

## ***Interactive comment on “Storm pulses of particulate and dissolved organic carbon in a forested headwater stream and their environmental implications – importance of extreme rainfall events” by B.-J. Jung et al.***

**B.-J. Jung et al.**

jhp@ewha.ac.kr

Received and published: 5 August 2014

Many of the comments offered by three reviewers are overlapped, so author responses are combined here and revisions are also indicated with references to the revised manuscript.

### 1. Summary of the major changes in the revision

We appreciate constructive comments offered by three reviewers and have thoroughly revised the manuscript to address major concerns raised by the reviewers. Three major

C4086

changes are summarized below and responses to all review comments are detailed in the following sections. All changes made in the revised manuscript have been marked by a blue color in the text.

First, the primary focus has been placed on ecological and environmental implications of storm-enhanced export of DOC and POC, namely potentials of DOC and POC for biodegradation and disinfection-byproduct formation, with commensurate changes in the title and manuscript structures (particularly Discussion). As all three reviewers commonly commented, storm pulses of POC have received much less attention than DOC export. In the revised manuscript, we wanted to go one step further and placed more emphasis on the implications of the storm-enhanced export of DOC and POC, because differential storm responses of DOC and POC have already been addressed in our previous publications (Jeong et al., 2012; Jung et al., 2012) and other studies (e.g., Dhillon and Inamdar, 2013).

Second, we used only “direct” measurements of DOC and POC concentrations to build more robust relationships between hydroclimatic variables and organic C concentrations or fluxes (Fig. 2). Although we are still confident in using optical measurements of TOC with careful correction measures as described in our Author Comment (AC C2793), optical measurements are not used any more in this revision to incorporate the suggestions of Reviewer 1 and 2. The newly established relationships in Fig. 2 were described by best-fit regressions. Although these relationships are now based on a smaller number of storm events (13 instead of 50), our message (importance of extreme storm events for storm-enhanced export of POC) remains unaltered. Please keep in mind that the primary objective of this manuscript is not simply to depict these relationships but to explore the implications of storm-enhanced export of organic C in headwater streams, particularly during extreme storm events.

Third, Table 1 (summary of regression equations) has been replaced by a new table summarizing characteristics of analyzed storm events and Fig. 4 (Q-C plots) has been removed to incorporate reviewer comments.

C4087

## 2. Responses to the Reviewer 1's comments

The manuscript of Byung-Joon Jung and colleagues addresses the question if exports of particulate organic carbon (POC) contribute substantially to total organic carbon exports in headwaters during stormflow events. This is a relevant topic, as compared to dissolved organic carbon (DOC), POC exports are not adequately considered in many carbon flux and budget calculations.

However, I have concerns with respect to the optical method used to measure the POC concentrations. POC is derived here from the difference between total organic carbon (TOC) and DOC. Both, DOC and TOC were measured in situ by light attenuation. While DOC can be monitored fairly well by UV absorption ( $R_2$  typically around 0.75, 0.84 in Jeong et al. 2012 as cited in the manuscript), optical TOC estimates include high uncertainties. First, there is large variation in the relationship between (VIS) light attenuation and particulate matter quantity depending on e.g. particle size or surface quality. Secondly, suspended particulate matter consists not only of organic carbon (POC) but also of mineral fractions. Changing concentrations of minerals between events seriously affect TOC estimates and therefore calculated POC values. DOC and POC concentrations were calculated and corrected here on the basis of water samples analyzed in Jeong et al. 2012 (p. 6882 lines 22-26, Jeong et al. 2012, G03013 p. 4). However, the present study obviously includes a much higher number of events (6888 line 19 – p. 6889 line 2) exhibiting “large magnitudes and variations in POC” (p. 6889 line 3). Because of the uncertainties associated with optical measurements I am not confident if empirical validations of the method in Jeong et al. 2012 can be extrapolated to the larger dataset of this study. Different events potentially mobilize POC and DOC of different quality and composition from soil layers or aquatic sediments of a catchment. Heavy rainfall can increase soil erosion and can change the contribution of mineral soil particles to suspended particulate matter. In conclusion, the uncertainties in POC values appear too high. A direct measurement of POC after filtration is strongly recommended.

