

Interactive  
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## ***Interactive comment on “Organic matter sources, fluxes and greenhouse gas exchange in the Oubangui River (Congo River basin)” by S. Bouillon et al.***

### **Anonymous Referee #1**

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#### General comments

In the manuscript “Organic matter sources, fluxes and greenhouse gas exchange in the Oubangui River (Congo River basin)” Bouillon and colleagues present data from a one-year long, biweekly sampling of the Oubangui River, a tributary of the Congo River. The Oubangui River at the chosen sampling site (Bangui) is a large river with a pronounced annual discharge regime ranging in the thousands of m<sup>3</sup> s<sup>-1</sup> and draining a catchment of appr. 500.000 km<sup>2</sup> dominated by savannah vegetation. The data presented describe riverine carbon biogeochemistry: concentrations and d<sup>13</sup>C signatures of DOC, POC and DIC; pCO<sub>2</sub> derived from alkalinity and pH; a range of lignin deriva-

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Interactive Discussion

Discussion Paper

tives; gaseous CH<sub>4</sub> and N<sub>2</sub>O concentrations. The data are presented with great detail and almost always in relation to the hydrograph, which gives the manuscript a focus on seasonal succession and temporal evolution of these variables over the hydrological year. Interpretations are sound and extensive. The authors also use their temporally well-resolved data to compute annual average transport loads and downstream fluxes. The data presented in this manuscript are clearly a valuable contribution to our understanding of tropical rivers in the carbon cycle, especially given the limited research efforts so far undertaken in African rivers, and I can recommend this manuscript for publication given one major and some minor points of concern are addressed in a revision.

A major issue of critique concerns the computation of CO<sub>2</sub> evasion fluxes from pCO<sub>2</sub> and wind speed data. For this, the authors use an empirical relationship published by Raymond and Cole (2001), a paper focusing on estuaries (!) and pinpointing the problem of estimating water-atmosphere gas exchange (gas transfer velocity  $k$ ) for the computation of evasion fluxes. Given the high fluctuations of discharge reported for the Oubangui in the submitted manuscript (water depth changes by as much as 6 m!), the mere use of wind speed to estimate  $k$  seems really inappropriate as  $k$  is presumably heavily influenced by hydrology. E.g. Melching (1999) (Reaeration equations derived from US geological survey database. Journal of Environmental Engineering-Asce, 125, 407-414.) report a clear relationship of gas exchange efficiency with discharge. The approach chosen by Bouillon et al uses an almost constant  $k$  (as wind speed does not change much over the sampling year) and makes CO<sub>2</sub> evasion a simple function of pCO<sub>2</sub>. Though certainly the difficulties associated with properly estimating  $k$  in a large river as the Oubangui are substantial, such an approach can only produce very inaccurate estimates and as such may do more harm than good to our current efforts of understanding riverine contributions to the carbon cycle. I strongly advise to either drop the computed CO<sub>2</sub> evasion fluxes completely or at least strongly highlight their inaccuracy and give them less prominent space in the manuscript (including the title). Also, acknowledging discharge effects on gas exchange could actually greatly help

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Interactive  
Comment

to explain the observed seasonal changes of pCO<sub>2</sub>. Alkalinity, pH and pCO<sub>2</sub> indeed show pronounced variations with the hydrograph without the hysteresis effects shown for other variables (e.g. DOC, POC). This suggests a hydrological control by discharge on these variables, in agreement with lower exchange efficiency at higher discharge. Seasonal patterns of δ<sup>13</sup>C of DIC and N<sub>2</sub>O can also be reinterpreted in this light.

Minor points of critique include the used mixing models (whose mechanics are unclear to me), a probably overinterpreted hysteresis effect for DOC (which should be reported with greater caution), issues with the postulated role of phytoplankton during low discharge, and some structural improvements applicable to the order of topical text sections and figures. See below for specific comments and suggestions. The manuscript is relatively long and could benefit a lot from more economic word use. Some passages are clearly redundant. I find the text lengthy and surprisingly difficult to read given the clear and simple data situation. Readability can most probably be improved by a cleaner order of arguments and graphs, and less “hard” data numbers interwoven into the text. References given in the text but missing in the bibliography are a nuisance.

