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.**
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Interactive comment on "Revisiting the disappearance of terrestrial dissolved organic matter in the ocean: a d13C study" by K. Lalonde et al.
Anonymous Referee #2
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Discussion

In this paper, the authors study the effects of photobleaching and microbial processing on the stable carbon isotopic composition of dissolved organic carbon (DOC) deliver from rivers to oceans in order to better constrain the isotopic signature of terrestrial-DOC end-member and to quantify its contribution to the oceanic DOC pool. According to this aim, an experimental irradiation followed by a bioassay is performed on water samples from ten large world rivers. The authors show that the photomineralization of riverine DOC results in a loss in DOC concentrations associated with an enrichment of 13C about 1.5‰ in the remaining DOC (whereas microbial processing does not). This observation is in accordance with previous studies showing that the photo-chemical degradation removes preferentially the isotopically depleted 13C-DOC fraction. However, this study provides a first worldwide overview of the importance of the photobleaching effects for the contribution of the terrestrial DOC pool to the oceanic reservoir, and points that the contribution of the terrestrial DOC is underestimated by about 20%.

The authors used the average isotopic fractionation of 1.5‰ due to photobleaching to re-evaluate the contribution of terrestrial-DOC to the oceanic pool based on literature data. If the experimental results are convincing, the extrapolation of an average isotopic fractionation of 1.5‰ for the estimation of riverine DOC in the ocean using a two endmember 13C mixing model is quite simple. Indeed, the isotopic fractionation ranges from 0.48 to 2.29‰ in the experiment, and the isotopic decomposition approach is extremely sensitive to the isotopic composition chosen for the DOC end-members (an example of such sensibility is shown in Lambert et al., 2013). Moreover, the use of a single value for the marine end-member (-20‰) seems oversimplified. Both spatial and temporal variations in the isotopic fingerprints of riverine and marine DOC pools need to be considered in this model and therefore estimations in Table 2 should be considered with caution.

As explained above in our responses to the first two reviewers, the model and extrapolation to the global ocean was removed from our revised manuscript.

Concerning the organization of the manuscript, the subdivision of the section Results and Discussion in two sections (Results then Discussion) should greatly improve the readability of the paper.

The Results and Discussion sections are now presented separately.

Comments:

It should be interesting to compare the DOC concentrations and isotopic signature of riverine waters sampled in this study and measured after 80-390 days of storage with previously published data when available.

As described in the manuscript, this was done for the St. Lawrence River, the only sample for which the total DOC and NL-DOC fractions were available. The results agreed very well with the literature estimates of the labile DOC fraction.

Are the data representatives of the temporal variation of these rivers?

We only analyzed one sample per river, which of course does not capture temporal variability. However, since these rivers are large, temporal variability in stable isotope signatures of DOC are expected to be small (less than 1‰ for the St. Lawrence River). Stable C isotope measurements of the NL-DOC fraction also show that the vast majority of the DOC in these samples is terrestrial in origin. Temporal variability is thus not expected to affect our conclusions.

Moreover, as samples were stored unfiltered, it is difficult to assess if physico-chemical reactions affect both DOC concentration and composition during the storage. The temperature of storage after sampling should also be specified.

Yes, storage of unfiltered and non-acidified riverine water does affect DOC concentrations (less than 20% decrease) and composition, although to a limited extent. Microbes consume the most biologically available DOC fraction (simple sugars, amino acids and small peptides), leading to a decrease in DOC concentration and the removal of the labile DOC fraction. However, these changes do not affect the δ^{13}C signatures of the DOM pool. The transportation and storage temperature was added to the method section.

Whereas the authors argued that the isotopic fractionation produced by microbial processing of the labile DOC produced by photomineralization is negligible, some samples show strong variations in their isotopic signature after the bioassay (-2.45 and -0.84 ‰ for Parana and Congo River, respectively). This point needs to be cleared.

As explained above (response to a comment of Rev. 1): We agree that the isotopic signature of these two samples changed upon microbial degradation of the photobleached DOC. We now acknowledge this fact in our new version. The conclusions remain the same however since the signature of the residual DOC (following photobleaching and microbial degradation) are still more enriched in ^{13}C than the initial NL-DOC fraction (by 0.47 to 1.59‰ for the five samples with *a sufficiently high DOC concentration following microbial inoculation and degradation to allow δ^{13}C-DOC measurement).*

Moreover, the decrease of nearly 1‰ observed in the dark control is quite surprising and need to be discussed.

As explained above (response to a comment of Rev. 1): The sample shown in Figure 3 is the Amazon River (now indicated in the caption). We added a comment in the new section regarding the change in the δ^{13}C signature of the dark control in Figure 3A; in short, the difference is likely due to the preferential microbial degradation of ^{13}C-enriched biochemical such as (poly)saccharides and peptides/amino acids, leaving behind ^{13}C-depleted biochemical, resulting in lower δ^{13}C values.

