Please find below a list of major / minor comments:

Line 17: You can't have a DOM concentration – just DOC.

REPLY: This has been corrected.

Line 19: "stretch in" is poor English. I'm not editing English throughout but there is a lot of minor editorial English correction required.

REPLY: "stretch" has been replaced by "transect". Overall, we have carefully read the manuscript to improve English.

Line 20: "second river in the world" for what? Discharge, basin size, number of people?

REPLY: "in terms of drainage basin area and water discharge". However this sentence has been removed in the revised manuscript in order to reduce the length of the abstract and to avoid repetition with the introduction and methods.

Lines 23-28: This is all speculation for which no evidence is presented. I'll come back to this below.

REPLY: We recognize that our manuscript doesn't include experimental evidence from incubation in controlled conditions that could confirm our interpretations regarding the impact of photodegradation and microbial degradation on DOM composition in the Congo River Basin. Such experiments pose logistical difficulties in the field and bringing large volumes of waters to our laboratories in Belgium holds the risk of modifying the natural conditions during transport and thus DOM composition. The abstract of the revised manuscript has been modified to accommodate this comment. That being said, we respectfully disagree that our interpretation can be considered as "all speculation". The application of PARAFAC modeling on a large spatial scale allows us to characterize the compositional features of DOM, and, more importantly, to identify specific fractions of DOM and their associated reactivity/origin (see Table 2). Thus, the identification of PARAFAC components previously identified as highly photodegradable (e.g. C3), photo-produced (e.g. C5), or produced during microbial reworking of terrestrial DOM (e.g. C2) significantly enhances the potential interpretations of our dataset. Moreover, the spatial and temporal variations in our dataset are interpreted alongside with other measurements including biogeochemical parameters (e.g. pelagic respiration, pH) and changes in environmental conditions (e.g. landscape morphology), and some of our conclusions are highly consistent with concepts evidenced in experimental studies (e.g. the link between photodegradation of terrestrial DOM and pelagic respiration, see Fig. 7). Consequently, despite the lack of experimental incubations, we argue that the interpretation of our data and ensuing conclusions are based and supported by recent literature. Overall, we attempted to improve the revised manuscript by pointing out how the variability observed in our dataset is consistent with recent literature (and also to enhance the general language flow as suggested by reviewer #2).

Lines 101-105: So what is the difference in WRT between the two seasons? If you are going to postulate WRT as a major driver it would be good to know at least how much it varies.

REPLY: WRT in the Congo River between Kisangani and Kinshasa has been roughly estimated to increase about $\sim$5 days between FW and HW (Descy et al., 2016) but is likely not uniform along the transect: because the main tributaries are all located downstream, the increase of WRT is probably more important upstream of Oubangui compared to downstream. We have specified this explicitly in the revised manuscript.

Lines 132-135: Samples were collected during the declining limb of a secondary discharge maxima which has its source in the southern part of the Basin and so this makes sense for comparison for samples near the mouth to the major discharge maxima. As you move upstream towards Kisangani on the map how is seasonality changing there for example – does this hydrograph have any bearing on what is happening there? It is unclear to me if this hydrograph (i.e. timing of high and low waters) is the same for all the sites – it seems not from what is written so what is really been compared in terms of seasonality / WRT?

REPLY: Water level of the Congo River follows similar seasonal variations at Kisangani and Kinshasa (Fig. 1 (revised Fig. 2)). Thus, timing of high and low waters are similar for the sites located along the mainstem although changes in WRT are likely more important upstream of Oubangui as outlined in the previous comment. We have specified this explicitly in the revised manuscript, as well as revising Figure 2.

Lines 141-149: Samples for DOC and 13C-DOC were filtered and acidified so were stable. Samples for optical analysis were just filtered – were they then refrigerated or frozen – it is unclear? A major concern here is that these samples were just filtered (even at 0.2um we see 3% of the microbial community get through the filter and it rebounds in a few days) and then basically were degrading until they were analyzed. Please provide details of how samples were stored, I appreciate this is probably a logistically very difficult part of the world to work in but more details on sample storage and analysis are required to assess the validity of the optical data.

