

Author comments (ACs) to the referee comments (RCs) on the manuscript “High-frequency productivity estimates for a lake from free-water CO₂ concentration measurements”, by Provenzale et al. (bg-2017-412)

The authors would like to thank the referees for the time they invested in reading and assessing the manuscript, and for the comments they provided. We believe that the feedback from the referees has allowed us to substantially improve our work. The authors would also like to thank the editor for the time and consideration.

In the following file, the blue colour denotes our answers to the reviewers, the orange colour denotes the changes we made to the manuscript.

Attached after our answers is the marked-up version of the manuscript.

RC1

Provenzale and co-authors describe a study in which they use high-frequency CO₂ measurements to estimate lake net ecosystem production (NEP) and describe variation in NEP using water temperature and light in the upper mixed layer. The authors constrained their study to well-stratified periods so as to satisfy assumptions of CO₂ transport in the lake. Michaelis-Menten model fits to the estimated NEP were very good and parameters varied between years, for reasons which the authors speculate (e.g. algal community composition). This study advances CO₂ metabolism research in lakes; however, I think the results and discussion sections need a lot of restructuring to effectively describe the important results of this study. I make several suggestions below that I think will improve the manuscript.

We thank the referee for the suggestions. We followed them to restructure the Results and Discussion sections.

Hanson et al. (2003, *Limnology & Oceanography* 48: 1112-1119) also estimated GPP, R, and NEP using CO₂ measurements for 2-4 days in each of their study lakes, so this isn't the first time CO₂ measurements have been used for metabolism studies other than Hari et al. (2008).

We added this information to the manuscript.

The manuscript now reads: “our study is an important step towards testing and developing the approach so that it becomes more general, also given the scarcity or even lack of high-frequency direct CO₂ measurements for productivity studies (we are aware of only one other study where free-water CO₂ measurements were used for metabolism studies (Hanson et al., 2003).”, P12 L22-25 in the new version of the manuscript, P13 L26-28 in the marked-up version.

Do the authors have evidence that lateral transport of CO₂ negligible in their study lake? Are there stream or groundwater inflows to the lake that may transport CO₂? Even in lakes that are fairly isolated from the surrounding landscape, lateral transport of CO₂ can be significant. (see Vachon et al. 2016 doi: 10.1002/lno.10454), and some autotrophic lakes can have significant CO₂ outgassing, indicating a decoupling from NEP and CO₂ dynamics (Bogard and del Giorgio 2016 doi: 10.1002/2016GB005463). More details on lake hydrologic characteristics and the influence of lateral transport or lack thereof would be good. What is the lake water residence time? Are there significant inlet streams? Etc..

We added the hydrologic characteristics of the lake.

The manuscript now reads: “Most of the inflow is through a permanent stream in the northern end, while the role of groundwater is small during summer. Temporary inflows appear at snowmelt, through several small ephemeral streams. The outflow is located at the southern end. The residence time was 522 days in 2011 and 655 days in 2013.”, P3 L28-31 in both versions of the manuscript.

As for the lateral transport, Dinsmore et al. (2013) studied the CO₂ concentration discharge in six sites, including lake Kuivajärvi. They concluded that most of the CO₂ discharge for this site happens at snowmelt or during strong rain events in the autumn. The assumption that lateral transport of CO₂ is, under our conditions, negligible is also confirmed by the fact that the CO₂ concentrations in the mixed layer only exhibit a diurnal cycle, and no long-term trend is observable (see the Figures in the supplemental information).

We added this information in the manuscript, which now reads: “The lateral transport of CO₂ had to be ruled for the sake of the calculations. A similar challenge is encountered in forest ecology studies as well, where the lateral transport in the air (advection) is also usually neglected. We are of course fully aware of the lake being a 3D dynamic system. Besides, since this study focuses on the summer periods when the lake was stably stratified and there were no high winds or rains, the lateral transport is not expected to play a significant role here. This assumption is supported by Dinsmore et al. (2013), who showed that for lake Kuivajärvi most of the CO₂ discharge happens at snowmelt or during heavy rains in the autumn. It is also supported by the mixed layer CO₂ concentration time series, which show no sign of a long-term trend on top of the diurnal cycles (see Figg. S5-S14 in the supplemental information).”, P10 L25-31 in the new version of the manuscript, P11 L8-21 in the marked-up version.

I also think it would be useful to indicate when or for what type of lakes that this method might be useful. This is the second lake that has tested this method, but do the authors think that this method can be applied to every lake? If not, then why not?

In principle, we think that the method could be applied to any lake under any conditions, with an expansion of the instrumental set-up.

We added this information to the manuscript, which now reads: “At the current stage, the method we present here is still very system specific, and assumptions about lateral and vertical CO₂ exchange and photo-oxidation had to be made (negligible lateral exchange and photo-oxidation, no in-lake vertical exchange). However, the method can in principle be applied to any lake and under any condition, with an expansion of the instrumental set-up. Measurements or estimates of F_u , the CO₂ flux from the deeper layer to the surface layer of the lake, would be needed in order not to limit the analysis to isothermal (as in Hari et al., (2008)) or stable stratification (as here) conditions. This could be achieved for example adding water column turbulence measurements to the CO₂ concentration and temperature measurements. Chemical measurements would be needed to apply the method in clear-water lakes, where photo-oxidation could play an important role. Finally, information about CO₂ discharge would be needed for lakes or periods when lateral transport is not negligible.”, P11 L34-P12 L8 in the new version of the manuscript, P12 L33-P13 L8 in the marked-up version.

Page 4 and 5: NEP is the net biological conversion of organic carbon to inorganic carbon while NEE is equal to NEP + inorganic sinks/sources of CO₂. So I think it is incorrect to state that negative NEE is the same as NEP on page 4 line 30. See Lovett et al. (2006 doi: 10.1007/S10021-005-0036-3) for an in-depth discussion of terminology and Stets et al. (2009, doi: 10.1029/2008JG000783) for an application to lakes. I think it is correct to say that NEP = -NEE if lateral transport of CO₂ (and other inorganic sinks/sources) are negligible, so equation 3 seems correct, but only under this assumption.

We agree.

The manuscript now reads: “Provided that there are no inorganic sinks or sources of CO₂, the NEP is the opposite of the net ecosystem exchange (NEE)”, P4 L32-P5 L1 in both versions of the manuscript.

I don't see how this manuscript harmonizes terrestrial vs. aquatic studies other than using a similar term (M-M dynamics as harmonizing isn't very convincing). And the authors don't give any good reasons for why harmonizing terrestrial and aquatic C cycling research is needed. Sprinkling in forest ecology references here and there (e.g. page 7 line 8, Figure 2 legend) seems like a cheap connection to make to terrestrial systems. I think this paper would be stronger if the authors did not try to compare to terrestrial systems and instead focused on the merits of using CO₂ in addition to or in place of O₂ to estimate metabolism in aquatic systems (e.g. respiratory quotient different than 1, etc. . .).

We agree that we did not clearly state what we meant. Our effort was to harmonize the procedures that are used to calculate productivity from measurements in different ecosystems (and not specifically M-M dynamics, which we used here as a validation for our calculated NEP, together with other models (Smith (1936) and Jassby and Platt (1976), see the supplemental information)).

We stated our intentions more clearly. Also see the answer to the "Page 5 lines 19-27" comment.

Page 2 line 29: What do you mean "the NEP was not mathematically parameterized" in the Hari et al. (2008) analysis? Does this mean that NEP was not explained by PI curves?

A PI curve is reported in Hari et al. (2008) Fig. 4, with the data points and a modelled NEP curve. However, the mathematical expression of the modelled NEP curve is not provided, and neither is information on its agreement with the data.

Page 5 line 7: It is unclear if h_{mix} was set at 1.5m for the entire study period (due to stable stratification and setting F_u to zero) or if this is calculated at the frequency of the temperature measurements. If it is calculated at a high-frequency interval, do the authors account for vertical entrainment of hypo CO₂ into epi when thermocline deepens and epi CO₂ into hypo when thermocline shallows?

h_{mix} was set to 1.5 m for the entire study period.

The manuscript now reads: "the average value for the entire study period was $h_{mix} = 1.5$ m", P5 L10 in the new version of the manuscript, P5 L10-11 in the marked-up version.

Page 5 line 19: is "e.g." supposed to be NEP?

"e.g." stood for "for example", we agree that it was unclear.

The manuscript now reads: "considering for example forest EC calculations", P5 L24-25 in the new version of the manuscript, P5 L25 in the marked-up version.

Page 5 lines 19-27: I don't think equation 4 and the paragraph surrounding it adds very much to the MS and is distracting to the methods section. It is also unclear what the 'gap with terrestrial ecology' is and how using CO₂ measurements reduces this undefined gap. Was using different methods of ecosystem productivity really creating a separation between terrestrial and aquatic studies?

We believe that the idea of finding a common language between different fields (aquatic and terrestrial productivity studies) is important. Ongoing European projects and infrastructures such as ICOS and RINGO for example have tasks related to this harmonization need. For these reasons, we decided to keep the equation and the paragraph. However, we now explain in a hopefully clearer way what the gap is and why in our opinion it is important to harmonize the methods.

The manuscript now reads: "High-frequency measurements for productivity are common in forest ecology. They are, however, less common in aquatic ecology, where traditional approaches are still widespread despite their limitations (low temporal resolution, unnatural conditions). Having different methodologies and different time resolutions creates a gap between the two fields, and

makes comparing the estimates more difficult. Given that the terrestrial and aquatic ecosystems are a continuum through which carbon is cycled, using shared procedures is a step in the direction of connecting and integrating these ecosystems, in order to have more precise carbon budgets and a deeper knowledge of the carbon cycle.”, P5 L29-P6 L4 in the new version of the manuscript, P5 L30-P6 L6 in the marked-up version.

Page 6 lines 1-4: F_a was not possible at 30 min resolution; did you ever compare to a model of gas flux and fill in data gaps that way? i.e. why not use Heiskanen et al. (2014) gas flux model?

We compared the available EC data with the model from Heiskanen et al. (2014), but for the analysed periods we did not find a good agreement between them, with the model underestimating the fluxes. This might be due to our analysis being focussed on the periods with low wind speeds (even though we did take that into account, and also tried using the median k value reported in Heiskanen et al. for low wind conditions). Given the poor agreement between model and data, we decided not to use the model to fill the gaps, but resort to average F_a values.

Page 6 line 28: I'm assuming Q_{10} is set to 2, but the authors should be explicit to make this clear.
We agree.

The manuscript now reads: “ Q_{10} is a non-dimensional temperature coefficient whose generally accepted value (and the value we used) for freshwater communities is 2; in the literature, values between 1.88 and 2.19 are reported”, P7 L7-8 in both versions of the manuscript.

Page 7: The results section is not very well organized and is a combination of results that do seem to fit in the same paragraph. For example, the first paragraph covers results from Figure 2-5 and table 1 and does not flow well together. Break these up into individual paragraphs with topic sentences so that the reader knows what point the authors are trying to make with the paragraph.

We agree.

The assessment section is now further divided into four subsections, and some of the subsections are further divided into paragraphs. The Discussion section is also now divided into two subsections.

Page 7 line 6: do not use colloquial language such as “Anyhow, . . .”
Changed to “However, . . .”, P7 L24 in both versions of the manuscript.

Page 7 line 12-13: remove “Figure 3 displays the NEP versus PAR.”
Removed, P8 L3 in the marked-up version of the manuscript.