## Specific comments

**Abstract:** The abstract generally suffers from poor structure and readability. There are too many numbers/results and main findings are poorly connected. Tell seasonal changes first. Then oppose the low and high discharge phases, followed by variables showing a hysteresis effect. Offer an explanation for the hysteresis effect and an interpretation of the lignin data. Move the annual flux estimates to the end. Page 65, line 5: “starting” instead of “since” Line 12: What are “elements”? Maybe better “measures” or “variables”? Line 14–20: Immediately, the reader wonders: . . . And what is the situation during high flow like? Line 23: The lignin data shows marked differences between discharge states. . . and what? Interpretation? Implications?

Page 68, line 7: reword “parameters and analyses have been examined” Line 9: see

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Interactive  
Comment

general comments above, not sure as to how much “gas exchange with the atmosphere” was actually investigated!? Line 19ff: With regard to catchment characteristics it would be interesting to learn about how much human influence can be expected, the amount of settlements in the catchments, agriculture, the degree of disturbance, etc. The very last sentence of the paper refers to the catchment as “pristine”. For how much of the catchment is this actually true? Line 21: delete “the” before “Bangui”.

Page 70, line 8: exact meaning of “air-dried”? Line 14: No data for oxygen isotopes are presented anywhere. Line 18ff: Frankignoulle and Borges 2001 are not in the bibliography. If this is Aquatic Geochemistry, 7, 267-273, then I do not find any thermodynamic constants there, only a lot of other references. Greater detail would be appreciated. The given accuracy is enormous and hard to believe, how was it evaluated? Usually, very small pH changes can already affect pCO<sub>2</sub> to a much greater extent. The data for the Oubangui would also be very valid and valuable with a greater measurement error... Line 23: Source for the atmospheric pCO<sub>2</sub> value? Line 25: Raymond and Cole 2001 are not in the bibliography. Given that k estimated by wind speed is a really coarse approach, I would at least try to report some sort of a bracket estimate.

Page 72, line 1ff: how much “filtered water”? With regard to lignin, it would be helpful to give some information about how the various lignin fractions and ratios can be interpreted, BEFORE the results are presented. The discussion section has a paragraph on this, which could be transferred here as a whole almost. Line 25: move “excellently” before “matched”.

Page 73, line 19ff: TSM and POC show a “clear” hysteresis. Could this be shown in an appropriate plot similar to Fig. 8? Does this also apply to %POC? With regard to %POC, I actually expected at least a graph in the Supplement, but there is only raw data. If the strong seasonal variation of %POC is mentioned in the text, it would be nice to show it somewhere.

Page 74, line 5, Figure 8B: I actually find the hysteresis of DOC not at all so “clear”, it

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is based on only 4 data points! Greater caution would probably be applicable. What is the error associated with DOC measurements? Any chance for coinciding shipping dates for samples to explain the mysterious DOC drop right at the center of the peak flow?

Discussion: I suggest restructuring the discussion section: (1) Start with seasonal patterns of TSM, POC and DOC following the hydrograph, (2) interpret with regard to POC and DOC origin, (3) upscale to annual downstream fluxes, (4) greenhouse gases.

Page 76: line 13ff: Part of this paragraph is fully redundant with the methods section, and another obvious part should be moved to the results section.

Page 77, line 24: “thus”? What is the logical linkage between the previous and this sentence?

Page 78, line 11: Put “87.5%” and not the misleading “~88%” Line 18: The “riverine C fluxes” are only the downstream export fluxes, here! Line 23: If so “striking” (there is a whole paragraph devoted to this here) why is this data only presented in the Supplement as raw data? Line 27: “and” or “and/or” instead of “or”?

Page 79, line 2-3: “due to the dominance of...river systems” – I do not understand how this can be understood as an argument for validity on a global scale. Line 10: are these C:N ratios molar or mass-based? Line 18: “some” values are actually only TWO values! Line 20ff: I do not understand how this can be taken as supporting the phytoplankton argument! Why would phytoplankton contribution be so much more variable?