REPLY: Among the different preservation techniques, we have chosen to just filter samples without acidification and to store the samples at cold temperature. Acidification of samples (or addition of $HgCl_2$) could have significant effects on the colored and fluorescent fractions of DOM due to change in the ionic strength (leading to flocculation or complexation) and/or through the release of DOM of biological origin due to senescence of microorganisms, and freezing has been shown to significantly affect the composition of DOM, especially when surface water are enriched in aromatic DOM (Fellman et al., 2008, STE). In order to limit potential degradation, samples were stored just after filtration at 4°C in a refrigerator placed on the boat until transport toward Belgium. Once received, samples were again stored at 4°C until analysis, the latter being performed during the week after arrival. Potential storage and degradation effects were assessed by analyzing a series of contrasting samples after 3 months (see one example of absorbance spectra in Fig. 2). The differences in optical proxies (a350, SUVA254 ad SR) were less than 5% (n=22) and no significant differences were observed by comparing excitation-emission matrices, validating therefore both the preservation technique as well as the quality of the data. These details as well as the figure (revised supplementary Fig. 2) have been added in the revised manuscript, and should eliminate the doubts raised about sample/data integrity.

Lines 204 -207: SUVA is a linear sliding scale, there is no hard and fast cut off between aromatic and aliphatic: higher values = greater percent aromaticity.

REPLY: We have modified the text in the revised manuscript.

Lines 378-383: A general increase in DOC is reported along the axial transect related to inputs from flooded forest (Fig 4). The authors are stating that flooded forest extent controls DOC export, which makes sense, and so how then does it not control DOM composition? If the composition is varying independently of DOC concentration you cannot invoke processes like photochemistry as that would also impact DOC concentration. This gives me concern about the DOM composition data as its storage history is not clear.

REPLY: In fact we found significant differences in the longitudinal increase in DOC concentrations between FW (0.0002 mgDOC km-1) compared to HW (0.0012 mgDOC km-1) in the upper part of the transect (these details have been added in the revised version), and these changes were accompanied with changes in DOM composition (already mentioned in the manuscript). We recognize that we cannot rule out that lateral exchanges between the central water masses of the Congo River and DOM-rich waters from tributaries can be driven by water level fluctuations in the Congo River (comment included in the revised manuscript). That being said, the occurrence of greater photodegradation during FW compared to HW is supported by several of our results (reformulated in the revised manuscript), including (1) the lower %C1 and %C3 during FW compared to HW (both these components are associated with highly aromatic molecules of high MW known to be sensitive to photodegradation), (2) the more important decrease in %C3 (consistent with the well documented high photosensibility of this component relative to other terrestrial humic-like components) and (3) the

PCA analysis that clearly separates stations collected in the mainstem between HW (negative scores) and FW (positive scores) along the PC2. Along PC2, PARAFAC components are distributed with C1 and C3 as negative loadings and C4 and C5 as positive loadings. C1 and C3 has been identified as photo-sensitive (Yamashita et al., 2010; Lapierre and del Giorgio, 2014) while C4 and C5 are respectively considered as photo-resistant (Massicotte and Frenette, 2010; Ishii and Boyer, 2012) and produced by photodegradation (Lapierre and del Giorgio, 2014). Therefore, we interpret positive values of PC2 as indicative of photo-degradation. The results of the PCA analysis (i.e. the meaning of PC2) have been detailed in the revised manuscript.

Lines 397-436: This is all highly speculative and ok so WRT is changing but by how much? TSS and phytoplankton growth are leading to less light penetration but in the Congo your light penetration is likely controlled by CDOM as its low TSS year round apparently. So if you have high CDOM year round (i.e. your river is colored) you have lots of substrate for photochemical reactions but its self regulating as your absorption is so high in the water column that only the very surface will degrade. . .when you look at any reference except the Cory Science paper they see very little evidence for photochem in freshwaters. . .they are typically either mechanistic (i.e. we put this in a bottle and degraded it) or they are in coastal systems where your colored waters are diluted out in optically clear marine waters and so see more light (i.e. self-shading goes away). I'm very skeptical that in a colored river like the Congo photochem actually can meaningfully degrade DOM so it shows up compositionally between seasons – maybe though if the WRT increases by weeks / months it could but this is not described.

