Responses to interactive comments on "Revisiting the disappearance of terrestrial dissolved organic matter in the ocean: a d13C **study" by K. Lalonde et al." by Patrick Albéric, Ron Benner, and an anonymous reviewer.**
Karine Lalonde and Yves Gélinas

Interactive comment on "Revisiting the disappearance of terrestrial dissolved organic matter in the ocean: a _13C **study" by K. Lalonde et al.**
R. Benner (benner@mailbox.sc.edu)
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The authors present data for the stable carbon isotopic composition of riverine DOC after extensive photochemical and microbial degradation. Photomineralization selectively removed isotopically depleted C, resulting in an enrichment of 13C (1-2‰ in the remaining DOC. These results are similar to those observed in previous studies (Opsahl and Zepp 2001, Spencer et al. 2009).

We agree with Dr. Benner that similar results have been reported before, as mentioned in our original manuscript (both references were cited, recognizing this fact). We believe that the global relevance of our sample set (10 of the most important rivers of the world) gives added value to our work and builds on these pioneering studies.

Photochemical degradation is chemically selective and primarily removes the chromophoric components of DOC that absorb UV light, such as lignin. Microbial degradation can preferentially remove isotopically enriched C (Benner & Kaiser 2011), but the authors observed minor shifts in carbon isotopic compositions during microbial degradation of riverine DOC that has been extensively photodegraded. The authors extrapolate these observations using a two-end member 13C isotopic mixing model to estimate the potential contribution of riverine DOC in the ocean. They conclude riverine DOC could account for up to 25-30% of the DOC in the Atlantic and Pacific Oceans. The model is oversimplified by using a marine end member del13C of -20‰ and a riverine photooxidized DOC end member del13C of -26.63‰. There is considerable range (~10‰) in both marine and riverine end member del13C compositions. The authors should include this in the model and calculations to provide a more realistic range of riverine DOC contributions to the ocean DOC reservoir.

We agree. The model was meant to simplify the effect of UV light on $\delta^{13}C$. It is apparent from this and other reviews that we did not adequately stress that we were simply examining the effect of photobleaching on apportionment calculations of terrestrial and marine DOC using stable carbon isotopes, and not trying to precisely quantify the terrestrial DOC content of the ocean. We chose to use frequently cited $\delta^{13}C$ signatures for the two end-members, though in agreement with Drs. Albéric and Benner, we acknowledge the fact that the $\delta^{13}C$ of the two end-members can vary over a broad range. We have now removed the extrapolation calculation to the world ocean (and Table 2) and centered this part of our discussion on the effect of photobleaching on the $\delta^{13}C$ signatures of the terrestrial end-member.

The values presented in Table 2 suggest the riverine DOC contributions to the Atlantic and Pacific Oceans are similar, which is odd because the Atlantic receives ~3.6-times greater riverine discharge than the Pacific (Opsahl and Benner 1997). Lignin phenol concentrations have been measured in the same ocean regions and are ~2.5-times higher in the Atlantic than the Pacific (Hernes and Benner 2006,

Opsahl and Benner 1997). Differences between the results obtained using different tracers of riverine DOC need to be discussed in the manuscript.

Our calculations were carried out using data available in the literature for the Pacific Ocean. Druffel et al. (1992) reported a series of $\delta^{13}C$ values that varied between -20.1 and -22.4 per mil. Some of this variation could have resulted from the incomplete oxidation of the DOC by UV (the method used in their work) or instrumental error. As shown in our work as well as in the papers cited above, UV preferentially decomposes the more $\delta^{13}C$-depleted components of total DOM, producing CO_2 that is more depleted in ^{13}C than the total DOC pool and hence artificially overestimating the terrestrial character of the total DOC pool. When using the more enriched signature reported by Druffel et al. (-20.1 per mil), the proportion of terrestrial DOC calculated for the Pacific Ocean is about 4 times lower than for the Atlantic Ocean (deep Sargasso Sea sample), in agreement with the difference in riverine discharge between the two oceanic basins.

Please note that these global ocean calculations were removed in the new version of our manuscript.

Water samples were not collected near the mouths of the rivers. The sample representing the Amazon River is a composite sample collected from the Rio Solimoes and Rio Negro, which are about 1000 km upstream. In addition, unfiltered water samples were stored in plastic carboys for 80-390 days prior to processing and use in experiments. The operationally defined labile fraction of DOC is removed within weeks, so additional components of DOC were remineralized during sample storage. Overall, these samples are not representative of the DOM discharged by rivers to the ocean, and it is not known how the C isotopic composition of the remaining DOC compares with values in the rivers. It would be useful to include previously published measurements of DOC concentrations and stable C isotopic compositions of DOM in Table 1.

