

Associate Editor Decision: Reconsider after major revisions (19 Jun 2017) by Gwenaël Abril

Comments to the Author:

Decision on MS BG 2017-56

Dear authors,

I have now read your answers to the reviewer's comments and projected changes to the manuscript. Because I found reviewer's comments were at some places superficial, I made my own detailed reading of your submitted paper. Although it was clear to me that the presented dataset is of high quality for publication, my major concern comes from the lack of well-defined objectives of the paper and the justification of the choices made in the way data are analysed and presented. What are the important new insights provided by the study? How can this paper help future CO₂ and CH₄ fluxes measurements in lakes? These questions must be answered more clearly in your revised MS. It was not evident to me if your paper was focussed on the comparison between EC, FC and k methods, on the validity of different parameterization of k, on the diurnal variations of fluxes at the study site, or on the difference between stratified and mixed periods at the study site, etc...

Thank you for your comments. The research objectives are now made clearer and the paper focuses in comparison of the three flux measurement methods and making recommendations for future flux measurements over lakes. The new insights come from frequent sampling that allows us to examine the differences between day and night-time fluxes, with all three methods. We find that the old, widely used, gas transfer coefficient model gives substantially lower fluxes than the other methods, and there are differences between manual and automatic gas concentration measurements. All these affect the resulting flux calculation, and especially current global up-scaled flux estimates have deficiencies, as they are mostly based on the old gas transfer model and daytime concentration measurements.

To that respect, I recommend you consider very seriously the general comment by Ref.#1: "some aspects of the discussion elements should be reworded to make the main conclusions more evident. Some of the conclusions, for example on the difference between day and night time, do not seem so evident based on the figure analysis. Those figures should also be improved to ease comparisons between fluxes and controlling parameters on one side, and between approaches on the other side."

Figures are improved to make comparison between daytime and night-time more clear and in addition a new table is added where average daytime and night-time fluxes are listed for the stratified and mixing periods separately.

I also fully agree with review#1's comment "If you have floating chamber measurements and mixing ratio of CO₂ and CH₄ in the water, you should try to calculate a site specific k value and compare it to the one calculated from Cole and Caraco"

I would add that k could be calculated from EC and FC fluxes and compared to those calculated with the different BLM. If the paper deals with performance of methods (maybe not), calculations of k can be done separately for CO₂ and CH₄, normalised with the Schmidt Number and compared one with the other. This would allow a comparison of performance of methods, even when fluxes are extremely low for CH₄ but not for CO₂ (due to larger delta CO₂ between air and water). In your respond to this comment, you mention a second paper in preparation. Your dataset is indeed strong enough to produced two papers, but splitting the data in two papers must be done according to well-defined specific objectives.

We thought about this aspect thoroughly, but came to the conclusion that we will still write two separate manuscripts. The current one is focused on flux measurement method comparison and gas fluxes in general, whereas the second one will focus more on the physics of gas transport, for which site specific k calculation is more appropriate and calculated with other methods as well.

Five Figures (6-10) report “median” diurnal variations of fluxes and driving parameters. If I understood properly, these are composite data averaging values at the same hour but different days, so these data include natural day-to-day variations. I was not convinced that using such composite median values was the best way of comparing the efficiency of the different methods, which could be done using individual synchronous values.

Daily median values of each flux are compared in Table 1. Using daily median values for comparison instead of half-hour synchronous values produces a less noisy comparison. Diurnal variation is studied for the two time periods (lake mixing and stratification) separately, because the variation considerably differs between these two periods. Figures 4 and 5 show that especially during lake stratification there is not much day-to-day variation.

To summarise, I am happy to encourage you to proceed with the revision of your manuscript, but I would like to stress that this should be done after re-think profoundly the objective of your study and the way the data are analysed. Needs some work. The paper must be re-focused. Separating the results section from the discussion section will probably help your writing.

