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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.

S. Bouillon et al.

steven.bouillon@ees.kuleuven.be

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REF: In the manuscript “Organic matter sources, fluxes and greenhouse gas exchange in the Oubangui River (Congo River basin)” [. . .] I can recommend this manuscript for publication given one major and some minor points of concern are addressed in a revision. REPLY: Thanks for the constructive feedback and detailed comments.

REF: A major issue of critique concerns the computation of CO₂ evasion fluxes from pCO₂ 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

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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 CO₂ evasion a simple function of pCO₂. 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 CO₂ evasion fluxes completely or at least strongly highlight their inaccuracy and give them less prominent space in the manuscript (including the title).

REPLY: Raymond and Cole (2001) is based on a compilation of data in rivers and estuaries and provides estimates of K that are based on a parameterisation based on wind speed. Hence, this approach indeed supposes that wind is the main generator of turbulence in rivers. However, it is well established that turbulence in rivers proportional to current speed (flow) and inversely proportional to depth (Alin et al. 2011; Butman & Raymond 2011). These quantities are linked by slope, and in general small streams are much more turbulent than large rivers (Alin et al. 2011; Butman & Raymond 2011). To accommodate this comment, we have now also computed the fluxes using a gas transfer parameterization based on depth and water current that was developed for rivers and streams (O'Connor and Dobbins 1958), an approach that has been verified independently by field data in tidal rivers by Zappa et al. (2003) and Borges et al. (2004). Water current and river depth was recomputed from discharge data, based on relationships established from data reported by Olivry (1989). Average river depth ranged between 3.5 and 8.7 m, and surface flow rates between 0.09 and 0.98 m s⁻¹. The corresponding k values ranged between 2.82 and 5.78 cm/h – obviously increas-

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ing with river discharge. Overall, the resulting annual CO₂ estimate was ~2-fold that of our initial approach (Raymond & Cole 2001). We would strongly prefer to keep these flux estimates in the manuscript, but will adequately describe both approaches.

Reference: Olivry JC (ed.) Opération Grands Bassins Fluviaux : premiers résultats, années 1987 à 1989. Note d'information n°3, septembre 1989. Montpellier : ORSTOM, 1989, 124 p.

REF: Also, acknowledging discharge effects on gas exchange could actually greatly help to explain the observed seasonal changes of pCO₂. Alkalinity, pH and pCO₂ 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 $\delta^{13}\text{C}$ of DIC and N₂O can also be reinterpreted in this light. REPLY: Although less pronounced than for some other parameters, our Figure 8A does show that TA also exhibits hysteresis. Moreover, the hydrological control on TA does not imply that pCO₂ values are strongly influenced by residence time – outgassing does not affect TA values.

REF: 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. REPLY: These are dealt with in more detail in subsequent separate comments and replies.

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REF: 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. REPLY: We have restructured the abstract.

REF: Page 65, line 5: “starting” instead of “since” REPLY: corrected.

REF: Line 12: What are “elements”? Maybe better “measures” or “variables”? REPLY: “elements” seems correct to us, refer to different chemical elements or their speciation (POC, DOC, PN, . . .)

REF: Line 14-20: Immediately, the reader wonders: . . . And what is the situation during high flow like? REPLY: we have restructured and rewritten the abstract.

REF: Line 23: The lignin data shows marked differences between discharge states. . . and what? Interpretation? Implications? REPLY: we have restructured and tried to clarify the abstract.

REF: Page 68, line 7: reword “parameters and analyses have been examined” REPLY: this was rephrased.

REF: Line 9: see general comments above, not sure as to how much “gas exchange with the atmosphere” was actually investigated!? REPLY: We have added a 2nd approach to estimate gas exchange, and feel this adequately answers this comment. As outlined elsewhere, we do not agree with the hypothesis that seasonality in pCO₂ would be mainly due to differences in water residence time and set by prior degassing.

REF: 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

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this actually true? REPLY: We have added the following in the catchment description: Although we did not find land-use data specifically for the Oubangui catchment, deforestation rates in the Central African Republic are reported to be among the lowest in Africa (net deforestation of 0.06 % y⁻¹, Duveiller et al. 2008). According to FAO statistics (<http://faostat.fao.org/>), agricultural land use has increased only 8% in the last 4 decades, and makes for ~8 % of the total land area. Considering a national population density of ~7 inhabitants km⁻², these figures support classifying the Oubangui catchment as relatively pristine.

REF: Line 21: delete “the” before “Bangui”. REPLY: OK, done.

REF: Page 70, line 8: exact meaning of “air-dried”? REPLY: = simply dried, no oven used. Changed to “dried in ambient air”.

REF: Line 14: No data for oxygen isotopes are presented anywhere. REPLY: Correct, this has been deleted. There are a wide range of additional parameters measured apart from those discussed in this manuscript, the d18O-H₂O data will be used in another context.