Page 80, line 5: end member is 28.5 permil then? Line 13: Perhaps you should make clear that more “distant” means more grasses? Line 1-13: Maybe just a line of thought: I wonder if phytobenthos eroded from smaller streams during onset of the flooding season could be an important part of POC during the rising part of the hydrograph. Line 28: “predominant” instead of “predominantly”. Line 29: Is this the two-component

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mixing model shown in Fig 9? How is this model set up and computed?

Page 81, line 11-12: “These” instead of “The latter” Line 20: I see this mysterious sharp backfall of DOC occurring almost right at the center of the hydrograph rather than at the end of the peak flow. Line 22: The mixing model mechanics are unclear to me. What are the end-members? Line 23-25: From the information given it is not clear to me why a 3-source model would be insufficient. Line 26-28: With regard to “variability over time” – Isn’t this what the flushing actually is? Variable over time? DOC builds up in top soil layer “reservoirs” during dry periods, then gets flushed out and later stormflow finds less DOC to flush out of the soil (e.g. Boyer 1996)?

Page 82, line 4-18: consider moving to the methods section to allow the lignin-illiterate reader to actually understand the results before having it made through the discussion. Line 11: move “respectively” to end of sentence. Line 15: I don’t understand “in the absence of phase changes that can cause fractionation issues”. Line 20-23: To use Q and DOC thresholds to exchangeably define states or phases is slightly misleading with regard to the postulated “clear” hysteresis of DOC over the hydrograph.

Page 83, line 4: “much higher” is a little exaggerated. . . I find the mixing curves captures the data not too bad. . .

Page 84, line 1-10: Partly redundant to introduction. Line 23 ff: The strong linkage to hydrological conditions without hysteresis effects really points towards effects of in-river (!) hydrology on gas exchange! On the one hand, this offers an opportunity for interpretation of seasonal patterns of pCO<sub>2</sub> (which are poorly explained so far). On the other hand, however, it seriously compromises the undertaken efforts to compute evasion fluxes!

Page 85, line 2: “sometimes” is in fact “twice”! Line 4: Don’t use “significant” unless with a statistical meaning. I find this sentence formulated in a slightly exaggerated way. Line 15: Carbonates come at what d<sup>13</sup>C signature? Line 5-20: The d<sup>13</sup>C of DIC data can eventually also be reinterpreted in the light of hydrological effects on gas

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exchange. Limited gas exchange at higher discharge can be expected to also prevent isotopic equilibration with the atmosphere, thus causing lower  $d_{13}C$  signatures of DIC. This effect probably just adds to the CO<sub>2</sub>-evasion effect following Doctor et al. (2008).

Page 86, line 4: or outgassing that has already happened and leaves an imprint? And/or gas exchange and atmospheric equilibration, which happen more efficiently at low Q? Line 11: “rivers” instead of “reivers” Line 27 ff: With regard to N<sub>2</sub>O, the concentrations vs. the hydrograph also point towards a limitation of gas exchange effects at higher discharge. Also here this could help to explain the seasonal patterns.

Page 87, line 8-9: which numbers of this range for the N<sub>2</sub>O flux come from which reference? Line 11 ff: The discussion of CO<sub>2</sub> equivalents for N<sub>2</sub>O AND CH<sub>4</sub> in comparison to CO<sub>2</sub> should not be part of the N<sub>2</sub>O-paragraph. Consider moving it to the end. Instead link the next paragraph with NO<sub>3</sub>-effects to the N<sub>2</sub>O paragraph.

Figures: Set up a figure order which parallels the presentation of data in the text. While reading, I found myself repeatedly switching back and forth between the graphs with the hydrograph timeline and superimposed variables, and the graphs showing the hysteresis effects. Consider combining them in a single graph with multiple panels (e.g. for TSM, POC, DOC, probably also %POC). Give legend information (which symbol or line shows what) consistently (!) either in the graph as a graphical legend OR in the text legend below.

Figure 3: Is each point a single sample? Any idea about the associated measurement error?

Figure 4 and 6: “dotted line” instead of “dotted lines”, or put “discharge” in graphic legend.

Figure 5: Add symbols for TA and pCO<sub>2</sub> as graphic legend similar to other figures.

Figure 9: should be one of the last figures, it is only referenced to in the discussion section.

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Figure 11: It seems the correlation is relevant here. Why the rising and falling stage arrows?

End of review.

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