Page 7 lines 18-19: get rid of “In case of . . . it was not necessary.” This doesn't add anything to the fact that there was no photoinhibition.

Removed, P8 L10-11 in the marked-up version of the manuscript.

Page 7 line 20-21: why is respiration more negative with hotter years? Be explicit. Because R_h is more temperature dependent than GPP?

Yes.

The manuscript now reads: “Year 2014 was particularly hot, so the strongly negative NEP can be due to increased respiration rates, given the strong dependency of R_h on temperature”, P8 L10-11 in the new version of the manuscript, P8 L11-13 in the marked-up version.

Page 7 line 26: change Figg. to Figure

We removed it altogether, P8 L20 in the marked-up version of the manuscript.

Page 7 line 31-32: Get rid of “An in-depth analysis. . . some comments are possible.” Since you do spend three paragraphs of the results discussing these parameters. Replace with a more constructive topic sentence.

We agree.

The manuscript now reads: “We then focused on the inter-annual variability of the values of the model parameters (reported in Table 1).”, P8 L24 in the new version of the manuscript, P8 L26 in the marked-up version.

Page 8 line 7-10. Move to methods rather than results
Moved, P7 L16-19 in both versions of the manuscript.

Page 8 line 13-14: get rid of “In general, we can say that there are statistically significant differences between the years.”

Removed, P9 L13-14 in the marked-up version of the manuscript.

Page 9 line 11: but see Lovett et al. 2006 where NEP does not equal –NEE.

We specified it and added the reference, P10 L22-24 in the new version of the manuscript, P11 L5-7 in the marked-up version.

Page 9 line 21-22: “This is in agreement with. . .” who? The citations in parenthesis? And what is in agreement with them? That lakes are heterotrophic when NEP is negative? Or that many lakes are heterotrophic?

We rephrased and also moved the sentence to make it clearer. The references were supporting the fact that many lakes at higher latitudes are supersaturated with respect to CO₂, as is our lake.

The manuscript now reads, where the general results are first commented: “the net productivity values are almost always negative, meaning that the ecosystem, overall, is heterotrophic and a source of CO₂. In fact, the daytime and nighttime average values of the CO₂ flux were also always positive, albeit having lower values during the day than during the night. This is not surprising: many lakes, especially at high latitudes, are supersaturated with respect to CO₂ (Cole et al., 1994; Sobek et al., 2003); as a result, the CO₂ flux is from the lake to the atmosphere also during the day, when the aquatic primary producers are photosynthesising and absorbing CO₂.”, P7 L24-28 in both versions of the manuscript.

Page 10 line 10-16: This is a confusing paragraph. The authors state that 1) more info on algal communities was needed to explain differences in fitted parameters, but 2) this isn’t needed because the whole point of this method is to be simple and parsimonious, but 3) this method should be applied in many lakes to make links between parameters and environmental conditions / algal communities. I don’t know what point the authors are trying to make with this paragraph.

We rephrased the paragraph, we hope our point is now clearer.

The manuscript now reads: “In this study, we could not clearly link the environmental variables to the changes in the Michaelis-Menten model parameters, and more information on the algal communities living in the lake would have been required in order to expand the analysis. However, it is important to stress that the simplicity of this method lies in the fact that to estimate the parameters, which can then be used to calculate the productivity, information on the algal communities is not needed. It is needed only when widening the scope of the productivity studies: when, for example, the parameters themselves and their relationship with the environmental conditions or the specific phytoplankton communities are investigated. Knowledge on the algal communities would also help when extending the productivity calculation to the whole year.”, P11 L24-30 in the new version of the manuscript, P12 L18-29 in the marked-up version.

Page 10 line 28-29: How is there a comparison between the calculated NEP and modeled NEP when you fit the model to the calculated NEP? To make a statement like this, it seems like you should be training the model on a set of the calculated NEP data and then verifying with a separate set of the calculated NEP data. Also, what do you mean calculated NEP vs. modeled NEP was compared for first time? Compared for the first time using the MM method? I know there are many other examples where predictor variables are used to model lake NEP, so the authors will have to be more specific here.

We agree. We added the out-of-sample comparison.

In the manuscript there is now a new subsection in the Results section, which reads: “The analysis we performed was based on an in-sample comparison, since our goal was to check whether our method to calculate the NEP was in agreement with the PI models typically used (Michaelis-Menten, Smith (1936) and Jassby and Platt (1976) equations). However, for the Michaelis-Menten model, we also ran an out-of-sample validation for each year, in order to further verify the correspondence between the calculated NEP and the model. For each year, we randomly selected half of the data points and used them for the fit, to calculate the model parameters. Then, for the other half of the sample, we estimated the NEP using the equation and the parameters we had obtained, and compared it to the originally calculated NEP. We both evaluated the correlation coefficient r between the two NEPs (the one calculated from the data, and the one calculated from the model trained on half of the data points, then discarded), and the RMSE of the validations. The results are reported in Table 2, and show that the two NEP values compared well. The correlation coefficient r varies between 0.84 and 0.92 and the RMSE varies between 0.15 and 0.31 $\mu\text{mol}(\text{CO}_2)\text{m}^{-2}\text{s}^{-1}$.”, P10 L8-17 in the new version of the manuscript, P10 L19-28 in the marked-up version.

The “first time” in the comparison referred to the NEP calculated with this method. It has been calculated with this method only in Hari et al. (2008), and in that paper there is no quantitative evaluation of the modelled NEP vs the calculated NEP.

We rephrased it to make it clearer, P12 L14-15 in the new version of the manuscript, P13 L15 in the marked-up version.

Page 10 lines 32-33: this is not a clear sentence.

We rephrased and expanded the sentence, we hope it is now clearer.

The manuscript now reads: “Overall, we believe that the method proposed in Hari et al. (2008) and further tested and developed here represents an improvement over the traditional approaches (bottle method and ^{14}C technique), given its time resolution and the fact that it is a free-water approach. We also think it is promising compared to the other more common free-water approach, the O_2 method, since it is direct and the respiratory quotient is not needed”, P12 L18-21 in the new version of the manuscript, P13 L19-25 in the marked-up version.

I don't think figure 1 is necessary.

Removed (P18 in the marked-up version of the manuscript).

Figure 2-5: each dot represents a day or a 30 min interval? Please specify in legend

Each dot represents a 30-min interval.

The legend now states that (P17, P18, P19 and P20 in the new version of the manuscript, P18, P19, P20, and P21 of the marked-up version).

Can tables 1 & 2 be combined? It would just add 5 more columns.

Yes.

The tables are now combined (P21 in the new version of the manuscript, P22 in the marked-up version).

RC2

The manuscript “High-frequency productivity estimates for a lake from free-water CO₂ concentration measurements” presents a method to assess NEP in aquatic ecosystems. While interesting, the method requires an independent measurement of (1) the flux of CO₂ between the atmosphere and the water surface, (2) usage of high-frequency in situ CO₂ sensors, and – at least in the present approach – (3) conditions under which lateral advection fluxes (both within the water column and in the atmosphere) are limited. Overall, the methodological approach and science appear sound, but of limited utility due to known issues with eddy covariance and chamber methods for determining water to atmosphere fluxes of CO₂. That is, the atmospheric turbulence required for eddy flux determination is often not present at night, while the stratification required for the water column (i.e. to satisfy the assumption of no lateral fluxes in the lake) would be violated under higher wind speeds. Thus, the overall measurements are constrained to a methodological “sweet spot”. The authors do not explore the potential limitations of only making measurements during these ideal conditions, which were identified for 10 summer days over a number of years for a lake in Finland. While the results for the measured days are interesting, there should be some effort to describe what these NEP rates represent relative to the other seasons (early open water after thaw, etc.), as well as efforts towards uncertainty estimates of the NEP rates and how this uncertainty cascades into the least-squares regressions for modeled parameters.

We thank the referee for the good points. We tried to follow the suggestion to describe what the NEP rates represent relative to the other seasons and to estimate the uncertainty in the NEP rates.

For the first part, the manuscript now reads: “In our case, for example, the NEP rates and hence the parameters are representative of the late summer. In lake Kuivajärvi, where diatoms are abundant, it can be expected for the productivity to have a peak in the spring and another smaller peak in the autumn, at the turnover. More measurements at those times would be needed, in order to understand whether the parameterization is still valid under those conditions.”, P11 L30-33 in the new version of the manuscript, P12 L29-32 in the marked-up version.

For the second part, see the answer to the later comment about NEP uncertainty.

We would like to point out that the ideal conditions were identified in 40 days, not 10, as is specified already in the original manuscript (see P1 L9, P3 L6, P5 L22, P9 L6, P12 L11 in the new version of the manuscript, P1 L9, P3 L6, P5 L22, P9 L19, P13 L12, in the marked-up version).

The authors present in essence a case study of implementation of a method presented by Hari et al (2008), with the suggestion that the method has been overlooked and has not been used for NEP because of limited testing (P 2 L35 – P3 L1). This logic seems a bit circular, and misses the point that there are few eddy covariance studies over aquatic systems. The authors suggest that determination of the atmospheric flux of CO₂ could be made with chambers rather than by eddy flux, but do not discuss limitations of chamber measurements, which are not insignificant. Some discussion on how chamber measurements and in situ measurements could be co-located would be useful. As well, the study makes the assumption that CO₂ is uniform in the mixed layer, but this assumption does not appear to have been tested for confirmation.

We added a sentence about the potential benefit of co-locating chamber measurements and in situ measurement. However, we would like to stress that this manuscript is focused on a direct way to measure the CO₂ concentration in the water and on the equations used to calculate the NEP from these measurements. The flux between the lake and the atmosphere is needed in order to close the mass balance, but the methodology used to measure it (and hence a comparison of the possible methods) is beyond the scope of this paper. We tried to make this clearer in the manuscript.

The manuscript now reads: “The calculations could be improved with a better EC data set. Different methods could also be adopted to estimate the flux between the lake and the atmosphere. Chamber measurements could be used, but the time resolution could be an issue. They would need to be performed regularly. They could, however, be used to integrate the EC data set for example. Surface renewal models could also be used (e.g. Heiskanen et al. (2014)). For further information on the comparison between different flux measurement methods, see Erkkilä et al. (2018).”, P11 L18-22 in the new version of the manuscript, P12 L12-16 in the marked-up version.

Regarding the uniformity of CO₂ in the mixed layer, for years 2010 and 2011 we had a second CO₂ probe at 0.5 m, whose readings matched the ones from the probe at 0.2 m.

We added this information to the manuscript: “For years 2010 and 2011, another CO₂ probe was located at a depth of 0.5 m, and its readings were consistent with those from the probe at 0.2 m, hence showing homogeneous CO₂ concentrations in the mixed layer.”, P5 L11-13 in the new version of the manuscript, P5 L12-13 in the marked-up version.

It seems problematic that the authors calculate NEP based on time varying dC/dt , but use mean values for daytime and nighttime fluxes of the atmospheric flux (essentially static values). Perhaps there is additional information in the eddy flux data that could be used to propagate uncertainty in NEP calculations? For example, the standard deviation of the F_a term for each day could be useful. We agree. We calculated the uncertainty on the average values of F_a . We decided not to use the standard deviation, since the 30-min EC data are characterised, as often happens, by large scatter. Instead, we recalculated the averages randomly selecting only half of the available data, and then we repeated the process 100 times. We then checked how far apart the calculated average values were.

