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Point-by-point response to the reviews

Review 1

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 (m1, m2) 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.

Response: 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 simultaneous 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)." (revised MS P11/L27-P12/L3).

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.

Response: To respond to this reviewers comment, we assessed the effect of humic lake water filtration through 0.7 µm GF/F filters vs. 0.2 µm Supor filters on CDOM absorbance. Integrated 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 µm 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." (revised MS P4/L6-9).

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 in 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).

Response: 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/L3-8.

In the revised manuscript we focus less on the model parameterisation using the monthly measured AQY spectra to acknowledge 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.

Response: 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 CO_2 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.

Response: We agree with the reviewer that it is valuable for the manuscript to include the methods and more data about the total CO_2 emissions measured from the study lake. Hence, we included a method description in the revised manuscript (P10/L11-27). We also prepared a new figure (Fig. 5) where we show a box-plot for the total CO_2 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 CO_2 efflux measured from a Swedish brownwater lake.

Given the stronger emphasis on the comparison with CO_2 flux data and inclusion of further data (Fig. 5), Sivakiruthika Natchimuthu, who conducted the CO_2 flux measurements, analysed the data and contributed to this study in several detailed discussions, should be included as a co-author.

Minor comments

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.

Response: 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.

Response: 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".

Response: 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.

Response: 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 that the change in production. Avoid using "significant" here as it implies the change 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.

Response: 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 (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.

Response: We removed this statement as suggested by the reviewer.

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

Response: We agree and rephrased the sentence, specifically (P15/L1-2): "This suggests that the longer wavelengths contributed more to DIC photoproduction later in the season."

Review 2

General Comments:

The role of photochemical oxidation of DOM in natural waters in releasing CO2 has been studied since the 1980s. However, many questions remain regarding the nature of the process and it rates – the latter of which the present study addresses. Their study reports valuable findings on the high seasonal variability of the apparent quantum yield (AQY) that is an integrated index of wavelength-specific photochemical reactivity of DOM. By making monthly experimental measurements of AQY in a humic Swedish lake and running photochemical rate modeling exercises, they conclude that the photochemical production of CO2 is a minor fraction of the over- all CO2 production in humic Swedish lakes that is presumably dominated by biological respiration. Advancing the discussion of these findings to low-latitude lakes with *less seasonality and including considerations of loading of CDOM with variable reactivities based on the nature of the different biogeochemical backgrounds of their watersheds would enrich this study.*

Response: 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", and greatly value the suggestions and comments given by the reviewer. Below, we provide detail on how the manuscript has been revised in response to the comments.

Details:

1. Title: The title describes the subject well, but reveals nothing of the findings. Suggest changing the later part of the title as follows: "large temporal seasonal variability with minor contribution to CO2 production".

Response: We agree that the title could be more informative concerning the main findings of the study. We revised the title to: **"**Photochemical mineralisation in a boreal brownwater lake: Considerable temporal variability and minor contribution to carbon dioxide production".

2. Abstract: Good.

3. Introduction: Nice introduction to the problem.

4. Methods: Sufficient detail is given.

5. Results: Results are well presented, and I have no suggestions to make here.

Response: We are pleased about the positive comments concerning these manuscript parts.

6. Discussion: Nice discussion points. Advancing the discussion of these findings to low-latitude lakes with less seasonality and including considerations of loading of CDOM with variable reactivities based on the nature of the different biogeochemical backgrounds of their watersheds would enrich this study.

Response: Although no study has yet measured AQY spectra in low-latitude lakes, we acknowledge that a few studies have investigated seasonal variability in photochemical DOC mineralisation. We now include a paragraph in the discussion devoted to a comparison between the effect of seasonality in high-latitude and low-latitude systems, referring to a recently published article by Vachon et al. (2016) on temporal variability in temperate and boreal systems and articles by Amado et al. (2006) and Suhett et al. (2007) on tropical systems, specifically:

"Similarly, rainfall and input of fresh terrestrial material increased CDOM photoreactivity in tropical lakes (Amado et al., 2006; Suhett et al., 2007). For tropical systems, which receive an even dose of sunlight throughout the year, the importance of photochemical reactivity in regulating temporal variability in photochemical DIC production may be expected to be higher than in boreal lakes, where temporal changes in photochemical reactivity interact with the pronounced seasonality in irradiance. Accordingly, CDOM photoreactivity and irradiance explained a similar amount of variability in photochemical mineralisation across seasons for three boreal and northern temperate lakes (Vachon et al., 2016)." (revised MS P16/L2-10).

7. Furthermore, a simultaneous study of both ecosystem respiration and photochemical oxidation rates would have been very helpful. The authors should at least attempt a literature review – perhaps in the shape of a Table and discuss the take home message and how it relates to the current study.

Response: During June to October 2012 and April to November 2013, total CO_2 emissions were measured from the same lake using floating chambers (Natchimuthu et al., unpublished data). In the originally submitted manuscript, we had compared the mean simulated DIC photoproduction to the mean observed CO_2 emissions (P17140/L22-29 and P17141/L1). Moreover, we compare the simulated DIC photoproduction from our study to four more studies from boreal Sweden (Jonsson et al., 2001, Humborg et al., 2010, Koehler et al., 2014, Chmiel et al., 2016; P17141/L1-10). To address this reviewers comment, and a similar comment by reviewer #1, we placed more emphasis on relating our study to the total CO_2 flux measurements. Specifically, we included the methods for the total CO_2 flux measurements, and prepared a boxplot comparing the mean total CO_2 emissions to the simulated photochemical DIC production (new Fig. 5), illustrating that simulated photochemical DIC production made just a minor contribution to the total observed CO_2 emissions from this boreal brownwater lake. Given that we use the total CO_2 emissions fluxes more extensively we extended the author list, including S. Natchimuthu. The take-home message is discussed on original P17141/L15-20, and revised MS P16/L30-P17/L4.

8. Refs: O.K. I consider this work to be of considerable interest to the readership of BG. The overall approach has merit, and these experimental measurements covering seasonal variability and modeling of photochemical mineralization of DOM reveal lower than expected rates of photomineralization of carbon, help advance our understanding of photochemical reactivity of DOM in natural waters and brings better context to its diminished but still important role in the carbon cycle of Earth's watersheds. I suggest revision including a more robust Discussion of the findings as noted above.

Response: We revised the discussion section of the manuscript according to the reviewers suggestion, as detailed above.

Review 3

General comments:

This manuscript by Groeneveld et al. describes a seasonal study of the photochemical degradation rates of dissolved organic matter (DOM) in a humic northern (Boreal) lake in Sweden by looking at "in situ" photochemical dissolved inorganic carbon (DIC) production estimated rates and modeled estimated rates. Also, the manuscript focused on the apparent quantum yields (AQY) over a temporal scale. The study is well designed and developed and bring interesting data that might contribute to the general current knowledge of the DOM photochemistry dynamics in lakes and also points out that it is reliable to evaluate the photochemical contribution to lakes carbon budget using modeling methods. Thus, in my opinion the manuscript is suitable for publication in Biogeosciences.

Response: 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", and greatly value the suggestions and comments given by Dr. Amado. Below, we provide detail on how the manuscript has been revised in response to the comments.

I acknowledge here that reviewer # 1 did a great job reviewing the manuscript raising questions and pointing out really relevant issues (regarding technical aspects of the research) to be addressed before acceptance and I totally agree with all these comments. Also, I noticed that the authors already addressed these concerns, which I believe have greatly improved the manuscript quality.

Response: We agree that the comments provided by reviewer # 1 were very helpful in improving the manuscript.
On the other hand, in my opinion it is necessary to better explore the main message of the manuscript regarding the title and the discussion structure. Thus, I'll recommend the manuscript for publication after the consideration of the aspects that will be detailed below.

