

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.

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General comment:

This study summarizes findings after one year of intense and detailed hydro-biogeochemical monitoring in a small stream in temperate climate draining a forested catchment. The manuscript focuses on dissolved organic matter. More specifically on identification of “spatial sources” of DOM within the catchment. The topic is of interests for Biogeosciences readers and the data set is really powerful. However, precisely because the data set is extremely interesting, I miss the formulation of more ambitious questions and a more deep data analysis exercise. Perhaps the weakest objective is

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that that attempt to “to investigate the implications of the short term variations for the calculation of DOC export fluxes at the annual scale” (pag 11930, lines 16-17). The impact of the sampling frequency on solute fluxes estimation is a technical topic analyzed in depth by several researches. In my opinion this question does not derive into new information/findings. In addition the manuscript is not a technical note and this section can be easily removed without threatening the most essential results and conclusions.

Below I detailed all my questions and doubts related to the manuscript.

The main objective of this study consists to identify “spatial sources” of DOM. However, in my opinion, “spatial” is not the appropriate term, because sources are not explicitly located in some spatial domain.....Obviously, “riparian wetland soil” is spatially located along the stream edges, however, authors do not provide any information about location or size/area of this compartment .“Compartment sources” fits better. It is interesting to note that the adjective “spatial” appears in the abstract, introduction and M&M.then it disappears and appear the more hydrological terms “compartment” and “end members” (M&M, discussion and table 1).

Results and discussion DOC concentrations According Fig. 3, the data set is split into two clusters according seasons: “Summer, Autumn” and “Winter, Spring” (Fig.3). Authors refer, in the “Study site” section, that a “substantial snow cover develops regularly” (pag. 11930, lines 1,2) in the studied catchment. Therefore, the snowmelt is integrated within the “Winter, Spring” group. Minding that snowmelt episodes typically generated clockwise no-lineal hysteresis loops in alpine catchments (several papers appear in the reference list of the manuscript), it would be interesting to highlight the snowmelt response in your monitoring and discuss it if it is similar/different to that responses clustered within the same season or are similar/different to that reported in literature from other snowmelt catchments. A rough inspection of Fig. 3 it seems that the highest storm episode (a snowmelt episodes according page 11936 (line 12) generates lowest DOC vs. Q slope and the loop seems to be quite lineal.It would be interesting to make more evident these patterns. There exist intuitive descriptors

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that allow to synthesize the hysteresis loops shapes (namely, hysteresis loop area, a measure of the magnitude of the non-linearity of the response; the rotational pattern, clockwise/counterclockwise/no rotation; and the solute concentration. vs. Q, a measure of the flushing/dilution magnitude). In Butturini et al. (in your reference list or, *J. Geophysical Research-Biogeosciences*, 113(G3), DOI: 10.1029/2008JG000721, 2008) you can find an application of these descriptors to describe the loops variability/heterogeneity. In your case, the implementation of these simple descriptors might help to evidence the differences in slope and area (Fig 4) that exist among events and to demonstrate that these differences are driven by seasons and perhaps to highlight the hysteresis behaviour of the snowmelt episode. The discussion section start stating that “DOC concentrations. . .] . . . were highly variable at hourly to daily time scales”, but, in the result section, DOC variability is related to storm events only. Does this hourly frequency DOC variability appear under basal discharge condition as well? Why, this interesting and available information is not analysed in detail?

DOC quality (M&M and results) At pag. 11934, line 25 and forward), authors stated that omitted to “discussion about chemical quality of the DOC of the respective sources”. They justify this decision because the “chemical molecular interpretation of the PARAFAC components identified by Cory and McKnight (2005) has become a matter of discussion (Macalady and Walton-Day, 2009). Without any doubt the interpretation of DOM fluorescence signal is a theme of debate, and work of Macalady and Walton-Day is one of the large list of studies that feedback this debate. Specifically, these authors refer to the insensitivity of the reducing index to describe the redox status of some natural organic matter samples that were experimentally manipulated under reducing and oxidizing conditions and criticize the use of PARAFAC to analyse the redox conditions of quinone-like signal in DOM. However, to cite the work of Macalady and Walton-Day to avoid performing a biogeochemical analysis and interpretation of the EEMs seems to me a rather drastic decision. Note that the authors in the discussion (11939, lines 5-18) refer to “Ketal or Acetal Carbon,” aliphatic carbon”, “refractory” ,” tryptophan-like fluorescence”. Therefore they cannot really omit

