

Interactive comment on “Linkage between the temporal and spatial variability of dissolved organic matter and whole stream metabolism” by S. Halbedel et al.

Anonymous Referee #4

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There are already opinions of 3 different reviewers on this manuscript, I will therefore try to limit my comments and critique on additional issues rather than underlining points of criticism already pointed out by other reviewers. In general, I believe, this manuscript presents interesting data, especially on the linkage between DOM and metabolism. These data are of interest to the readers of Biogeosciences and I support publication in this journal. However, in its current state the manuscript is clearly unacceptable for the targeted journal: It is extremely lengthy to read, contains a lot of speculation and speculative language and is linguistically absolutely unsatisfying. A lot of the results on seasonal or site differences are either not very robust or not adequately analysed in terms of statistics. Most of these results are also not very new to the scientific com-

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munity. The linkage between DOM and metabolism is the only really interesting part of the manuscript and a revised version should clearly focus on this topic, essentially exploiting the gradient of DOM-quality and metabolism across seasons, sites and systems (rather than reporting about this gradient itself in terms of a landcover or seasonal effect, etc. . .).

The submitted manuscript is not yet in a state requiring detailed copy-editing or similar corrections, it clearly has to change markedly before this should be done. A couple of more specific points, which need to be addressed and maybe have not been pointed out by the previous reviewers:

1) Please clearly distinguish between a fluorescence pattern and the potentially (!) underlying chemical information. Currently, there are a lot of statements referring to chemistry like “low-molecular weight substances”, etc. All these statements are based on previously published correlative relationships between fluorescence patterns and chemistry. More cautious wording is necessary here. Also, a certain component may dominate in terms of fluorescence, but this does not mean that the underlying population of molecules actually dominate the DOM matrix as the various populations may have very different fluorescent yields per molecule or per amount of carbon. This is a problem at multiple places throughout the manuscript.

2) There is a severe methodological issue with the propane additions used to compute the reaeration coefficients. The authors report that travel time t was determined by a salt slug injection, and then propane was bubbled into the stream for a minimum time of one t before sampling for propane concentrations along the experimental reach. One t is definitely too short to reach equilibrium (“plateau”) conditions along the entire reach. In fact, the peak time of a salt slug corresponds to the time point of maximum conductivity change (slope) of a metered (continuous addition), i.e., in the middle of the rising limb of the breakthrough curve of conductivity but potentially far from plateau conditions. The propane addition is a metered addition, it can therefore by no means be assumed that equilibrium conditions are reached after one t . There are usually

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two strategies to solve this problem: Run a metered salt addition alongside propane and sample propane when conductivity reached plateau conditions at the most downstream point. Or use a salt slug (as the authors of this study did) but then wait for a reasonable additional (!) time (2-4 times the travel time seems to be a literature-wide acceptable time, but ideally this factor is determined independently for the system at least once). This methodological shortcoming may be a severe problem in the present study (depending on how often waiting times were actually too short, which I cannot judge from the current information), which could greatly compromise the GPP and CR24 estimates. A possible solution could be to model the diurnal DO-curves (e.g. Holtgrieve et al, L&O) and model the reaeration coefficient as well. The experimentally determined reaeration coefficients could be used as model starting parameters (the “prior” in the Bayesian setting of the Holtgrieve model). A probably minor point: please specify how propane samples were taken “with an air headspace”.

3) The authors compute both P/R and NEP to give information about the relative importance of GPP and CR24. However, in their argumentation P/R and NEP are almost used in a redundant way, not respecting the actual differences between the two in terms of their relative and absolute meaning (e.g, page 18268, first paragraph). The same is true for the PARAFAC components, where once a ratio and then an absolute fluorescence is used, seemingly without any underlying reasoning other than achieving nice correlations. Furthermore, to examine the linkage between metabolism and DOM, it would make intuitive sense to combine ratios of P/R with ratios of fluorescent components, or to combine an absolute fluorescence of C2 with an absolute measure of metabolism such as GPP. But also here, authors seem to “pick” nice correlations, rather than follow a hypothesis-driven approach (see Fig. 9 for instance).