Aspects of the general message to be addressed:

1. The title describes what the study aimed, but does not bring the message of the manuscript. As I understand, the photochemical mineralization contribution to to the total carbon dioxide (CO2) production in the lake is minimal and that was the expected from the literature (e.g. Jonsson et al. 2001) and thus, the authors may feel that it does not calls great attention to the *paper. However, this study brings this confirmation in a very consistent way due to a more complete time-scale approach because it considers the seasonal variation of the photochemical DOM degradation and total CO2 production. On the other hand, this work also highlights the relevance of considering the temporal (seasonal) variation to estimate the AQY rather than time-limited observation/estimates. That brings a reliable modeling approach (demonstrated through the comparison with the "in situ" measurements) to study the photochemical contribution to CO2 production in lakes for broader time and spatial scales. Raised these aspects, the authors should pick what they believe as being the most relevant aspect of the work as the main take-home message to acknowledge in the title (and make it more attractive and informative).*

Response: In response to this comment, and to similar comment by reviewer #2, we revised the manuscript title to **"**Photochemical mineralisation in a boreal brownwater lake: Considerable temporal variability and minor contribution to carbon dioxide production", highlighting both main findings of the study.

2. The discussion of the manuscript does a great job in presenting the patterns found in the research, adding the data in the literature results perspective and discussing it altogether. However, in my opinion it is not clear in the discussion what is the main message of the work, following the thoughts line in my previous comment. Thus, my suggestions to the authors are: a) Think through the paper and considering the literature (state of art of the research topic) to clearly recognize what should be the take-home message of the paper: either the confirmation of the low contribution of the photochemically produced CO2 to the whole lake carbon budget in the humic boreal lakes considering the seasonal variation or the possibility of using modeling tools to study this photochemical contribution in lakes with good confidence. In my opinion, the first one should be adopted as the main message and better exploited in the title of the paper and the second one should be clearly stated in the discussion;

Response: We revised the manuscript title, which now states that the contribution of photochemical mineralization to carbon dioxide production in the studied boreal brownwater lake was minor (see also response to comment above above).

b) In the discussion, write an introductory paragraph where the authors would clearly state the main message and secondary messages of the paper so the reader can be better guided in the discussion to what is the contributions of the paper. As I mentioned in the previous comment (A), the low contribution of photochemical degradation to the total CO2 in the humic lake is an important finding and could be the pointed as the main message. Also the possibility of other studies be carried out in different lakes from different regions (such as tropical lakes with high sunlight incidence all over the year) to evaluate the AQY and CO2 photochemical *production through modeling estimates should be stimulated as this paper shows that it is an important and reliable approach.*

Response: We agree with the reviewer, and have included a new introductory paragraph in the discussion section where we stress the main message of the manuscript and aim to facilitate the understanding of the reader:

"The apparent quantum yield (AQY) spectra for photochemical DIC production, measured monthly between June and November 2014 in a boreal brownwater lake, showed considerable seasonal variability, with the slope of the spectrum decreasing over the open-water season. Photochemical DIC production, simulated using photochemical rate modelling, made a minor contribution to the total CO_2 emissions observed from the same lake (Fig. 5). Hence, similar results from earlier studies in boreal Sweden (Jonsson et al., 2001; Koehler et al., 2014; Chmiel et al., 2016) were corroborated when considering temporal variability in photochemical reactivity as well as in total lake CO_2 emissions. Moreover, the good match between photochemical DIC production observed in situ and simulated rates (Fig. 2) supported that photochemical rate modelling is a suitable approach to investigate photochemical DOM mineralisation in lakes and its contribution to carbon cycling on broader temporal and spatial scales. This highlights the potential to use a similar method for studying this process also in other climate zones, e.g. for tropical lakes, where the role of photochemical mineralisation for lake carbon cycling remains even less constrained than in boreal and temperate systems." (revised MS P13/L23-P14/L7)

List of all relevant changes made in the manuscript

- The title has been changed to: “Photochemical mineralisation in a boreal brownwater lake: Considerable temporal variability and minor contribution to carbon dioxide production” (revised MS P1/L1-3).

- Because we included methods and more data on total CO_2 fluxes from Lake Erssjön, measured and analysed by S. Natchimuthu, we included her as a co-author (revised MS P1/L5).

- We included two more literature reference on seasonal variability of photochemical reactivity in the introduction, specifically (P3/L13-15): “For example, studies in a tropical systems observed the largest and smallest photochemical mineralisation rates during rainy and dry season, respectively (Amado et al., 2006; Suhett et al., 2007).”

- We also now refer to a recently published article by Vachon et al. (2016) in the introduction and discussion.

- Fig. S2 has been moved to the main text as the new Fig. 1, and also includes a map of Sweden as well as the locations of the chambers for total CO_2 measurements.

- Information on the effect of Supor filters on CDOM absorbance has been included in the methods (revised MSP4/L6-9).

- We conducted chemical actinometry to verify the calculated CDOM absorbed photons of our irradiation setup for AQY determination. We included this aspect in the methods description (section 2.3, revised MS P7/L3-12).

- We included new statistical analyses to assess changes in the AQY fit parameters and temporal variability in AQY spectra, and to assign confidence intervals to the AQY spectra (P7/L22-P8/L9).

- 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 included a method description for the total CO_2 measurements in the revised manuscript (P10/L11-27). We also prepared a new figure (Fig. 5) where we show a box-plot of the total CO_2 fluxes next to boxplots of the simulated minimum and maximum photochemical DIC production.

- Rather than calculating a pooled AQY spectrum from the average fit parameters of the six monthly AQY measurements, 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 R^2 of a linear regression between observed and predicted DIC photoproduction as indicator, together with the normalised root mean squared error. To expand the indicator set we now also included the slope estimates of the linear regressions in Table 3 (revised MS P12/L3-5). 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 (Table 3).

- We added the results from the new analyses (see above) to section 3.2 (revised MS P11/L27-P12/L3), and included new Fig. 2 and S2.

- We revised section 3.4 (‘Photochemical rate modelling’) to place less emphasis on the model parameterisation using monthly mean AQY spectra. Instead, we focus on the model parameterisations when using the least and most photoreactive water sample for simulation of photochemical DIC production (previous P17137/L17-26, revised MSP12/L21-P13/L8). We also show daily photochemical DIC production rates using the AQY spectrum with the highest photochemical reactivity, lowest photochemical reactivity, and using the monthly measured AQY spectra for month-long time periods around the sampling date in the new Fig. S3.

- 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 (revised MS P13/L9-21).

- To improve clarity, the old Fig. 3 is now presented in two panels, in new Fig. 4.

- We have included a new introductory paragraph in the discussion section where we stress the main messages of the manuscript (revised MS P13/L23-P14/L7).

- In the discussion, we added a few lines on temporal variability in tropical systems to discuss to results from our boreal study lake in a wider context (revised MS P16/L2-10).

Photochemical mineralisation in a boreal brownwater lake: Considerable temporal variability and minor contribution to carbon dioxide production

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Abstract

Sunlight induces photochemical mineralisation of chromophoric dissolved organic matter (CDOM) to dissolved inorganic carbon (DIC) in inland waters, resulting in carbon dioxide (CO_2) emissions to the atmosphere. Photochemical rate modelling is used to determine sunlight-induced CO_2 emissions on large spatial and temporal scales. A sensitive model parameter is the wavelength-specific photochemical CDOM reactivity, the apparent quantum yield (AQY). However, the temporal variability of AQY spectra within inland waters remains poorly constrained. Here, we studied a boreal brownwater lake in Sweden. We measured AQY spectra for photochemical DIC production monthly between June and November 2014 and parameterised a photochemical rate model. The total AQY between 280 and 600 nm increased about threefold during the open water period, likely due to a high rainfall event with consecutive mixing in autumn that increased availability of highly photoreactive CDOM. However, the variability in AQY spectra over time was much smaller than previously reported variability in AQY spectra between lakes. Yet, using either the AQY spectrum from the least or from the most photoreactive water sample resulted in a 5-fold difference in simulated annual DIC photoproduction (2012-2014), with 2.0 ± 0.1 and 10.3 ± 0.7 g C m^{-2} yr^{-1}, respectively. This corresponded to 1 and 8% of the mean CO_2 emissions measured from this

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lake. We conclude that (1) it may be recommendable to conduct repeated AQY measurements throughout the season for more accurate simulation of annual photochemical DIC production in lakes and (2), in agreement with previous studies, direct CDOM photomineralisation makes only a minor contribution to mean CO_2 emissions from Swedish brownwater lakes.