We added this to the manuscript, which now reads: “We also estimated the uncertainties on the daytime and nighttime average values of F_a . We decided not to use the standard deviation, since individual 30-min data EC data are characterised by significant scatter. Instead, we recalculated the daytime and nighttime averages randomly choosing only half of the data in the sample, and repeated the process 100 times. Then we checked how far apart the minimum and maximum average values we obtained were, and used that as uncertainty.”, P6 L28-31 in the new version of the manuscript, P6 L30-34 in the marked-up version.

The authors state (P6 L13) that the CO₂ flux is expected to have similar daily cycles across the analysed days, but it is not clear that the magnitude of the fluxes should be similar across days. What is the basis for this assumption?

We agree that it was not written clearly in the manuscript. It is not an assumption, but an observation, from analysing the available EC data for the studied years, and the data from years with more complete EC data sets.

We rephrased it in the manuscript, which now reads: “Under these circumstances (i.e. warm and sunny summer days without strong wind events), the CO₂ flux is expected to have similar daily cycles across the studied days, as is shown by the available EC data and by the EC data from years with more complete data sets.”, P6 L20-22 in the new version of the manuscript, P6 L22-24 in the marked-up version.

Specific comments

P1 L11: Here, the model fit is described as “excellent”, while later it is described as “very good” on P7 L28. Providing some metrics that would qualify as excellent should be included in the abstract.

We agree.

We changed “excellent” to very good in the abstract, and provided some metrics ($R^2 \geq 0.71$), P1 L11 in both versions of the manuscript.

P1 L19: change to “. . . in gaseous form (primarily as CO₂).”

We changed it, P1 L19 in both versions of the manuscript.

P4 L5: What is the permeability of silicone to CO₂ relative to the diffusion rate of CO₂ in water at the temperatures experienced in this study?

Laboratory tests on the same set-up were run for the original paper (Hari et al. (2008)). When the silicone tube was transferred rapidly from a water bath with low CO₂ concentration to one enriched in CO₂, the response time of the whole system was < 5 min (Hari et al., 2008).

P6 L29: It would be helpful to present more information describing how p_{\max} , b and r_0 are determined. Which equations were used to solve for these three unknowns?

The parameter values are obtained fitting the model to the data.

We added this sentence to the manuscript, which now reads: “their values can be obtained fitting the model to the data.”, P7 L12 in both versions of the manuscript.

Also see, already in the original version of the manuscript, “After calculating the NEP, we plotted the NEP versus irradiance curves. We then fitted the model (Eq. (5)) to the NEP data with the least-squares fitting method, in order to check the agreement between the data and the model and in order to estimate p_{\max} , b and r_0 .”, P7 L13-15 in both versions of the manuscript.

P7 L26: “The curves in Figg. 2-5 have the expected trends, and this confirms that. . .” – this sounds like confirmation bias.

“confirms” was changed to “suggests”, P8 L18 in the new version of the manuscript, P8 L20 in the marked-up version.

P7 L29: “This clearly indicates that the method used here allows the NEP to be accurately parameterized as a function of irradiance and water temperature.” What seems to be missing here is uncertainty assessment on NEP. If NEP is not well constrained (since it is calculated from Eqn 3 assuming static rates for the daytime and nighttime CO₂ fluxes between the lake and the atmosphere), how can the model fits be characterized without consideration of the uncertainty in the “measured” NEP vs. the modelled fit?

We agree. We removed “accurately” (P8 L24 in the marked-up version of the manuscript), and we addressed this issue in the Discussion session.

The manuscript reads: “Our analysis was hindered by issues in the EC data set: due to inherent EC limitations and technical problems, the data set had many gaps and average daytime and nighttime F_a values had to be used. The relative uncertainty on them was, on average, 50%. This uncertainty propagates to NEP through Eq. (3), and therefore to the parameter values as well. However, it does not undermine the good agreement between the model and the data, given that the average F_a values were calculated putting together all the periods of the same year. Therefore, each NEP data point has the same uncertainty and the same weight in the fit.”, P11 L13-18 in the new version of the manuscript, P12 L2-12 in the marked-up version.

P8 L10: “The value of b does not change significantly between any of the years” – but Table 1 and 2 show it to vary by 50% between years. This seems rather significant. The later statement that p_{\max} and r_0 are more sensitive to variation seems to be a statement that wasn’t formally tested through sensitivity analysis.

We performed a statistical test to check whether the variations in the parameter values between the

years were statistically significant. See P8 L7-10 in the original manuscript, P7 L16-19 in the new and marked-up versions. The changes in the value of b are indeed large but so is the uncertainty on the value of b itself, which makes these changes not statistically significant.

P9 L14: “We hope in the future to further develop the method” – this kind of statement doesn’t belong in a Discussion section.

We removed it, P11 L10-11 in the marked-up version of the manuscript.

Compare P9 L6-7: “the changes of PAR and water temperature cannot fully account for the changes in the model parameters” with P7 L29 “the method used here allows the NEP to be accurately parameterized as a function of irradiance and water temperature.”

The method does allow the NEP to be parameterized as a function of PAR and water T , through the calculation of the model parameters. The model parameters change between the years, and their changes are not fully explained solely by the changes in water T and PAR, indicating that they depend on other variables as well, such as the algal community composition for example. We rephrased it to make it clearer.

The sentence from P7 L29 in the original version of the manuscript now reads: “From what is said so far, the changes of PAR and water temperature alone cannot fully account for the changes in the model parameters. The long-term variations of the parameters probably have other drivers too, such as the composition of the algal communities”, P9 L28-30 in the new version, P10 L5-7 in the marked-up version.

P11 L7: I would not describe eddy covariance over a water surface as “relatively inexpensive”. “relatively inexpensive” refers to the CO₂ probes. The next sentence in fact reads: “The method requires at least a concomitant estimation of the CO₂ flux from the lake to the atmosphere. In our case the EC technique was used, which is expensive and can be laborious in the data processing phase. However, chamber measurements or surface renewal models could be equally good options.”.

We tried to make it clearer in the manuscript, P12 L27-30 in the new version of the manuscript, P13 L31-P14 L1 in the marked-up version.

P17 Fig 3 for 2014: What explains the large separation between NEP values for low values of PAR and the jump in NEP just as PAR increases a bit?

The large separation is explained by choosing a PAR threshold between “night” and “day”, and then having different F_a average values for night and day.

We made it clearer in the manuscript, which now reads: “Note that both in Fig. 3 and Fig. 4 and especially for years 2010 and 2014 there is a large separation between NEP across the chosen PAR threshold between night and day. This is caused by having to resort to daytime and nighttime average values for F_a .”, P8 L15-17 in the new version of the manuscript, P8 L16-18 in the marked-up version.

High-frequency productivity estimates for a lake from free-water CO₂ concentration measurements

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Abstract. Lakes are important actors in biogeochemical cycles and a powerful natural source of CO₂. However, they are not yet fully integrated in carbon budgets, and the carbon cycle in the water is still poorly understood. In freshwater ecosystems, productivity studies have usually been carried out with traditional methods (bottle incubations, ¹⁴C technique), which are imprecise and have a poor temporal resolution. Consequently, our ability to quantify and predict the net ecosystem productivity (*NEP*) is limited: the estimates are prone to errors and the *NEP* cannot be parameterized from environmental variables. Here we expand the testing of a free-water method based on the direct measurement of the CO₂ concentration in the water. The approach was proposed already in 2008, but was tested on a very short data set (3 days) under specific conditions (autumn turnover); despite showing promising results, it has not been used ever since. We tested the method under different conditions (summer stratification, typical summer conditions for boreal dark-water lakes) and on a much longer data set (40 days), and quantitatively validated it comparing our data and productivity models. We were able to evaluate the *NEP* with a high temporal resolution (minutes) and found ~~an excellent agreement~~ a very good agreement ($R^2 > 0.71$) with the models. We also estimated the parameters of the productivity-irradiance (PI) curves that allow the calculation of the *NEP* from irradiance and water temperature. Overall, our work shows that the approach is suitable for productivity studies under a wider range of conditions, and is an important step towards developing it so that it becomes even more general.

1 Introduction

Lakes are very important actors in the local and global carbon cycles (Battin et al., 2009; Tranvik et al., 2009). They both fix carbon, through the photosynthesis of the in-lake primary producers, and release it, through the respiration of all the aquatic organisms (primary producers, consumers and microbes), through photochemical reactions and by transmitting the received carbon from the catchment (lateral transport) back to the atmosphere in gaseous form (primarily as CO₂). Many lakes - especially the oligotrophic ones typical of high latitudes - are net heterotrophic systems where the rate of community respiration exceeds that of primary production (Cole et al., 1994; Sobek et al., 2003); this contributes to make lakes one of the most im-

portant natural sources of greenhouse gases (Raymond et al., 2013). However, they are not yet fully integrated in the local and global carbon budgets, and the lacustrine carbon cycle is still poorly known (Cole et al., 2007).

In freshwater ecology, productivity studies have usually relied on the light and dark bottle method (Gaarder and Gran, 1927) and the ^{14}C labeling technique (Steeemann Nielsen, 1951; Peterson, 1980; Bender et al., 1987; Søndergaard, 2000). The first provides estimates both of the gross and the net primary productivity, whereas the latter gives an estimate that is between the gross and the net productivity, depending on the incubation time. These traditional methods require time- and effort-demanding measurements and have a poor temporal resolution. Periods of high productivity are easily missed (Karl et al., 2003) and, because of the low temporal resolution, the non-linear relationship between photosynthetically active solar radiation (*PAR*) and photosynthesis cannot be properly investigated. As a consequence, carbon balances may be imprecise and for instance the net ecosystem productivity (*NEP*) cannot be parameterized robustly as a function of ambient variables. Moreover, communities enclosed in bottles experience light and nutrient conditions far from the natural ones, since the movement of water or of the organisms themselves is limited (Mallin and Paerl, 1992; Reynolds, 2006), and the results can be unrealistic. Thus, advances in the methodology are necessary, to better estimate freshwater ecosystems productivity and to expand our understanding of the carbon cycle in the water column.

In the last 15 years, free-water methods, not requiring sampling and incubation, have become more common. These methods, however, are usually based on the measurement of the O_2 concentration in the water, which is then used as a proxy for CO_2 (Hoellein et al., 2013; Solomon et al., 2013): this introduces uncertainties (Staehr et al., 2010). The respiratory quotient that has to be applied when transforming rates from O_2 to CO_2 has, in fact, large variations (Berggren et al., 2012).

To study the in-water photosynthesis and respiration, Hari et al. (2008) proposed a free-water method based on the direct measurement of the CO_2 concentration in the water with non-dispersive infra-red (NDIR) CO_2 probes, associated with a concomitant assessment of the CO_2 flux between the lake and the atmosphere. The probes are designed to measure the CO_2 concentration in the air, but by building a gas collection system the concentration in the water is obtained. Similar probes have been used also in Johnson et al. (2010), albeit not for productivity studies. The temporal resolution is of five seconds, more than a hundredfold improvement over the traditional approaches. A requirement of the method is the concomitant assessment of the CO_2 flux from the lake to the atmosphere. Information on the in-lake vertical CO_2 flux is also needed (and, ideally, on the lateral transport as well). If such data are missing the method can be applied under specific conditions (e.g. stable stratification); it still allows the parameterization of the *NEP* from *PAR* and water temperature, from which the *NEP* can then be calculated under different conditions.

