Biogeosciences Discuss.,
doi:10.5194/bg-2015-558-AC1, 2016

Interactive comment on "Controls of longitudinal variation in δ^{13}C-DIC in rivers: A global meta-analysis" *by* K. A. Roach et al.

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Received and published: 9 March 2016

Dear Anonymous Reviewer 1,

We have made extensive revisions to our manuscript "Controls of longitudinal variation in δ13C-DIC in rivers: A global meta-analysis." The excellent suggestions allowed us to critically review the manuscript, and as a result the paper is much improved. We have increased the number of studies from our meta-analysis from 26 to 31. We also changed one of the covariates in our GAMMs from DIC concentration to bicarbonate (HCO3-) concentration. We did this because we originally used DIC as a proxy for weathering, following Bade et al. (2004), however we realized that substituting DIC for HCO3- would increase the number of data points included in the GAMMs from 889 to 2,087, resulting in much better geographic coverage. In addition, we appreciate the suggestion to provide our data-base as a supplement for future studies. Below are detailed comments justifying how the manuscript was revised. We are ready to submit our revised manuscript and data-base upon request by the editor. We hope that you will find the revised manuscript suitable for publication in Biogeosciences.

Sincerely, Katherine A. Roach on behalf of the authors

Reviewer comment: I suggest that the authors make their data-base public (as a supplement) for future studies and comparisons. The compilation is far from complete, the authors missed numerous papers (see below). I was not convinced from such a broad analysis that cyanobacteria have a major influence on the delta13C-DIC distribution in rivers.

Author comment: We will provide our dataset to Biogeosciences as supplementary material so other researchers can use it in the future. As explained below, we could not include all of the studies that this reviewer recommended. In the manuscript, we clarified that we constrained the δ13C-DIC data to only include samples that measured temperature, pH, and one of the following variables that could be used to assess the relative concentrations of H2CO3, HCO3-, and CO32-: DIC concentrations, alkalinity, or HCO3- concentrations in rivers with low to neutral pH. We agree the assertion that cyanobacteria have a major influence on δ13C-DIC in rivers is speculative. However, intense photosynthesis by cyanobacteria has been shown to produce fractionation that results in low δ13C-DIC values when pH is high and pCO2 is low (Herczog and Fairbanks, 1987), and our results indicated that δ13C-DIC values were low in rivers with high pH and low pCO2 values. Following the addition of new data, sites with the highest pH no longer tend to have low δ13C-DIC values, therefore we removed the discussion of cyanobacteria from the Discussion section.

Herczog, A.L., and Fairbanks, R.G. Anomalous carbon isotope fractionation between atmospheric CO2 and dissolved inorganic carbon induced by intense photosynthesis, Geochim. Cosmochim. Acta, 51, 895–899, 1987.

Reviewer comment: I suggest the authors use the term "isotopic composition" instead of "isotopic signature". A signature is individual and invariable, which is not the case of stable isotopes.

Author comment: As a result of this comment, we realized that the term "stable isotope signature" is the terminology that is most commonly used by biologists, whereas "stable isotope composition" seems to be the terminology that is most commonly used by biogeochemists (e.g., Mayorga et al., 2005). Our paper focuses on dissolved inorganic carbon, therefore we revised the terminology "δ13C signature" to "δ13C composition" or "δ13C values."

Reviewer comment: L 23: What's the difference between "decomposition" and "respiration"?

Author comment: By decomposition, we meant methanogenesis followed by methane oxidation, which would produce CO2 that is highly depleted in 13C. However because methane oxidation by methanotrophs is a form of respiration, we changed the terminology "decomposition" to "respiration" throughout the manuscript. Furthermore, we added the following sentences to the Introduction section to make more explicit why DIC from heterotrophic respiration is depleted in 13C: "The δ13C of the CO2 that is produced during heterotrophic respiration is similar to the δ13C of the energy source. In rivers the energy source is often plants, which are relatively depleted in 13C (Deines, 1980; Kohn, 2010). Furthermore, methanogenesis in anaerobic sediments produces methane that is extremely depleted in 13C, and this methane can then be oxidized to CO2 by methanotrophs (Conrad et al., 2011)."

Conrad, R., Noll, M., Claus, P., Klose, M., Bastos, W.R., and Enrich-Prast, A. Stable carbon isotope discrimination and microbiology of methane formation in tropical anoxic lake sediments, Biogeosciences, 8, 795–814, 2011.

Deines, P. The isotopic composition of reduced organic carbon, in: Handbook of Environmental Isotope Geochemistry, Vol. 1, edited by: Fritz, P., and Fontes, J.C., New

York, Elsevier, 329–406, 1980.

Kohn, M.J. Carbon isotope composition of terrestrial C3 plants as indicators of (paleo)ecology and (paleo)climate, Proc. Natl. Acad. Sci. USA, 16, 19691–19695, 2010.

Reviewer comment: L 55: HCO3- is also formed from weathering of silicate rocks.