1 Introduction

Inland waters play a substantial role in carbon cycling (Cole et al., 2007; Battin et al., 2009; Tranvik et al., 2009). The major carbon fluxes occurring in inland waters are burial in sediments and mineralisation followed by carbon dioxide (CO_2) emission into the atmosphere. A substantial fraction of the CO_2 emissions is attributed to microbial mineralisation of dissolved organic carbon (DOC) (del Giorgio et al., 1997; Duarte and Prairie, 2005). Also, sunlight contributes to CO_2 production via photochemical mineralisation of chromophoric dissolved organic matter (CDOM) (Granéli et al., 1996; Bertilsson and Tranvik, 2000). According to the first global upscaling study, up to about one tenth of the CO_2 emissions from lakes and reservoirs are directly sunlight induced (Koehler et al., 2014). However, the importance of sunlight for carbon processing varies strongly between systems and studies (Granéli et al., 1996; Molot and Dillon, 1997; Ziegler and Benner, 2000; Cory et al., 2014).
Measuring photochemical DOC mineralisation, equivalent to photochemical production of dissolved inorganic carbon (DIC), in the field is challenging and seldom conducted (Salonen and Vähätalo, 1994; Graneli et al., 1996). Photochemical rate modelling is used to obtain DIC photoproduction estimates at large spatial and temporal scales. Model parameterisation requires wavelength-specific irradiance, CDOM absorbance, attenuation and photochemical CDOM reactivity, i.e. the apparent quantum yield (AQY) defined as DIC produced per mol photons absorbed (Fichot and Miller, 2010; Koehler et al., 2014). The AQY is a sensitive model parameter but until now spectra have only been published from a small number of lakes (Vähätalo et al., 2000; Vähätalo & Wetzel, 2004; Koehler et al., 2014; Cory et al., 2014; Vachon et al., 2016), and temporal variability of AQY spectra within individual systems is even less studied (Cory et al., 2014; Vachon et al., 2016). Given the limited knowledge on spatial and temporal variability of AQY spectra the first large-scale modelling study of photochemical CDOM mineralisation in inland waters assumed that AQY spectra determined

Deleted: (2.0 ± 0.1 and 10.3 ± 0.7 g C m^{-2} yr^{-1}, respectively). Using the monthly measured AQY spectrum to simulate DIC photoproduction for month-long time periods resulted in an apparent time lag between irradiance and DIC photoproduction. This suggested that temporal variability in AQY spectra occurs on shorter time scales. Therefore, we parameterised the model with the pooled AQY spectrum of six monthly measurements. Simulated DIC photoproduction for three years (2012–2014) averaged 4.5 ± 0.2 g C m^{-2} yr^{-1}, which represented 3 % of the mean CO_2 emissions from this lake.

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for single systems and on single occasions represented photochemical reactivity on larger spatial and temporal scales (Koehler et al., 2014).

Deleted: The AQY is a sensitive model parameter but until now only a few spectra have been published from lakes (Vähätalo et al., 2000; Vähätalo and Wetzel, 2004; Koehler et al., 2014; Cory et al., 2014). Besides this very limited knowledge on variability of AQY spectra across differing lakes, their temporal variability within individual systems has not yet been studied. The modelling studies so far assume that AQY spectra determined for single systems and on single occasions represent photochemical reactivity on larger spatial and temporal scales (Cory et al., 2014; Koehler et al., 2014).

However, temporal variability in AQY spectra is to be expected. For example, photochemical DIC production can increase with increasing CDOM aromatic content, increasing iron concentrations or decreasing pH (Gao and Zepp, 1998; Bertilsson and Tranvik, 2000; Anesio and Granéli 2004; Stubbins et al., 2010). An important process that may influence CDOM quality on a seasonal scale is photobleaching, where CDOM is transformed to less coloured and less aromatic compounds (Brinkmann et al., 2003; Müller et al., 2014). Consequently, CDOM can become less photoreactive after light exposure (Lindell et al., 2000; Gonsior et al., 2013), and this “light dose dependence” may be especially important at high latitudes (Zhang et al., 2006). Temporal fluctuations may also be caused by photoreactive terrestrial CDOM entering aquatic systems through heavy rainfall and runoff (Spencer et al., 2010; Hughes et al., 2013). For example, studies in a tropical systems observed the largest and smallest photochemical mineralisation rates during rainy and dry season, respectively (Amado et al., 2006; Suhett et al., 2007).

In this study, we examined temporal variability in photochemical reactivity and photochemical DIC production in a small brownwater lake in Sweden. We then evaluated differences in photochemical DIC production simulated using a photochemical rate model with time-constant vs. repeatedly measured AQY spectra. Finally, we assessed the contribution of mean annual photochemical DIC production to total mean CO_2 emission from this lake.

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2 Material and methods

2.1 Study lake and sampling

Erssjön (58°37´ N, 12°16´ E) is a small brownwater lake (59 997 m^2, mean depth 1.3 m, maximum depth 4.4 m) in the Bäveån catchment in southwest Sweden (Fig. 1a). The lake is mostly surrounded by forest, mainly spruce and birch, and some agricultural land, and is part of the Skogaryd Research Site (Klemedtsson et al., 2010). In 2014, the ice disappeared from lake Erssjön on 25 February (S. Peter, personal communication, 2014) and the lake remained ice-free until 31 December. For this study, 2L of surface water was grab-sampled into acid-

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washed polyethylene bottles in the middle of the lake, monthly between April and November 2014. The samples were kept dark and cold (<10°C) until and during transport to Uppsala University within one to three days. Upon arrival, the water was filtered sequentially through pre-combusted glass fibre filters (Whatman GF/F, GE Healthcare, Little Chalfont, Buckinghamshire, UK) and 0.2 µm polyethersulfone membrane filters (Supor®-200, Pall Corporation, Ann Arbor, Michigan, USA) into glass bottles. Filtration through the 0.2 µm 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. The samples were wrapped in aluminium foil and kept at 4°C until further analysis within three weeks.

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2.2 Chemical and optical water properties

DOC concentrations were measured with a total carbon analyser (Shimadzu TOC-L, Shimadzu Corporation, Kyoto, Japan), as non-purgeable organic carbon (NPOC) concentration. UV-Vis absorbance spectra (200 to 600 nm) of filtered water were measured in a 1 cm quartz cuvette using a Lambda35 UV-VIS Spectrometer (PerkinElmer Lambda 25, Perkin Elmer, Waltham, USA). Based on the Beer–Lambert law, absorption coefficients a (m^{-1}) were calculated as:

$$a = \frac{A \ln \mathbf{10}}{L} \quad (1)$$

where A is absorbance (dimensionless) and L is optical path length (m) (Kirk, 2010). The specific UV absorption coefficient at 254 nm ($SUVA_{254}$; L mg C^{-1} m^{-1}), a commonly used indicator of DOC aromaticity (Weishaar et al., 2003), was calculated as the ratio between a_{254} and the DOC concentration ($mgCL^{-1}$). Synchronous fluorescence scans were obtained using a FluoroMax-4 Spectrofluorometer (FluoroMax-4, Jobin Yvon, Horiba, Kyoto, Japan), with excitation-emission matrices (EEMs) between excitation wavelengths 250 to 445 nm with 5 nm increments, and emission wavelengths 300 to 600 nm with 4 nm increments. The EEMs were blank-subtracted using a sample of Milli-Q water run on the same day, corrected for instrument biases and inner filter effects and normalised to Raman units (Lawaetz and Stedmon, 2009; Kothawala et al., 2013). Three commonly used indices were calculated at fixed excitation/emission wavelength pairs or regions (Coble et al., 2014; Gabor et al., 2014).

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All fluorescence corrections and analyses were performed using the FDOMcorr toolbox for MATLAB (Murphy et al., 2010).