In Hari et al. (2008), the method was tested on a small boreal lake in Finland over three days only, during the autumn turnover. A cross-comparison was carried out between different measurement methods, but the *NEP* was not mathematically parameterized and the method was not quantitatively verified. Despite the very short data set and the specific conditions, the results were promising: the relationship between *PAR* and *NEP* was clearly visible, the measured respiration rate was 16 times higher than with the bottle method and the measured productivity was 5 times higher than with the ^{14}C technique. The numbers are in line with previous studies: Pace and Prairie (2005) reported similar discrepancies between an oxygen-based free-water approach and the bottle method in small lakes in Michigan, and a tendency of the ^{14}C method to underestimate the productivity is

well known (Howarth and Michaels, 2000). However, the method has been overlooked and has not been used for productivity calculations since 2008, possibly because of the limited testing.

Here we tested the method of Hari et al. (2008) on a different boreal lake, under different conditions and on a much longer data set, quantitatively verifying it. We continuously collected data for four summers, and then we focused on the periods when the lake was stably stratified, i.e. summer conditions typical of boreal dark-water lakes, in order to rule out the lateral CO₂ flux and the CO₂ flux from the deeper layers of the lake. Overall, we analysed 40 days of data. We calculated the *NEP* using the equations that are typically used in forest ecology, where high-frequency measurements are more common, in an effort of harmonizing the procedures between different fields. Once we had the *NEP* with a high temporal resolution, we verified the relationship between the *NEP* and irradiance, using a saturating Michaelis-Menten model. We found an excellent agreement between the data and the model. From that, we could also estimate the parameters of the productivity-irradiance (PI) curves, specific to the in-lake communities. These parameters are very important because they allow the calculation of the *NEP* from *PAR* and water temperature.

Whilst our efforts were mainly focused on method testing and development, we also checked whether the parameters of the PI curves we estimated changed significantly between the years. Our goal was to gather information on how sensitive the parameters are to variations in the communities living in the lake or in the environmental conditions. We investigated whether their behaviour could be related to their main drivers, water temperature and irradiance.

2 Materials and procedures

2.1 Study site

The study site is the boreal lake Kuivajärvi, in southern Finland (61°50.743' N, 24°17.134' E). Lake Kuivajärvi is typical dark-water boreal lake. It is small and oblong, and it is surrounded by managed coniferous forests. Its surface area is 0.62 km² and its length is 2.6 km; its mean depth and maximum depth are 6.3 m and 13.2 m respectively. The lake is humic (surface median DOC concentration = 11.8 mg l⁻¹ in 2011) and mesotrophic (surface median annual total nitrogen concentration = 370 μg l⁻¹ and annual total phosphorus concentration = 14 μg l⁻¹ in 2011), with a chlorophyll *a* concentration in the surface layer usually between 3 and 5 μg l⁻¹ (median 4.8 μg l⁻¹ in 2011), with summer values that can reach 30 μg l⁻¹ (Miettinen et al., 2015). The lake is dark coloured: the Secchi depth ranges from 1.2 to 1.5 m (Heiskanen et al., 2015). The lake is dimictic and it is frozen for five months every year on average; the spring turnover occurs immediately after the ice out in late April or early May, and after the turnover a thermocline starts developing. The thermocline deepens until the autumn turnover, and finally the lake freezes over in late November or early December (Heiskanen et al., 2015; Mammarella et al., 2015). Most of the inflow is through a permanent stream in the northern end, while the role of groundwater is small during summer. Temporary inflows appear at snowmelt, through several small ephemeral streams. The outflow is located at the southern end. The residence time was 522 days in 2011 and 655 days in 2013. A map with the location and bathymetry of the lake is available in the supplemental information (Figg. S1 and S2).

2.2 Measurements

All the instruments were mounted on a raft, which was moored in the middle of the lake (see the supplemental information, Fig. S2, for the exact position of the raft on the lake). To measure the CO₂ concentration in the water, a closed system consisting of a NDIR probe (CARBOCAP® GMP343, Vaisala Oyj, Vantaa, Finland) for the CO₂ concentration in the air, gas impermeable tubes (stainless steel and teflon) and a submerged gas permeable tube (silicone rubber, Rotilabo 9572.1, Carl Roth GmbH and Co. KG, Karlsruhe, Germany) was built; the air was circulated continuously in the system by a diaphragm pump (KNF Neuberger Micro gas pump, KNF Neuberger AB, Stockholm, Sweden). Analog voltage outputs were used, logged with a Nokeval RMD680 serial transmitter to a ASCII-file on a Windows-based computer. Since silicone rubber has an excellent permeability to CO₂ (Carignan, 1998; Hari et al., 2008), the concentration of CO₂ in the air circulating in the system equilibrated with that in the water around the submerged tube. Hence, the CO₂ concentration in the water could be obtained from that in the air using the dependence of CO₂ solubility on temperature and pressure. The CO₂ concentration in the water C_{CO_2} (dissolved CO₂), in $\mu\text{mol m}^{-3}$, was calculated as

$$C_{\text{CO}_2} = \chi_{\text{CO}_2} P K_{\text{H}}, \quad (1)$$

where χ_{CO_2} is the CO₂ gas phase mole fraction in the tube measured by the probe (in $\mu\text{mol mol}^{-1}$), P is the total air pressure inside the system and K_{H} is Henry's law constant (temperature dependent). For more details on the setup see Hari et al. (2008), Heiskanen et al. (2014) and the supplemental information (Fig. S3). The CO₂ concentration in the water was measured at a depth of 0.2 m (determined by the depth of the submerged silicone tube). The system was operating continuously from May to September 2010-2014, but the data from year 2012 are not used here due to technical problems. The silicone tube was cleaned once a week to avoid biofouling and changed once a month. The CO₂ sensors were calibrated using span and zero gases. A thermistor chain of 16 Pt100 resistance thermometers (depths: 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, 7.0, 8.0, 10.0, and 12.0 m) was deployed and a *PAR* sensor (LI-192, LI-COR Inc., Nebraska, USA) for photosynthetic photon flux density (*PPFD*) was submerged in the water at the same depth as the CO₂ measurement (0.2 m). An eddy covariance (EC) system (with ultrasonic anemometer USA-1, Metek GmbH, Germany, and closed-path infra-red gas analyzer LI-7000, LI-COR Inc., Nebraska, USA, replaced in 2011 by enclosed-path infra-red gas analyzer LI-7200, LI-COR Inc., Nebraska, USA) was used to detect the CO₂ flux between the lake and the atmosphere. The fluxes were calculated and quality screened according to the standard procedures, see Vesala et al. (2006), Mammarella et al. (2009), Mammarella et al. (2015) and the supplemental information (Sect. S2). All the instruments were powered by mains electricity.

2.3 Calculation of the net ecosystem productivity

The net ecosystem productivity (*NEP*, $\mu\text{mol}(\text{CO}_2)\text{m}^{-2}\text{s}^{-1}$), also called net ecosystem uptake, can be defined as

$$NEP = GPP - R_{\text{h}}, \quad (2)$$

where *GPP* (gross primary productivity) is the amount of carbon fixed by the primary producers through photosynthesis and R_{h} (ecosystem respiration) is the amount of carbon lost through respiration, both autotrophic and heterotrophic. [The Provided](#)

that there are no inorganic sinks or sources of CO₂, the NEP is the opposite of the net ecosystem exchange (NEE), whose expression can be derived from the conservation of mass. Hence, considering the mass balance of CO₂ in the mixed layer of the lake, where most of the photosynthesis takes place, and assuming that lateral transport of CO₂ is of no importance, the NEP can also be expressed as

$$5 \quad NEP = -NEE = - \int_{-h_{\text{mix}}}^0 \frac{\partial C_{\text{CO}_2}(z,t)}{\partial t} dz - F_a + F_u; \quad (3)$$

~~see Fig. 1 for a schematic representation.~~ In Eq. (3), C_{CO_2} is the CO₂ concentration in the water calculated from Eq. (1), F_a is the CO₂ flux between the lake and the atmosphere (positive if from the lake to the atmosphere), F_u is the CO₂ flux between the deeper and the mixed layer of the lake (positive if upwards), t is time and z is depth. The integration is computed between the mixing depth h_{mix} and the surface. The mixing depth is defined as the depth at which the water temperature starts decreasing
 10 faster than one degree per meter (Staehr et al., 2010); in our study case the average value for the entire study period was $h_{\text{mix}} = 1.5$ m. Given the dark water colour and the resulting low light conditions in the lake, there was no benthic primary production in the profundal zone. For years 2010 and 2011, another CO₂ probe was located at a depth of 0.5 m, and its readings were consistent with those from the probe at 0.2 m, hence showing homogeneous CO₂ concentrations in the mixed layer. While C_{CO_2} was measured by the probe and F_a by the EC system, we had no precise way of measuring F_u . This is the main reason
 15 behind our choice to limit the analysis to the summer days when the lake was stably stratified and it was safe to assume no gas was exchanged through the thermocline: $F_u = 0$. The periods of stable stratifications were chosen on the basis of temperature plots and of the Schmidt stability of the lake, calculated with the LakeAnalyzer program, according to Read et al. (2011). For all the chosen days, the stability (Sc) is $> 100 \text{ Jm}^{-2}$. However, not all days with $Sc > 100 \text{ Jm}^{-2}$ were used: days with strong winds or stable atmospheric stratification were discarded because of their impact on fluxes (for more detailed information, see
 20 the end of this section). For the time series of isotherms for the whole summers (from 1 June to 31 August), and the time series of isotherms, Schmidt stability, CO₂ concentration and PAR at 0.2 m and air temperature for the periods of stable stratification chosen for analysis each year see the supplemental information (Figg. S4-S14). Overall, we analyzed 40 days in 10 periods occurring between mid-June and the end of July of each year.

It is worth pointing out that Eq. (3) resembles the equation used in terrestrial ecology to estimate the NEP . In fact, ~~e.g. in~~
 25 considering for example forest EC calculations (Foken et al., 2012), neglecting lateral transport, the NEP is

$$NEP = -NEE = - \int_0^{h_m} \rho_d \frac{\partial \chi_{\text{CO}_2}(z,t)}{\partial t} dz - \rho_d \overline{w' \chi'_{\text{CO}_2}}. \quad (4)$$

In Eq. (4), $\rho_d \chi_{\text{CO}_2}$ ($\rho_d =$ dry air density, $\chi_{\text{CO}_2} =$ CO₂ mixing ratio) replaces C_{CO_2} as the CO₂ concentration in the air instead of in the water, and z is the height (with $h_m =$ measuring height); $\rho_d \overline{w' \chi'_{\text{CO}_2}}$ is F_a , the CO₂ flux from the forest to the atmosphere, calculated as the covariance between the fluctuations of the vertical wind velocity and the gas mixing
 30 ratio. ~~From the analogy, we can see that using high-frequency CO₂ concentration measurements and Eq. (3)~~ High-frequency measurements for productivity are common in forest ecology. They are, however, less common in aquatic ecology ~~reduces the~~

gap with terrestrial ecology, where high-frequency measurements are common, and leads towards a greater uniformity in the equations and procedures, where traditional approaches are still widespread despite their limitations (low temporal resolution, unnatural conditions). Having different methodologies and different time resolutions creates a gap between the two fields, and makes comparing the estimates more difficult. Given that the terrestrial and aquatic ecosystems are a continuum through which carbon is cycled, using shared procedures is a step in the direction of connecting and integrating these ecosystems, in order to have more precise carbon budgets and a deeper knowledge of the carbon cycle.