One detail: P4L27-Final gas concentrations in the water were calculated using the Henry’s Law
Please mention what solubility coefficients you used for CO₂ and CH₄

Solubility constants are added to the text. The manuscript is now more focused and figures are improved. We still kept results and discussion in the same section, as it helps analyzing the results more deeply. However, we have added more text on both results and discussion in the manuscript!

Looking forward to reading a revised version of you MS.

With best regards
Gwenaël Abril, BG Associate Editor

Interactive comment on “Methane and carbon dioxide fluxes over a lake: comparison between eddy covariance, floating chambers and boundary layer method” by Kukka-Maaria Erkkilä et al.

Anonymous Referee #1

Received and published: 20 March 2017

Scientific significance: Good: It is not clear whether the whole data set is new, but the comparison between EC measurements and Boundary Layer Methods (BLM) offers new insights on these data

Scientific quality: Good: Applied method are valid, and the research group has a well expertise on this topic.

References are appropriate, very few might be added to support assumptions (see comments)

Presentation quality: Good: English is good, figures and tables are all necessary. Some of the figures could be improved to support discussion (see comments)

We thank the anonymous referee #1 for your very good and on point comments. We have carefully read through all the comments and prepared responses to all specific comments below.

+General comments:

This manuscript by Erkkilä et al deals with the important question of assessing CO₂ and CH₄ fluxes from water bodies, boreal lake in this case. This paper is fallen well in the scope of the Biogeosciences journal. MS present a set of Eddy Covariance flux measurements and BLM flux calculations, all data of interest for the research community and GHG inventory compilers. This MS is generally well written, is timely and interesting to understand the parameters of influence on carbon emissions from lakes. The authors have done a good job in data collecting and study design though the study period is quite short (15d), but still, interesting by the contrast it is showing between stratified and mixed conditions. Some aspects of the discussion elements should be reworded to make the main conclusions more evident. Some of the conclusions, for example on the difference between day and night time, do not seem so evident based on the figure analysis. Those figures should also be improved to ease comparisons between fluxes and controlling parameters on one side, and between approaches on the other side.

Thank you! The study period is short due to intensive manual data collection that was timed to the start of the lake mixing period. All the comments will be taken into account and the figures improved.

+Specific comments:

-Page 2, line 7: it is Heiskanen et al (2015) rather than 2014

Yes of course, this will be fixed.

-Page 2, line 11: ". . . a small part of a lake": rather vague. . .

Will be changed to "...is representative of the measurement point only"

-Page 2: lines 27-29: "Because current up-scaling estimates are based on these methods, comparison is needed to reduce the uncertainties in current estimates of the role of lakes in global carbon cycle". More generally, the role of freshwaters need to better assessed.

"lakes" will be changed to "freshwaters"

-Page 5, line 12: with 27% and 32 data coverage for CO₂ and CH₄ fluxes are quite low, though not critically low. What is the coverage for heat fluxes? Is there any estimate of the impact of gap filling with bulk model on those fluxes?

27% and 32% coverage for lake eddy covariance measurements is not that low, keeping in mind that we also have to discard data according to wind direction on top of other quality filtering. Coverage of heat fluxes was 83% and 80% for latent and sensible heat fluxes, respectively. The effect of gap-filling is probably not large, because the few gaps in heat fluxes most probably coincide with gaps in gas fluxes and will not affect the comparisons. The bulk-transfer relationships are widely used, and well-established in-situ coefficients are reported in Mammarella et al. (2015).

-Page 8, lines 2-5: do you assign difference in CO₂ concentration between the automatic and manual systems to the same reason as for CH₄ (too short time of equilibration in the automatic system?). With 40min, do you really think time of equilibration was too short? What percentage of dissolved CH₄ do you think you were retrieving? This issue needs to be discussed.