In the section 3.4, the authors propose to use the isotopic signature of riverine waters as a predictive tool for estimating the maximum potential photochemical and bacterial removal of riverine NLDOC in the ocean, based on the linear regression found in Fig. 5. However, as the authors say for the Congo River, this can be complicated by inputs of organic matter derived from C4 plants, and also by temporal variations in d13C values, which reflect changes in DOC composition and bioavailability (e.g. Neff et al., 2006; Raymond et al., 2007; Bouillon et al., 2012). The strength of the relationship in fig. 5 need to be discussed, as well as the values of -32.25 and -20.04 ‰ of the lower and higher limits.

The C4 plant material contributions to total DOC in large rivers are normally very low. Even in the St. Lawrence River, which drains a predominantly corn-intensive agricultural area covering most of southern Quebec and Ontario east of the Great Lakes, the $\delta^{13}C$ signature of DOC is about -26‰, very similar to soil DOC and to lake DOC from the boreal forest (surrounded by C3 plants almost exclusively). The contribution of C4 plant materials to total DOC in the rivers selected in this study is captured in the relationship shown on Figure 5, except maybe for the Congo River. To avoid any risk of confusion, we added a comment on possible deviations from this relationship in rivers draining large areas covered in C4 plants.

Pg 17118, line 22: Apportioning should be replaced by Differentiating

There is a small difference in the meaning of the two terms, with the former carrying the idea of a quantitative assessment of the relative importance of the two sources and the latter being more qualitative. We meant apportioning, not differentiating, and thus decided to keep the same word.

Pg 17123, line 7: due to the important time of storage (especially 390 days before experimentation), the sentence “the DOM fraction that was used at the start of the irradiation experiment corresponds to non-biologically labile DOM” should be moderated. Indeed, it is likely that some more refractory fraction of DOM have been microbially processed before experimentation.

The statement was modified slightly by adding “…at the start of the irradiation experiment mostly corresponds to…”. However, these fractions are operationally defined and thus, any compound microbially degraded during transport and storage is not part of the refractory pool.

Pg 17124, line 25 (and following): the indication “(mean+SD)” is not necessary.

The changes were made in the text.

Pg 17129, line 5: as the authors do not present 14C measurements, the sentence “14C-enriched materials…” is out of topic.

The sentence (and the reference) was removed in the new version.

Pg 17129, line 12: the definition of the R-DOC fraction should be presented before referring the figure 5 (pg 17129, line 5).

The definition now appears in the method section.

Tables and Figures: There are numerous errors in the tables and figures. Care should be taken to improve the quality of the manuscript.

The quality of the tables and figures was improved according to the comments of all three reviewers.

Table 1: what is the correct accuracy of isotopic measurements? Some values are shown to be significant to 0.01‰ whereas isotopic values measured after the bioassay are indicated to be 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.

d13C average values of residual DOC after bioassay is missing.

We had originally decided not to add it since we only five samples had sufficiently high DOC concentrations to allow isotopic measurements. Following the suggestion of the reviewer, we added the mean and standard deviation in the new version.

Fig. 1: Plots A: one of the initial or dark control absorption coefficient should be indicated in dashed line to improve the readability of the figure.

The change was made in the new version.

Fig. 3: the legend should be indicated also in the figure, not only in the caption. Plots of DOC concentration and d13C – NL DOC should be inversed. Put A and B in the corresponding plot and in the caption. The format of the X-axis should be replaced by days of irradiation and incubation (0-10-28/30 days). In the caption of the figure, the bioassay in indicated to cover 30 days whereas it is indicated 28 days in the text (ligne 1, p 17123). Please correct.

All these changes were made in the new version of the manuscript. The correct incubation time is 28 days (corrected in the caption).

Fig. 4: Y-axis should be d13C – NL DOC (‰)

The change was made in the new version.

Fig. 5: Plots of aCDOM and d13C should be inversed, following the order of reference in the text. Be careful to put A and B in the corresponding plot, as well in the caption. Please indicate the dimension of aCDOM350 (m-1) and precise d13C – NL DOC (‰)

These changes were all made in the new version.

References:

We thank Anonymous Reviewer 2 for these references. They are now cited in our text and have been added to our list of references.

Lambert et al., 2013. New insights from the use of carbon isotopes as tracer of DOC sources and DOC transport processes in headwaters catchments, Biogeosciences Disc., 10, 17965-18007

Neff et al., 2006. Seasonal changes in the age and structure of dissolved organic carbon in Siberian Rivers and streams, GRL, 33, L23401 C7616
Raymond et al., 2007. Flux and age of DOC exported to the Artic Ocean: A carbon isotopic study of the five largest artic rivers, Global Biogeo. Cycles, 21, GB4011