Author comment: We changed the sentence "Other physical processes influencing δ13C-DIC in rivers include carbonate mineral weathering and mixing of different water bodies" to "Other physical processes influencing δ13C-DIC in rivers include chemical weathering of rocks and mixing of different water bodies." We also explained that "The major source of DIC in most rivers is carbonate weathering, the formation of HCO3- via the dissolution of carbonate minerals (Raymond et al., 2008)."

Reviewer comment: L 55: CaCO3 precipitation can also occur in rivers at travertines (Hernan and Lorah 1987) or in highly eutrophic rivers (Abril et al. 2003).

Author comment: It would have been interesting to include Ca2+ as a covariate in the GAMMs to investigate if carbonate precipitation influences δ13C-DIC in rivers. Unfortunately, we only have data on Ca2+ in eighteen of the thirty-one studies in our meta-analysis. Most of the world's major river systems are not supersaturated in Ca2+ and HCO3- (Kempe 1982) thus carbonate precipitation at travertines likely does not have a large effect on δ13C-DIC in most fluvial ecosystems."

We also were interested in investigating if eutrophication had an effect on δ13C-DIC in rivers. However, variables that are associated with eutrophication, such as chlorophyll a or algal primary production, were rarely measured. We added the following sentence to the Discussion section: "Algal primary production or other processes that are associated with eutrophication might account for some of the unexplained variation in the GAMM analyses of $\Delta\delta$13C-DIC and δ13C-DIC. For example, calcium carbonate precipitation can occur in highly eutrophic rivers (Abril et al., 2003), and this process causes fractionation of DIC (Emrich et al., 1970)."

Emrich, K., Ehhalt, D.H., and Vogel, J.C. Carbon isotope fractionation during the precipitation of calcium carbonate, Earth Planet. Sci. Lett., 8, 363–371, 1970. Kempe S. 1982. Long-term records of CO2 pressure fluctuations in fresh waters. SCOPE/UNEP Sonderband 52:91-332.

Reviewer comment: L 269: replace "carbonate dissolution" by carbonate rock weathering.

Author comment: We replaced "carbonate dissolution" with "carbonate rock weathering."

Reviewer comment: L 284: statement "pCO2 in rivers tends to decline downstream" is to some extent correct in temperate rivers with limited wetlands. It is not correct in tropical rivers where the presence of floodplains and wetlands in lowlands leads to increases in pCO2 downstream (Abril et al. 2014; Borges et al. 2015a;b).

Author comment: Originally, most of the data in our meta-analysis were from temperate rivers, which is why we stated that pCO2 in these rivers tends to decline downstream. The additional data we added to the meta-analysis were almost all from tropical rivers. Furthermore, with the addition of the new data, pCO2 is no longer included in the GAMM of δ13C-DIC. Therefore, we removed this statement during manuscript revision.

Reviewer comment: L 286: statement "tropical rivers typically have higher concentrations of CO2 (aq) than temperate rivers" is not entirely true (anymore). Since the Aufdenkampe paper several studies have shown that pCO2 is very variable in tropical rivers (e.g., Borges et al. 2015a), and values are frequently lower than the "tropical average" given by Aufdenkampe.

Author comment: We appreciate this new information on global patterns in CO2 (aq) concentrations in rivers. With the addition of the new data, pCO2 is no longer included in the GAMM of δ13C-DIC. Therefore, we removed this statement during manuscript revision.

Reviewer comment: L 301-303: this statement is incorrect. The two largest rivers in the world (Amazon and Congo) have extremely low carbonate alkalinity values. The carbonate alkalinity is strongly a function of latitude (that co-varies with lithology). Refer to classic work by Meybeck or Gaillardet.

Author comment: Originally, most of the data in our meta-analysis were from temperate rivers, in which carbonate alkalinity has been documented to increase with increasing river size (e.g., Telmer and Veizer 1999). The additional data we added to the meta-analysis were almost all from tropical rivers. Furthermore, with the addition of the new data, Strahler order is no longer included in the GAMM of δ13C-DIC. Therefore, we removed this statement during manuscript revision. In addition, we clarified that "Most tropical rivers are highly weathered and thus their waters tend to be more dilute in dissolved materials than temperate rivers (Gaillardet, 1997)."

Gaillerdet, J., Dupré, B., Allègre, C.J., and Négel, P. Chemical and physical denudation in the Amazon River Basin, Chem. Geol., 142, 141–173, 1997.

Telmer, K.H., and Veizer, J. Carbon fluxes, pCO2 and substrate weathering in a large northern river basin, Canada: carbon isotope perspectives, Chem. Geol., 159, 61–86, 1999.

Reviewer comment: L 310: This is not entirely true. While there's abundant organic carbon, black water rivers also have very low nutrient concentrations (N,P) that limit bacterial growth (Castillo et al. 2003) in addition to low pH and low O2 conditions that are not favorable to bacteria. What is important for delta 13C-DIC is that these rivers have very low HCO3- and most of the DIC is CO2.

Author comment: We revised this sentence and explained that "In blackwater rivers, alkalinity is extremely low and the DIC pool is mainly composed of biogenic CO2 derived from respiration in organic sediments and soils which has a low δ13C signature (Rau, 1978; Tan and Edmond, 1993)."