REF: 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 pCO₂ to a much greater extent. The data for the Oubangui would also be very valid and valuable with a greater measurement error. REPLY: Information on thermodynamic constants has been updated. Regarding the estimated accuracy for DIC and pCO₂, we have added the following: “Using an estimated error for pH measurements of ± 0.01 pH units, ± 2 μM for TA data, and ± 0.1°C for temperature measurements, the propagated error is ± 1% for DIC, and ± 3% for pCO₂.”

REF: Line 23: Source for the atmospheric pCO₂ value? REPLY: The following information has been added – we now included measured values from Mt Kenya rather

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than a fixed value, although the differences are obviously minor so do not considerably influence our CO₂ exchange estimates: “Atmospheric pCO₂ from Mount Kenya (Kenya, -0.05°N 37.80°E) were retrieved GLOBALVIEW-CO₂ data-base (Cycle Greenhouse Gases Group of the National Oceanic and Atmospheric Administration, Earth System Research Laboratory). Atmospheric pCO₂ was converted from dry air to wet air using the water vapour algorithm given by Weiss and Price (1980).”

REF: 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. REPLY: Sorry, reference has been added. As discussed elsewhere, we have added an additional approach to estimate CO₂ exchange.

REF: Page 72, line 1ff: how much “filtered water”? REPLY: Typically 250 mL, this information has been added.

REF: 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. REPLY: Yes, a section on what the lignin composition can learn us has been moved to the introduction.

REF: Line 25: move “excellently” before “matched”. REPLY: OK.

REF: 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. REPLY: Yes, we have added an additional Figure 8 to show the hysteresis in TSM (the pattern being similar for POC), and the relationship between discharge and %POC.

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

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“clear”, it 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? REPLY: We don't really agree on this point – we find our data to clearly indicate hysteresis, and the fact that this fits well with earlier data by Coynel et al. (2005) reinforces this. Please also see Figure 5C in Coynel et al. (2005). Repeatability for DOC analyses is always better than 10%, usually within 5%. The drop in DOC concentrations does not match with sample shipment or pickup dates.

REF: 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. REPLY: We prefer to start with estimates of downstream fluxes as in the original version. In line with the suggestion of Ref#2, however, we have included an introductory paragraph recapturing the aims of the study and outlining the structure of the discussion, which we hope will help.

REF: 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. REPLY: OK – we have removed the redundancy and have introduced part of this section into the Results.

REF: Page 77, line 24: “thus”? What is the logical linkage between the previous and this sentence? REPLY: Not with previous sentence, but with the one before that. Still, we have removed it.

REF: Page 78, line 11: Put “87.5%” and not the misleading “_88%” REPLY: Done.

REF: Line 18: The “riverine C fluxes” are only the downstream export fluxes, here! REPLY: Yes.

REF: Line 23: If so “striking” (there is a whole paragraph devoted to this here) why is

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this data only presented in the Supplement as raw data? REPLY: A new Figure has been added.

REF: Line 27: “and” or “and/or” instead of “or”? REPLY: I prefer “or” since we’re listing two contrasting explanations, only one of them can be valid for a given system.

REF: 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.

REPLY: OK, this was perhaps not properly expressed. The point we wanted to make is that on a global level, POC in the majority of rivers is likely to be dominated by terrestrial material, whereby in situ production makes no substantial contribution and cannot be invoked to explain the global pattern in TSM vs. %POC. Thus, for the majority of data on a global level, the observed pattern can be explained by different contributions of litter/topsoil versus deeper (C-poor) soil layers. We have rephrased this in the revised version.

REF: Line 10: are these C:N ratios molar or mass-based? REPLY: They are mass-based – this was specified in the Results where POC/PN ratios are mentioned for the first time but now also in Table 1.

REF: Line 18: “some” values are actually only TWO values! REPLY: True – but still, this implies that the lower pCO₂ values are not solely due to a long residence time but that phytoplankton production is involved as this is the only plausible process in this system which can lower pCO₂ to values below saturation.

REF: 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?

REPLY: For POC dominated by terrestrial material, we expect short-term variations in δ¹³C signatures to be limited as it integrates POC delivered from a huge catchment area. However, short-term variations in δ¹³C_{POC} values are likely to occur when varying contributions of phytoplankton and/or short-term changes in their δ¹³C signatures occur, e.g. due to variations in growth rate or δ¹³C_{DIC}. This is mentioned in the original

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ms.

REF: Page 80, line 5: end member is 28.5 permil then? REPLY: No: we used both -28 and -29 ‰ to estimate this contribution – this translates into the range of estimated C4 contributions of 12-18 %. We will make this more explicit in the revised version.

REF: Line 13: Perhaps you should make clear that more “distant” means more grasses? REPLY: Yes- we’ve made this more explicit.

REF: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. REPLY: Good suggestion, but difficult to comment on this – there are no data on phytobenthos abundance.

REF: Line 28: “predominant” instead of “predominantly”. REPLY: Corrected.

REF: Line 29: Is this the two-component mixing model shown in Fig 9? How is this model set up and computed? REPLY: We have provided more details on the model in the revised version.

REF: Page 81, line 11-12: “These” instead of “The latter” REPLY: This has been replaced.

REF: 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. REPLY: This has been modified.

