

Interactive comment on “Photochemical mineralisation in a humic boreal lake: temporal variability and contribution to carbon dioxide production” by M. M. Groeneveld et al.

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Dear Dr. Maria Tzortziou,

we are pleased by the overall positive reception of our manuscript “Photochemical mineralisation in a humic boreal lake: temporal variability and contribution to carbon dioxide production” by the reviewer, and greatly value the suggestions and comments provided by the reviewer and in one additional short comment. Below, we provide detail on how the manuscript has been revised in response to the comments. We think that the manuscript has improved significantly following the revision.

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Major Comments

1. Temporal variability of the AQY: Too little is done to assess if the difference between AQY is significant beyond the uncertainty of the measurements. The authors need to provide some measure of the uncertainty in the calculated AQY and they need to demonstrate using statistics that the month-to-month variability is significant beyond the uncertainty bounds of the AQY calculations. Uncertainty bounds around the coefficients (m_1 , m_2) need to be included. This is particularly important here because the temporal variability of the AQY is at the core of this study. Furthermore, in the text the authors go back and forth on whether the difference between AQY is important or not, and this more rigorous assessment would help. Also, instead of a single figure 1b showcasing all AQY at once, I would suggest creating a 6-panel figure with each panel showcasing a single AQY with its 90% confidence interval (one panel for each month). In each panel, the showcased spectra and its confidence interval would be in color and the other months' spectra would be shown as gray curves in the background, and the pooled AQY as a black curve. In addition to the statistics, this figure would help visualizing how uncertainties and temporal variability compare.

We fully agree with the reviewer in that there was potential and need to improve the statistical assessment of uncertainty and significance of the temporal AQY variability. In the revised manuscript, we used bootstrapping to estimate the 95% confidence intervals around the fit parameters m_1 and m_2 (eq. 2). These are reported in the revised Table 3, and the method is explained in the revised Sect. 2.3. In the original manuscript we reported that the parameter m_1 did not change over time while the parameter m_2 decreased over time (original MS P17136/L20-23). This is now visualised as well in the bootstrap distribution of parameter estimates, which we show in the revised Fig. S2c,d. We also used bootstrapping to calculate simultaneous pointwise 95% confidence intervals for AQY at five discrete wavelengths, midway between the cut-off wavelengths of the optical filters used in the irradiation experiments. We prepared a new 6-panel Figure 2 as suggested by the reviewer, where the monthly AQY spectrum with the si-

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multaneous pointwise confidence intervals is shown in colour, and can easily be compared to the AQY spectra of the remaining months shown as grey curves. The method is explained in the revised Sect. 2.3. Moreover, we used bootstrapping as well to simultaneously test for a temporal difference in the group of six monthly AQY evaluated midpoint between the cut-off filters. This analysis showed that temporal variability was significant beyond the uncertainty estimates. Based on the new analyses we revised the manuscript text in Sect. 3.2 to: “The monthly AQY spectra, evaluated at five discrete wavelengths and tested simultaneously, differed from each other ($p < 0.05$; Fig. 2). Specifically, while the AQY fit parameter m_1 did not change throughout the sampling period, the slope parameter m_2 decreased over time ($p = 0.005$; Table 3). This is also illustrated by the density of the bootstrap distribution of parameter estimates. The densities of m_1 overlapped for all months (Fig. S2c), while, for example, the densities of m_2 for June and July did not overlap with the densities of October and November (Fig. S2d).” We find that, in the revised version, uncertainty is well assessed, tested and visualised and are thankful for this constructive reviewers comment.

2. Use of Supor filters: In my experience, Supor Polyethersulfone filters strongly adsorb humic material, and can lead to a large decrease in the CDOM (effects were quite severe on the river waters that I have tested in the past). I would expect the problem to be exacerbated for water from humic lakes. I am therefore a little concerned about the effects of using these filters on the overall results from this manuscript. Ideally, the authors should try to assess and report the extent of the problem (in supplementary material and in main text) by comparing the effects of these filters with that of other, more adequate, types of membrane such as polycarbonate or nylon membrane. This is important here because this has potentially some important consequences for the findings of this study and can contribute to the AQY quantum yield and in the modeled DIC photoproduction rates.

To respond to this reviewers comment, we assessed the effect of humic lake water filtration through $0.7 \mu\text{m}$ GF/F filters vs. $0.2 \mu\text{m}$ Supor filters on CDOM absorbance. In-

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tegrated CDOM absorbance between 300 and 600 nm was 4.4% smaller in the Supor-compared to the GF/F filtered humic lake water, probably do to the difference in effective pore size and/or adsorption to the filters. This small loss of CDOM absorbance due to the use of this specific filter type should not have profoundly affected our estimates of AQY spectra and subsequent photochemical rate modelling. We have included a note about this in the Methods Sect. 2.1, specifically: “Filtration through the $0.2 \mu\text{m}$ membrane filters, which was conducted to minimise microbial abundance and hence microbial respiration during the irradiation experiments (Sect. 2.3), reduced the integrated CDOM absorbance between 300 and 600 nm by 4.4% compared to that of GF/F filtrate.”