Resuming our calculation of the *NEP* in aquatic ecosystems through Eq. (3), to increase the precision of the concentration data, half-hourly averages of C_{CO_2} from the raw 5-sec data were used. A 30-min resolution is enough to capture the variations caused by the biological activity and at the same time filter out the ones caused by the physical mixing of the water (Staehr et al., 2010). However, the EC data set, which also has a resolution of 30 minutes, had many gaps, due to inherent problems of the EC technique (wind not blowing along the lake, stability or not fully developed turbulence resulting in quality criteria not met) and technical problems (instrument failures). Approximately 70% of the data points for the summers were rejected or missing, with occurrences of consecutive days having no acceptable data points at all. Hence, for our data set, a point by point calculation of F_a in (3) was not possible. Even though in general it would not be needed, we had to use a daytime and a nighttime average value for F_a ; we ~~maintained~~ maintained the half-hourly calculation of the *NEP* to preserve the temporal resolution. The daytime and nighttime average F_a values were calculated separately for each year, combining all the studied periods of water stable stratification of the same summer. Before doing so, we checked that the environmental conditions (temperature and relative humidity cycles, incoming radiation, wind speed and direction, atmospheric stability) were similar for all the analysed days in the summer. In particular, since wind and atmospheric stability have the greatest influence on the fluxes (given that the lake water is thermally stratified), as verified in Heiskanen et al. (2014), we discarded any day with winds $> 5 \text{ m s}^{-1}$ or with stable atmospheric stratification. For the remaining days, the wind was always weak, with averages $< 2.5 \text{ m s}^{-1}$; at such low speeds, the influence of the wind on the flux is negligible (Cole and Caraco, 1998). Under these circumstances (i.e. warm and sunny summer days without strong wind events), the CO_2 flux is expected to have similar daily cycles across the analysed days studied days, as is shown by the available EC data and by the EC data from years with more complete data sets.

Day and night were defined on the basis of *PAR*. When using *PAR*, we are referring to the average *PAR* value in the mixed layer, obtained from the 0.2 m value through the lake light extinction coefficient (1.5). The threshold between day and night was set to $20 \mu\text{mol}(\text{ph}) \text{ m}^{-2} \text{ s}^{-1}$ and it was chosen by calculating the average value of *PAR* at which the CO_2 concentration in the water started decreasing in the morning after accumulating during the night, or increasing again in the evening. Using this procedure, "day" represents the fraction of the time series when photosynthesis dominates over respiration, and not the times when photosynthesis takes place in absolute terms. We also estimated the uncertainties on the daytime and nighttime average values of F_a . We decided not to use the standard deviation, since individual 30-min EC data are characterised by significant scatter. Instead, we recalculated the daytime and nighttime averages randomly choosing only half of the data in the sample, and repeated the process 100 times. Then we checked how far apart the minimum and maximum average values we obtained were, and used that as uncertainty.

At this point, we were able to calculate the half-hourly values of *NEP* for each period.

2.4 Relationship between *NEP* and *PAR*

In humic lakes, the photosynthesis is strongly driven by *PAR*, and the relationship can be described for instance by the Michaelis-Menten equation (Caperon, 1967; Kiefer and Mitchell, 1983). Assuming that the daytime respiration rate equals the nighttime respiration rate and that they depend exponentially on temperature (Carignan et al., 2000), the *NEP* can be expressed as

$$NEP = GPP - R_h = \frac{p_{\max} PAR}{PAR + b} - r_0 Q_{10}^{T/10}. \quad (5)$$

In (5), T is the water temperature (in °C) and Q_{10} is a non-dimensional temperature coefficient whose generally accepted value for freshwater communities (and the value we used) is 2; in the literature, values between 1.88 and 2.19 are reported: Reynolds (1984); Raven and Geider (1988); Davison (1991);. The parameters p_{\max} , b and r_0 represent the maximum potential photosynthetic rate, the half-saturation constant (i.e. the value of *PAR* at which the photosynthetic rate is half of the maximum rate) and the basal respiration rate, respectively. These parameters are important, since they allow the calculation of *NEP* from water temperature and *PAR*; their values can be obtained fitting the model to the data.

After calculating the *NEP*, we plotted the *NEP* versus irradiance curves. We then fitted the ~~*NEP* data to the~~ model (Eq. (5)) to the *NEP* data with the least-squares fitting method, in order to check the agreement between the data and the model and in order to estimate p_{\max} , b and r_0 .

Each year was handled separately, since the conditions (*PAR* and water *T*) varied. We then verified whether the changes in the parameter values between the years were statistically significant. To do so, we calculated the parameters difference and its confidence interval (calculated as the uncertainty of the difference, from the confidence intervals of the parameters themselves), and checked whether it overlapped 0. If it did not, then the values were statistically significantly different.

20 3 Assessment

3.1 General results

The *NEP* had the same trend as the incoming radiation, as expected; it had bigger negative values during the night, when only respiration took place, and smaller negative values during the day, when photosynthesis contributed with an uptake of CO_2 . ~~Anyhow~~ However, the net productivity values are almost always negative, meaning that the ecosystem, overall, is heterotrophic and a source of CO_2 . ~~Figure 2~~ In fact, the daytime and nighttime average values of the CO_2 flux were also always positive, albeit having lower values during the day than during the night. This is not surprising: many lakes, especially at high latitudes, are supersaturated with respect to CO_2 (Cole et al., 1994; Sobek et al., 2003); as a result, the CO_2 flux is from the lake to the atmosphere also during the day, when the aquatic primary producers are photosynthesising and absorbing CO_2 .

Figure 1 shows the CO_2 concentration change in time over the mixed layer (the first term in Eq. (3)), which is usually referred to as storage flux in forest ecology calculations, the *NEP*, the average daytime and nighttime values of the CO_2 flux ($F_{\text{a,day}}$ and $F_{\text{a,night}}$) and *PAR* for a sample period of stable stratification in July 2010, representative of the analyzed periods. The

nine-day period in Fig. 2-1 is the longest of the entire data set. Generally, stable stratification lasted from two to five days; its short duration is due to the oblong shape of the lake, that makes it sensitive to wind action: as soon as the wind increases the mixing is enhanced (although complete mixing takes place only in spring and autumn). Figure 3 displays For the NEP versus PAR curves (Fig. 2-3), as mentioned above, we decided to draw a different plot for each year, instead of combining all the data points from all the years, since the conditions (PAR and water T) varied from year to year. The figure also Figure 2 displays the model curve calculated using the average water T of the studied periods of each year. From the plots, we can see that for low values of PAR the NEP was strongly negative; then, as PAR increased, the NEP quickly increased as well; however, as already noted, the NEP always remained negative, indicating net heterotrophy. None of the years exhibited signs of photoinhibition: the NEP did not seem to decrease even at high ($> 500 \mu\text{mol}(\text{ph})\text{m}^{-2}\text{s}^{-1}$) values of PAR . In case of photoinhibition, the addition of a specific term accounting for it in (5) would have been needed, but here it was not necessary. Differences can be seen between the years, with 2014 showcasing the smallest values of NEP . Year 2014 was particularly hot, so the strongly negative NEP can be due to increased respiration rates, given the strong dependency of R_h on temperature; year 2010 though displays the highest values of NEP despite having an intermediate average water temperature. Figure 4 shows the same plots, but focuses 3 concentrates on the dependence of the NEP on T . The model is calculated for different values of water T , ranging from the minimum to the maximum water temperatures recorded during the studied periods of each year. The NEP decreases with increasing temperature, due to higher respiration rates. Note that both in Fig. 3 and Fig. 4 and especially for years 2010 and 2014 there is a large separation between NEP across the chosen PAR threshold between night and day. This is caused by having to resort to daytime and nighttime average values for F_a . Finally, Fig. 5-4 features 3D plots of the data and the curves, to visualize simultaneously the dependence of the NEP on PAR and water T . The curves in Fig. 2-5 have the expected trends, and this confirms that the data suggests that the measurement method and the equation used are proper tools for estimating the NEP at a high temporal resolution. The results of the fittings of the NEP versus PAR and T are reported in Table 1 below. Considering the assumptions we had to adopt, there is a very good agreement between the model and the data: the R^2 values range from 0.71 to 0.84. This clearly indicates that the method used here allows the NEP to be accurately parameterized as a function of irradiance and water temperature. An in-depth analysis-

25 3.2 Inter-annual variability

We then focused on the inter-annual variability of the values of the model parameters (reported in Table 1) and their inter-annual variability is beyond the scope of this paper. However, some comments are possible. The differences in the parameter values between the years are mainly statistically significant. Only the value of b does not change significantly between any of the years: this means that the algal communities adapted to the light conditions in a similar way every year. The values of the other parameters change: p_{max} is comparable only between 2011 and 2014, and r_0 is never comparable. The difference in p_{max} and r_0 can be due to different total algal biomass in the lake. In general, we can say that variations in the environmental conditions might have led to changes in the communities living in the lake, or the communities might have responded differently to the environmental conditions; p_{max} and r_0 seem to be more sensitive to variations than b . The maximum photosynthetic rate p_{max} ranged between 1.55 (2014) and 0.63 (2013) $\mu\text{mol}(\text{CO}_2)\text{m}^{-2}\text{s}^{-1}$, and it was higher in

2011 and 2014 than in 2010 and 2013. The half-saturation constant b ranged between 22 (2010) and 33 (2013) $\mu\text{mol}(\text{ph})\text{m}^{-2}\text{s}^{-1}$, being higher in 2011, 2013 and 2014 than in 2010. The values of b are relatively small. It indicates that the phytoplankton communities were well adapted to the low light conditions (boreal area and dark-water lake) and were able to start photosynthesising even when the incoming radiation was small. The basal respiration r_0 ranged between 0.228 (2010) and 0.482 (2014) $\mu\text{mol}(\text{CO}_2)\text{m}^{-2}\text{s}^{-1}$, being higher in 2011 and 2014 than in 2010 and 2013, as was the case with p_{max} . The parameters however do not appear to be strictly correlated to each other, and a clear and uniform pattern in their behavior cannot be identified.

~~We checked whether the differences in the parameter values between the years are statistically significant. This also gives an indication whether the parameters should be re-assessed each year or can be considered lake-specific. We calculated the parameters difference and its confidence interval (calculated as the uncertainty of the difference, from the confidence intervals of the parameters themselves), and verified whether it overlapped 0. The value of b does not change significantly between any of the years: this means that the algal communities adapted to the light conditions in a similar way every year. The values of the other parameters change: p_{max} is comparable only between 2011 and 2014, and r_0 is never comparable. The difference in p_{max} and r_0 can be due to different total algal biomass in the lake. In general, we can say that there are statistically significant differences between the years. Variations in the environmental conditions might have led to changes in the communities living in the lake, or the communities might have responded differently to the environmental conditions; p_{max} and r_0 seem to be more sensitive to variations than b .~~

Finally, we investigated whether the changes of the model parameters can be explained in terms of changes, during the analyzed periods, of the ambient variables that act as *NEP* drivers: water temperature and irradiance. The model parameters and the average, minimum and maximum values of water T and PAR for each year are reported in Table 2-1 (only the 40 analyzed days are considered in these statistics). In 2010 and 2011 the surface water temperature had similar average values, 22.9 and 22.7 °C respectively. Year 2013 was slightly colder, with an average value of 21.5 °C, while year 2014 was warmer, with an average value of 25.6 °C. The minimum temperatures of the study periods were similar for 2010 and 2013 ($\approx 20^\circ\text{C}$), slightly higher for 2011 (20.7°C) and notably higher for 2014 (23.2 °C). The maximum temperatures ranged between 23.5 (2013) and 28.3 (2014) °C. Overall, 2013 can be considered as a cold year, 2014 as a hot year, 2010 and 2011 as intermediate years. The temperature variation pattern between the years cannot be easily linked to the variations in b .

