Biogeosciences Discuss., 9, C4534–C4543, 2012
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Biogeosciences Discussions

Interactive comment on "Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements" *by* S. Strohmeier et al.

Anonymous Referee #1

Received and published: 5 October 2012

General Comments

This is a well-written paper that investigates the sources of stream DOC and the dynamics of DOC concentrations and fluxes from a forested temperate catchment, which is a relevant topic within the scope of BG. One of the strength of the paper is that is based on high frequency measurements of stream DOC concentrations (30-min freq). Moreover, the paper includes novel techniques for characterizing the quality of DOC in different catchment compartments. Although this paper may be of interest to the BG audience, there are several issues that the authors need to address before this manuscript can be accepted for publication. Therefore, I recommend the publication of

this paper after major revisions.

âĂć Some of the variables analyzed in the Results section as well as the statistical analyses used by the authors are poorly explained in the M&M section.

âĂć The authors need to be consistent with the terminology used to refer to the different catchment compartments through the text, figures, and tables. For example, the "shallow wetland groundwater" is referred as "riparian wetland soils", "riparian soils" or "riparian groundwater". In Table 1, for instance, they refer to "riparian wetland soil" for both, soil solutions collected at 0-30 and >30-cm depth, and for "shallow groundwater" (50-100 cm from the soil surface). However, the authors show that the "riparian groundwater level" is usually at <30-cm from the soil surface. Therefore, the main contributor of DOC to the stream runoff may be the "shallow wetland/riparian groundwater" rather than the "riparian soil", unless perched hydrological flow paths occur during high flows which seems unlikely in this temperate catchment.

âĂć The authors show that (i) the quality of DOC is substantially different between the shallow groundwater than from the deep groundwater, and (ii) the quality of DOC in stream water is more similar to the former than to the later. Based on these results, the authors conclude that the riparian wetland is the main source of DOC to the stream. However, these samples were collected during 4 occasions from April to June. Therefore, the authors need to be cautious with their conclusion. First, because the quality of DOC in the shallow groundwater of the riparian wetland as well as in the upland groundwater could be different during the July-March period compared to the April-June period. Second, because even assuming that the quality of DOC is constant over time in the considered pools, the relative contribution of these sources to stream runoff may change over time because of changes in hydrological flow paths. This is shown in Figure 6, where the comp-12 (associated to deep groundwater) is higher than com-1 (associated to rip groundwater) for low flows, which may happen during a substantial fraction of the time. Hence, the authors need to explain clearly the assumptions and limitations of their approach. The authors can find an example of the temporal

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variability in the contribution of water and nutrient sources over time in Bernal et al., Biogeochemistry, 2006.

âĂć The authors show that high frequency time series are more reliable than fortnightly time series when estimating annual DOC export from catchments. This is not a novel result and there is an increasing body of knowledge considering the benefits and new challenges of high resolution data (e.g., Neal et al., Sci. Total Environ., 2012; Halliday et al., Sci. Total Environ., 2012). Moreover, the collection of stream water samples at high frequencies during storm events have been done from time ago (see for instance Hinton et al., Biogeochemistry, 1997; Hagedorn et al., Biogeochemistry, 2000; Bernal et al, HESS, 2002). If the authors aim to explore the goods of using high frequency data, the paper will benefit of considering other time intervals (such as hourly, daily, weekly intervals) when calculating annual DOC export in order to identify the minimum time interval needed to ensure a reasonable estimation of annual DOC export (within a reasonable percentage of error). This analysis will be more helpful to the potential readers of the paper that may consider the possibility of analyzing stream DOC more often but that may not have the equipment/resources to do so at 30-min interval.

âĂć The authors show that DOC concentrations are higher in summer/fall than in winter/spring, and therefore, they argue that future changes on stream DOC dynamics induced by changes in the precipitation will be especially noticeable during summer. However, the authors discuss that increased DOC during summer/fall may be a temperature-effect. Therefore, one may hypothesized that increased temperature may have a more dramatic effect on DOC dynamics that precipitation itseld. Moreover, increases in temperature would have a dramatic impact on the snowpack dynamics (and thus on the hydrological regime). The influence of this warming-induced hydrological effect on catchment biogeochemistry (plus a warming-induced increase in DOC mineralization) could be of major importance for ecosystem functioning. See for instance Campbell et al., HP, 2010; Bernal et al., PNAS, 2012.

âĂć Many of the results already included in the Results section are repeated in the Dis-

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cussion section. The authors should work on rewriting a meaningful discussion based on interpreting the obtained results and comparing them with other studies worldwide for better understanding the processes and mechanisms underlying the patterns observed in their study catchment. Moreover, when comparing the value of DOC export for the study catchment with other values found in the literature, the authors need to be cautious because their study does not account for the inter-annual variability.