For total nitrogen (TN) analysis, all nitrogen species were oxidised to nitrate using potassium persulfate and sodium hydroxide at high pressure and temperature in an autoclave. TN was determined spectrophotometrically by subtracting a blank and absorbance at 275 nm from absorbance at 220 nm (PerkinElmer Lambda 40 UV- VIS spectrometer, Perkin Elmer, Norwalk, CT, USA). EDTA (disodium-dyhydrogen- ethylendiamine-tetraacetat) was used for the calibration curve (Rand et al., 1976). Total phosphorus (TP) was converted to orthophosphate using oxidative hydrolysis with potassium persulfate in acid solution at high pressure and temperature in an autoclave, and to phosphorus molybdate by reaction with ammonium molybdate, which was then reduced with ascorbic acid, accelerated by antinome. The samples were analysed spectrophotometrically at 882 nm as molybdate reactive phosphorus (PerkinElmer Lambda 40) (Menzel and Corwin, 1965; Murphy and Riley, 1958). TP concentrations measured for the LAGGE project were used (M. Wallin, unpublished data).

2.3 Apparent quantum yield

The wavelength-specific CDOM reactivity towards photochemical DIC production, i.e. the apparent quantum yield (AQY) defined as mol DIC produced per mol CDOM absorbed photons, was determined monthly between June and November 2014 similarly as described in Koehler et al. (2014). The measurements from April and May could not be used due to failure of the DIC analyser. Specifically, to minimise initial DIC concentration, the samples were acidified (10 % HCl to pH < 3), bubbled with nitrogen gas for 25 min to remove the CO_2, and re-adjusted to the original pH using 1M NaOH. The amount of HCl and NaOH added never exceeded 0.5 % of the sample volume. The water was re-filtered with 0.2µm Supor®-200 filters to minimise bacterial abundance and hence respiration during subsequent irradiation. During this filtration step the water, in which oxygen concentrations were reduced during bubbling with N_2, was also aerated again. The water was then filled into cylindrical glass vials with flat quartz top (50 mL volume; Fig. S1). The incubation vials were soaked in 10 % HNO_3 for at least ten hours and rinsed thoroughly with Milli-Q water before and after each experiment. To systematically manipulate the irradiance field, cut-off filters (CVI Laser Corporation, obtained from former Gamma Optronik AB, Sweden and Oriel Instruments, Newport Corporation, Irvine, California) that cut off irradiance with wavelengths below 455, 420, 380, 350, 320, 309 or 280 nm (Fig. S1) were placed on top of the vials. All filters and dark controls, where a black lid was attached to the vial, were used in triplicate. Thin needles were inserted through the septa covering one of the vial outlets to enable pressure release during irradiation in the solar simulator. Using three vials with and three vials without a needle through the septum, which were filled with a standard of 1500 ppb IC and left at room temperature for 24 h, we verified that this did not affect DIC concentration in the vessel (p = 0.113). Then, the samples were irradiated for five hours using a solar simulator (Q-Sun 1000 Xenon test chamber, Q-panel Lab Products Europe, Bolton, UK) set to 0.59 W m^{-2} at 340 nm (calibrated with the instrument's CR20 Calibration Radiometer). During irradiation, the samples were standing in a cooled water bath, maintaining the temperature around the vials at approximately 25°C. Initial and final DIC concentrations were measured from each vial with the Shimadzu TOC-L analyser, and the photochemical DIC production in each vial was calculated as the difference between the final and initial DIC concentration, minus the mean production in the dark controls. A calibration curve was created before each run, using the auto-dilution function to create six standards of different concentrations from a 5 or 10 ppm solution that was freshly prepared from a 1000 ppm IC stock solution ($R^2 \geq 0.998$) (Shimadzu user manual). DIC concentrations were measured in a minimum of five injections of 150 µL, resulting in SD < 0.5 ppb and/or CV < 2%. In the June experiment the "dark DIC production" was −0.2 to −17 ppb. We suspect this was due to a slight offset in the calibration of the instrument during the measurements and/or difficulty to detect very low DIC concentrations, and set the control values to zero. In the August experiment, the dark production of one control set was considerably higher than usual. Since the acid-washing step had been missed during cleaning of these three vessels we suspect the high concentrations were caused by contamination. Therefore, the values of the other control set were used for calculating photochemical DIC production. This affected the resulting AQY spectrum only to a minor extent (Fig. S2b in the Supplement). Across experiments, DIC production in the dark controls averaged 26.2 ± 4.6 ppb, corresponding to 3 and 24% of the average DIC production under the 250 and 455 nm cut-off filter, respectively. On eight occasions throughout the study period, irradiance spectra (280–600 nm) were measured at the location of each vial using a spectrometer (BLACK Comet UV-VIS, StellarNet Inc., Tampa, Florida, USA) equipped with

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a fibre optic cable (STEF600-UVVis-SR, StellarNet) and a cosine receptor for UV-Vis near-infrared irradiance (STE-CR2, StellarNet). Absorbed photons were calculated accounting for the inner filter effect (Hu et al., 2002). The calculated number of CDOM-absorbed photons was in good agreement with CDOM-absorbed photons determined using nitrite ultraviolet actinometry, where the photon exposure of an irradiated sample is quantified from the photochemical production of salicylic acid formed during reaction of the hydroxide radical with benzoic acid (Jankowski et al., 1999; Jankowski et al., 2000). The response bandwidth was verified, and the photoproduced salicylic acid was detected using fluorescence spectrophotometry (SPEX FluoroMax-4; Jankowski et al., 1999). CDOM-absorbed photons determined with the spectrally resolved calculation used during AQY determination and the broadband actinometry differed by a factor of 1.43 ± 0.04 under the complete irradiance spectrum in the solar simulator.

AQY spectra were calculated using weighted parameter optimisation (Rundel, 1983) to an exponential function

$$\Phi = e^{-(m_1 + m_2(\lambda - 290))} \qquad (2)$$

where Φ is the AQY of DIC photoproduction (mol DIC mol photons^{-1}), λ is the wavelength (nm) and m_1 and m_2 are fit parameters (Johannessen and Miller, 2001), using the Nelder Mead simplex minimisation algorithm (Nelder and Mead, 1965) implemented in the function *optim* in R 3.1.0 (R Development Core Team, 2014), and using a set of different starting values to verify stability of the solution. The total AQY (AQY_{total}) was calculated using the DIC production measured under full irradiance (280 nm filter) divided by CDOM-absorbed photons integrated from 280 to 600 nm. For uncertainty estimation we used bootstrapping (Ritz and Streibig, 2008; Crawley et al., 2012), where we resampled the monthly measured photochemical DIC production with replacement (6000 times), assigned the respective CDOM-absorbed photons, fitted AQY spectra to each bootstrap dataset. We give the 2.5% and 97.5% quantiles of the resulting bootstrap distribution of parameter estimates as 95% confidence intervals. Kernel density estimation was used to estimate the probability density function for the bootstrap distributions of parameter estimates. To obtain simultaneous pointwise confidence intervals (Fig. 2) we used the 6000 bootstrap parameter estimates to predict the AQY at five discrete wavelengths, about midway between the cut-off filters used during the irradiation experiments (295, 330, 365, 400 and 435 nm). The confidence level was Bonferroni-corrected to reduce the family-wise type I error rate according to $(1-\frac{\alpha}{n})\cdot 100\%$, where α is the significance level and *n* is the number of simultaneous calculations.

To statistically test the temporal variability in AQY we calculated the difference in the discrete AQY values calculated above between adjacent sampling months (i.e. comparing June to July, July to August, etc., including November to June). Again, the confidence level was adjusted for multiple testing using the Bonferroni correction. A temporal difference (p-value ≤ 0.05) exists when the obtained 95% confidence intervals of the differences between adjacent months exclude zero in at least one case.

