Biogeosciences Discuss., 11, C4025–C4031, 2014
www.biogeosciences-discuss.net/11/C4025/2014/

Biogeosciences Discussions

Interactive comment on "Partial coupling and differential regulation of biologically and photo-chemically labile dissolved organic carbon across boreal aquatic networks" *by* J.-F. Lapierre and P. A. del Giorgio

J.-F. Lapierre and P. A. del Giorgio

jfrancoislapierre@gmail.com

Received and published: 2 August 2014

Reviewer: The authors present an impressive dataset of freshwater DOM measurements and accompanying microbial and photochemical degradation potential measurements. The samples span a comprehensive range in water types and offer a unique opportunity to study cross system trends. The dataset represents a considerable body of work. In short they find a correlation between the photochemical and biological degradation potential of DOM in freshwater systems where terrestrial colored DOM dominate the DOM reservoir. In systems characterised with low CDOM input the two

degradation potentials are decoupled and the extent of photochemical degradation is limited. In general I agree with the findings and consider the discussion to support the findings of early studies, although this study is unique in its comprehensive nature.

Authors:

We thank the Reviewer for the positive comments and for the following constructive suggestions. Below we address all the comments, and we have included almost all the suggestions in the revised manuscript.

Reviewer:

1) I do not follow there arguments for not needing to normalise the photochemical degradation to the photons actually absorbed by each sample. There is a considerable range in CDOM absorption across the freshwater systems sampled and I do not see how this cannot influence greatly the actual amount of energy absorbed by each sample during the exposures. Higher CDOM will result in greater light absorption and greater photochemical reactivity. Some of this will likely explain the observed correlation between Pd-DOC and CDOM. This needs to be clarified better.

Authors:

It is clear from this (and other reviewers') comments that there was some ambiguity on whether we explored the concentrations of degradable DOC vs the degradability of DOC in some portions of the manuscript. It is true that normalising by the number of photons absorbed would give a better idea of DOC photochemical degradability, but here the main objective was rather to explore the patterns in the concentrations of photo-chemically degradable DOC. In order to clarify this point, we have edited several sentences and section titles (in the "Results" and "Discussion" sections) throughout the manuscript to remove this ambiguity (more specific examples are provided in our reply to Reviewer #4).

We certainly agree that higher CDOM results in greater light absorption and thus higher

photochemical processing; this explains why CDOM is the strongest predictor of the amount of Pd-DOC. Please note, however, that we did not present this result as novel or unexpected; perhaps what was less intuitive was that CDOM was also the best DOM-related variable that explained the concentrations in Bd-DOC.

Reviewer:

2) PCA analysis. Before performing a PCA the data should be appropriately preprocessed so that quantitative difference between samples are removed. PCA is a qualitative analysis so it should only reflect qualitative trends. It is unclear what preprocessing was applied and the fact that you have a concentration axis (PC1) suggest that maybe the appropriate preproscessing has not be done (mean centred and autoscaling). Please expand on how the data are scaled before performing the PCA.

Authors:

We now specify in section 2.5 that " Data have been centered and standardized before performing the PCA."

Reviewer:

3) Some interesting correlations are presented in Table 1. From the results in Figure 4 one might expect some of the predictor variables used in the MLR to be inter-correlated, which would render the MRL invalid. Was this tested? If so this should be mentioned in the table legend. I presume the JMP software does this automatically in the stepwise regression process. A dataset like this would be excellent for partial least squares modelling. This approach can cope with the intercorrelations between the measured input variable (e.g. CDOM and FDOM, or C6 and TN). It may also improve the predictiveability of the models.

Authors:

The software indeed takes co-linearity into account, and this why although C6 and TN individually explain around 40% of the variation in Bd-DOC, together they explain only

45%.

