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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

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We would like to thank the Reviewer for commenting on our reply. As with our previous exchange, there appears to be some ambiguity remaining in our description of the experimental set up and our data processing, as the Reviewer still appears to misunderstand what we have done, which is almost exactly as the Reviewer suggests in this second comment.

We would first like to point to two sections that are included in the submitted manuscript,

which contain key elements that address the Reviewer's first two points.

p6696. L10-20 (Appendix A)

"The solar simulator light had a total light dose of 750 Wm−2 and a spectrum representative of the sunlight (Fig. A1), which was used to calculate the total amount of light energy (in Wm−2)available in each section of the experimental tube by multiplying the incoming light dose by (1 – fraction absorbed (by glass and CDOM)). ONLY THE 300–450nm RANGE OF WAVELENGTHS WAS USED. The lamp emitted substantial amounts of longer wavelengths, which were not significantly absorbed by either the glass or CDOM, thus although those wavelengths (450–750 nm) contribute a large fraction of the total energy delivered, they typically do not contribute much to photochemical processes (Vähätalo et al., 2000). Including these wavelengths would thus tend to attenuate the cross-sample differences in average light dose."

p6680. L16-25 (Methods, section 2.4):

"Given the strong light dose and the small cross-section of the tubes, there was a negligible effect of the CDOM concentrations on the effective light dose inside the tubes, even for the most colored samples (See Appendix A for details). The amount of light energy available for wavelengths comprised between 300 and 450 nm, responsible for most photochemical processing of DOC (Vähätalo et al., 2000), averaged 130.8Wm−2 and did not vary substantially across samples (std. dev.= 9.2Wm−2; 10th and 90th percentiles= 118.4 and 140.4Wm−2, respectively) compared to the range of variation measured in the concentrations of photo-chemically degradable DOC (Pd-DOC), which spanned several orders of magnitude."

We are now going to reply to the individual points made by the Reviewer.

Reviewer:

The authors state that they have normalized Pd-DOC by taking into account 2 factors: (1) the absorption of light by the vials (same for all samples), and (2) the absorption

of light by CDOM (varies widely in this study). There are several problems with their assertion. First, (1) and (2) are wavelength dependent (Fig. A1), but they don't tell us which wavelength(s) were used or how their results are wavelength corrected (all light is lumped into "Watts per m2").

Authors:

As can be seen in both sections that we refer to above, we have used the 300-450 nm range to make these corrections, as this is where most photo-oxidation has been shown to occur in arguably comparable freshwater systems. We run a complete absorbance scan (230-700 nm, see p6679. L4,5) for every sample, as well as for the vials used for the experiment, so we did take into account the wavelength dependency, both in terms of the amount that passes through the vial and that is absorbed by CDOM within the vial.

Thus, for every wavelength in every sample, we have calculated the proportion of light that 1) passed through the vial and 2) remained in 10 consecutive equal sections within the vial. We have then multiplied this proportion by the incoming light dose (W m-2) emitted from the lamp AT EVERY WAVELENGTH. We had mentioned in the text the light dose at 340 nm (0.68 W m-2) only as a reference, but we used the corresponding light dose for every wavelength, according to the light spectrum of the lamp that is presented in Figure A1. This calculation yields a total light dose (in W m-2) for every sample in the 300-450 nm range, averaged to account for the loss of energy across the vial due to CDOM self-shading. Again, this has been done individually for every sample according to its own absorbance spectrum, and unless we are missing something here, this is precisely what the Reviewer suggests should be done. We will further clarify these points in the manuscript during the revision based on the above explanations.

Reviewer:

Second, if the light dose on the outside of the vials was constant at 130 W m-2 as stated by the authors, how is it possible that some of the samples received MORE light

(up to 140 W m-2), given that both the vials and CDOM absorb the incoming light?

Author:

The light dose outside the vial was not 130 Wm-2; this is the average light dose within the experimental vials for all samples, once it has been corrected for absorption by the vial and by CDOM within the vial. We acknowledge that this may not have been clear enough in the text, because it did not say that this was the light dose "within the vial". As an aside, had it been the light dose outside the vial, it could not have varied by 20% across 10th and 90th percentiles as we describe later in the same sentence (p.6680. L20-23).

In the manuscript (see specific sections reported above), we mention that the total light dose from the lamp is actually 750 Wm-2; this is for the whole spectrum. Of this total dose, only a certain proportion is included in the 300-450 range, and of the latter, a fraction is absorbed by the g glass and by the CDOM in the samples, as per the calculations explained above, all of which yielding an average light dose in the 300-450 nm range WITHIN THE VIAL of 130 Wm-2 across all the samples.