3. Lag between irradiance and DIC photoproduction when using the monthly measured AQY (abstract and discussion): This argument does not make sense to me. I do not understand how the apparent lag between modeled irradiance and calculated DIC photoproduction rates (when using monthly AQY) suggests that AQY spectra change on time scales shorter than a month. This needs to be more clearly explained, or reassessed. Second, the lag in the data mentioned by the authors is not clearly seen in the data (mostly because figure 3 and S3 are not very clear). The authors mentioned they used a cross-correlation function that suggested a lag of 2-3 week lag. The cross-correlation function needs to be shown in the body of the manuscript (if the argument about the lag holds somehow).

This reviewers comment made us re-evaluate the argument, and we agree that we may not conclude based on the simulated time lag between irradiance and photochemical DIC production that AQY differs on a shorter but monthly time scale. We therefore deleted this argument. In our study, the smallest photoreactivity was observed in June/July when irradiance was highest and, vice versa, the highest photoreactivity was observed in October/November when irradiance was lowest. We now describe this pattern in Results Sect. 3.4 P13/L1-6. In the revised manuscript we focus less on the model parameterisation using the monthly measured AQY spectra to acknowledge

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the fact that the first AQY spectra was measured in early summer (June), and hence photoreactivity was not determined during spring.

4. New figure: I would strongly encourage the authors to add a new figure showing the location of the lake on a map of Sweden, which could be combined with Figure S2, which I think would also benefit from being shown in the main body. This would be a figure linked to the methods and that would help the reader get a sense of the study area and experiment setup.

As suggested by the reviewer, we added a map of Sweden showing the location of the study lake to Fig. S2, which has now been moved to the main body (new Fig. 1). We also included in this figure the positions of the floating chambers used for measurement of total CO₂ emissions (see also reviewers comment 5).

5. Contribution to CO₂ fluxes (Page 17140, lines 24-28): The authors compared their calculated DIC photoproduction rates to CO₂ fluxes estimates that are referenced as unpublished data. If these numbers are presented, the methods and data for estimating the CO₂ fluxes should be presented as well.

We agree with the reviewer that it is valuable for the manuscript to include the methods and more data about the total CO₂ emissions measured from the study lake. Hence, we included a method description in the revised manuscript (P10/L8-24). We also prepared a new figure (Fig. 5) where we show a box-plot for the total CO₂ emission next to boxplots of the simulated minimum and maximum photochemical DIC production. This figure illustrates and emphasises one of our major discussion points, that photochemical DIC production makes a small contribution to the total CO₂ efflux measured from a Swedish brownwater lake. Given the stronger emphasis on the comparison with CO₂ flux data and inclusion of further data (Fig. 5), Sivakiruthika Natchimuthu, who conducted the CO₂ flux measurements, analysed the data and contributed to this study in several detailed discussions, should be included as a co-author.

Minor comments

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- Figure 1a: In general, CDOM absorbance data below 240 nm are not reliable so I would suggest to only show the spectra from 250 to 600 nm, or even from 290 -600 nm since the data are not used below 290 nm and the spectral ranges of the CDOM spectra would match the displayed AQY.

We have adopted this suggestion and now only show absorption coefficients between 290 and 600 nm (revised Fig S2a).

- Figure 3 (and S3): The large number of symbols shown on the figure make it difficult to see the patterns. I would suggest using continuous lines instead, and separate the integrated irradiance and DIC production into two panels (top and bottom). The current figure is a little muddled and not much besides the seasonal variability can be seen.

We agree with the reviewer that the clearness of this figure could be improved. We revised Fig. 3 (Fig. 4 in the revised manuscript) and S3 to present separate panels showing irradiance and photochemical DIC production. However, we kept symbols instead of lines which, when we tried it, looked unclear due to the high inter-daily variability.

- Abstract (line 15) (and throughout manuscript): Use “between” or “among” instead of “across”.

The wording has been changed throughout the manuscript.

- page 17129 (line 18): SUVA is not a “measure” of aromaticity. The word “indicator” would be more appropriate. - Equation (3): need to change “alpha” to “a” - page 17136 (line 9) (and throughout): Please make sure P is defined,...I would suggest using “p-value” instead of P to prevent ambiguity.

We have edited the text concerning these three comments as suggested by the reviewer.

- page 17136 (line 20): The change mentioned here might be significant but is smaller than the change in production. Avoid using “significant” here as it implies the change

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is significantly larger than the uncertainty. - page 17136 (line 21): remove "were similar",...not sure what is meant here and contrary to the statement they are increasing.