Concerning p_{max} , even though the largest value of p_{max} is associated with the warmest year (2014), and the smallest value of p_{max} with the coldest year (2013), years 2010 and 2011 had different values of p_{max} despite having similar temperatures. Besides, p_{max} and b are expected to depend more strongly on PAR than on T . Conversely, r_0 can be expected to be larger when temperatures are higher. This happened in 2011 and 2014, but not in 2010, which still had relatively high temperatures. Possible explanations are changes in the Q_{10} value, or the influence of other environmental variables. We did not investigate further possible changes in the Q_{10} value, both because we did not have an independent way to estimate it, and because its range is narrow according to the literature (Reynolds, 1984; Raven and Geider, 1988; Davison, 1991). Concerning PAR , in the analyzed periods the average values in the mixed layer ranged from 162 (2013) to 227 (2014) $\mu\text{mol}(\text{ph})\text{m}^{-2}\text{s}^{-1}$, being higher in 2010 and 2011 than in 2013, and notably higher in 2014 than in all the other years. Remarkably also in 2014, despite the high values of PAR , the communities did not show signs of photoinhibition (a PAR_{max} value of 741 for the mixed layer corresponds to a surface value of $\approx 1900\mu\text{mol}(\text{ph})\text{m}^{-2}\text{s}^{-1}$, given the light extinction coefficient of the lake of 1.5). Higher

average PAR values could be responsible for larger p_{\max} values, as observed in 2011 and 2014, and partially in 2010. However, the average PAR values are very similar in 2010 and 2011, while p_{\max} values are not. Still, the very low value of p_{\max} in 2013 could be explained by the low PAR_{ave} value. The variations of b between the years, though, cannot be linked to the changes in PAR : 2013 and 2014, despite having very different PAR values, had similar b values. The trend in r_0 also cannot be associated with the trend in PAR between the years. From what is said so far, the changes of PAR and water temperature alone cannot fully account for the changes in the model parameters. ~~A~~ The long-term variations of the parameters probably have other drivers too, such as the composition of the algal communities; as already stated a more extensive analysis would require more information on the algal communities living in the lake such information and is beyond the scope of this paper.

3.3 Model choice

10 In aquatic sciences, other models for describing the dependence of photosynthesis on irradiance are more commonly used than the Michaelis-Menten equation. The Michaelis-Menten equation was chosen in an effort of harmonizing productivity studies between aquatic and forest sciences, in order to study the carbon cycle consistently in the forest-lake continuum. However, we checked whether other models provided a better fit to the data. We used the equations by Smith (1936) and by Jassby and Platt (1976). Even though they agreed well with the data, they did not perform significantly better than the
15 Michaelis-Menten equation: the R^2 and $RMSE$ values of the fits were very similar. Hence, we decided to proceed with our first choice. The Smith (1936) and Jassby and Platt (1976) model equations and fit statistics are reported in the supplemental information (Sect. S3 and Table S1).

3.4 Out-of-sample validation

The analysis we performed was based on an in-sample comparison, since our goal was to check whether our method to calculate
20 the NEP was in agreement with the PI models typically used (Michaelis-Menten, Smith (1936) and Jassby and Platt (1976) equations). However, for the Michaelis-Menten model, we also ran an out-of-sample validation for each year, in order to further verify the correspondence between the calculated NEP and the model. For each year, we randomly selected half of the data points and used them for the fit, to calculate the model parameters. Then, for the other half of the sample, we estimated the NEP using the equation and the parameters we had obtained, and compared it to the originally calculated NEP . We both
25 evaluated the correlation coefficient r between the two NEP s (the one calculated from the data, and the one calculated from the model trained on half of the data points, then discarded), and the $RMSE$ of the validations. The results are reported in Table 2, and show that the two NEP values compared well. The correlation coefficient r varies between 0.84 and ~~as already stated is beyond the scope of this paper.~~ 0.92 and the $RMSE$ varies between 0.15 and 0.31 $\mu\text{mol}(\text{CO}_2) \text{m}^{-2} \text{s}^{-1}$.

4 Discussion

4.1 Assumptions and uncertainties

Firstly, it is important to notice that we are working under the assumption that the *NEE*, which is what can be measured, is equal in magnitude to the *NEP*. This concept is widely accepted in the scientific community (Aubinet et al., 2012), for forests
5 as well as for other environments such as lakes. The assumption is indeed strictly valid only when there are no sources and sinks of CO₂ that do not involve conversion to or from organic C (Lovett et al., 2006). Such sources and sinks, however, are usually negligible, except for oceans.

The lateral transport of CO₂ had to be ruled for the sake of the calculations; ~~we~~. A similar challenge is encountered in forest ecology studies as well, where the lateral transport in the air (advection) is also usually neglected. We are of course fully
10 aware of the lake being a 3D dynamic system, ~~and we hope in the future to further develop the method we used so that it will work under more general conditions.~~ Besides, since this study focuses on the summer periods when the lake was stably stratified and there were no high winds or rains, the lateral transport is not expected to play a significant role here. ~~A similar challenge is encountered in forest ecology studies as well, where the lateral transport in the air (advection) is also usually neglected. The daytime and nighttime average values~~ This assumption is supported by Dinsmore et al. (2013), who
15 showed that for lake Kuivajärvi most of the CO₂ flux were always positive, albeit having lower values during the day than during the night. This is not surprising: many lakes, especially at high latitudes, are supersaturated with respect to CO₂; as a result, the discharge happens at snowmelt or during heavy rains in the autumn. It is also supported by the mixed layer CO₂ flux is from the lake to the atmosphere also during the day, when the aquatic primary producers are photosynthesising and absorbing CO₂. The *NEP* values were in fact also always negative, confirming heterotrophy. This is in agreement with
20 (Cole et al., 1994; Sobek et al., 2003) concentration time series, which show no sign of a long-term trend on top of the diurnal cycles (see Figg. S5-S14 in the supplemental information).

Regarding oligotrophic lakes, it has been suggested that diurnal patterns in the epilimnion stratification and water convective motions (causing nighttime upwelling of CO₂) are important drivers of the diurnal variation of the surface water CO₂ concentration (Åberg et al., 2009). Lake Kuivajärvi though is mesotrophic (chl *a* 5-30 µg l⁻¹ during summer) and the primary production
25 can be assumed to be the main driver of the CO₂ concentration, as observed also in some other lakes with high chl *a* (Hanson et al., 2003; Huotari et al., 2009). Also, we implemented strict selection criteria of the analyzed periods to minimize the effect of upwelling CO₂: the thermistor data indicate that the winds, despite being weak, were strong enough to keep the top 1.5 m of the water column well mixed both day and night, without however disrupting the thermocline. Thus, no sign of hypolimnetic upwelling was detected. Under these conditions, diurnal stratification patterns and convective motions had a minor impact on
30 the mixed layer of our lake. It is also important to note that the photochemical production of CO₂ is generally negligible in humic lakes (Jonsson et al., 2001); its maximum contribution to the flux for a lake with similar characteristics as the one in our study lake was < 4% over the whole growing season, and was detectable only in the top 10 cm of the water column (Vähätalo et al., 2000; Ojala et al., 2011).

~~In aquatic sciences, other models for describing the dependence of photosynthesis on irradiance are more commonly used than~~

~~the Michaelis-Menten equation. The Michaelis-Menten equation was chosen in an effort of harmonizing productivity studies between aquatic and forest sciences, in order to study the carbon cycle consistently in the forest-lake continuum. Our analysis was hindered by issues in the EC data set: due to inherent EC limitations and technical problems, the data set had many gaps and average daytime and nighttime F_a values had to be used. However, the relative uncertainty on them was, we checked whether other models provided a better fit to the data on average, 50%. This uncertainty propagates to NEP through Eq. (3), and therefore to the parameter values as well. We used the equations by Smith (1936) and by Jassby and Platt (1976). Even though they agreed well with the data, they did not perform significantly better than the Michaelis-Menten equation: the R^2 and $RMSE$ values of the fits were very similar. Hence, we decided to proceed with our first choice. The Smith (1936) and Jassby and Platt (1976) model equations and fit statistics are reported in the supplementary information (Sect. S3 and Table S1).~~ However, it does not undermine the good agreement between the model and the data, given that the average F_a values were calculated putting together all the periods of the same year. Therefore, each NEP data point has the same uncertainty and the same weight in the fit. The calculations could be improved with a better EC data set. Different methods could also be adopted to estimate the flux between the lake and the atmosphere. Chamber measurements could be used, but the time resolution could be an issue. They would need to be performed regularly. They could, however, be used to integrate the EC data set for example. Surface renewal models could also be used (Heiskanen et al., 2014). For further information on the comparison between different flux measurement methods, see Erkkilä et al. (2018).

4.2 Limitations and further development

In this study, we could not clearly link the environmental variables to the changes in the Michaelis-Menten model parameters, and more information on the algal communities living in the lake would have been required in order to ~~extend~~ expand the analysis. However, it is important ~~for us~~ to stress that the simplicity of this method lies in the fact that to estimate the parameters, which can then be used to calculate the productivity ~~for each year, such information~~, information on the algal communities is not needed. ~~Besides, an extensive application of the method would also allow for a comparison of the parameters between different lakes and different times, and the understanding of the relationship between the parameters and the~~ It is needed only when widening the scope of the productivity studies: when, for example, the parameters themselves and their relationship with the environmental conditions or the specific phytoplankton communities ~~would improve. Our analysis was hindered by the problematic EC data set: due to inherent EC limitations and technical problems, the data set had many gaps and average flux values had to be used. The calculations could be improved with a better EC data set or chamber measurements performed regularly~~ are investigated. Knowledge on the algal communities would also help when extending the productivity calculation to the whole year. In our case, for example, the NEP rates and hence the parameters are representative of the late summer. In lake Kuivajärvi, where diatoms are abundant, it can be expected for the productivity to have a peak in the spring and another smaller peak in the autumn, at the turnover. More measurements at those times would be needed, in order to understand whether the parameterization is still valid under those conditions.

~~For further development, it would also be good to have measurements for~~ At the current stage, the method we present here is still very system specific, and assumptions about lateral and vertical CO_2 exchange and photo-oxidation had to be made (negligible

lateral exchange and photo-oxidation, no in-lake vertical exchange). However, the method can in principle be applied to any lake and under any condition, with an expansion of the instrumental set-up. Measurements or estimates of F_u , the CO₂ flux from the deeper layer to the surface layer of the lake, would be needed in order not to limit the analysis to isothermal (as in Hari et al. (2008)) or stable stratification conditions. For example, (as here) conditions. This could be achieved for example adding water column turbulence measurements could be added to the CO₂ concentration and temperature measurements. Chemical measurements would be needed to apply the method in clear-water lakes, where photo-oxidation could play an important role. Finally, information about CO₂ discharge would be needed for lakes or periods when lateral transport is not negligible.