C4088

Response: Aforementioned, only direct measurements are used in this revision.

Further comments p. 6878 lines 2 and 3. It was not immediately clear to me how “erosion-related sinks of CO<sub>2</sub>” and “biodegradation of recalcitrant organic materials” is related to the issue of this work (POC and DOC export). I suggest starting with the importance of extreme events or of extreme monsoon rainfalls for matter transport on a regional/global (?) scale.

Response: The sentence was rewritten to emphasize ‘the importance of extreme rainfall events for organic carbon export to inland waters’ (Page 1, Lines 17-18).

p. 6878 lines 12 and 13. The Abstract does not contain the information that POC and DOC were not measured directly but derived from optical measurements.

Response: Now we have only ‘direct’ measurements.

p. 6878 lines 25 and 26. This sounds a bit like an exaggeration to set up the conclusions. It is now generally accepted that rivers are not passive conduits. Please see also p. 6881 lines 13-14.

Response: Yes, it is now generally accepted that rivers are not passive conduits. However, some studies have suggested that rivers in monsoon Asia passively transport POC exported during monsoon rainfall events (e.g., Galy et al., 2007; Goldsmith et al., 2008). This regional difference has clearly been indicated in the second part (P 4, L 11-12). The part in the abstract was removed to enhance readability.

p. 6879 line 14. Why “contrasts”? Both, dynamic transformation and high C sequestration can occur.

Response: The sentence now starts with a different phrase “Other studies have suggested...” (P 2, L 24).

p. 6880 line 13. Please insert “in” situ.

Response: Thanks, “in” has been inserted (P 3, L 15).

C4089

p. 6882 line 6. This study included data “from 2008 through 2011”. In Jeong et al. 2012, data from May 2008 until January 2011 from the same catchment were analyzed. The authors should explain in the Methods which data were already published.

Response: In this manuscript (Fig. 2) we use original data of DOC and POC concentrations from 8 events that were published elsewhere to calculate event mean concentrations and fluxes and this is noted in Table 1.

p. 6882 line 11. Although published in Jeong et al. 2012, I found the phrase “in-stream C analyzer” not applicable for a device measuring light absorption.

Response: Optical measurements are not used any more in the revision.

p. 6884 lines 6-10. Were filter blanks processed without suspended solids?

Response: Yes. This is now indicated in P 6, L 10-11.

p. 6885 line 1. Please consider “The” inoculum...

Response: “The” has been inserted in P 6, L 31.

p. 6886 line 9 and Fig. 2. Except C export vs. rainfall, there seems to be no statistical relationships above the threshold value of 100 mm precipitation.

Response: This sentence is not used anymore, because we now have a new data set.

p. 6886 lines 17-19. “Above the threshold precipitation ... POC concentrations and fluxes increased drastically...” Can you exclude that this important observation was based on nonlinear light attenuation relationships with increased turbidity (internal filter effects), instrument settings and corrections? Was it supported by conventional POC measurements?

Response: Yes, our new data set corroborates the same pattern.

p. 6887 line 16. Please consider Fig. 5 instead of Fig. 4?

Response: The wrong reference was replaced by the correct one (P 8, L 31-32).

C4090

p. 6887. I found parts of the manuscript difficult to read. Some sentences contained too much information (e.g. p. 6887 lines 22-25).

Response: The whole manuscript has thoroughly been revised for clarity. The specified sentence was split and then rewritten to enhance readability (P 9, L 7-11).

p. 6888 line 19. The start of the Discussion typically summarizes the most important findings. Here it starts with “The result ... expands our previous results obtained from a smaller number of storm events...” I suggest rewriting the paragraph to indicate that this study represents a valuable contribution.

Response: Thanks for the suggestion! The starting sentence was revised to indicate the contribution of major findings (P 10, L 3-8).

p. 6891 line 13-15. “...aged humic materials...”. Is the meaning of ‘aged’ old (i.e. analyzed by radiocarbon) or refractory and less available?