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Reviewer comment: L 336: Abril et al. (2014) showed that root respiration by living macrophytes also contributes directly to CO2 in the water. Regarding the importance of C4 inputs in tropical watersheds refer to Marwick et al. (2014).

Author comment: We added a sentence explaining that "The period of floodplain inundation is associated with heterotrophic respiration of organic matter and root respiration by living macrophytes (Richey et al., 1988; Langhans and Tockner, 2006; Abril et al., 2014) that lowers $\Delta\delta$13C-DIC and δ13C-DIC."

We revised the manuscript to focus on the importance of respiration of organic matter of terrestrial origin (rather than focusing on C4 grasses and C3 plants separately) to δ13C-DIC in tropical rivers. In doing so, we added a sentence stating that "Studies in tropical rivers have found that terrestrial plants contribute a large amount of material to both the inorganic and organic carbon pools (Mayorga et al., 2005; Marwick et al., 2014)."

Abril, G., Martinez, J.M., Artigas, L.F., Moreira-Turcq, P., Bernedetti, M.F., Vidal, L., Meziane, T., Kim, J.H., Bernardes, M.C., Savoye, N., Deborde, J., Souza, E.L., Albéric, P., Landim de Souza, M.F., and Roland, F. Amazon River carbon dioxide outgassing fuelled by wetlands, Nature, 505, 395–398, 2014.

Langhans, S.D., and Tockner, K. The role of timing, duration, and frequency of inundation in controlling leaf litter decomposition in a river-floodplain ecosystem (Tagliamento, northeastern Italy), Oecologia, 147, 501–9, 2006.

Marwick, T.R., Borges, A.V., Van Acker, K., Darchambeau, F., and Bouillon, S. Disproportionate contribution of riparian inputs to organic carbon pools in freshwater systems, Ecosystems, doi:1007/s10021-014-9772-6, 2014.

Richey, J.E., Devol, A.H., Wofsy, S.C., Victoria, R., and Ribeiro, M.N.G. Biogenic gases and the oxidation and reduction of carbon in the Amazon River and floodplain waters, Limnol. Oceanogr., 33, 551–561, 1988.

Reviewer comment: It could be useful to try to include wetland/floodplains into Figure 8.

Author comment: We also thought it would be interesting to classify each of the sites to reflect whether they were located on a floodplain. We previously considered using the following global inundation map to classify our sites using the mean annual maximum land surface inundation extent:

Fluet-Chouinard, E., Lehner, B., Rebelo, L.M., Papa, F., and Hamilton, S.K. Development of a global inundation map at high spatial resolution from topographic downscaling of coarse-scale remote sensing data, Remote Sens. Environ., 158, 348–361, 2015.

We contacted the first author for directions on how to download the map and she told us "A word of warning: GIEMS-D15 isn't accurate on the local scale and include various other types of inundated areas than simply floodplains. Depending on the geographical extent of your sampling sites it'll be important not to over-interpret the presence of GIEMS-D15-MAMax over your sites. I am currently working on a classified version of GIEMS-D15 that will separate major wetland categories, but that is still very much in the works."

We decided against classifying our sites using a map that is not accurate at the local scale and includes areas other than floodplains.

Reviewer comment: There are numerous studies that were missed in the data compilation that should be updated. A much more scrupulous search of literature is needed. Here's a list that came from the top of my mind: Abril et al. (2013), Balagizi et al. (2015), Borges et al. (2014), Brunet et al. (2009), Darling et al. (2016), Dubois et al. (2010), Polsenaere and Abril (2012), Teodoru et al. (2015)

Author comment: We appreciate the suggestion to add these papers to our meta-analysis. As indicated in the Methods section, we collated data from the scientific literature using the search engines Google Scholar and Web of Science and using the search terms “river”, “stable isotope”, and “dissolved inorganic carbon”. We did not find any of these papers during our search, however we should have been more explicit about the dates that were searched. We included the following sentence in the Methods section to be more explicit: "Papers included in our meta-analysis were published prior to the year 2016." We included Balagizi et al. (2015), Brunet et al. (2009), Dubois et al. (2010), and Teodoru et al. (2016) in our revised meta-analysis. We did not include Abril et al. (2013) or Borges et al. (2014) because Abril et al. (2013) sampled the Amazon estuary and Borges et al. (2014) sampled Lake Kivu, a large lake in East Africa, whereas our meta-analysis focused on rivers. Darling et al. (2016) is not yet published in the journal Hydrological Processes. According to the journal, the final edited and typeset version of record will appear in the future. Polsenare and Abril (2012) developed a model to predict CO2 degassing in small headwater streams using pCO2, DIC, and δ13C-DIC. The original data used to develop the model was published in: Polsenare, P., N. Savoye, H. Etcheber, M. Canton, D. Poirier, S. Bouillon, and G. Abril. 2013. Export and degassing of terrestrial carbon through watercourses draining a temperate podsolised catchment. Aquatic Sciences 75:299-319. Polsenare et al. (2013) did not provide information on pH, a key variable in our meta-analysis.

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