Biogeosciences Discuss., 10, C2116–C2119, 2013
www.biogeosciences-discuss.net/10/C2116/2013/

Biogeosciences
Discussions
Open Access

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

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 experiment might be significantly influenced by interactive micro-

bial/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.

-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).

-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.

-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).

-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 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?

-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?

-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).

- 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).

-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 clfodder for discussion about other factors that may affect photodegradation rates (e.g. p 5989, line 15-16).

-I do not really understand the rationale for comparing the photoreactivity of DOM col-

lected up- and downstream to test the effect of previous DOM exposure on photoreactivity. 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.

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