

Interactive comment on “Revisiting the disappearance of terrestrial dissolved organic matter in the ocean: a $\delta^{13}\text{C}$ study” by K. Lalonde et al.

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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 ^{13}C (1–2‰ in the remaining DOC. These results are similar to those observed in previous studies (Opsahl and Zepp 2001, Spencer et al. 2009). 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

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isotopic compositions during microbial degradation of riverine DOC that has been extensively photodegraded. The authors extrapolate these observations using a two-end member ^{13}C 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 $\delta^{13}\text{C}$ of -20 ‰ and a riverine photooxidized DOC end member $\delta^{13}\text{C}$ of -26.63 ‰. There is considerable range ($\pm 10\%$) in both marine and riverine end member $\delta^{13}\text{C}$ 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.

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.

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.

The amount of light absorbed by CDOM (particularly UV radiation) during the pho-

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todegradation 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.

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

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 can not be recognized using the currently available optical methods”.

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

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.

Water samples were filtered through 0.2 μm pore-size filters, but this does not indicate the incubations were sterile. Sterile techniques were not used in the processing of

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water samples, and it can be assumed bacteria were present in the samples during irradiation experiments.

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‰.

Tables 1 & 2 – Define the values given in parentheses

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

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.

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