REF: Line 22: The mixing model mechanics are unclear to me. What are the end-members? REPLY: We have added end-member values in the section describing the lignin mixing curves, and refer to these here.

REF: Line 23-25: From the information given it is not clear to me why a 3-source model would be insufficient. REPLY: If we look at Figure 9, and would add a third end-member (e.g. either a low DOC, low d13C-DOC one for the falling stage, or an intermediate

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DOC, high d13C-DOC one to cover the rising stage), we would still end up in each case with a ‘curved’ triangular area where some of the data always fall outside.

REF: 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)?
REPLY: Yes, correct. The Boyer (1996) flushing principle assumes that DOC concentrations in the lower soil layer is constant, but variable over time in the upper layer. We have mentioned this in the revised version.

REF: 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.
REPLY: Good suggestion – we have moved this to higher up in the ms (introduction).

REF: Line 11: move “respectively” to end of sentence.
REPLY: this has been moved.

REF: Line 15: I don’t understand “in the absence of phase changes that can cause fractionation issues”.
REPLY: We have rephrased this.

REF: 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.
REPLY: We tried to consistently use a distinction between low and high discharge periods; but these obviously still correspond to low and high DOC concentrations.

REF: Page 83, line 4: “much higher” is a little exaggerated. . . I find the mixing curves captures the data not too bad.
REPLY: For these samples, the mixing model predicts 0.47-0.50 but measured values are 0.64 to 0.79.

REF: Page 84, line 1-10: Partly redundant to introduction.
REPLY: We have shortened this paragraph.

REF: Line 23 ff: The strong linkage to hydrological conditions without hysteresis effects

really points towards effects of inriver (!) hydrology on gas exchange! On the one hand, this offers an opportunity for interpretation of seasonal patterns of pCO₂ (which are poorly explained so far). On the other hand, however, it seriously compromises the undertaken efforts to compute evasion fluxes! REPLY: We do not agree with this line of thought, even if it is tempting at first sight. For example, variations in d13C-DIC and pCO₂ closely follow those of TA which is not expected to be influenced by outgassing or photosynthesis; therefore we propose different contributions of source waters (with different sources of inorganic C, different TA and pCO₂) and in situ biological processes to be the main drivers of variations in pCO₂, TA, and d13C-DIC.

REF: Page 85, line 2: “sometimes” is in fact “twice”! REPLY: Yes – but we still feel this is worth mentioning explicitly. Was replaced with “occasionally”.

REF: Line 4: Don't use “significant” unless with a statistical meaning. I find this sentence formulated in a slightly exaggerated way. REPLY: this was replaced with “substantial”

REF: Line 15: Carbonates come at what d13C signature? REPLY: We assume these to be around 0 ‰ was added to the text.

REF: Line 5-20: The d13C of DIC data can eventually also be reinterpreted in the light of hydrological effects on gas exchange. Limited gas exchange at higher discharge can be expected to also prevent isotopic equilibration with the atmosphere, thus causing lower d13C signatures of DIC. This effect probably just adds to the CO₂-evasion effect following Doctor et al. (2008). REPLY: While we do not exclude this process from playing a role, we do not feel our data should necessarily be interpreted in this context. We argue that different sources of DIC rather than outgassing are responsible for the seasonality in d13C-DIC – given that their variations follow those of TA which is not influenced by outgassing.

REF: 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

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low Q? REPLY: See similar comments – we do not see any evidence for this.

REF: Line 11: “rivers” instead of “reivers” REPLY: This has been corrected.

REF: Line 27 ff: With regard to N₂O, 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. REPLY: We do not see any strong evidence for this, as for CO₂ and CH₄ (the latter shows a pattern inconsistent with this hypothesis).

REF: Page 87, line 8-9: which numbers of this range for the N₂O flux come from which reference? REPLY: The reported range is for tropical rivers, from Guérin et al. (2008, their Table 3). This is now specified.

REF: Line 11 ff: The discussion of CO₂ equivalents for N₂O AND CH₄ in comparison to CO₂ should not be part of the N₂O-paragraph. Consider moving it to the end. Instead link the next paragraph with NO₃-effects to the N₂O paragraph. REPLY: This was moved to the end of the paragraph as suggested.

REF: 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. REPLY: 2 new Figures were added and we have organised them to be consistent with their first mentioning in the text.

REF: Figure 3: Is each point a single sample? Any idea about the associated measurement error? REPLY: Yes, each point is a single sample. We have not systematically analysed replicates to check the overall error – which will be a combination of sampling/handling + analytical errors.

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

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legend. REPLY: This has been corrected.

REF: Figure 5: Add symbols for TA and pCO₂ as graphic legend similar to other figures.

REPLY: These have been added as a legend.

REF: Figure 9: should be one of the last figures, it is only referenced to in the discussion section. REPLY: With an extra Figure added, we have changed the numbering of the Figures and positioned them according to first occurrence in the text.

REF: Figure 11: It seems the correlation is relevant here. Why the rising and falling stage arrows? REPLY: We added the arrows just to be consistent with other Figures and to allow the reader to follow the data throughout the hydrograph.

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