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

Anonymous Referee #2

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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.

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.

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.

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?

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 mached 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.

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?

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.

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.

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.

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.

Tables and Figures: Tables were fine and informative, though Table 2 contained extraneous 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.

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