

# *Interactive comment on* "Old carbon contributes to aquatic emissions of carbon dioxide in the Amazon" by L. E. Vihermaa et al.

### L. E. Vihermaa et al.

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#### Referee 1

We thank the referee 1 for the appreciating the scope and the findings of the manuscript.

Referee 2 We are pleased that referee 2 agrees with the importance of our study and the significance of aquatic CO2 emissions in general. We thank the reviewer for helpful comments that improved the manuscript.

Responses to more detailed comments:

Comment 1 Ln 1 p.1775. I have problems with the wording "ecosystem-derived car-

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bon". I understand that the authors would like to exclude fossil carbon, but I do not think the wording ecosystem-derived does.

- We used the term "rapidly-cycled ecosystem-derived carbon" to describe the fraction of carbon dioxide efflux that previous studies concluded to be derived from recentlyfixed organic matter. Using "ecosystem-derived carbon" in conjunction with "rapidlycycled" excludes the older ecosystem-derived carbon pools that have longer turnover times, but we agree with the reviewer that old organic carbon deposits such as eg. kerogen, do exist and therefore the term "ecosystem-derived" alone would not be sufficient in describing these fractions. We suggest that the manuscript is not altered.

Comment 2 Ln 10-14 p. 1778. I am not familiar with this method and think it definitely needs to be better explained. The relationship between silicate weathering and 14C age of the C emitted CO2 is a major finding that is presented in figure 3. Due to that I find the method description very poor, and why is not Silica measured??? It is hard to redo a study but at least the method/assumptions used need much better support.

- We apologise for insufficient explanation. Since manuscript submission we have measured the Si concentrations and find that the systems with the oldest ages have the highest silica concentrations. However interpretation of a concentration alone as a measure of where weathered material is coming from is not simple as the concentration reflects the contemporaneous processes of uptake, production and hydrology (dilution; concentration by evaporation). Thus the approach that calculates the importance of different rock weathering to a catchment hydrochemistry can provide a clearer understanding as accommodates these within-stream controls. For these reasons we think geochemical studies (eg. Meybeck 1987, Gaillardet et al. 1999) use the major cations (Ca and Mg) or the major anion (bicarbonate) in river water to deduce the major lithology that is weathering in the catchment. Meybeck 1987 had studied catchments consisting of pure lithologies to derive the expected in stream concentrations for carbonate and silicate rock end members. These end-member concentrations can be used in a simple mass balance mixing model to estimate the relative contributions of the weathering of these rock types at a given study site. These end member studies do not seem to use silica in these calculations. The end members defined by Meybeck 1987 have been used in previous publications to define weathering contributions (eg. Polsenaere and Abril, 2012; Han Lu et al., 2014).

Comment 3 Ln 12 p.1779. It is said that the SIAR package was developed for stable isotope endmember analysis (in this case 13C) and then the authors just use it for radioactive isotopes (in this case 14C). This should be clarified. I am not familiar with the analysis tool but I assume also 14C data is suitable to use.

- The SIAR package or other end member mixing models can be used for a variety of data types. For example, electrical conductivity measurements could also be used in this type of analysis if two sources have different signatures. The model simply needs the concentrations for the sources and the resulting mixture to then estimate the relative contributions from the different sources. The advantage of SIAR package is that it uses Bayesian statistics and allows uncertainties in the source compositions to be included which is not common.

Comment 4 Ln22 p1779. Waldron et al., 2007 is not in the reference list.

- Waldron et al., 2007 added to the reference list

Comment 5 Ln 1 p. 1782. "reflect young", what is young and how can a 13C signature indicate the age. It is obviously of biogenic origin but could still be up \_10,000 years old even though these environments probably have a quicker cycling rate. Still think this need to be clarified though. - It is absolutely correct that 13C signature cannot indicate an age. The young in this sentence was referring to the 14C content mentioned in the earlier part of the sentence. Sentence revised to make this clearer.

Comment 6 Ln 15-20 p. 1784. Even though a change in C source could be expected with a rising water level in the stream/soil, the change in 13C signature with increasing water level could also be linked to a change in emission rate with subsequent fraction-

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#### ation.

- The degree of evasion that a parcel of water has been subjected to can certainly change the isotopic signature, and change in evasion intensity could cause temporal variation in the isotopic signature of the dissolved CO2 remaining in the water. However at high water level we would expect an increased rate of evasion due to faster and more turbulent flow. Increased evasion would then lead to more kinetic fractionation and a more 13C-enriched signature in the remaining dissolved CO2 (since 12CO2 will have been preferentially evaded); however we observed the contrary. Therefore we interpreted that more terrestrial C is present in the DIC pool as despite fractionation during evasion the signature remained depleted. The manuscript has been revised to include these points.

Comment 7 Discussion: This paper identifies a very important pathway for mobilized old carbon to be transferred to the atmosphere. The authors provide a complementing picture of the different C sources and processes in the Amazon Basin and make a valuable effort to integrate the finding of the manuscript within the existing literature on the Amazon Basin. In addition to justify the conclusions of the manuscript and even though the dataset it relatively small, I think the authors could expand the discussion a bit to also include comparison to other systems in a more global context. What are the likelihood for this old carbon contribution to be observed in other river systems and if it has already been observed or not? Is this to be expected for all areas with carbonate containing bedrock?

- To produce an overview of existing studies on CO2 evasion age (or dissolved CO2 and DIC as a predictor) and description of regions lacking information and potential for evasion of fossil carbon either due to carbonate deposits or other factors we suggest the following text to be added in the discussion (starting line 17 p 1787): Globally information on CO2 evasion age is still scarce. Ages exist from temperate (Billett et al., 2007; Garnett et al., 2012; 2013; Leith et al., 2014) and boreal (Billett et al., 2012) streams draining peatland and forest (Tittel et al., 2013), some with agricultural land

(McCallister and del Giorgio, 2012), North American rivers (Raymond et al., 2004; Zeng and Masiello, 2010) and streams (Han Lu et al., 2014). The studies vary in their methodologies from direct measurement of evasion CO2 to measurement of dissolved CO2 and DIC. The ages range from modern to  $\sim$ 2800 BP, but there is high spatial and temporal variability in the evasion age, which needs to be understood in detail to better understand the terrestrial-aquatic-atmospheric continuum. Furthermore data are lacking from many regions. There are large areas of carbonate lithology in Asia (Copard et al., 2007) with major rivers such as Changjiang, Xijiang, Mekong, Brahmaputra and Ganges characterised with carbonate weathering contributions higher than those found in the Amazon river (Gaillardet et al., 1999). Also some large European rivers (Seine, Rhone, Rhine and Po) have higher carbonate weathering inputs (Gaillardet et al., 1999), and here outgassing of aged carbon can be prevalent. Additionally, large deposits of organic-rich shales are found in the Himalayas (Copard et al., 2007). Old C may also come from the ecosystem more directly. For example, disturbed peat swamps in SE-Asia are exporting old DOM (Moore et al., 2013), which if respired may result in aged CO2 evasion. Clearly, to obtain a global understanding on the importance of slow carbon cycling in various ecosystems the age of C fuelling CO2 efflux has to be considered.

Comment 8 Figure 1: Why is the EC tower noted in the figure and mentioned in the caption? If not relevant for the study I suggest remove it. Please note the distance of the scale bar in the figure, not just in the caption.

- Mention of the flux tower removed from the caption and the diagram. The figure has been revised to include the scale bar length.

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Fig. 1.