We agree and revised this paragraph to improve clarity and provide more detail regarding the uncertainties around the fit parameter estimates in the form of confidence intervals (please see response to major comment 1).

- page 17138 (line 20): The in situ rates could be calculated for the depth interval corresponding to the submerged tube. I suggest removing this statement.

We removed this statement as suggested by the reviewer.

- Page 17139 (line 10): "relatively more DIC produced",... confusing,... consider changing wording

We agree and rephrased the sentence, specifically (P14/L14-15): "This suggests that the longer wavelengths contributed more to DIC photoproduction later in the season."

Further minor revisions

In addition to the revisions which we performed based on the reviewer's comments, we conducted the following minor changes in the manuscript:

- Rather than calculating a pooled AQY spectrum from the average fit parameters of all measurement, we have now calculated a pooled AQY spectrum by fitting through the data from all six measurement occasions simultaneously. The new pooled AQY spectrum is shown in Fig. S2b and details about this model parameterisation are shown in revised Table 3. The use of this new pooled AQY in photochemical rate modelling resulted in slightly higher DIC photoproduction (7.3 g C m⁻² yr⁻¹) than when the old pooled AQY spectrum was used (5.3 g C m⁻² yr⁻¹).

To assess accuracy of our fitted AQY spectra to reproduce photochemical DIC production during the irradiation experiments we used the R² of a linear regression between observed and predicted DIC photoproduction as indicator, together with the normalised

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root mean squared error. To expand the indicator set we now also included the slope estimates of the linear regressions in Table 3. In addition, we also give these model diagnostics when each AQY was used to predict photochemical DIC production from all measurement occasions. This was done to show how each individual AQY spectrum would perform when tested against all measurements. Moreover, given that our first AQY spectral measurement was conducted in June, and that we hence lack information about photoreactivity during spring, we decided to place less emphasis on the model parameterisation using monthly mean AQY spectra. Instead, we focus on the model parameterisation when using the least and most photoreactive water sample for simulation of photochemical DIC production. Following these changes, previous P17137/L17-26 was revised, now reading: "To assess which AQY spectrum was most representative for the photochemical reactivity observed throughout the open-water period of 2014 we used the monthly AQY spectra as well as the pooled AQY spectrum to predict the DIC photoproduction observed in all six irradiation experiments. This revealed that the AQY spectra of the more photoreactive water samples (October and November) gave the best prediction, considerably better than the pooled AQY spectrum, which according to this evaluation underestimated the observed DIC photoproduction (Table 3). We therefore used the AQY spectrum from the most photoreactive water sample (November) in photochemical rate modelling for the year 2014, which gave a simulated DIC photoproduction of 12.2 g C m⁻² y⁻¹ (Table 3, Fig. S3a). Using the AQY spectrum from the least photoreactive water sample (July) for annual simulation the estimate would be 5.6-fold smaller (Table 3, Fig. S3b), and using the monthly measured AQY spectra for periods of one month around the sampling date the estimate would be three times smaller (Table 3; Fig. S3c). The rather small estimate when using the monthly measured AQY spectra for month-long time periods is related to the facts that 1) the comparatively small photochemical reactivity measured during the first sampling in June was used to simulate photochemical mineralisation also for the open-water period prior to June, and 2) observed photochemical reactivity was smallest during summer when irradiance is maximal, and highest during late autumn when

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irradiance is low (Table 3, Fig. S3d).”

- When we compare model simulated photochemical DIC production rates to those measured in situ we assume that the incubation tubes do not interact with the irradiance field. We noted that we did not state this assumption in the original manuscript, and now included it in the Methods (P10/L5-8): “We assumed that the quartz tubes did not interfere with irradiance. While, in reality, the quartz tubes will affect the number and optical path length of the photons entering the tube we considered this effect minor compared to other uncertainties during the in-situ measurements (see Discussion).”

- We conducted chemical actinometry to verify our calculated CDOM absorbed photons. We included this aspect in the methods description (section 2.3, P7/L3-12).

- We included one more literature reference on seasonal variability of photochemical reactivity in the introduction, specifically (P3/L13-15): “For example, a study in a tropical lagoon observed the largest and smallest photochemical mineralisation rates during rainy and dry season, respectively (Suhett et al., 2007).”

- We moved some information about the photochemical rate modelling for 2012-2014 from the Methods to the Results section because we found it would facilitate understanding of our approach for the reader, and slightly edited this paragraph (new P13/L10-22).

All additional minor text edits throughout the manuscript are tracked in the manuscript, which indicates the changes we made during revision.

We thank you for acting as editor for our study, and are looking forward to hearing from you about our manuscript!

Yours sincerely,

Marloes Groeneveld and co-authors

Interactive comment on Biogeosciences Discuss., 12, 17125, 2015.

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