4) I do not agree that the inner filter effect can be neglected in this study. The methods associated with EEMs are pretty straightforward and follow widely agreed standards in the scientific community. It is not difficult to carry out an IFE correction and I don't see any reason why this should not be done here. A lot of PARAFAC-argumentation

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boils down to comparison of identified components with components published in the literature. How can we expect this to be successful if methods for EEM correction differ among studies?

5) Some of the fluorescent indices require measurements at wavelengths outside the reported EEM ranges. Similarly, 254 is a used wavelength for computations but was not measured according to methods. Please explain or correct.

6) Statistics: Please pick Spearman or Pearson correlation but don't use both. A lot of the regression analyses should rather be correlation analyses, as there is no clear identification of independent and dependent variable.

7) Landcover and seasons: A difference between non-forest and forest streams can not be statistically tested. First, the non-forest streams differ substantially with regard to discharge at least, so should not be regarded replicates. The “landcover” effect may as well be a discharge effect. Second, the real sample size for both forest and non-forest is only 2. Plots like the boxplots in fig 10 suggest a much more powerful statistical analysis, which however has to be considered as almost completely built on pseudo-replicated data (e.g. measurements from two consecutive dates and multiple seasons from the same system). Unless seasons and consecutive dates are accounted for as within-subjects factors in some sort of ANOVA or similar model a valid analysis is not possible. Then, however, I also note that the same season may actually mean very different dates for the different streams (sampling dates were up to 1.5 months apart for two systems in the same season, a considerable time distance especially for spring). I therefore do not think that seasons can nor should be compared, nor that this allows the use of “season” as a factor in any analysis (or at least this must be done with great caution).

8) Some of the statistical analyses (e.g., page 18266 last paragraph; page 18270 second paragraph) make the impression of a not very responsible combination of working with selected variables (and excluding others) and simultaneous exclusion of “outlier”

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cases (season-stream combinations). This gives some of the analysis a trial-and-error touch, which seems irresponsible and not very hypothesis-driven. If there are any outliers, I would prefer to see them in a graph still, maybe the correlation can still be computed without the outlier when indicated as such. "Outlier" data should not be considered "wrong" simply because it does not fit a model.

9) If GPP is a function of light and TP, why did the authors not just consider a multivariate regression model? Maybe some of the outliers are not really outliers then. . .

10) Some of the fluorescent components are interpreted as if having two fractions (e.g. ,page 18268, chapter 3.3.). I do not think that this is correct. Rather, one population of chemically similar molecules must be considered to produce manifold fluorescent signals. The same molecule may indeed produce two peaks in an EEM, as I believe. I am however, not an expert on this.

11) Component ratios and "regressions" with components: I was totally confused by the report of these results on page 18268, where C1:C2 meant something different as C1/C2. Please clarify. Also, regression analysis seems really inadequate here, as independent and dependent variables cannot be clearly identified. Rather, correlation analysis should be chosen here. Then, the stronger a relationship turns out, the more likely it is that these two components come from the same source. Reading this paragraph I also think that it could be worthwhile to consider a ratio $(C1+C3)/C2$, this should give very similar information as beta:alpha.

12) Table 1: can you add velocity to this table? It must be quite small and I am not sure if this is correct (e.g. about 1-3 cm/s for the first two entries in the table).

13) Table 2: Can you give literature sources for each component separately?

14) Fig. 3: The y scale on some graphs here need attention, consider a break, otherwise some of the data cannot be seen at all.

15) Fig. 5: According to my understanding there should be a maximum of 16 points in

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this graph. There are much more. Where are these coming from? What is the meaning of "samples" in the legend?

16) Fig. 7-9: All these graphs should show correlations rather than regressions. Modeled lines are therefore not adequate.

Interactive comment on Biogeosciences Discuss., 9, 18253, 2012.

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