2.4 In situ photochemical DIC production

During 23 to 25 July 2014, we determined in situ photochemical DIC production rates similarly as described in Granéli et al., 1996. Specifically, we filled filtered lake water (0.2 µm membrane filters) into quartz tubes (38 mL, 2 cm diameter) and corresponding borosilicate dark control tubes wrapped in aluminium foil. Three quartz and two to three dark tubes were attached horizontally to steel wire racks, which were secured to a floating wooden frame that was kept in place with two anchors. This setup was duplicated and the two frames were positioned in the lake at least 50 m from the shoreline (Fig. 1b; red dots). The racks with the tubes were positioned such that the centre of the tubes was positioned at 1, 4 and 8 cm water depth and well within the frame, so that no shading occurred (Fig. 1c). During the 2 day incubation period the anchors sank into the sediment and pulled the frames down by approximately 1 cm. After incubation, all tubes were wrapped in aluminium foil, placed with cooling blocks in cooling boxes for transport, and stored at 4°C until analysis at Uppsala University within two days. Initial DIC concentration was measured from one water sample taken and filtered at the start of the incubation as described above, and kept cold and dark until analysis after three days. Final DIC concentrations were measured directly from the incubation tubes and averaged for the three pseudoreplicate tubes. In one case the measured value of one of the dark triplicates was about 35% higher than all other dark values. This sample was considered to be contaminated and excluded from the calculations. The DIC production at the different water depths was then calculated as the mean of the two set-ups and standardised to mg C m^{-3} d^{-1}.

Deleted: *mle2* in R 3.1.0 (R Development Core Team, 2014). In addition, the wavelength-integrated AQY was calculated using the DIC production measured un- der full irradiance (280 nm filter) divided by CDOM-absorbed photons integrated from 280 to 600 nm.

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2.5 Photochemical rate modelling

Using photochemical rate modelling (Eq. 3), DIC photoproduction was simulated for the open water periods of 2012 to 2014 as:

$$\Psi_{DIC}^{day} = \int_{\lambda_{min}}^{\lambda_{max}} E_{od}^{day}(\lambda, 0^{-}) a_g(\lambda) e^{-(K_d(\lambda)z)} \phi(\lambda) d\lambda \qquad \text{(eq. 3)}$$

The model calculates the daily photochemical DIC production rate (Ψ_{DIC}^{day}, mol C m^{-3}d^{-1}nm^{-1}) over water depth (z, m) based on daily-integrated downwelling scalar irradiation just below the water surface ($E_{od}^{day}(\lambda,0^{-})$, mol photons m^{-2} d^{-1} nm^{-1}), CDOM absorption coefficient (a_g, m^{-1}), vertical attenuation coefficient for downwelling irradiance (K_d, m^{-1}) and the apparent quantum yield ($\Phi(\lambda)$, mol DIC mol photons^{-1}) over the photochemically relevant wavelength range (λ, 280–600nm) (Fichot et al., 2010; Koehler et al., 2014). Daily-integrated clear-sky irradiance spectra were obtained using the libRadtran model (version 1.6) for radiative transfer (Mayer et al., 2005), parameterised and cloud corrected as described in Koehler et al. (2014). For the year 2014, for which monthly AQY spectra were measured between June and November, we used four different AQY parameterisations and assessed their influence on the simulated photochemical DIC production. In the first parameterisation, we assumed that the measured AQY and absorbance spectra were representative for one month around the sampling dates. The spectra measured in June were also used for the open-water period prior to June, and the spectra measured in November were used until the end of the open water period in December. In the second parameterisation, we assumed that the AQY spectrum fitted through all data points obtained between June and November is a representative description of the photochemical reactivity in the lake. The absorbance spectra were again used for one month around the sampling dates. In the third and fourth parameterisation, we assumed that the observed most and least photoreactive water sample was representative throughout the whole open water period, respectively.

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$SUVA_{254}$ was calculated for the years 2012 to 2014, using data from this study as well as absorbance spectra and TOC concentrations measured in 2012 and 2013 (M. Wallin, unpublished data). Since no actual ice-on and ice-off dates were available for lake Erssjön in 2012 and 2013, the long-term average (1970–2007) ice-cover dates for the nearby (19 km) lake Ellenösjön were used (3 April to 7 December; SMHI, 2013).

Deleted: $SUVA_{254}$, as well as DOC concentrations and water colour (a_{420}) were stable across these three years (see Sect. 3.4). Therefore, we assumed similar photoreactivity as observed in 2014 and also used the pooled AQY spectrum of 2014 throughout this study (unless stated otherwise) to simulate photochemical DIC production for the years 2012 and 2013, in combination with the measured absorbance spectra and simulated irradiance.

We also compared simulated photochemical DIC production with the in situ measured rates. In order to compare with the rates measured in the incubation tubes, we integrated the simulated sunlight-induced DIC production rates over the respective depth intervals and for the same time period as the in situ measurement. Since the duration of the incubation was only two days, hourly rather than daily irradiance spectra were used. 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). The absorbance coefficients and apparent quantum yield were obtained from water sampled on the last day of the incubation (the July sample of this study, Fig. 1).

2.6 Total CO_2 emissions

Total CO_2 emissions from the lake surface were measured using plastic floating chambers of volume 6.3 L and area 0.07 m^2, which were covered with aluminum tape to reflect sunlight thereby minimising internal heating, equipped with Styrofoam collars to enable floating and anchored to the lake bottom. The chamber walls extended 3 cm into the water on deployment. Mini CO_2 sensors (CO_2 Engine® ELG, SenseAir AB, Sweden; measuring range 0-10000 ppm) were fitted inside the chamber and programmed to log CO_2 concentrations every 5 minutes (Bastviken et al., 2015). Three chambers were deployed over water depths of 0.5, 2.5 and 4 m (Fig. 1b; white dots). Before flux measurements, the chambers were vented using a 20 cm long PVC tube fitted with a 3-way luer-lock stopcock (Becton-Dickinson, USA). After venting, the chambers were closed for 30 minutes, and the rate of change in CO_2 concentration inside the chamber was calculated using linear regression. When the change of CO_2 concentrations over time was nonlinear, with $R^2 < 0.9$, we discarded the time series. The rates were converted to moles using the ideal gas law and divided by area and time to obtain emissions. Measurements were made approximately every two weeks during June to October 2012 and April to November 2013. During each visit, emissions were measured on two consecutive days.

2.7 Statistical analyses

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Two sample *t* tests were used to test for differences between DIC production under the cut-off filters and the dark controls, and to compare DIC concentrations in the incubation vials with and without a needle through the septum. Linear mixed effects models were used to test for changes in the total AQY, the AQY fit parameters and the chemical and optical water properties over time. The R^2 of a linear least squares regression between DIC photoproduction observed under the cut-off filters and predicted using the fitted AQY spectrum as well as the normalised root mean squared error was used to assess performance of the fitted AQY spectra to reproduce the observations. In all statistical tests, differences were considered significant if *p-value* < 0.05. Mean values are reported with ±1 standard error. Analyses were conducted using R 3.1.0 (R Development Core Team, 2014).

3 Results

3.1 Chemical and optical water properties

Water chemical and optical properties were similar in lake Erssjön from April to July 2014 (Table 1; Fig. S2a). Sampling in August was preceded by a period of high rainfall with 46 mm precipitation within seven days. This corresponded to almost 5% of the annual rainfall in 2014, and another 97 mm precipitation was observed during the remainder of the month (SMHI, 2015). Subsequently, from August until November, DOC concentrations and absorbance coefficients were approximately 50% higher than earlier in the year (p_{DOC} = 0.022, p_{a254} = 0.009, p_{a420} = 0.025), while pH and $SUVA_{254}$ remained similar. TN and TP were similar across the open-water period with the exception of August, when TN was approximately twice as high. The fluorescence index (FI) increased slightly throughout the study period (P = 0.003) whereas the freshness index ($\beta : \alpha$) showed no apparent pattern over time. The humification index (HIX) decreased in spring and early summer, increased towards autumn and then decreased again (Table 1). DOC concentrations, a_{420} and $SUVA_{254}$ were similar during 2012–2014 (Table 2).

3.2 Apparent quantum yield

The DIC production under full irradiance (p = 0.002) and the AQY_{total} (p = 0.008) increased throughout the sampling year, while there was no significant change in CDOM-absorbed photons (Table 3). 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

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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). For each measurement, the fitted AQY spectra reliably predicted the observations, with R^2 of a linear regression between observed and predicted DIC photoproduction ≥ 0.96, slopes close to unity and nRMSE ≤ 7% (Table 3).

