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Interactive comment on "Seasonal changes in photochemical properties of dissolved organic matter" *by* P. Porcal et al.

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Interactive comment on "Seasonal changes in photochemical properties of dissolved organic matter" by P. Porcal et al., bg-2013-124

Anonymous Referee #1 Received and published: 22 May 2013

In this manuscript, Porcal and colleagues look for seasonal changes in the photoreactivity of dissolved organic matter in three boreal streams. The topic is relevant, though not really as novel as the authors claim it to be (p5979, line 12-14). There are at least a couple of earlier studies addressing exactly this topic and it would of course have been useful to frame the present study with the quite relevant findings from these earlier studies (see for example two papers in Can. J. Fish. Aquat.Sci; Lindell et al. 2000

57:875-885 and Suhett et al 2007 64:1266-1272). The observation of substantial seasonality in DOM photoreactivity reported here is potentially important (and also agree with these earlier studies), but I have some major reservations about the experimental design addressed below.

The references were added.

-The experiment might be significantly influenced by interactive microbial/photochemical processing of DOM. The filtration described here (0.5 micrometer cutoff) does NOT remove bacteria effectively. Because there is extensive synergistic effects between solar radiation and bacteria in DOM degradation (Miller & Moran, 1997. L&O 42:_1317-1324), this confounding factor cannot be accounted for by looking at dark controls. This effect may furthermore vary over the year depending on the in situ microbial abundance, size distribution and activity. At the very least this need to be discussed and acknowledged when interpreting the results.

It is possible but it is necessary to take into account that during irradiation microbial processes are mostly inhibited and the microbial growth starts when the light is turned off.

This was added to the manuscript on page 10: "The initial filtration (0.5 μm) does not remove all bacteria. There is some possibility of synergistic effect of bio- and photodegradation of DOC during irradiation due to formation of easily biodegradable photo byproducts (Miller and Moran, 1997). A recent review by Ruiz-Gonzáles et al. (2013) showed variability in bacterial response during irradiation ranging from stimulation to inhibition. However, most of the reported studies irradiating with a full range of artificial UVA and UVB inhibited microbial growth, perhaps due to photoproduction of singlet oxygen and other reactive oxygen species (Zepp et al., 1977; Scully et al., 2003). Singlet oxygen is the primary agent of photo-oxidative stress in microorganisms (Glaeser et al., 2011) and high concentrations may delay consumption of readily microbially decomposable organic matter until dark conditions prevail. In our experiments, irradiation with a full range of UV was continuous, the intensity used was high, the microbial community was reduced in size via filtration and the experiment duration was short (i.e., 48 hours is a short period of time for the remaining microbes to adapt to harsh conditions). Hence, it is reasonable to assume that the effect of residual microbial activity in filtered samples was very low and photochemical rates were not corrected for residual microbial activity.

-The authors did take some measures to assess the irradiance in the experiment. However, the spectral irradiance and the screening effect of the bottles do not provide any information on the amount of radiation actually being absorbed in the water. Unless the water is extremely colored, small bottles behave as cuvettes where the portion of the incident radiation absorbed in the bottle is proportional to the color of the water. If a variable portion of the radiation pass the cuvette without being absorbed, the photoreactivity of water with less colored DOC (low SUVA) will be systematically underestimated. The authors need to take this into account, at least if (as stated in title) the aim is to probe variation in DOM properties (photoreactivity).

We calculated the normalized rate constants (Figure 1 of this response). The normalization was done by dividing the rate constants (in m2 GJ-1) by the absorbance measured at 254 nm (in m-1).

But we think that it is not necessary to add this figure to the manuscript, because K has already been normalized for total DOC in equation 1 (K is the slope of ln(DOC/DOCo) vs energy) so it shouldn't be normalized again with another DOC proxy like absorbance. The bottles were small so irradiation intensity should not vary significantly between stream experiments.

We can add this figure if you whish.

-With only three systems studied, I would not highlight the type of trees (coniferous vs. deciduous) as a decisive factor for photoreactivity (line 9-10 in abstract). I'm sure there are many characteristics that differ between the studied streams. Replication (more

catchments) would be needed to support this conclusion.

This statement was omitted from the abstract and Introduction.

-The single reference to microbial and photochemical processes as the two principal sinks of DOM (the Stumm and Morgan textbook) is really not appropriate for this statement. Quantitative studies are needed to support this statement (there are several such studies published).

This statement was omitted from the Introduction.

-The precision (reproducibility and limit of detection) of the DOC analyses is not reported anywhere although this is of critical importance for this type of seasonal analysis. I am also missing the statistics for how good the first order decay model fits the observed data.

The R2 for the first order decay model ranged from 0.78 to 0.99 in all samples. It was added to the results on page 12 (lines 22-23).

-The authors acknowledge that DOM can aggregate to form POM. Such a process would be observed as a decrease in DOC (because of the filtration through the 0.4 micrometer nylon filter). How is this accounted for?

All work was done with filtered samples, thus all POC was removed at the beginning of the experiment. It is possible that the decrease in DOC was not only due to production of DIC but also of POC (Porcal et al., 2013). This is mentioned on page 12, lines 10-14.