The PLS is an interesting suggestion. We performed the analysis (using the "pls" package in R, (Mevik & Wehrens, 2007) following the Reviewer's suggestion, but given the high number of samples and the low number of variables included in the MLR models presented in Table 1, the results were exactly the same. From our understanding, the PLS is most efficient compared to other techniques when the number of variables in the model is high compared to sample size. In this regard we explored how a PLS including all our variables would predict the concentrations in Bd-DOC and Pd-DOC. While it is true, as suggested by the Reviewer, that these overall models had better predictive power than the individual models presented in Table 1, we did not consider that the (somewhat low) improvement in r^2 out-weighted the added complexity in terms of interpretability.

Reviewer:

4) Comparison of the components with those identified in earlier studies would be very useful. A passing comparison to Kotawalla et al 2013 is made in the discussion but this could be more quantitative by directly comparing the fluorescence spectra of the components in each study. Murphy et al 2014 (doi: 10.1039/c3ay41935e) published an online resource for this (http://www.openfluor.org) and I can see that the Kotawalla data is available there.

Authors:

We thank the Reviewer for the suggestion. We now refer to published PARAFAC components that strongly match our spectra and refer to Murphy et al. paper. (section 3.2, 1st par.)

Reviewer: Minor points, Abstract Line 16. Rephrase to “The concentration of colored DOM (CDOM), which in this case could be used as a proxy for contribution of terrestrial DOM, :...

Authors: done

Reviewer: Introdcution Line 3. Replace “throughout” with “through”.

Authors: done

Reviewer: Page 6678. Line 5. Report at which wavelength this CDOM value corresponds to.

Authors: done

Reviewer:

Methods A description of how the inorganic nutrient samples were stored is missing. As it reads at the moment it would appear that they were measured from the TN/TP samples after storage cool for one month. This is not appropriate if this is the case.

Authors:

We now specify that inorganic nutrients samples were actually treated the same way as DOM samples, i-e they were filtered and analysed within two weeks. (section 2.1)

Reviewer:

Line 14. On page 6679. SUVA is traditionally not calculated on the absorption coefficients but on the absorbance (so not multiplying by 2.303). Your SUVA values may be a factor of 2.303 too high when you compare with previous studies.

Authors:

This is a good point to keep in mind. However, SUVA is only used in the PCA and we do not report actual SUVA values in the manuscript so that should not be a problem.

Reviewer: Line 18. P6679. Spell out PARAFAC first time you use it.

Authors: done

Reviewer:

Line 26. A recent study has shown that inner filter effects can be corrected for samples with greater absorbance. Kothawala et al 2014 (doi: 10.4319/lom.2013.11.616) which would question the findings of the Miller paper.

Authors:

We thank the Reviewer for pointing out this study, we now cite it in order to make the point that the bias, if any, is actually less than what is suggested by Miller et al. 2010 (section 3.2, 2nd par.)

Reviewer: P6680 line 5. Replace “than” with “that”.

Authors: done

Reviewer:P6680. Line 26. “alter” instead of “alters”.

Authors: done

Reviewer: P668A1. Lines 11-14. Move the regression results into a table to facilitate reading.

Authors: done

Reviewer:

P6683. And elsewhere. Using the term concentration for the fluorescence intensities of each component identified by the PARAFAC model is miss leading. It would imply that if C1 had a higher fluorescence signal in a sample than say C2, that C1 also had a higher concentration. As we do not know the fluorescence efficiencies of the responsible structures/compounds, one can not state this. So I think it is best to rephrase this.

Authors:

We agree, and this relates to a comment by Reviewer #5. We have inserted the following statement at the end of section 2.3:

"We express the "concentrations" of fluorescence components as the maximum fluo-

rescence intensity at the peak. These represent relative concentrations that may be used to explore the cross-sample patterns for a given component, but this does not necessarily mean that one unit of a given component represents an equal amount of DOM compared to one unit of any other component."

Reference cited: Mevik, B.-H. & Wehrens, R. (2007) The pls package: principal component and partial least squares regression in R. Journal of Statistical Software, 18, 1-24.

Interactive comment on Biogeosciences Discuss., 11, 6673, 2014.