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some chemical interpretation of EEMs results. I would invite the authors to describe in more detail their PARAFAC results. In this section the DOM fluorescence is used as a tracer to discern the hydrological sources of DOM for stream water. Obviously from a hydrological point of view is questionable to use a reactive solute to tracer water and solute inputs in a stream. Why authors do not add information about some more classic conservative tracer (i.e. Cl, or electrical conductivity, for example) to discern the relevance of one hydrologic source with respect to another one? In the discussion (at the end of page 11941) information about nitrate dynamic is unexpectedly revealed to support the “bypass effect” hypothesis. I strongly believe that all available information that is indispensable to support or refuse some hypothesis should be described at the result section. In any case, from fig. 5 it is reasonable to conclude that DOMrunoff = DOMriparian wetland. However I found this section excessively simple and I believe that it be might strongly improved. Hundred of EEM and thousand of fluorescence data are reduced to describe only the ratio between a humic-like peak (component 1) and a quinone like peak (component 12). In the section “2.4 DOC quality”, authors should to argue the reasons that justify why these two components are considered “tracers”. Note that the explanation appears in the discussion (pag. 11939 lines 5-10). It should appear before in M&M because this information is necessary to create figs 5 and 6. What about others components? How the remaining components change over time or among water bodies during a storm episode/basal discharge conditions? Does in stream water appear some new fluorescence signal that can not be explained by input from other hydrological compartments? Some additional information appears in the discussion (pag. 11939, lines 13-20). This suggests that information exists but, for some reason, is not explained in results. Furthermore there exist several fluorescence indices that provide information about origin, humification degree, and freshness of DOM (see Felmann et al., *L&O*, 55 (6) ,2452-2462). These index might be integrated in the data analysis. Without any doubt, the relevance of the manuscript would strongly benefit from a more exhaustive explanation of the decomposition of fluorescence signal. Sampling for DOM quality was performed under basal (27/04; 18/05) and high

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discharge conditions (02/06 and 16/06; I suppose after visual inspection of fig. 1). In any case, during this period, groundwater showed the lowest levels (i.e. soft drought?). Therefore, hydrological connection between stream water and riparian groundwater was, in some moment more weak than usual. Does the difference in DOM fluorescence between stream water and surrounding riparian groundwater is more (or less) evident during this period? Does the stream runoff recharge the riparian groundwater during this period? Hence, does the few outliers (star symbols) that appears in Fig 5 might be associated to these potential anomalous moments? In short, the data set is extremely powerful and it can be used to explore these, and additional, questions that might be extremely interesting from a biogeochemical point of view. Another think to consider: DOC quality analyses cover a short temporal window, under relatively "drought" conditions. It is important to remark that conclusions obtained from this period might change if a different hydrological period is selected, for instance the snowmelt. It might be an interesting speculation exercise (in the discussion) to attempt to use the available information to hypothesize how would change the DOM fluorescence signal during more humid conditions. In the discussion, at page 11942 (lines 12-16) authors hypothesized that water flow paths might changes over seasons. . . .this speculation might be useful to link both DOC quantitative and qualitative aspects.

Conclusions Authors conclude suggesting that "Future changes in the hydrological regime, . . .[] . . .will influence the DOC dynamics in this catchment, with largest effects in the summer/fall season". It would be interesting to explore more this argument. It exists an apparent "hot" (and some time reiterative) debate about causes of the increase of DOC concentration in north Europe and America in several acid impacted freshwater ecosystems (for details and a synthesis see Clark et al, STONEN, 408(13), 2768-2775.). How can you integrate your results into this debate?

Technical/Formal considerations/suggestions Referee # 1 already generated an excellent list of specific comments. I will be not so detailed and precise. Just few items.

DOC quality: DOM quality was explored during four sampling (27/04; 18/05; 02/06 and C5037

16/06). These sampling were executed in spring and not "summer" as indicated by authors.

Fig. 1 I would be useful for readers to mark the sampling period for DOC quality

Figures 5, 6 and 7 (and associated legends) should be improved. In fig. 5 and 6 I would suggest to enlarge the symbol size. The grey symbols are nearly invisible. Fig. 6: How do you get the interpolated lines? Specify in the legend. Fig. 7 Gray line is nearly invisible.

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