-References to figures in the text are wrong. There is no figure 10, 11, 12, 13 in this study. I guess figure "13" refer to Figure 5?

We are very sorry but we used automatic numbering of figures in Microsoft Word and did not turn it off when exporting the file. All figure numbers were corrected.

-When reporting the results, it would be better to start with the central component of the study (the photoreactivity) and then later on report the data that can be used to explain the seasonality in this central DOM feature (pH etc).

The order has been changed.

- DOC can be measured in several ways on the Shimadzu instrument. More details (or a reference) is needed. There are also some inconsistencies in the description of the molecular weight assessment. The method do not appear to be exactly the same as in Köhler et al. 2002. There is furthermore no information about what wavelength was used for the detection. Natural DOM is complex and not all portions of the material absorb equally. If this was done at 254 nm (which is common practice), this could explain the positive correlation between apparent molecular weight and SUVA254 (specific absorbance of DOC at 254 nm).

The reference for DOC measurement was added to page 7, line 12.

The text on page 8 has been revised: determination of molecular weight from measured data was done according to Köhler et al. 2002. The instrumental method itself was done according to Wu et al. 2003. The reference to Wu et al. 2003 was moved from the end of the description of the method to the beginning for better understanding.

-Page 5989, line 1: The study by Brinkmann et al (2003) only report increased photobleaching (not necessarily the same as photodegradation) in the presence of elevated iron concentrations. There are however other (earlier) studies that report a positive correlation between total iron concentration and photodegradation of DOM in surface water (Gao & Zepp, 1998, Env. Sci. Technol 32:2940-2946; Bertilsson &Tranvik, 2000 L&O 45:753-762). These references would be more appropriate here. These studies also provide fodder for discussion about other factors that may affect photodegradation rates (e.g. p 5989, line 15-16).

The new references and discussion were added to the text on page 17, last paragraph.

-I do not really understand the rationale for comparing the photoreactivity of DOM collected up- and downstream to test the effect of previous DOM exposure on photoreac-

tivity. This relies on the quite unrealistic assumption that there is no exchange of DOM between the water and the sourrounding catchment (or the sediment/periphyton for that matter) as the water travels downstream. I do not know these streams well enough to say whether or not this might be the case, but I would need some data supporting this to be convinced. A much better test would actually be to repeatedly expose water to the controlled UV and see if photoreactivity changes. I suspect it will.

We revised the manuscript on pages 17 (last paragraph) and 18. Alternative explanations are mentioned.

Anonymous Referee #2 Received and published: 26 May 2013

This manuscript provides a comparison of seasonal trends in optical and chemical properties of DOM in small tributaries to three well-studied lakes in Canada. The title itself is misleading and should acknowledge the focus is on small boreal streams and that "photochemical properties" is misleading. What really was studied here was an artificial and inherent (more on this later) photodegradation rate constant. The seasonal results were interesting and the manner in which the K value was calculated would be comparable across other ecosystems. However, the authors have also omitted some freshwater lake and stream photodegradation work from the late 1990's and early 2000's that I think they should consider and results which may provide context for their interpretations here.

The title has been revised to include small boreal streams and the additional references have been added to the manuscript. We used 'photochemical properties' in the title rather than 'photochemical degradation' because seasonal variation in molecular weight and specific absorbance, properties that can be related to photochemical reactivity, were also examined.

I don't understand why several figures referred to in the manuscript did not match the figures submitted with the manuscript. I only found 8 figures total, yet the authors refer to Figures 10-16. So clearly there is a problem here they need to sort out before decision can be made on publication. I have the following comments should the authors decide to revise.

We are very sorry but we used automatic numbering of figures in Microsoft Word and did not turn it off when exporting the file. All figure numbers were corrected.

P#,L# P5979,7: I don't understand how DOC can be degraded to something larger like POC. Is this just an issue with wording? DOC could be incorporated into microbial biomass but this is not degradation. DOC could be adsorbed to particles but this also is not degradation. As written this is wrong.

The concentration of dissolved organic carbon can decrease by direct photodegradation but also by formation of particles which can also be a photoinduced process. Organically bound metals are released and can form insoluble hydroxides and coagulate DOC. This is explained on page 12, lines 10-14.

P5981,5: Were the samples collected for the Dillon et al. (1991) paper used in this study? Why are the ion concentrations shown in Table 2 but never discussed in the rest of the manuscript?

The samples were collected at the same sites as in Dillon et al. (1991) in 2007 and 2008. The ion concentrations are presented in this manuscript to help characterize the water samples as dilute but they are not discussed. Views of reviewers on this matter differ; we were asked to add them to another paper even though we felt the information was not terribly relevant and so we decided to leave the table in this manuscript.

