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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

Anonymous Referee #3

Received and published: 24 June 2014

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.

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[Interactive Discussion](#)

[Discussion Paper](#)



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. There are however some points that need to be considered by the authors.

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 can not 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.

2) PCA analysis. Before performing a PCA the data should be appropriately pre-processed 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 preprocessing has not be done (mean centred and autoscaling). Please expand on how the data are scaled before performing the PCA.

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 predictive ability of the models.

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

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Discussion Paper



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.

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, ...

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

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

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.

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.

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

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.

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

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

P6681. Lines 11-14. Move the regression results into a table to facilitate reading.

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

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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.

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

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