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.
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bg-2013-512 Revisiting the disappearance of terrestrial dissolved organic matter in the ocean: a _13C study (K. Lalonde, A. V. Vähätalo, and Y. Gélinas)

General comments

The authors present an experimental approach to quantify the impact of photobleaching on stable carbon isotope composition of terrestrial organic matter dissolved in river waters. The point is of prime importance to evaluate terrestrial contributions to the dissolved organic carbon (DOC) pool present in ocean water. Experimental and worldwide sampling of riverine waters used in this study appear well appropriate with regard to the objectives. Output data are original and give a relatively large worldwide basis for a re-evaluation of the recalcitrant terrestrial DOC pool in ocean. By considering +1.5‰ fractionation on d13C-DOC values of non labile terrestrial DOC due to the residual-enrichment effect of photobleaching, the authors calculate a terrestrial DOC contribution in ocean multiplied by about 1.22 (as a whole). Although experimental is convincing, application to direct calculation of terrestrial DOC percentages present in oceanic total DOC using a unique two end-member isotopic mixing system may sound exaggerated. The choice of a unique value for the pure algal marine DOC end-member, i. e. -20‰ looks as an over simplification, may be not applicable everywhere in the ocean? Likewise, unalterated (-28.11‰ or photobleached (-26.63‰ d13C-DOC endmembers values for riverine contribution which are average values may fail to compute significantly local mixing percentages. The authors should prefer to stress the 20% increase of DOC terrestrial contribution in ocean which is calculated if photobleaching is taken into account (according to their data) than to proposed absolute values of that contribution like in Table 2. Calculated riverine contribution for literatures values would be taken more as an example to illustrate the photobleaching effect on that evaluation.

The calculation that appeared in Table 2 in our original paper (extrapolation to the total ocean) was not well received by all three reviewers for the reasons broached here and below (other two reviewers). We have removed this section in the new version of our manuscript. As suggested by Reviewer 1, our discussion now stresses the effect of photobleaching on the calculation of the terrestrial contribution to marine DOC without extrapolating to the whole ocean. We believe however that the δ^{13}C-DOC values that we have used are reasonable estimates of the average signatures for the end-members selected in this study, even though we are aware that these signatures can vary over a fairly broad range.

A welcome improvement of the manuscript should to reorganise the Results and Discussion section by first presenting the results.

The Results and Discussion sections have been reorganized in our new version.

Specific comments

The assumption that mineralization of labile photoproducts was not associated to an isotopic shift is balanced by the data found for the Parana River (and Congo River), that is 2 out of 5!

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 $\delta^{13}C$-DOC measurement).*

You should also comment the -1‰ found for the dark control in Fig 3A (and precise from which river the sample came from?).

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

R-DOC should be introduced in this section (3.3).

The definition for the R-DOC fraction now appears in the Methods section on lines 193-195.

In Figure 5 B, extrapolation of d13C-DOC values to fraction 0 or 1 seem perhaps unnecessary (since not used later) if any correct if a sigmoid function is considered instead a straight line. Anyway the sense of the -32.35 and -20.04‰ values respectively calculated for the pure mineralized and the pure R-DOC fractions should be discussed.

We now added a more thorough explanation for the extrapolation, and on the interpretation of the meaning of the $\delta^{13}C$ values corresponding to these fractions in section 3.3. Aside from one data point, the system behaves like a two-component mixture, which allows determining the characteristics of each end-member by extrapolation to 0 or 1. Also, we see no scientific reason to use a sigmoidal fit to the data of Figure 5B aside from obtaining a higher correlation coefficient. We acknowledge the fact that the photochemical sensitivity might not be the same for all the compounds photobleached during the UV treatment; however, the harsh photobleaching conditions used in this study most likely compensated for potential differences in photodegradation kinetics between photodegradable components, which could have affected the slope and/or fit of the data in Figure 5B.

How is calculated the fraction of R-DOC comprised in the NL-DOC could be specified.

The explanation was added in the caption of Figure 5.

Technical corrections (suggestions)

Line 27: less depleted should be preferred to more enriched.

The change was made.

Line 54: Hedges 2002 is missing in the list of references.

The reference was added.

Line 146: one set irradiated + one dark control make not a duplicate?

We meant to say "one set of duplicate irradiated samples, and one set of duplicate dark control samples". This was clarified in the new version.

Line 158: reference? (Chu and Liu 2009?).

The reference was added.

Line 223: Amazon? Black or White waters or mix? Put here information given in Table 1 caption.

The reviewer is right: this information should have been given in the text. Rather than inserting it in the Results section however, it was added on lines 128-131 in the Methods section.

Line 232: sentence starting by L-DOC was not... should be placed at the end of the §line238.

The sentence was moved accordingly.

Line 241: this statement cannot apply in case of mixing of different sources of DOC with different biodegradability.