REPLY: We agree with the reviewer that light penetration is likely controlled by CDOM. However, while the depth of UV light penetration decreases with increasing level of CDOM, the average rate of light absorption by CDOM increases in parallel (Hu et al., 2002). In this case, high rate of photodegradation can occur in ecosystems rich in CDOM such as the Congo Basin even if UV light penetration is low (Cory et al., 2015). Furthermore, an increase of ∼5 days in WRT between FW and HW is likely sufficient to significantly enhance DOM photodegradation as this degradation pathway can significantly processed terrestrial DOM over short time scale (e.g. ∼12h of sunlight alteration; Cory et al., 2015). Clearly, further research is needed in order to quantify rate of photodegradation in the Congo River and the relative importance of this process on C cycling in the Congo Basin, but this was beyond the scope of the present study. We have mentioned this explicitly in the revised manuscript. Moreover, without considering experimental incubation studies (such as the Cory Science paper) that represent the most easy and common way to investigate this process, it should be noted that several field studies carried out in "natural conditions" have illustrated the occurrence of photodegradation in freshwaters. The most relevant of these studies, conducted in the St Lawrence River (Massicotte and Frenette, 2011) and the Okavango Delta (Cawley et al., 2012), have thus related longitudinal changes in DOM composition to the impact of photodegradation on the aromatic and colored fraction of DOM during its downstream transport through notably the characterization of DOM by PARAFAC modeling.

Lines 467-551: Again this whole section is really speculative with just the optical data to suggest things – there are no incubations to support any of the trends. I appreciate the authors are just trying to explain their data but in reality its always fairly aromatic dominated. When I look at all the data I see a highly terrestrially dominated system and I'm not sure I'd dare get too much into seasonality with just two time periods. This needs scaling back to reflect this as a minimum.

REPLY: We agree with the reviewer that the Congo River Basin is fairly dominated by terrestrial and aromatic DOM during the two periods. This point has been added in the revised manuscript. That being said, this does discard our results and interpretations that are based on the patterns of PARAFAC components that can be used a tracers of source, origin and processing of DOM according to an increasing body of literature (Fellman et al., 2010; Jaffé et al., 2008 and other references cited in the manuscript). Moreover, patterns of PARAFAC components are interpreted along with measurements of environmental variables known to drive DOM reactivity (e.g. pH) that provide addi-

tional support for our interpretations. Finally, this section of the manuscript is focused on the downstream transformation of DOM during its transport in the fluvial network and not on seasonality (that would require monitoring at high frequency).

Lines 552-583: Again highly speculative – isn't the Cuvette constantly connected and so its not like it flushes like the varzea on the Amazon? If its always connected shouldn't the DOM coming out of it always look compositionally similar and so there should be no flood pulse?

REPLY: We respectfully disagree that the comparison made in our study with the conceptual model proposed by Creed et al. (2015) can be qualified as speculative as we used the same approach than these authors to investigate the relative influence of terrestrial inputs versus biogeochemical transformations across a gradient of Strahler order. Our results show that the Cuvette Centrale have a major control on DOM biogeochemistry at the scale of the Congo Basin. Although the seasonal variations of water level are modest in the Congo compared to the Amazon, and that the Cuvette Centrale Congolaise (CCC) does not flush as in the Amazon, there are several rivers that drain the CCC (Ruki, Likuoala aux herbes, Sangha), that bring large amounts of water and DOM to the river (The Ruki is the second tributary after the Kasai). DOM is therefore fairly dominated by aromatic compounds, but shows some differences in composition between the two periods because of changes in WRT. Overall, our results highlight the critical importance of river-floodplain connectivity in lowland tropical rivers as postulated in the flood pulse concept of Junk et al. (1989) in controlling DOM concentration and composition (see also Battin, 1998; Zurbrügg et al., 2013; Lambert et al., 2016). Patterns of other data acquired during the same cruises such as CO_2 and CH_4 also show the influence of inputs of these quantities from the Cuvette Centrale Congolaise (Borges et al. 2015). This is markedly different from the Chemostat Hypothesis of Creed et al. (2015), the latter being built on the river continuum concept (Vannote et al. 1980) that is typically applicable to rivers at temperate latitudes (devoid of large wetlands). This section has been clarified, and two references have been added (Moreira-Turcq et al., 2003; Zurbrügg et al., 2013).