âĂć In general the captions of figures and tables need to be better explained. IN addition, some variables included in the Tables need to be defined in the M&M section. There are some Figures and Tables that do not contribute substantially to the development of the paper, and thus, they can be combined or removed.

Specific Comments

P11926, L23-24. The obtained results do not support this conclusion.

P11930, L26. Specify frequency of sampling.

P11930, L26. Do you mean "riparian wetland soils" and "soil solution beneath the Oa horizon in the upland forest soil"? Please, be consistent with terminology through the text, tables, and figures. This would facilitate the fluency of the paper.

P11930, L28. Where and how was sampled this deep groundwater? Where and how was sampled the shallow groundwater in the riparian wetland soils included in Table 1?

P11931, L1. This subsection is lacking a description of the variables used to characterize the storm events as indicated in Table 2. Moreover, the authors should explain which criterion was used for separating storm flow and base flow in order to calculate Qsum for each storm event.

P11931, L13. Change "spectrolyser measurements" by something like "DOC concentrations estimated with the spectrolyser".

P11931, L18-19. A strong R2 is not enough to conclude that DOC concentrations esti-

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mated with the spectrolyser are similar to those obtained by thermo-catalytic oxidation. The slope of the regression needs to be not significantly different from 1.

P11932, L23. This sentence is repetitive. Delete.

P11932, L20. If one of the objectives of the paper is "to investigate the implications of the short term variations of DOC for the estimation of DOC export fluxes at the annual scale", the authors need to consider other time intervals between 30-min and 15-days interval in order to establish the minimum time-interval required to obtain a reasonable estimation of the annual export. As it is now, the exercise that the authors are proposing is not interesting enough and the conclusion is not novel. In fact, there are several studies from the last decades based on high frequency analysis of solutes during storm events (see refs in general comments) because it was already acknowledge that some solutes change not linearly with discharge during storms. Moreover, the authors are testing two different things at the same time. First, the effect of the frequency of the data on the estimation of the annual export. Second, the goodness of the Walling and Webb method (eq-1). It will be fairer to compare the annual export between the 30-min interval and the xx-min interval time series using either Eq-1 or either interpolating DOC concentration between dates, or both.

P11932, L9-12. Some of this information is already included in the Results section. Please, reorganize.

P11933, L8. The information about where, how, and when water samples were collected needs to be reorganized. Otherwise, it is difficult to get a clear picture of the information contained in Table 1 (the major part of this info is now in the Study Site section).

P11933, L11. Add "riparian" before "wetland" here and from here on.

P11933, L9-18. These two paragraphs need to be combined, and the information clarified. (1) Still not clear from where this shallow groundwater was sampled? Did

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you pump water from the piezometer where the sensor was located? Shallow groundwater from the riparian wetland area is more correct than shallow groundwater from the riparian wetland soil, because soil water and groundwater may not have the same chemistry. (2) Did you sample 4 wells of 1 well of deep groundwater (3-15 m-depth) in the upland areas? (3) How did you get 28 and 26 samples of shallow groundwater and downstream runoff in 4 occasions? Did you take several replicates each time? (4) Why do you refer these samples to the summer period when the sampling period comprised from April to June? This would comprise both winter/spring and summer/autumn periods according to how the results are presented. Where theses samples collected during base flow or high flow conditions? (5) What do you mean by "downstream runoff"? and, (6) To which runoff are you referring in Table 1 with "catchment runoff" to upstream or to downstream runoff? Are the authors assuming that DOC quality from April to June is representative of the DOC quality over the year? So, the underlying assumption is that there are no changes in DOC quality over time?

P11935, L2. Please specify which tests were you applying and for testing what.

P11935, L15. It is almost impossible to appreciate this flashiness in Fig.1

P11395, L23. Is this result based only a visual inspection of the data?

P11936, L3. No need to refer to Fig.2. This result is clear from data included in Table 2.

P11936, L5. What was the purpose of analyzing the correlation between the DOC delay and the variables in Table 2? Please, include this data analysis in the 2.5 section, and relate it to the objectives of the study. Otherwise, delete.

P11936, L28. By "riparian wetland soils" do you mean "shallow groundwater from the riparian wetland area"?

P11937, L1-4. Not sure what the authors mean by "runoff samples lined up between deep groundwater and the shallow groundwater from the riparian wetland area". This is

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not what is shown in Figure 5 were almost the 26 of "(downstream) runoff" laid between the shallow groundwater of the riparian wetland area.

P11937, L12-14. The Y-axis in Figure 6 does not correspond to the axis in Fig.5 In particular the comp-1 for the 26 "downstream samples" plotted in Fig. 5 ranges between 10-13%, while the comp-2 ranges between 4-10%. However, the Y-axis in Fig 6, ranges from something around 3 to something around 8%. Please, check. What represent the lines included in Fig. 6? Explain in the M&M and in the caption. Add "in the downstream runoff" or something like that after "discharge".