Reviewer:

Third, giving the authors the benefit of the doubt that (1) and (2) above are just a misunderstanding, I assumed they normalized their Pd-DOC values using a light screening factor. I assumed they calculated this light screening factor by multiplying the incoming light dose (assuming 1 mW m-2 at 300 nm), by e(-a_) (where a_ is the absorption coefficient of CDOM at a given wavelength and z is some depth in the vial).

Authors:

It indeed appears that the above concerns were due to misunderstanding; we appreciate that the Reviewer would give us the benefit of the doubt and further expands on their reasoning because the key concerns with which we fundamentally disagree lie in the following comments.

As an aside, we have to precise here that the lamp emitted no light at 300 nm; it emitted 0.3 Wm-2 at 320 nm, 0.68 Wm-2 at 340 nm etc. (see FIgure A1 for the complete spectrum).

Reviewer:

I calculate that this light screening factor ranges from $\sim$ 0.3 at 300 nm to 1 at 600 nm (and depending on the CDOM in the sample). Instead of correcting for the maximum light screening factor (0.3), as is the minimum approach used by some in the literature to correct for differences in light absorption by CDOM, I suspect that the authors used the average light screening factor across all wavelengths (300-600 nm or so ...), which is a factor of about 0.7-0.8 for a high CDOM sample, consistent with their assertion that the "maximum" effect of differences in initial CDOM is $\sim$ 20%.

Authors:

This is what we did, but for wavelengths ranging from 300-450 nm, not from 300 to 600 nm as the Reviewer assumed. Please note that this was explicitly stated in the manuscript sections that we have highlighted above. The numbers provided by the Reviewer match very well with our own calculations of the amount of light remaining AT Z = 24mm; please keep in mind, however, that we calculated the AVERAGE light dose within the vial from Z = 0 mm to Z = 24 mm for 10 equal sections.

We excluded wavelengths > 450 nm precisely for the reason mentioned below by the Reviewer: " although those wavelengths (450–750 nm) contribute a large fraction of the total energy delivered, they typically do not contribute much to photochemical processes" p. 6696. L15-20

Reviewer:

However, this average light-screening factor is large underestimate of the effect of differences in CDOM concentration because as has been shown in the literature, most of the mineralization of CDOM is driven by absorption of light in the UVB or low UVA

range (i.e. 300-320 nm), where the correction factor is much larger than 20% (more like 70%).

Authors:

Older and recent literature in freshwater environments comparable to ours, however, suggest that most of the photochemical mineralization of CDOM (or DOC) does not occur in the 300-320 nm range, as the Reviewer mentions, but rather rapidly peaks from 300 to 320-330 nm then slowly declines to wavelengths up to 550 nm, when incoming sunlight, apparent quantum yield and light attenuation in the water column are taken into account (see Vahatalo et al. 2000 (Figure 7), Koehler et al. in press (Figure 4)). As a consequence, the results presented in these studies suggest that there is nearly twice as much photochemical processing of DOC at WL > 320 nm than at WL < 320 nm in natural environments, and more importantly, that most photo-oxidation occurs at wavelengths comprised between 300 and 450 nm, which is why we decided that a 300-450 nm range was more appropriate to quantify potential biases due to CDOM self-shading in the incubation vials.

These technical details are indeed important, and we agree with the Reviewer that the magnitude of the potential biases due to CDOM self-shading need to be assessed, which is what we have done here. The Reviewer, however, not only dismisses our attempts to assess this technical problem, but finally concludes that all the patterns that we show in this paper are essentially driven by this potential technical problem, a conclusion that is fundamentally wrong.

The Reviewer bases their conclusion on the fact that the effective light dose at the critical wavelengths might vary up to 70% between the highest and lowest CDOM samples, and that this difference will drive all the patterns in the amount of Pd-DOC that we show here. The point that we would like to make here is that this difference in light dose as a result of CDOM self-shading cannot possibly drive the patterns that we report here. Whether there is a 20% or a 70% difference in the light dose to which the highest and

lowest CDOM samples are exposed to during our experiments makes almost no difference when comparing Pd-DOC concentrations ranging three orders of magnitude, from 0.05 to 10 mg L-1, i.-e. a 20 000 % variation.

In this regard, we had originally tried to illustrate this point with Figure A2, which shows the difference between the standardized and the non-standardized Pd-DOC concentrations, but the variation around the relationship was so small that the Reviewer concluded that there was either a misunderstanding on our part or an error in the calculations. This was not the case. Above we have attempted to clarify our calculations, and in order to further show how this potential bias cannot meaningfully affect our patterns, we present in this comment another, more conservative version of this figure (attached), which based on the Reviewer's comment now includes lower wavelengths.