5 Conclusions

The high-frequency direct CO₂ concentration measurement method suggested in Hari et al. (2008) and tested only on 3 days of data under autumn turnover conditions was tested more extensively and under different conditions here, on a dataset of 40 days and under stable stratification conditions of stable stratification typical of summer for dark-water lakes. The method proved to be suitable for lake productivity studies under isothermal (Hari et al., 2008) or stable stratification conditions: its high temporal resolution allowed us to calculate the net ecosystem productivity at a temporal scale of minutes. A quantitative comparison between the ~~calculated~~ *NEP* calculated with this method and the modeled *NEP* was also carried out for the first time, and it showed a very good agreement between the two, further validating the method. From that, we were able to accurately parameterize the net productivity as a function of the ambient variables, estimating the productivity parameters typical of the communities in the lake.

Overall, we believe that the method proposed in Hari et al. (2008) and further tested, verified and developed here, with the explicit parameterization of the *NEP* from *PAR* and water *T*, represents a great improvement over the traditional approaches (bottle method and ¹⁴C technique). At the present stage it is still very system specific, and assumptions about lateral and vertical CO₂ exchange and photo-oxidation had to be made (negligible lateral exchange and photo-oxidation, no in-lake vertical exchange method, since it is direct and the respiratory quotient is not needed. However, at the present stage it still can be applied under a limited set of conditions (isothermal or stable stratification). Still, our study is an important step towards testing and developing the approach so that it becomes more general, also given the scarcity or even lack of high-frequency direct CO₂ measurements for productivity studies (we are aware of only one other study where free-water CO₂ measurements were used for metabolism studies (Hanson et al., 2003)). We are looking for further contributions by the research community and we think the method should be widely adopted, in order first to gather more information about its usability under different conditions and then also to have a broader network of productivity studies on lakes. This is all the more true given that it is the CO₂ probes are also easy to set up and relatively inexpensive. Its only requirement is The method requires at least a concomitant estimation of the CO₂ flux from the lake to the atmosphere. In our case the EC technique was used, which is expensive and can be laborious in the data processing phase. However, chamber

measurements ~~for example are an equally good option~~ or surface renewal models could be equally good options.

5 Additionally, the method also relies on equations that are typically adopted in terrestrial ecology studies for the calculation of the *NEP*, where high-frequency measurements are more commonplace than in aquatic research. Extensively applying the method would reduce the gap in the CO_2 exchange measurements between aquatic and terrestrial ecology, which is beneficial in the framework of integrating research in different ecosystems, for which purpose a common language between different disciplines is needed. It would also help us achieve a better understanding of the biological processes behind the CO_2 exchange. This, in turn, would expand our knowledge on the carbon cycle in the water, which is still limited, and would lead to a better integration of aquatic ecosystems in the local and global carbon budgets.

Code and data availability. The data sets and the codes used in this paper can be obtained from the authors upon request.

10 *Competing interests.* The authors declare that they have no conflict of interest.

Acknowledgements. This study was funded by the University of Helsinki and the Finnish Cultural Foundation - Häme fund (Hämeen rahasto - Suomen Kulttuurirahasto). Support also came from the Academy of Finland, through the Academy Professor projects (1284701 and 1282842), the CarLAC project (281196), ICOS-Finland (1281255) and the Finnish center of Excellence in Atmospheric sciences, and from the EU project GHG-LAKE (612642).

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A schematic representation of the mass balance in the mixed layer of the lake. C_{CO_2} is the CO_2 concentration in the water, F_a is the CO_2 flux between the lake and the atmosphere (positive if from the lake to the atmosphere), F_v is the CO_2 flux from the deeper to the mixed layer of the lake (positive if upwards), t is time, z is depth and h_{mix} is the mixed layer depth.

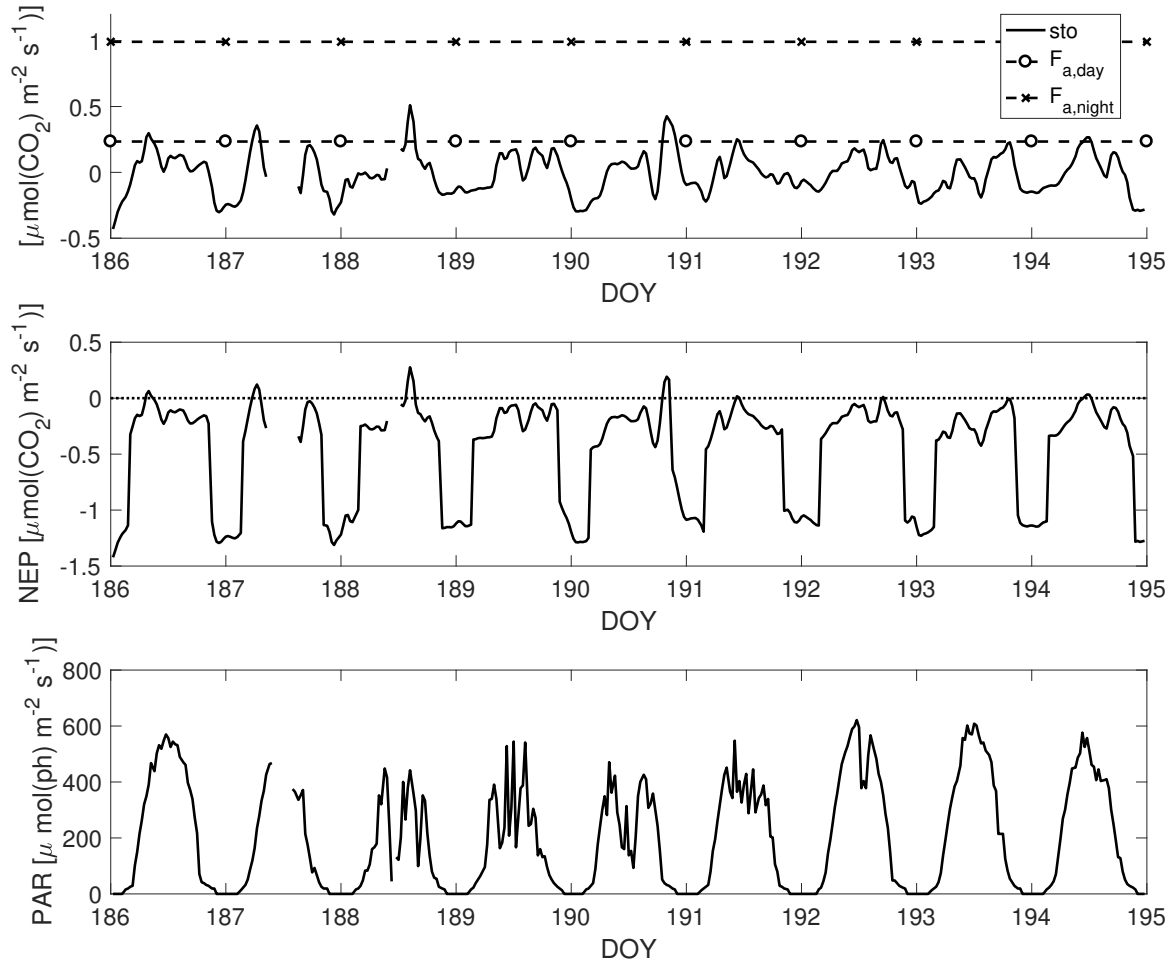


Figure 1. A sample period of stable stratification in July 2010, representative of the studied periods. In the upper panel the solid line (sto) is the first term of Eq. (3), the CO_2 concentration change in time over the mixed layer, which is usually referred to as storage flux in forest ecology calculations; the dashed horizontal lines are the daytime and nighttime average CO_2 fluxes from the lake to the atmosphere (F_a). In the central panel, the solid line is the NEP and the dotted line is the zero rate. In the lower panel the solid line is the PAR (photon flux density measured in the PAR wavelength range) average value in the mixed layer. [The resolution is 30 minutes, except for the \$F_a\$ average values.](#)

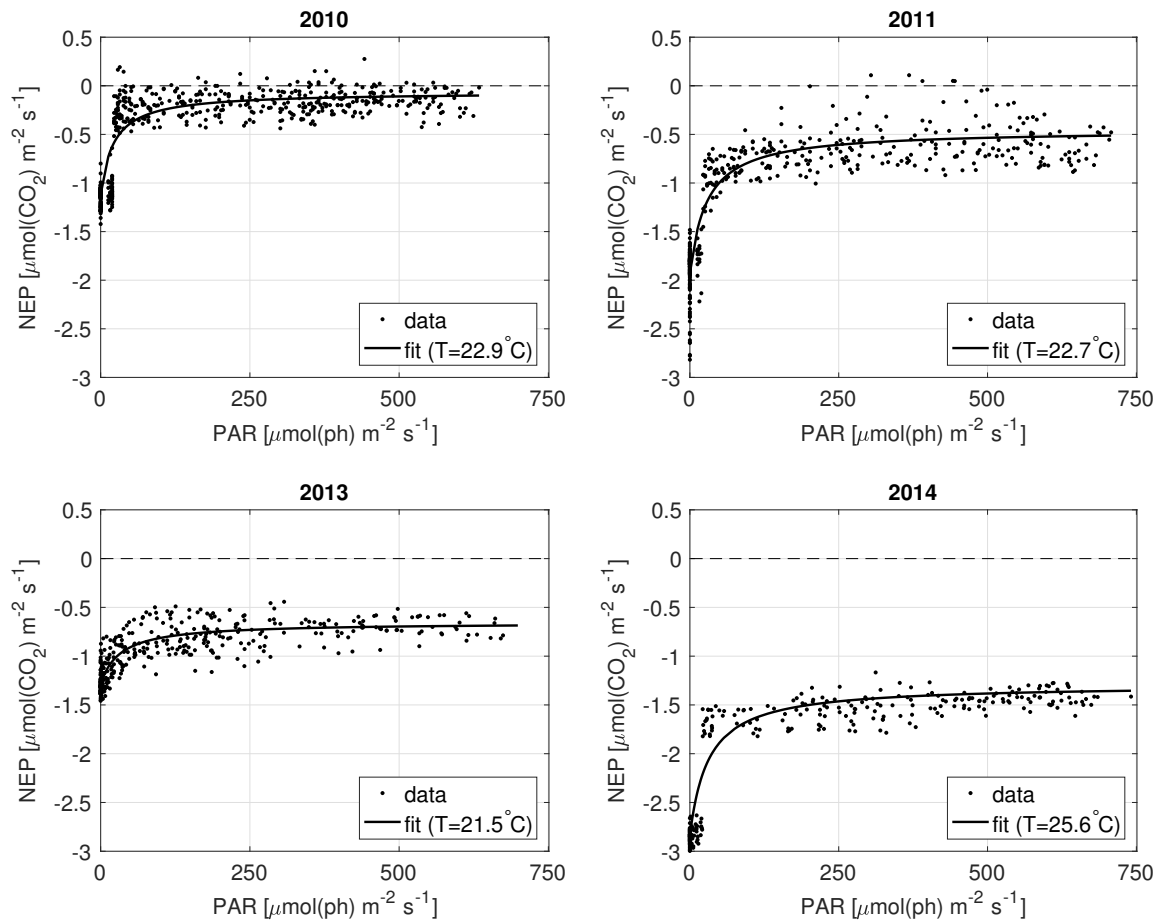


Figure 2. The *NEP* versus *PAR* plots for each year; the each dot represents a 30-min interval. The fitted curve shown is calculated using the average water *T* of the studied periods of the year.