Response: The meaning was clarified (old humic materials that are enriched in  $^{13}\text{C}$ ) in P 12, L 22-23.

p. 6901 Table 1. This table can be omitted. R2 and P were already included into Fig. 2. The regressions itself appear questionable (please see above). I would prefer a table characterizing the rainfall events and other hydrological situations, which were sampled. This can include information, which data were already published in Jeong et al. 2012 (please see above).

Response: As the reviewer suggested, Table 1 was omitted and R2 and P values were included in Fig. 2. A new table was included to summarize rainfall events.

### 3. Responses to the reviewer 2's comments

This manuscript covers an interesting and important topic, namely POC fluxes, in catchments. Thus, it is highly relevant to the scientific community and suitable for publication in Biogeosciences. So far, there is only few studies available providing datasets

C4091

of POC fluxes along with parallel DOC fluxes, to allow for comparison and interpretation of the relevance of both of these fluxes. Generally, the manuscript is well written, although the structure in general may need some improvements according to my point of view (see below). My major concerns about the study that I wish the authors to comment on are the following:

Comment: Regarding the title I expected detailed analysis of DOC and POC exports during flow events, along with high frequency data. As the title states that the manuscript will report on the environmental implications, I expected a detailed discussion about the relevance of DOC and POC fluxes in comparison, under high flow and low flow conditions. However, in the manuscript the environmental implications are DOC production from POC and, even further, the production of disinfection by-products by POC and DOC. From my point of view, these last points go well beyond what the title would make the reader expect. It broadens the discussion of the manuscript very much, which limits the space of a thorough discussion and interpretation of the POC and DOC fluxes themselves. This is already reflected in the results section, where the section about the fluxes is about 13.5 lines of text (one paragraph only), while the disinfection by-product formation makes up one page of the results section (although based on the title this is only one side aspect).

Response: We appreciate the reviewer's comment on the title and main theme of the manuscript. The reason we opted for the quite comprehensive title was simply because we wanted to add up the new aspect of storm pulses of POC, namely biodegradation and DBP formation potential. As the reviewer 3 commented, recent reports including our papers have already addressed the issue of storm-induced surges of POC export exceeding the otherwise dominant DOC export. With a back-up of our four-year monitoring results, we wanted to emphasize the importance of extreme storm events in providing labile organic components that can either biodegrade or contribute to forming DBPs upon chlorination. In this context, we have revised the title and related discussion parts to make clear study objectives and the implications of major findings.

C4092

As a second point, I want to mention, as already mentioned by another reviewer, that I find the calculation of the POC fluxes a bit problematic. Firstly, as the calculations of DOC and POC are essential for the manuscript, I think it is not enough to just say that the concentrations were calculated according to an already published manuscript, without giving any short summary about how this was done. This implies that in this manuscript there was a very sophisticated method applied that cannot be presented here due to space limitations. However, when looking up in the reference, the calculation is just based on a simple regression equation. Moreover, the regression becomes noisy and inexact at high concentrations of 20-40 mg /L. Nevertheless, the authors use the equation to predict POC concentrations as high as 50 mg/L (event 2) without any comment on the validity of the applied regression. I think this is not a valid approach. here and, as already commented by another reviewer) this needs to be crosschecked by parallel sampling. Another point: The authors state that they have recorded a high frequency dataset. Where is the time resolution and how do they make use of this high resolution data?

Response: We now use only direct measurements of DOC and POC concentrations during 13 storm events. Original measurements were conducted with samples collected at two hour intervals (indicated at P 5, L 1). We used these original measurements to calculate discharge-weighted event mean concentrations and fluxes that were analyzed in Fig. 2.

In the discussion of the storm pulses of POC export, I also missed a deeper discussion about POC and DOC fluxes in parallel. The authors state that there is little data available, but there is hardly any comparison based on numbers: how much is mobilized in which form under which conditions? How much do we miss if we do not measure POC? In the conclusions the authors mention to have analyzed 50 storm events. Where is this data? I think a thorough analysis of the POC fluxes during storm events would suffice to write a conclusive and thoughtful paper with important implications about C fluxes. The part about DBP is in current state too large and obscures the important

C4093

facts about C fluxes.