P5981,20: I think it important the authors state throughout the manuscript that they are calculating inherent and not actual photodegradation. The solar simulator provides the possible photodegradation during June but not at other times of the year. The scalability done on the global horizontal radiation data is fraught with uncertainty because day-to-day variability in UV-B and to some degree UV-A (the former which drives DOC photodegradation but not necessarily photobleaching, which largely controls the latter)

is not incorporated. So these K values and the rather arcane delta value calculated in Eqn 2 are rough estimates of the inherent photodegradation of DOC samples collected from these streams seasonally. This must be communicated more effectively because the bulk of the discussion purports that actual in-stream photodegradation (which would presumably be extrapolated to CO_2 photoproduction) is being described. And it certainly is not. I think a way to express what I think the authors would like to express is what the photodegradation potential for lake water in the catchments receiving flow from these streams (each is matched to a lake) is how the results should be incorporated. But it must also be recognized that these are only inherent possible estimates of photodegradation under the best possible conditions (no ozone, clouds, consistent sunlight). Daily variability of sun angle is not included either. So these considerations must be made.

We agree and added the following section to the Methods section (page 10, lines 10-15). "Photodegradation rate constants, K, presented in this study were derived from DOM exposed in solar simulators to constant spectral quality and are therefore a valid measure of changes in photochemical reactivity potential. Since in situ K will not vary with irradiation intensity for reasons discussed above, it will not vary with changes in canopy thickness or cloud cover unless spectral quality changes. K will, however, differ with time of day and year because of significant changes in spectral quality in relevant regions of the solar spectrum."

P5982,L23: was the decadal absorption used, this is what is described, for SUVA? Please clarify. A254 is absorbance, a254 is absorption coefficient. Also, was any correction made in SUVA for the Fe in these samples?

Absorbance at 254 nm was measured and used in calculation. The description is on page 7, last paragraph.

P5987, 15: It is no wonder a weak correlation was found and I was surprised it was significant because if you pooled all samples, Fig 7-8 show that there were positive and negative trends with K. So it is odd to me that it would be portrayed in such fashion. Move the Figs 7,8 up in the manuscript to describe these seasonal trends.

This part was moved.

P5989,4: Equation 4 is fine, but why isn't this just incorporated here. citing unpublished work hardly allows a reader to evaluate the statement that the relationship was "thoroughly studied" and what rationale can you provide that the parameters of Eqn 4 hold for all three streams? And even within one stream itself because of the variability shown in the SUVA values.

Unpublished work is cited because it is a part of a manuscript in preparation. Better description and rationale were added.

P5990,6: Use of the integrated dose in this manner is problematic. Action spectra should be calculated for each stream to make an effective estimate of K. There is too much uncertainty in the approach taken despite the performance of the empirical model in Eqn 4. Also, while the empirical formula to related K to Fe and pH was interesting, I recommend doing this individually for each system and then exploring the coefficients for Fe and pH in relation to the properties of each stream.

This section was removed.

P5991,26: can the authors speculate on the role of Fe and/or pH in causing these altering patterns. I disagree that previous irradiation reduces K because both SUVA254 and MW are increasing. Both of these chemical measurements suggest greater photoreactivity. However, if Fe exerts a primary control on photodegradation of DOC in these streams, then Fe dynamics (perhaps in response to particles, DO, pH) might also influence K. I would expect this insight can be gained by use of Eqn 4 with the data on hand.

The Discussion was expanded. See pages 18 and 19.

Tables and Figures: Tables were fine and informative, though Table 2 contained ex-

traneous information not explained or referred to in the manuscript. Figure 2-5 were the most informative and showed the comparable trends between the tributaries during the year. Figure 6 Figures 7-8 were confusing in terms of what was shown. Plot the appropriate figures on similar scales.

Scales in Figures were changed.

It was recommended to do some structural changes in manuscript so the revised version of manuscript is also attached as a supplement pdf file for referees to see the changes.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/10/C2866/2013/bgd-10-C2866-2013-supplement.pdf

Interactive comment on Biogeosciences Discuss., 10, 5977, 2013.

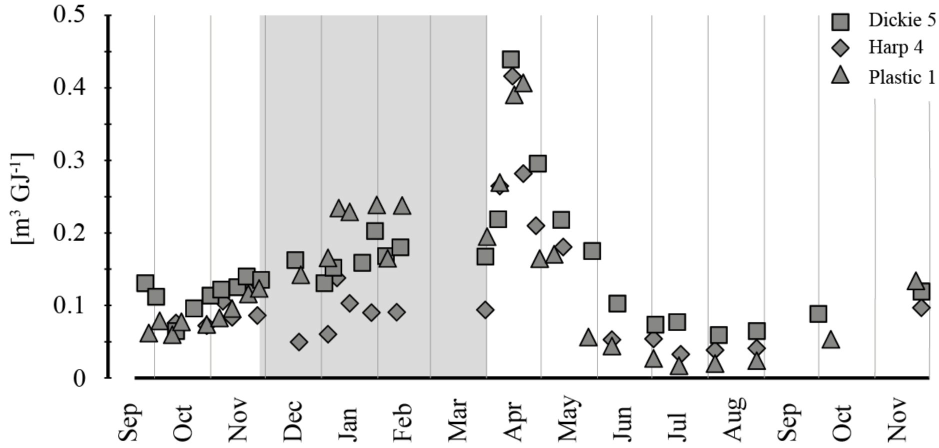

Fig. 1. Normalized rate constants