We agree with Dr. Albéric that there could be situations in which this statement does not apply; however, in most large rivers such as those included in this study, the overwhelming majority of the DOC is terrestrial in origin, at least with respect to its $\delta^{13}C$ signature. The statement would not apply in rare situations where, for instance, a labile C4 plant-derived DOC fraction (less depleted in ^{13}C) would be mixed with a more recalcitrant C3 plant-derived DOC fraction (more depleted in ^{13}C). In such situation, the microbial degradation of the labile DOC fraction would result in a more ^{13}C-depleted DOC fraction. We were referring to the general situation here however, not to less likely exceptions to the general rule.

Line 259: light absorption.

The change was made in the text.

Line 272: please put references at the end of the sentence or move backward the sentence. Lines 288-291 "Naturally ...".

The change was made in the text.

Line 290, rephrase to avoid double brackets.

The change was made in the text.

Line 308: "data not shown" really not shown or in Fig 3B?

Dr. Albéric is right: Figure 3B shows the data for one sample (the Amazon River). What we meant is that the data was not shown for all samples. We added the reference to Figure 3B on line 308.

Lines 315-317: average data are not available on last column in Table1? The shift seems quite large for Parana River: -2.5‰ in Table 1, comment please. In Fig 3A dark control recorded a 1‰ shift during the microbial degradation step following photooxidation, is this significant? Comment please. Also in Fig 3 caption, you mention data from "a representative riverine sample" but you should indicate which River?

Please see the response to the general comments referring to these issues above.

Line 318: new subtitle? 3.4?

Reviewer 1 is right. We added the sub-section number.

Line 320: rephrase.

The sentence was rephrased.

Lines 321-323: 14C..., do you mean young material or mass dependant 14C enriched material? This section is not clear and not at its right place in the text.

This sentence was removed, as suggested by the other two reviewers.

Line 323-325: move to next paragraph.

We are not sure why Dr. Albéric would prefer to see the sentence moved to the next paragraph as it introduces the text that follows in the same paragraph. We decided to keep the text as it was, but reworked this paragraph and the following paragraph to improve the flow of the text.

Line 329: prefer (R-DOC is less 13C-depleted).

The change was made in the text.

Line 330: what is "model II" ?

A model II regression is a regression analysis between two dependant/error prone variables. We do not think that it should be explained in the text as this is a common type of regression analysis for which the definition/explanation is broadly available.

Line 332: do not repeat (R-DOC).

The change was made in the text.

Line 340: References?

A reference was added.

Line 341-343: move before line 321. Results are not sufficiently exposed before to be discussed.

Please see note for lines 323-325 above: this section was entirely reworked to better present the results.

Line 343: avoid excessive bracketing.

The double brackets were removed.

Lines 343-346: Where are the data you comment? Which are the Rivers you are talking about?

We added a reference to the data with a short explanation.

Line 349: plant materials.

The change was made in the text.

Line 350: less depleted.

The change was made in the text.

Line 355: new subtitle? 3.5?

Dr. Albéric is right. We added the sub-section number.

Line 369: do not repeat (R-DOC).

The change was made in the text.

Line 385: no useful data could be taken from phytoplankton?

The C3 cycle is the predominant carbon fixation pathway in phytoplankton, therefore the information cited in the text does pertain to phytoplankton. We added more information specifically linked to the natural variability of phytoplankton $\delta^{13}C$ *signatures in the next sentence.*

Lines 388-394: too long, rephrase.

The sentence was rephrased and shortened.

Line 397: which d13CDOC end-members values are used?

This section was entirely deleted (see response to general comments above).

Line 407: 22%? data from Table 2?

This section was entirely deleted (see response to general comments above).

Line 413: which are the "others".

They are “microbial degradation” and “salt-induced coagulation and precipitation”. These were added in the text.

Are lines 415 to 427 the Conclusion?

Yes. A new subtitle (plus section number) was added.

Lines 415-419: not at there place, move to Introduction?

This information already appears in the Introduction on lines 59-64. We think it is helpful to repeat it here, using a slightly different form.

Lines 424: which "new proxies, methods and ..." ? References?

Three references were added here and in the References section.

Line 444: actualise reference data.

This reference was deleted along with some of the text in the Discussion section.

Table captions

Table 1: Total and 2 NL-DOC ... instead of "various". Do not repeat information concerning L-DOC removal and move to the plain text information concerning Amazon River sampling.

These changes were all made in the new version of the manuscript.

In Table 1, last column, does % of microbial degradation are also "% loss"?

They are. The word “loss” was added to the heading of the column.

Table 2: Why unalterated or photobleached CDOC end-members values taken for calculation (respectively -28.11 and -26.63‰ differ from average values in Table 1 (respectively -28.07 and -26.57‰? less depleted instead of "most enriched" line 3

Following the suggestions of the three reviewers, we removed the section pertaining to the extrapolation of our results to the global ocean (and thus Table 2).

Figure captions

Figure 1: Put (a) and (b) at the beginning of the sentence sections

The changes were made in the caption.

Figure3: Y-axis Fig 3b : NL-DOC (mg/L); Fig3a: NL-DOC d13C

The changes were made in the figure.

Figure 5: (A) and (B) have been inverted in the text of the caption precise NL-DOC d13C Y-axis

The changes were made in the figure.

Figure 4B: Congo plot mark in Fig5A should be in black as in Fig5B rearrange X-axis label

The changes were made in the figure.