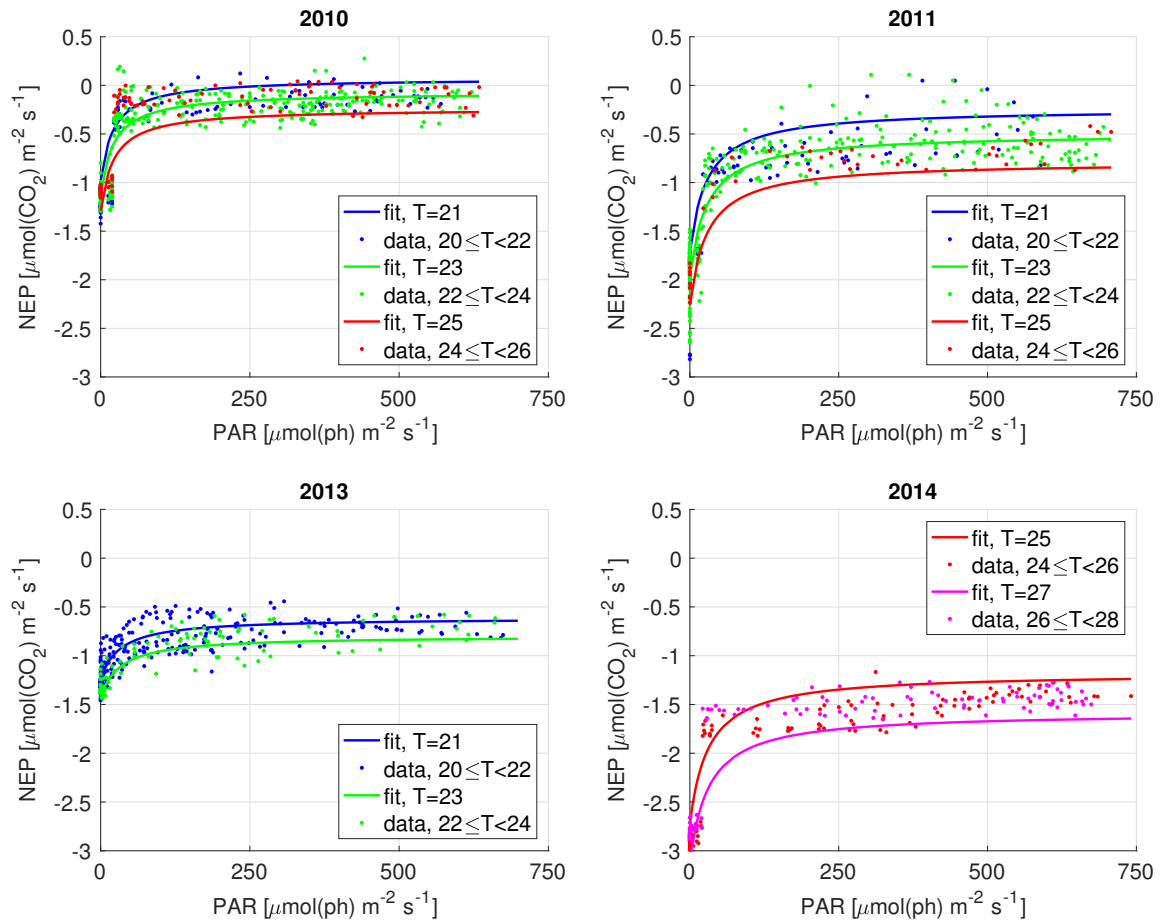


Figure 3. The *NEP* versus *PAR* plots for each year. Data points are Each dot represents a 30-min interval, color-classified according to water temperature classes, and the curves are calculated for the different temperatures; note, Note that the curves are not individual fits, but are the result of the year's 3D fit, evaluated for the different temperatures. Water *T* is in °C.

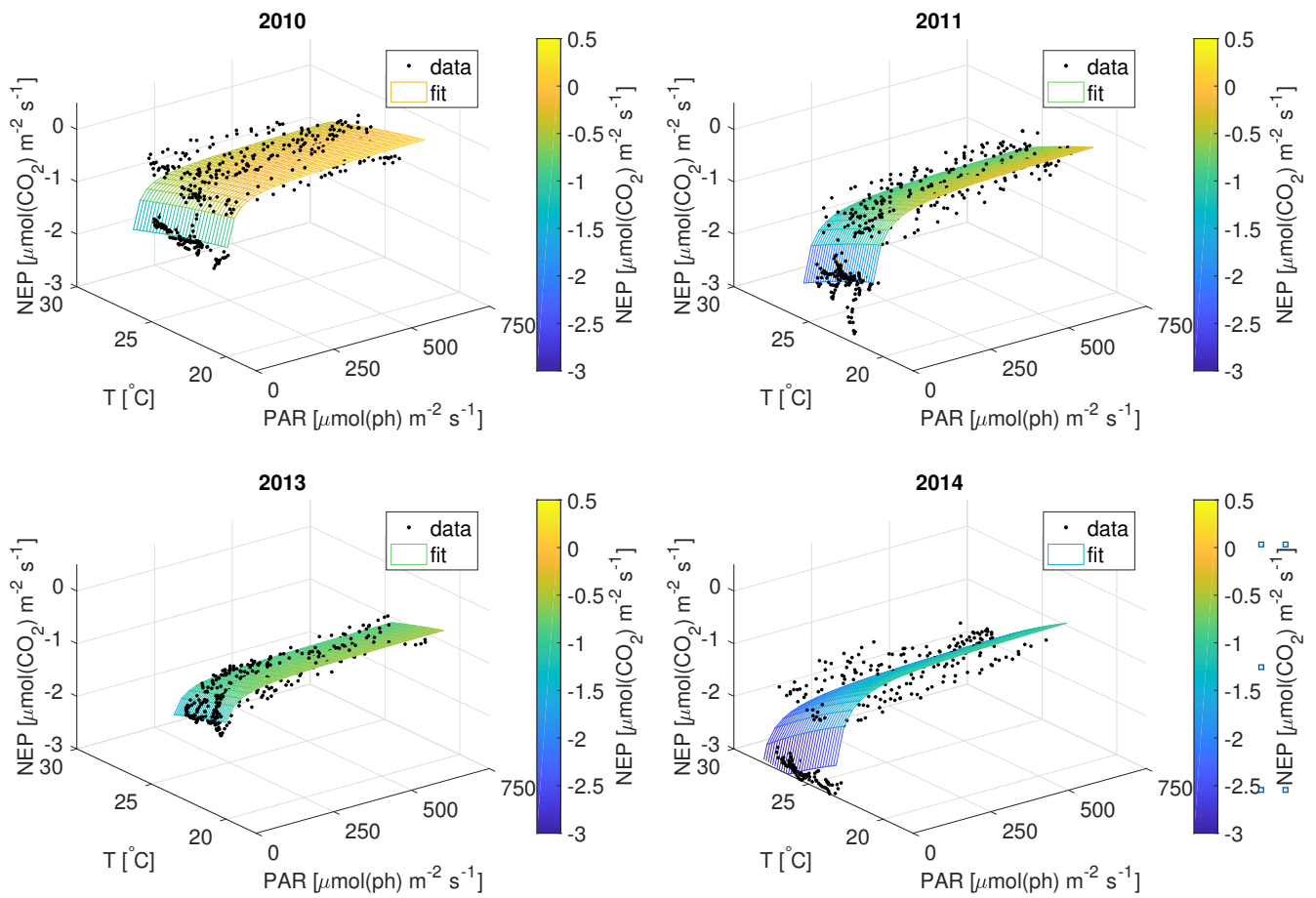


Figure 4. Data and fitted *NEP* versus *PAR* and water *T* 3D-curves for each year; each dot represents a 30-min interval.

Table 1. ~~Parameters~~ Fit statistics, parameters of the *NEP* vs *PAR* and water *T* model with 95% confidence intervals (from Eq. (5)), ~~with 95% confidence intervals~~ and average, minimum and fit statistics ~~maximum values~~ maximum values of water *T* and *PAR* in the mixed layer for the studied periods of each year. *RMSE*, p_{\max} and r_0 in $\mu\text{mol}(\text{CO}_2)\text{m}^{-2}\text{s}^{-1}$, *b* and *PAR* in $\mu\text{mol}(\text{ph})\text{m}^{-2}\text{s}^{-1}$, *T* in $^{\circ}\text{C}$.

Year	R^2	<i>RMSE</i>	p_{\max}	<i>b</i>	r_0	R^2 T_{ave}	<i>RMSE</i> T_{min}	$[\mu\text{mol}(\text{CO}_2)\text{m}^{-2}\text{s}^{-1}]T_{\text{max}}$	$[\mu\text{mol}(\text{ph})\text{m}^{-2}\text{s}^{-1}]T_{\text{max}}$
2010	<u>0.73</u>	<u>0.23</u>	1.05 ± 0.05	22 ± 5	0.228 ± 0.008	0.73 <u>22.9</u>	0.23 <u>19.9</u>	<u>26.2</u>	<u>195.3</u>
2011	<u>0.84</u>	<u>0.25</u>	1.47 ± 0.06	29 ± 6	0.399 ± 0.009	0.84 <u>22.7</u>	0.25 <u>20.7</u>	<u>25.3</u>	<u>197.3</u>
2013	<u>0.71</u>	<u>0.14</u>	0.63 ± 0.04	33 ± 10	0.290 ± 0.007	0.71 <u>21.5</u>	0.14 <u>20.0</u>	<u>23.5</u>	<u>162.3</u>
2014	<u>0.74</u>	<u>0.33</u>	1.55 ± 0.10	31 ± 11	0.482 ± 0.013	0.74 <u>25.6</u>	0.33 <u>23.2</u>	<u>28.3</u>	<u>227.3</u>

Table 2. The model parameters as in Table 1 Fit statistics (p_{\max} , R^2 and r_0 in $\mu\text{mol}(\text{CO}_2)\text{m}^{-2}\text{s}^{-1}$, b in $\mu\text{mol}(\text{ph})\text{m}^{-2}\text{s}^{-1}$ $RMSE$) calculated for half of the sample, average, minimum correlation coefficient r and maximum values of water T ($^{\circ}\text{C}$) and PAR in validation $RMSE$ using the mixed layer ($\mu\text{mol}(\text{ph})\text{m}^{-2}\text{s}^{-1}$) for the studied periods other half of each year the sample. $RMSE$ in $\mu\text{mol}(\text{CO}_2)\text{m}^{-2}\text{s}^{-1}$.

Year	p_{\max}	R^2	b	$RMSE$	r_0	r	T_{ave}	T_{min}	T_{max}	PAR_{ave}	PAR_{max}	validation $RMSE$
2010	1.05	0.72	220	23	0.228	0.85	22.919	9.926	21.956	340	23	
2011	1.47	0.84	290	25	0.399	0.92	22.720	7.253	19.770	80	25	
2013	0.63	0.71	330	15	0.290	0.84	21.520	0.023	5.162	699	14	
2014	1.55	0.77	310	31	0.482	0.88	25.623	2.228	3.227	741	31	