P11937, L18. Not clear when the snowmelt period was. Was it monitored in the catchment?

P11937, L16-21. Not clear how useful the information in Fig. 7 is. Which is the purpose of presenting these cumulative curves? The authors need to do a better job relating this figure to the results about DOC fluxes; otherwise delete.

P11937, L25-26. All the figures and results are referred to winter/spring and summer/autumn periods, and not to growing season/dormant season. Please, be consistent with the selection of periods; otherwise explain in the M&M the reasons why the data is organized differently depending on the analysis.

P11938, L1-3. As already mention the authors need to do a better job to address the objective 3; otherwise it will be better to delete this piece of information from the manuscript. P11938, L6-9. These are results already included in the Results section.

P11939, L1-7. These are results already included in the Results section.

P11939, L19-P11940, L2. This discussion section is a continuation of the idea developed in P11938, L15-22. Please, reorganize text to improve clarity.

P11938, L21-22. A reference is needed for supporting this assertion.

P11939, L28-P11940, L11940. Is this assertion based on a visual inspection of the

time series only, or else, it is based on some sort of data analysis not specify in the M&M or in the Results section? As this relationship could be an empirical evidence of one of the main conclusions of the paper (that riparian wetland soils or shallow wetland groundwater is one of the main contributors of DOC to stream runoff), it may be worth analyzing the data set more thoughtfully.

P11938, L5. Modify the title of subsection 4.1 in concordance with the changes made.

P11940, L26-P11941, L4. Move the new results to the Results section and delete those that are already included in the Results section.

P11941, L13-L15. Explain better why do you mean and on which results support the assertion "the relation DOC-discharge during the rising limb seems to be depend on the preceding groundwater level in the wetland soils".

P11941, L19-P11942, L3. The authors propose that low DOC concentrations during the rising limb of the hydrograph could be explained by the input of water from the ditches to the stream that bypasses the wetland soils. The authors argue that peaks of nitrate concentrations at the beginning of rain events support this explanation because there is no nitrate in the riparian wetlands. Is this water high nitrate and low DOC coming directly from atmospheric sources, or from upland areas? Do the authors have some idea of the DOC concentrations/quality of this water? This may help to support their hypothesis. Another issue that the authors need to think about is that stream DOC concentrations during base flow conditions are as low as 3-5 ppm. However, the riparian groundwater level during base flow conditions is often at 30-cm or even at 10-cm below the soil surface during base flow conditions (as shown in Figure 1). The soil solution at 10-cm depth ranges between 10-150 ppm (Table 1) Therefore, one may expect higher DOC concentrations during base flow conditions (as well as during the rising limb of the hydrograph) if the riparian wetland soils are the main contributors of DOC and water to stream runoff, as suggested by the authors. The fact that stream DOC concentrations are low during base flow conditions suggest that the stream is

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partially fed by a deep groundwater component, at least during base flow conditions and during the first part of the storm hydrograph. This explanation does not exclude the potential influence of ditch water but may help explaining the low DOC concentrations during base flow conditions.

P11942, L18-19. This result is already included in the Results section.

P11942, L 18-21. The annual DOC export for the study catchment is based on only one water year. The authors need to take into account that there might exist a substantial inter annual variability on annual DOC export depending on climatic variability (temperature and precipitation), especially when considering that temperature is a driving factor of organic matter mineralization.

P11943, L1-3. Please explain better the calculation for the annual export from wetland soils of 240kgC/ha/r.

Figures and Tables

Table 1. The terminology used in this Table needs to be consistent with the terminology used through the text and Figures.

Table 2. It is not clear whether the Start and End, and duration refer to the precipitation events, or to the stream storm events. There is no need to include in such detail the Start and End of each event. The day/month/year would be enough for identifying the event. The description of the variables included in this table needs to be specified. The authors need to explain in the M&M the procedure followed for separating the storm flow and the base flow.

Table 3 is not needed.

In general, figures are better read if standard procedures are used. The standard way of presenting figure is to plot X-and Y-axis from 0, and that the X- and Y-axis intersect each other.

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Figure 4. This figure could be combined with Figure 3. It could be an inset. Please use the same color code for the two figures. Explain arrows in captions.

Figure 5. Be consistent with terminology. The axes do not represent the quality of DOC. Improve the caption.

Figure 6. Check the Y-axis for inconsistencies. Explain in the caption what the lines are.

Figure 7. Not sure how useful this Figure is.

Technical corrections

P11935, L10. Used either rainfall or rain fall consistently through the text. P11935, L18. Delete 2010/2011. P11937, L1. Add “deep” before “groundwater”. P11938, L23-27. Please, rewrite this sentence for improving readability. P11941, L6. This “what”. P11941, L12. Either “counter-clockwise” or “counterclockwise”. Be consistent through the text.

Interactive comment on Biogeosciences Discuss., 9, 11925, 2012.