Response: Aforementioned, ecological and environmental implications of storm-enhanced DOC and POC export represent the main focus of the revised manuscript. We hope that the revision has successfully addressed the reviewer's concern.

Fig.2: The choice of the regression equations is not clear to me. Based on which criteria the authors chose a quadratic or even cubic equation? How would you interpret this relationship in terms of a physical basis?

Response: Cubic equations have been determined as 'best-fit' regressions, i.e. regressions that best explain the new relationships established between hydroclimatic variables (precipitation or discharge) and C concentrations or fluxes in Fig. 2.

Fig.3: What is the temporal resolution here? Maybe also a Q-C plot for the events would be interesting.

Response: The temporal resolution of all measurements is described in the figure legend and Methods (P 5, L 1). Q-C plots were shown in the previous version (Fig. 4), but have been removed in the revised version according to the suggestion of Reviewer 3. We also thought that Q-C plots did not add much to the information conveyed in Fig. 3.

Generally, I find the topic of this manuscript very interesting. However, in its current state it is not well elaborated to really get a conclusive "message" from this manuscript. I would suggest to revise the manuscript and to decide whether to focus on C fluxes (then deepening the discussion here and showing more data), or focusing on DBP (then changing the title accordingly). Therefore, I recommend major revisions.

Response: We hope that our revision strengthens the main message of storm-enhanced export and reactivity of POC in mountainous headwater streams.

#### 4. Responses to the reviewer 3's comments

C4094

Comment: Overall, this is an interesting paper that explores the contributions of POC to OM exports during large events and the potential of POC for DBP formation. I thought that the biodegradation of POC and its contribution to DBP formation was the novel aspect of this work. The contributions of POC during large events has already been demonstrated by the authors previous publications and other published articles. I think the article could have been stronger if more storm-event measurements were available for POC biodegradation and DBP analyses. As it stands in this article, only a few limited samples were analyzed and presented for DBP formation (Figure 5).

Response: We also agree that more storm-event measurement could strengthen our findings on POC potentials for DBP formation and biodegradation, but stochastic characteristics and harsh storm sampling conditions did not allow us to conduct more measurements. The limitation of small sample numbers, along with future research needs, have been discussed in more detail (P 11, L 30-32).

Specific comments: The authors should thoroughly revise the paper for sentence structure and grammar. Some of the sentences were too long and confusing.

Response: The manuscript has been revised thoroughly for sentence structure and grammar. Responses to the specific comments are provided below.

Page 6878, line 20-21 – sentence needs to be revised, very difficult to understand.

Response: The sentence has been revised in P 2, L 5-8.

Page 6885, line 1 – "To inoculmn: : ." Something not correct here.

Response: 'To' was corrected to 'The' (P 6, L 31).

Lines 5-10 – please simplify and revise; very difficult to understand. Only two laboratory incubations were performed? Isn't this a limited analysis for this study?

Response: The sentences have been revised to provide clearer descriptions of three treatments (P 7, L 3-7). As described in response to the general comment, the limita-

C4095

tion of the small number of measurements was discussed in P 11, L 30-32.

Page 6887, line 16 – are you referring to Figure 5?

Response: Yes, it has been corrected (P 8, L 31).

Figure 2 – some of the fitted lines look very weird. Would an exponential fit to all plots be preferable?

Response: New 'best-fit' regressions were established in Fig. 2.

Figure 3 – middle panel – can this figure be improved for clarity?

Response: The figure has been revised to enhance visual clarity.

Figure 4 – is this figure necessary? I would recommend taking it out.

Response: The figure is not used in the revised manuscript.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/11/C4086/2014/bgd-11-C4086-2014-supplement.pdf>

---

Interactive comment on Biogeosciences Discuss., 11, 6877, 2014.