3.3 Observed vs. simulated photochemical DIC production rates

Deleted: The AQY spectra determined monthly were similar throughout the sampling year (Fig. 1b) but the slope of the spectra, i.e. the fit parameter m_2 in Eq. (2), decreased over time (P = 0.005; Table 3). Across measurements, the fitted AQY spectra reliably predicted the observations (R^2 of a linear regression between observed and predicted DIC photoproduction ≥ 0.96 and nRMSE ≤ 7%; Table 3).

The in situ photochemical DIC production rates decreased sharply by about a factor of five from just below the water surface to 4 cm water depth (Fig. 3, black numbers). At 8 cm depth, DIC production did not differ between the irradiated and the dark tubes, i.e. the photochemical DIC production was below the detection limit. The simulated photochemical DIC production also decreased sharply with increasing water depth (Fig. 3, red curve). When assuming that the experimental tubes remained at the intended depth of incubation, the simulated photochemical DIC production differed by 114% at 1 cm and by 22% at 4 cm from the observed rates, and, in accordance with the measurements, was small at 8 cm depth (Fig. 3, red numbers). However, the racks to which the tubes were attached were pulled down by approximately 1 cm over the course of the two-day incubation period as their anchors sank into the sediment. If the depth intervals of integration are taken to be 1 cm lower than the intended depths, the simulated DIC photoproduction rates differed by 38% at 2 cm and by 9 % at 5 cm from the observed values (Fig. 3, red numbers in parentheses).

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3.4 Photochemical rate modelling

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

CDOM absorbance, as well as $SUVA_{254}$ and DOC concentrations, were similar throughout 2012 to 2014 (Table 2). Therefore, we assumed that photoreactivity was similar as observed in 2014 and also used the least and most productive AQY spectra measured in 2014 to simulate photochemical DIC production for the years 2012 and 2013, in combination with the measured absorbance spectra and simulated irradiance. Interannual variability in irradiance was very small (Fig. 4a) and hence, in combination with similar CDOM absorbance and the assumption that photoreactivity was similar as in 2014, simulated DIC photoproduction was similar across the years (Table 2; Fig. 4b). Simulating irradiance over the years 2004 to 2014 showed that the irradiance that lake Erssjön received in 2012 to 2014 was representative for the decadal mean ($4.10 \times 10^5 \pm 0.15 \times 10^5$ Wh m^{-2} yr^{-1}). During simulations we assumed that irradiance was not transmitted into the water column during the ice-covered period. If we instead would assume that the ice fully transmits irradiance or ice cover was absent, the yearly simulated photochemical DIC production would increase by 11 to 14%.

4 Discussion

The apparent quantum yield (AQY) spectra for photochemical DIC production, measured monthly between June and November 2014 in a boreal brownwater lake, showed considerable seasonal variability, with the slope of the spectrum decreasing over the open-water season. Photochemical DIC production, simulated using photochemical rate modelling, made a minor contribution to the total CO_2 emissions observed from the same lake (Fig. 5). Hence, similar results from earlier studies in boreal Sweden (Jonsson et al., 2001; Koehler et al., 2014; Chmiel et al., 2016) were corroborated when considering temporal variability in photochemical reactivity as well as in total lake CO_2 emissions. Moreover, the good match

Deleted: Using the pooled AQY spectrum in photochemical rate modelling for the year 2014 resulted in a simulated DIC photoproduction of 5.2 g C m^{-2} yr^{-1} . Using the monthly measured AQY spectra for periods of one month around the sampling date reduced the simulated rate by 25 % (3.9 g C m^{-2} yr^{-1}). When the monthly measured AQY spectra were used, there was an apparent time lag between irradiance and DIC photoproduction (Fig. S3a). This was confirmed by a cross-correlation function, which indicated a time lag of around two to three weeks. Assuming the highest observed photochemical reactivity (November) was representative throughout the open-water period would result in a 5-fold higher estimate (12.2 g C m^{-2} yr^{-1}) than when the lowest observed photochemical reactivity (July) was used (2.2 g C m^{-2} yr^{-1}). Irradiance and simulated photochemical DIC production rates were similar in 2013 and 2014, and slightly lower in 2012 (Table 2, Fig. 3). If we would assume that the ice fully transmits irradiance or ice cover was absent, the yearly simulated photochemical DIC production would increase by 11 to 14%. Simulating irradiance over the years 2004 to 2014 showed that the amount of irradiance that lake Erssjön received in 2012 to 2014 was representative for the decadal mean ($4.10 \times 10^5 \pm 0.15 \times 10^5$ Wh m^{-2} yr^{-1}).

between photochemical DIC production observed in situ and simulated rates (Fig. 2) supported that photochemical rate modelling is a suitable approach to investigate photochemical DOM mineralisation in lakes and its contribution to carbon cycling on broader temporal and spatial scales. This highlights the potential to use a similar method for studying this process also in other climate zones, e.g. for tropical lakes, where the role of photochemical mineralisation for lake carbon cycling remains even less constrained than in boreal and temperate systems.

The DIC photoproduction rates observed in situ in the studied boreal brownwater lake (Fig. 3) were comparable to rates in a Norwegian dystrophic lake (100 and 40mgC m^{-3} d^{-1} at 1 and 10 cm depth, respectively; Salonen and Vähätalo, 1994), five Swedish lakes (100–300 mg C m^{-3} d^{-1} at 1 cm depth; Granéli et al., 1996), and in a Finnish humic lake (300 and 180 mg C m^{-3} d^{-1} at 1 and 2.5 cm depth, respectively; Vähätalo et al., 2000). However, it is difficult to accurately measure DIC photoproduction rates in situ. Wind and wave action make it hard to exactly measure, adjust and stabilise the tubes at the intended depths of incubation. This is especially relevant in the case of a brownwater lake like Erssjön, where DOC photomineralisation is confined to the upper centimetres of the water column and photochemical rates decrease rapidly with increasing water depth (Fig. 3; Granéli et al., 1996; Vähätalo et al., 2000; Koehler et al., 2014). Nevertheless, the simulated and observed DIC photoproduction rates were similar (Fig. 3), giving confidence in the model parameterisation. Given the experimental difficulties, photochemical rate modelling is an attractive method for estimating photochemical DOC mineralisation, especially on large temporal and spatial scales.

The wavelength-specific photochemical reactivity is a critical and sensitive parameter in photochemical rate modelling (Fichot & Miller, 2010; Koehler et al., 2014; Cory et al., 2014). However, knowledge on its variability remains scarce. So far, AQY spectra for photochemical DIC production have only been reported for a small number of Arctic, boreal and temperate lakes (Vähätalo et al., 2000; Vähätalo and Wetzel, 2004; Koehler et al., 2014; Cory et al., 2014; Vachon et al., 2016). Information about temporal variability in AQY spectra across seasons within single lakes is even more rare, with only two studies so far where lake AQY spectra were repeatedly determined during the open-water season (Cory et al., 2014; Vachon et al., 2016). In this study, the AQY spectra determined monthly in a boreal brownwater lake showed a decrease in slope (fit parameter m_2, eq. 2) from June to November (Table 3; Fig.

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S2b,d in the Supplement). This suggests that the longer wavelengths contributed more to DIC photoproduction later in the season. However, the variability in AQY spectra over time (CV = 0.11 at λ_{300}) was much smaller (Fig. 1b) than the variability in AQY spectra between lakes of differing CDOM quality and quantity reported so far (CV = 0.52 at λ_{300}; Vähätalo et al., 2000; Vähätalo and Wetzel, 2004; Koehler et al., 2014; Vachon et al., 2016; AQY_{300} of Toolik Lake from June 29, 2012, R. Cory, personal communication, 2014). Yet, given the high sensitivity of simulated DIC photoproduction towards both magnitude and slope of the AQY spectrum, applying AQY spectra measured at different times to the whole open-water period of 2014 resulted in up to 5.6-fold differences in simulated annual DIC photoproduction. Hence, depending on scale and scope of the study as well as feasibility, it may be recommendable to conduct repeated measurements of AQY spectra throughout the season for more accurate simulation of annual photochemical DIC production in lakes, as recently conducted in studies in the Arctic (Cory et al., 2014) and northern temperate and boreal Canada (Vachon et al., 2016).