We agree that the lag time between water sampling and the UV treatment in Finland is quite lengthy; we unfortunately had to deal with severe fieldwork constraints (cruise availability and difficulty in the shipment of samples) to obtain this unique series of samples. Aside from the Amazon River, all the samples were collected close to the river mouths and were thus representative to the DOM discharged to the coastal ocean at the time of sampling. We clearly acknowledged the constraints associated with this sampling strategy in the paper using published data and actual measurements for the St. Lawrence River sample (which agreed with the published data). Although impossible to demonstrate, we firmly believe that the operationally-defined NL-DOC and R-DOC fractions identified in our work roughly correspond to an operationally-defined semi-labile and recalcitrant DOC fraction, respectively. The separation of the total DOC pool into reactivity classes was also carried out by Dr. Benner himself in previous publications.

We also agree that adding literature values for DOC concentrations and $\delta^{13}C$ signatures would be informative; they were added in the new version of our manuscript.

The amount of light absorbed by CDOM (particularly UV radiation) during the photodegradation experiments was not determined in this study. However, 10 days of exposure at 1 cm depth in the solar simulator used in this study is a very large dose. The authors state this is equivalent to about a half-year dose of UV radiation. However, this estimate is not representative of the light absorbed by CDOM in the surface mixed layer of ocean. The extinction of UV radiation with depth is rapid in the ocean, and the mixed layer in the ocean is typically 40-60 m deep. What should be estimated is the exposure time within the mixed layer of the ocean for an equivalent UV dose used in these experiments.

Again, we agree with Dr. Benner's comment. However, the UV treatment was not designed to represent the actual UV dose to which terrestrial DOM is exposed in the surface ocean, but rather a dose that results in the total oxidation of coloured DOM, as explained in the method section. We were interested in quantifying the maximal potential effect of photobleaching on the $\delta^{13}C$ signatures of the DOM pool. Calculating exposure time to UV is important when extrapolating to the global ocean; since this section was removed from our manuscript, we did not attempt to calculate it in this work. We did however add a comment in the last section of our discussion, in which the effect of photobleaching on the $\delta^{13}C$ signatures of DOM is presented and discussed in detail.

Pg 17119, lines 9-14 - the photochemical degradation of dissolved lignin and the resulting shift from high to low molecular weight photoproducts was first observed in the study by Opsahl & Benner 1998

This was an oversight. We added the correct reference here and in the reference section.

Pg 17119, lines 15-24 - strong linkages between photobleaching and the molecular transformation of dissolved lignin were observed by Fichot and Benner 2012. These authors demonstrate how optical properties are useful indicators of the photobleaching of lignin. The authors also present a quantitative optical tracer for dissolved lignin, so it is incorrect to state the "terrestrial origin cannot be recognized using the currently available optical methods".

This is another oversight. In our new version of the paper, we have acknowledged the work of Fichot and Benner and corrected our statement regarding the recognition of terrestrial DOM using the currently available optical methods.

Pg 17127, lines 20-22 – the depletion of 13C in lignin relative to carbohydrates and bulk plant carbon was demonstrated by Benner et al. 1987

The Benner et al. (1987) reference was added here and in the methods section.

Pg 17130, lines 16-21 –exposure of DOM to solar radiation in estuaries and river plumes is typically minimal due high particle loads and short residence times in these waters. There is little photochemical and microbial DOC removal in these mixing zones. Conservative mixing of DOC has been observed across the salinity gradients from the mouths of rivers into the coastal ocean. The statement that 2/3 of the NL-DOC is removed in this mixing zone is incorrect and should be removed.

We corrected the statement to acknowledge that (i) such removal takes place in the surface ocean and not in these mixing zones, and (ii) that this value represents the theoretical maximal effect of photobleaching, and that the real exposure to UV (time and wavelengths) should be calculated to estimate the actual effect of photobleaching.

Water samples were filtered through 0.2 um pore-size filters, but this does not indicate the incubations were sterile. Sterile techniques were not used in the processing of water samples, and it can be assumed bacteria were present in the samples during irradiation experiments.

As indicated in the paper, staining tests were negative for bacteria in the "sterile" incubations. While it is true that sterile techniques were not used in the processing of the samples, care was taken to minimize contamination and to keep the bacterial abundance to a minimum during UV exposure.

Stable C isotopic measurements reported in table 1 are shown to be significant to 0.01‰ Is this correct? Why are some values significant to 0.1‰

All stable carbon isotopic measurements were significant to the 0.1‰ per mil level. We corrected the values in Table 1.

Tables 1 & 2 – Define the values given in parentheses

The values are now defined.

Figure 3 - Why does the concentration of DOC increase during incubation in the dark?

The increase in DOC concentration is not significant (within measurement error).

Overall, there are numerous errors relating statements in the text to specific references.
The authors need to go through the manuscript and carefully match statements with the correct references.

We have revised our reference section to better match our statements to the correct references. This new version is much better in this respect.