The left panel shows the distribution of the individual % differences in the concentrations of Pd-DOC obtained without considering self-shading (using a calculated light dose at Z = 0 mm for WL 300-350 nm of 18.4 Wm-2), and considering self-shading due to CDOM, as described above. Please note that the lamp emitted no light at 300 nm and that very little light passed through the glass at 320 nm, so it would make little sense to use only the 300-320 range suggested by the Reviewer, as this range could not explain much of the Pd-DOC that we measured. Thus, we extended the range to 350 nm for this analysis.

The left panel shows that indeed there may be a bias in the effective light dose of up to 80% for the highest CDOM samples, that there is little difference for the lowest CDOM samples, and that there is typically a 20% difference (line shows median) between corrected and uncorrected samples regarding self-shading. The right panel, however, shows that when these individual differences are put in perspective of the whole set of Pd-DOC data, which ranges over several orders of magnitude, the amount of variation that is generated by self-shading is barely noticeable. Please note that the right panel is NOT the same as Figure A2. It was redrawn and now only includes lower wavelengths in order to emphasize how little difference in the patterns can be generated by the

wavelengths chosen.

Reviewer:

In summary, the results of this study are biased and can't be assessed or compared with the photochemistry literature because the authors still have not correctly considered the effect of CDOM absorbance on the amount of DOC available to be broken down by sunlight.

Authors:

There is a certain level of bias in high CDOM samples, which we have quantified. More importantly, we demonstrate that at that scale, this potential bias due to CDOM-induced self-shading cannot have a meaningful effect "on the amount of DOC available to be broken down by sunlight". Even more importantly, based on the evidence we provide above, we conclude that self-shading can in no way affect the PATTERNS in the concentration of Pd-DOC that we report here, in particular, the relationships that exist between Pd-DOC, Bd-DOC and their drivers. Considering that one of the main objectives of our study is to explore the coupling between Bd-DOC and Pd-DOC, we decided to present the uncorrected Pd-DOC data (in mg L-1) since these units are more intuitively comparable to the concentrations in biologically degradable DOC, thus more easily interpretable. We should further point out that several previous freshwater, estuarine and even marine studies of photodegradable DOC have taken a similar approach, so our results are still comparable to an abundant literature.

We would further like to point out that the current manuscript is one on the large-scale patterns and underlying drivers of degradable DOC in boreal freshwaters. Our group has a paper in preparation that is addressing the more technical photochemical aspects underlying the patterns reported here, but this is simply beyond the scope of the current study.

In order to avoid the type of misunderstanding that we had with the Reviewer, we will

make sure we clarify the methods underlying this section of the manuscript, and we will update the Appendix and Figure A2 according to above comments.

Links to cited papers:

http://aslo.org/lo/toc/vol_45/issue_3/0664.pdf

http://onlinelibrary.wiley.com/doi/10.1002/2014GB004850/abstract

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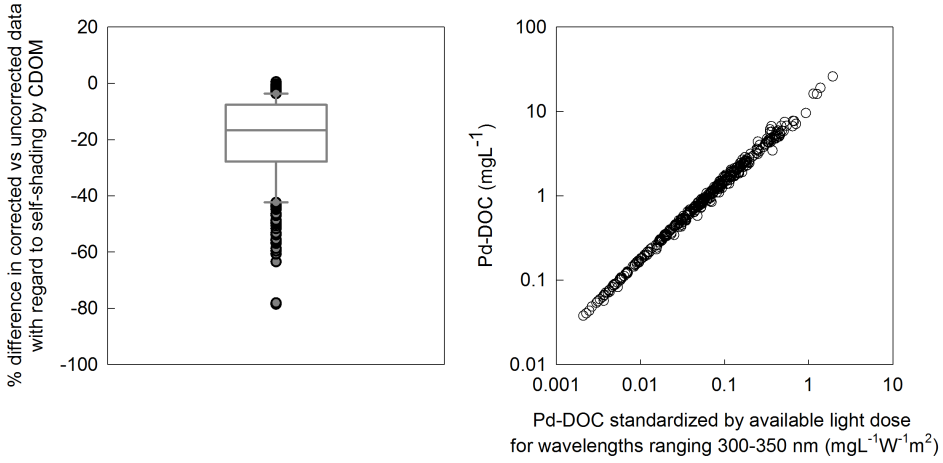

Fig. 1.