While photobleaching is a relevant process regulating CDOM absorption on a seasonal scale in some humic boreal lakes (Müller et al., 2014), we did not observe net photochemical bleaching with a potentially associated reduction in DOM photoreactivity (Lindell et al., 2000). However, AQY spectra were only determined from June onwards, leaving the spring, in which photoreactivity may be high (Gonsior et al., 2013; Vachon et al., 2016) and bleaching most prevalent (Lindell et al., 2000; Zhang et al., 2006; Gonsior et al., 2013), unstudied. Values for the fluorescence index were around 1.3 throughout the season, indicating that the fluorescent DOM was mostly of terrestrial origin. Also the freshness index was stable, suggesting no major temporal changes in the proportion of recently produced fluorescent DOM from microbial origin (Gabor et al., 2014). A marked increase in DOC concentrations and absorbance in autumn (Table 1; Fig. S2a in the Supplement) was preceded by a high rainfall event (SMHI, 2015) and consecutive mixing of the lake (S. Peter, personal communication, 2014). Consistent with the observed simultaneous increase in the humification index (Table 1), this event likely added a substantial amount of humified material to the lake, both from land and from the bottom water of the lake itself (Spencer, 2010; Gonsior et al., 2013; Hughes et al., 2013). Hence, rainfall events, mixing of the lake and potentially a shorter residence time towards autumn may have added fresh and more

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Deleted: We used the mean AQY fit parameters from six monthly measurements in 2014 to simulate photochemical DIC production rates for 2012 to 2014. This was reasonable because the measured AQY spectra showed small changes over time (Fig. 1b), AQY spectra were not determined prior to June, and testing different AQY parameterisations showed that using the measured monthly AQY spectra for month-long time periods resulted in an apparent time lag of two to three weeks between irradiance and DIC photoproduction. This time lag suggested that the monthly measured AQY spectra were not representative for an entire month but likely varied on shorter time scales. By using the pooled AQY we evened out the impact of short-term events, e.g. a heavy rainfall event days before sampling, on photochemical reactivity.

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photoreactive material to the lake. Possibly, this masked photobleaching while increasing photoreactivity (Fig. 2). Similarly, rainfall and input of fresh terrestrial material increased CDOM photoreactivity in tropical lakes (Amado et al., 2006; Suhett et al., 2007). For tropical systems, which receive an even dose of sunlight throughout the year, the importance of photochemical reactivity in regulating temporal variability in photochemical DIC production may be expected to be higher than in boreal lakes, where temporal changes in photochemical reactivity interact with the pronounced seasonality in irradiance. Accordingly, CDOM photoreactivity and irradiance explained a similar amount of variability in photochemical mineralisation across seasons for three boreal and northern temperate lakes (Vachon et al., 2016).

Considering that photoreactions are constrained to a shallow top layer of the lake, the relative contribution of photochemistry to overall dynamics of DOC is uncertain. To address this, we compared the DIC photoproduction with the total CO_2 emissions that were measured from the lake. Assuming that all photoproduced DIC was emitted as CO_2 to the atmosphere, the mean simulated DIC photoproduction ($7.9 \pm 0.3 – 41.3 \pm 2.9$ mg C m^{-2} d^{-1}; 2012–2014) contributes 1 – 8% to the mean observed CO_2 emissions of 562.2 mg C m^{-2} d^{-1} (Fig. 5). Hence, the results of this detailed study in one Swedish brownwater lake are in agreement with a large-scale modelling study for 1086 Swedish lakes, in which the contribution of mean annual DIC photoproduction to CO_2 emissions was about 12% (Koehler et al., 2014). Also in agreement, direct photo-oxidation contributed about 7% to the total DOC mineralisation in a large humic lake in northern Sweden (Jonsson et al., 2001), and 6% in a small brownwater lake in central Sweden (Chmiel et al., 2016). In a study based on 21 463 observations from lakes across Sweden, CO_2 emission ranged from 31.9 to 88.3 g C m^{-2} yr^{-1} (Humborg et al., 2010). Comparing our low and high estimate of simulated DIC photoproduction to these numbers would suggest a directly sunlight-induced contribution of 2 to 6% and 12 to 32% to the total CO_2 emission, respectively. Besides the here studied direct effect of sunlight on DOC mineralisation, sunlight can also stimulate bacterial respiration by partially photo-oxidising DOC. The magnitude of this indirect effect can be as large as that of the direct effect (Lindell et al., 1995; Molot and Dillon, 1997; Bertilsson and Tranvik, 1998; Cory et al., 2014), resulting roughly in a doubling of the estimates presented here. We conclude that the contribution of sunlight to the CO_2 emissions from the studied Swedish brownwater lake was

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small. This was also the case when taking temporal variability of AQY spectra into account. Even when using the AQY spectrum from the most photoreactive water sample for annual simulation and considering photostimulation of DOC mineralisation, the contribution of DOC phototransformations to the in-lake carbon cycling would still be minor.

The Supplement related to this article is available online at doi:10.5194/bgd-12-17125-2015-supplement.

Author contributions. B. Koehler designed the study. M. Groeneveld conducted laboratory and field experiments assisted by B. Koehler and L. Tranvik. M. Groeneveld and B. Koehler conducted photochemical rate modelling and data analysis. S. Natchimuthu conducted the total CO_2 flux measurements and analysed the flux data. M. Groeneveld wrote the manuscript with contributions and revision by B. Koehler, L. Tranvik and S. Natchimuthu.

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Tables

Table 1. Chemical and optical water properties of lake Erssjön during the study period of 2014

Month	DOC (mg L^{-1})	TN (mg L^{-1})	TP (µg L^{-1})	pH	a_{254} (m^{-1})	a_{420} (m^{-1})	$SUVA_{254}$ (L mg C^{-1} m^{-1})	FI	HIX	FRESH
April	18.8	NA	NA	5.5	210.5	21.0	11.2	NA	NA	NA
May	17.9	1.06	31	5.4	208.3	20.4	11.6	1.29	14.22	0.46
June	17.4	0.87	34	6.2	201.8	18.9	11.6	1.29	12.55	0.46
July	17.7	0.97	29	5.9	207.4	22.2	11.7	1.30	12.18	0.49
August	25.5	2.21	32	5.6	283.6	27.2	11.1	1.30	12.70	0.46
September	30.6	1.02	28	5.9	341.4	35.2	11.2	1.32	14.77	0.46
October	28.8	NA	33	5.0	309.3	28.7	10.7	1.33	14.86	0.47
November	NA	1.11	37	4.8	311.3	28.8	NA	1.32	13.60	0.46
Mean ± SE	22.4 ± 2.2	1.20 ± 0.2	32 ± 1	5.5 ± 0.2	251.7 ± 20.6	25.3 ± 2.0	11.3 ± 0.1	1.31 ± 0.01	13.55 ± 0.46	0.47 ± 0.004

DOC: dissolved organic carbon; TN: total nitrogen; TP: total phosphorus; a_{254}: absorption coefficient at 254 nm; a_{420}: absorption coefficient at 420 nm; $SUVA_{254}$: specific UV absorption coefficient at 254 nm; FI: fluorescence index; HIX: humification index; FRESH: freshness index.

Table 2. Mean (± SE) background variables (n=8 in 2012 and 2014, n=12 in 2013), and simulated irradiance and photochemical DIC production rates assuming lowest (left) and highest (right) photochemical reactivity measured in 2014.

