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Interactive comment on "Revisiting the disappearance of terrestrial dissolved organic matter in the ocean: a δ^{13}C 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 pointes 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 end-member 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.

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.

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. Are the data representatives of the temporal variation of these rivers? Moreover, as samples were stored unfiltered, it is difficult to assess if physic-chemical reactions affect both DOC concentration and composition during the storage. The temperature of storage after sampling should also be specified.

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

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 δ13C 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.

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

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.

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

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

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

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

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‰δ13C average values of residual DOC after bioassay is missing.

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.

Fig. 3: the legend should be indicated also in the figure, not only in the caption. Plots of DOC concentration and δ13C – 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.

Fig. 4: Y-axis should be δ13C – NL DOC (‰)

Fig. 5: Plots of aCDOM and δ13C 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 δ13C – NL DOC (‰)

References:

Bouillon et al., 2012. Reference in the manuscript

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

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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

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