Comment on bg-2021-92
Anonymous Referee #2

In their manuscript, Spray and co-authors investigated the effect of light exposure and microbial activity on the degradation of dissolved organic matter (DOM) in tropical headwater streams. They conducted in-situ experiments, with containers fulfilled with unfiltered water and covered or not by a lid to mimic dark (microbial degradation only) or ambient (photochemical + microbial degradation) conditions. Containers were anchored at each site (3 sites), and experiments were performed three times. Changes in dissolved organic carbon (DOC) and DOM composition (using absorbance and size exclusion chromatography) were investigated after 12h of incubation. In order to separate the effects of photodegradation from microbial processing on DOC losses and changes in DOM composition, "the values from the ‘ambient’ container, which theoretically represent the combined effects of both photochemical and microbial influences, were corrected by subtracting the values from the ‘dark’ container” (lines 176-178). Based on this approach, the authors observed higher DOC losses in “ambient” treatments while no clear trend was identified upon microbial degradation processes. The authors concluded that photodegradation has a larger influence on DOC degradation than microbial activity.

The relative importance of photochemical mineralization versus microbial degradation is still an unresolved question, and thus the topic addressed by this study is relevant. The experimental setup is original in that sense that more classical studies use incubation in laboratory-controlled conditions, and therefore diverge from field conditions. However, I found several issues with the approach that may affect data interpretation and conclusions. Furthermore, the structure of the manuscript could be improved significantly. In its current state, the results section contains a lot of interpretation. The authors could merge the results and discussion section as a Results and Discussion section, or better differentiate the two sections. I detailed my comments below and hope that they will be useful.

My main concern is about the calculations made to separate photochemical degradation from microbial degradation outlined lines 176-183, where values from the ‘ambient’
container are corrected by subtracting the values from the ‘dark’ container. By doing so, the authors made the underlying assumptions that photochemical and microbial degradation are cumulative processes and that the microbial degradation of DOM is not affected by photochemical reactions. In other words, this approach suggests/implies that DOM microbial degradation is similar between “dark” and “ambient” treatments. However, there is clear evidence of interactions between photochemistry and biological degradation where sunlight exposure of DOM can either increase or decrease its bioavailability (Bertilsson and Tranvik, 1998; Kaplan and Cory, 2016 for a short synthesis; Moran and Zepp, 1997). Given the experimental setup, the authors cannot exclude the fact that the dynamic of microbial degradation (both in terms of decay constants but also changes in DOM composition) differed across treatments. Therefore, I don’t know what really mean the ambient – dark calculation from a conceptual point of view, but I am not convinced that it represents photochemical effects solely as interpreted by the authors along the manuscript (e.g. fig 2, lines 199, 206, 209-211, 225, 273, 275-277,…). In consequence, several interpretations and conclusions are not supported by the data presented. For instance, the authors concluded that there was no photo-stimulated biodegradation (lines 322-324) or that “photodegradation is a more influential process on the complete mineralization of DOC than biodegradation” (lines 418-420), yet the two processes cannot be so easily distinguish by the ambient-dark calculation. Maybe directly comparing treatments after incubations would be more appropriate to highlight the influence of light exposure on DOM degradation.

The interest of the experimental setup is that it is closed to field conditions. However, it is not possible to determine how other processes (POC-DOC exchanges, primary production) may affect the results obtained as water were unfiltered. Primary production (and DOM release) may also have been affected by light exposure. I would appreciate that the authors discuss the limitation of their study. Finally, a direct comparison of “photodegradation rates” with previous literature should be done with caution. It is hard to compare results obtained from different studies as the protocols may be very different, especially in this study.

Specific comments

Line 14: “from from”

Line 15: the authors should present the mean instead of the higher values measured and used it to compare to previous studies (keeping in mind the limitation of such comparison). Mean DOC loss are 5%, and the 9% loss is more like an outlier than a real pattern.

Lines 130-137: I would not have expected significant difference across treatments during the night since photochemical reactions and biological uptake are very rapid processes.

Line 201: “The upper limit of this degradation exceeds those observed...” Please use the
mean instead of the higher value, this is not representative.

Lines 210-211: “non-aromatic compounds were preferentially removed by sunlight” ...or consumed by microbial communities. Overall, the ambient-dark calculation is interpreted as being solely due to photochemical processes along the manuscript, but this is misleading as biological activity was also occurring. This echoes my main concern about the approach used by the authors.

Lines 225-228: Sites are located in the same river networks and close to each other, DOM collected at BBR comes from BC1 and BC2 headwaters as shown by similar initial composition (table 1 and figure 3), so it is not surprising that composition and reactivity are similar despite differences in drainage areas.

Lines 322-325: as said above, I am not surprised that no difference was observed during the night because photodegradation reactions are very quick, and labile compounds potentially produced are likely consumed also quickly and thus do not accumulate in the water column. Moreover, the authors cannot conclude that there was no photo-stimulated biodegradation due to the experimental setup and the limits of their calculation.

Lines 456: fig 6?

Figure 3: there are errors in the caption.

References

Bertilsson, S. and Tranvik, L. J.: Photochemically produced carboxylic acids as substrates for freshwater bacterioplankton, Limnol. Oceanogr., 43(5), 885–895, doi:10.4319/lo.1998.43.5.0885, 1998.

Kaplan, L. A. and Cory, R. M.: Dissolved organic matter in stream ecosystems: forms, functions, and fluxes of watershed Tea., in Stream Ecosystems in a Changing Environment, pp. 241–320, Academic Press., 2016.

Moran, M. A. and Zepp, R. G.: Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter, Limnol. Oceanogr., 42(6), 1307–1316, doi:10.4319/lo.1997.42.6.1307, 1997.