	2012		2013		2014	
DOC (mg L^{-1})	23.5 ± 1.6*		21.1 ± 0.4		22.4 ± 2.2$^{\#}$	
a_{420} (m^{-1})	25.8 ± 3.0		20.3 ± 0.8		25.3 ± 2.0	
$SUVA_{254}$ (L mg C^{-1} m^{-1})	10.2 ± 0.3*		10.1 ± 0.2		11.3 ± 0.1$^{\#}$	
Irradiance (Wh m^{-2} yr^{-1})	$3.88 \cdot 10^5$		$4.19 \cdot 10^5$		$4.18 \cdot 10^5$	
DIC_{areal} (mg C m^{-2} d^{-1})	7.2 ± 0.3	35.5 ± 1.5	8.2 ± 0.3	43.3 ± 1.7	8.3 ± 0.4	45.0 ± 1.9
Range	0.3 – 19.3	1.7 – 102.8	0.3 – 19.7	2.1 – 102.7	0.3 – 20.0	1.6 – 111.3
DIC_{areal} (g C m^{-2} yr^{-1})	1.8	8.9	2.0	10.8	2.1	11.2
DIC_{lake} (kg C yr^{-1})	126.8	625.3	143.5	762.0	146.5	791.7

DOC: dissolved organic carbon; a_{420}: absorption coefficient at 420 nm; $SUVA_{254}$: specific UV absorption coefficient at 254 nm; Irradiance: irradiance integrated over the wavelength range 280-600 nm; DIC_{areal} and DIC_{lake}: areal and total lake DIC photoproduction rate simulated for the open water season, 249 days between the average ice-off and ice-on dates; * n=6; $^{\#}$ n=7.

Table 3. Mean (± SE) photochemical DIC production under the full irradiance spectrum in the solar simulator, and absorbed photons as well as the total AQY in the wavelength range 280-600 nm; parameter estimates for the fitted AQY spectra (eq. 2), information on performance to reproduce the observations (R^2, regression slope and nRMSE) and areal photochemical DIC production in 2014 using the respective AQY spectra. Values in parentheses give diagnostics and simulation results when single AQY spectra were used to predict photochemical DIC production observed during all six irradiation experiments

AQY	DIC production under full irradiance (μmol L^{-1} h^{-1})	CDOM-absorbed photons$_{280-600}$ (mol m^{-2} h^{-1})	AQY_{total} (mmol DIC mol $photons^{-1}$)	m_1	m_2
June	9.28 ± 0.72	3.12 ± 0.23	0.138 ± 0.003	$5.776^{+0.518}_{-0.429}$	$0.032^{+0.007}_{-0.007}$
July	7.54 ± 0.42	3.77 ± 0.26	0.093 ± 0.006	$5.985^{+0.373}_{-0.454}$	$0.033^{+0.006}_{-0.004}$
August	17.57 ± 0.90	3.97 ± 1.81	0.206 ± 0.007	$5.846^{+0.156}_{-0.168}$	$0.023^{+0.002}_{-0.002}$
September	19.90 ± 1.26	4.52 ± 0.31	0.204 ± 0.004	$5.839^{+0.137}_{-0.166}$	$0.022^{+0.001}_{-0.001}$
October	29.41 ± 1.76	4.02 ± 0.28	0.341 ± 0.016	$5.782^{+0.282}_{-0.316}$	$0.018^{+0.003}_{-0.003}$
November	33.87 ± 0.98	4.21 ± 0.24	0.375 ± 0.014	$5.967^{+0.176}_{-0.218}$	$0.015^{+0.002}_{-0.002}$
monthly measured	NA	NA	NA	NA	NA
pooled	NA	NA	NA	$6.350^{+0.672}_{-0.639}$	$0.017^{+0.006}_{-0.005}$

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Table 3. *Continued.*

AQY	R^2	slope	nRMSE (%)	DIC_{areal} (g C m^{-2} yr^{-1})
June	0.98 (0.58)	1.03 (0.32)	5.89 (25.91)	(3.0)
July	0.96 (0.57)	0.99 (0.24)	7.27 (28.94)	(2.2)
August	0.99 (0.60)	1.01 (0.55)	3.35 (17.42)	(5.8)
September	0.99 (0.60)	1.01 (0.60)	3.42 (16.87)	(6.4)
October	0.97 (0.60)	1.01 (0.87)	5.71 (24.67)	(10.1)
November	0.99 (0.61)	1.01 (0.92)	4.30 (30.94)	(12.2)
monthly measured	NA	NA	NA	(3.9)
pooled	(0.61)	(0.52)	(16.97)	(7.3)

AQY: apparent quantum yield; DIC: dissolved inorganic carbon; CDOM: chromophoric dissolved organic matter; AQY_{total}: DIC production measured under full irradiance (280 nm filter) divided by CDOM-absorbed photons integrated from 280 to 600 nm; m_1 and m_2: fit parameters with 95% confidence intervals; R^2 and slope: R^2 and slope of a linear regression between observed and predicted DIC photoproduction; nRMSE: normalised root mean squared error between observed and predicted DIC photoproduction; DIC_{areal}: areal DIC photoproduction rate simulated for the open water season of 2014, 310 days between the ice-off and ice-on dates.

Figure legends

Figure 1. a: Map of Sweden showing the location of lake Erssjön (blue star). b: Aerial photo of lake Erssjön, indicating the locations of the two floating frames used during in situ measurement of DIC photoproduction (red dots) and the location of the flux chambers (white dots) (image obtained from Google maps; Imagery ©2015 Lantmäteriet/Metria, Map data ©2015 Google). c: Floating frame with the quartz and control tubes positioned at three different water depths.

Figure 2. Apparent quantum yield (AQY) spectra for a. June, b: July, c: August, d: September, e: October, and f: November, including simultaneous pointwise 95% confidence intervals at 295, 330, 365, 400 and 435 nm. For comparison, the AQY spectra of the other months are added in grey in each panel.

Figure 3. Photochemical DIC production rates observed in situ (± SE; black numbers) and simulated using photochemical rate modelling (red curve and average values over the intended depths of the experimental tubes). The frame to which the tubes were attached sank into the sediment by about 1 cm during the two incubation days. Simulated values adjusted to this change in incubation depths are given in parentheses.

Figure 4. a: Daily irradiance integrated over the wavelength range 280-600 nm. b: Daily photochemical DIC production rate from 2012 to 2014 using the AQY spectrum with highest (November; primary y-axis) and the lowest productivity (July; secondary y-axis) measured in 2014. The grey shaded areas mark the ice-covered periods of the lake, during which we set DIC photoproduction to zero assuming no irradiance transmission (Petrov et al., 2005).

Figure 5. Box-and-whiskers plots of total measured CO_2 emissions, and minimum and maximum simulated photochemical DIC production, showing the median and 1st and 3rd quartiles with the whiskers set at ±1.5 times the interquartile range and data outside this range

given as circles. Note the log scale on the y-axis.

Figure S1. Determination of the apparent quantum yield (AQY) spectrum. Position of the cut-off filters with respect to the irradiance spectrum, and an exemplary AQY spectrum calculated based on the photochemical DIC production and CDOM-absorbed photons for each cut-off filter. Inset: Glass incubation vial with quartz top, sides covered with black insulation tape to avoid irradiance to enter laterally.

Figure S2. Monthly determined spectra from Lake Erssjön during the open-water period of 2014 for (a) filtered UV-vis absorbance (April-November) and (b) apparent quantum yield (AQY) (June-November). The blue dashed line in (b) gives the August AQY if the high dark control values, which we excluded due to suspected contamination, were included (see Sect. 2.3). The black dashed line in (b) shows the pooled AQY spectrum, which was fitted through all data points. The densities of the bootstrap distribution of parameter estimates, which was used to obtain 95% confidence intervals for the parameter estimates (eq. 2, Sect. 2.3), are shown for the fit parameters of the AQY spectrum m_1 (c) and m_2 (d).

Figure S3. a: Daily photochemical DIC production rate using the AQY spectrum with highest productivity (November). b: Daily photochemical DIC production rate using the AQY spectrum with lowest productivity (July). c: Daily photochemical DIC production rate using the monthly measured AQY spectra for month-long time periods around the sampling date, where the spectrum measured in June was also used for the open-water period prior to June, and the spectra measured in November were used until the end of the open-water period in December. The vertical lines indicate when the AQY spectra were measured and are colour-coded as in Fig. 2. d: Daily irradiance integrated over the wavelength range 280-600 nm for 2014. The grey shaded areas mark the ice-covered period of the lake, during which we set DIC photoproduction to zero assuming no irradiance transmission (Petrov et al., 2005).