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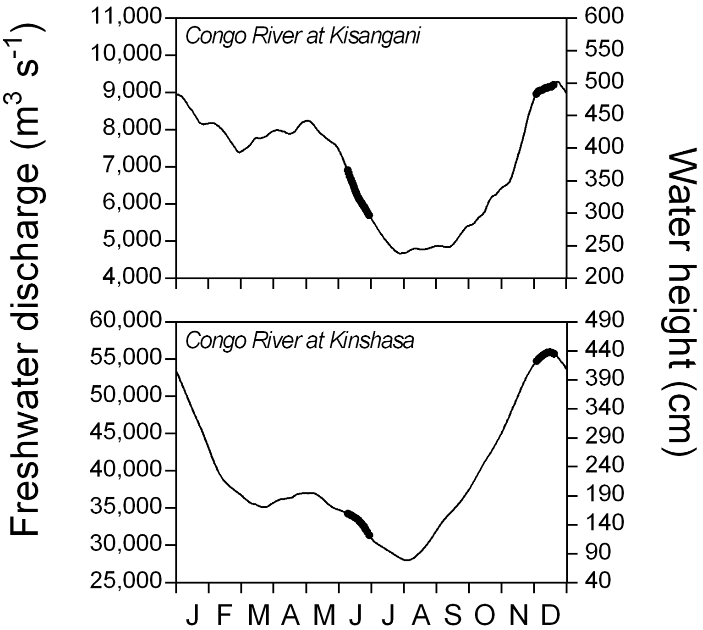

Fig. 1. Revised Fig. 2

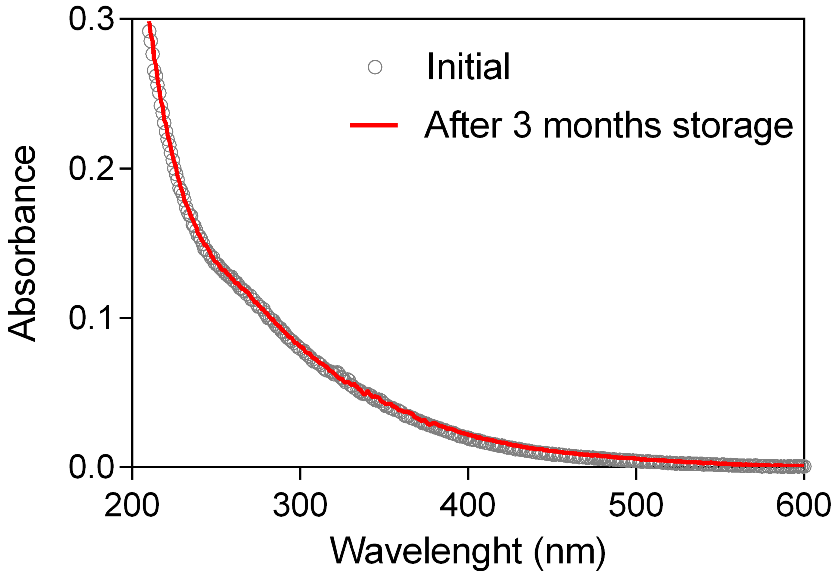

Fig. 2. Supplementary Fig. 2