We don't know if the equilibration time was too short or not but this a possibility. This is why we included the manual headspace samples to get a feeling for the uncertainty of the absolute values. Headspace samples were taken at different locations than the automatic system, so some variation between the two samples is expected. Without additional headspace samples close to the automatic system it is impossible to say anything absolute about the accuracy, but we still trust the gradient.

-Page 8, from line 23, section 3.2.1 There is a main issue here in defining detection limit, uncertainties, errors. If detection limit is approximately 2 nmol m⁻² s⁻¹, then you cannot write that "CH₄ fluxes. . . were small (less than 1 nmol m⁻² s⁻¹)". Identically, you cannot say that "the difference between manual and automatic BLM fluxes remained below 0.4 nmol m⁻² s⁻¹". All this is not consistent. You should give indications on how you determine the flux detection limit.

Detection limit was not calculated for this site but a reference was taken from Peltola et al. (2014) to have a rough estimate of detectable flux by this analyzer. A site specific detection limit may be calculated as the standard deviation of the cross-covariance function values far from the maximum values (flux), as was developed in Wienhold et al. (1995), and added to the text. As the EC fluxes are presented as daily median values, the detection limit should be scaled by \sqrt{n} where n is the number of measurements per day (n=48), giving a daily flux detection limit of approximately 0.29 nmol m⁻² s⁻¹. We will take a closer look on the detection limit and make the text more clear on this.

-Page 8, lines 18-20: you expect an enhancement of CO₂ concentration at the surface due to up-welled methane. You mean CO₂ from oxidised CH₄? There is at least a factor 10 between CO₂ concentration at the surface and CH₄ concentrations at 11m depth, so the proportion of CO₂ to be expected from methane oxidation between 11m and the surface would remain low in all cases...

I mean the upwelling water that would also bring CO₂ to the surface from deeper waters. However, the CO₂ concentration difference between surface and 11m is not as drastic as for CH₄ (surface water CH₄ concentration is only 3% of the 11m concentration whereas surface water CO₂ concentration is 20% of the 11 m concentration) and thus upwelling water does not make such a big rise in the surface water CO₂ concentration. This will be made more clear in the text.

-Page 8, line 34: why more frequent sampling should necessarily lead to higher fluxes than the ones reported by Miettinen et al? Give explanations.

More frequent sampling would include also nighttime cooling periods and perhaps windier daytime episodes in the measurements. When all kinds of weather conditions and cooling periods are included, the fluxes might end up being higher.

-Page 8, line 34: Give value of high fluxes reported by Ojala et al.

The high fluxes after rain events were about $6 \text{ nmol m}^{-2} \text{ s}^{-1}$, which is much higher than we measure during the stratified period. The value will be given in the text as well.

-Page 9, line 1: please add reference to support hypothesis on lateral CH₄ transport from catchment linked with precipitation event.

Ojala et al. (2011), Rantakari & Kortelainen (2005), will be added to the text.

-Page 9, line 3: ". . . that kTE and kHE were similar. . .": add "and comparable to EC measurements" to that sentence.

Will be added.

-Page 9, line 8: detail explanation in Schubert et al for lower kCC results, if relevant for this study.

Eddy covariance and floating chambers gave 8 and 7 times higher cumulative fluxes than kCC method in Schubert et al. (2012). This will be added to the text.

-Page 9, lines 11-13: make consistent, CO₂ flux or fluxes, singular/plural

Will be made consistent.

-Page 9, line 16: EC increase seems be lower than a factor 3. See Table 2.

This value is not seen from the table. Table 1 & 2 give linear fit values to the comparison between EC and BLM fluxes for CH₄ and CO₂ fluxes, respectively, during the whole measurement period. CO₂ flux increases from about $0.5 \mu\text{mol m}^{-2} \text{ s}^{-1}$ to $1.7 \mu\text{mol m}^{-2} \text{ s}^{-1}$, thus a factor 3 increase.

-Page 9, line 20: $3 \mu\text{mol m}^{-2} \text{ s}^{-1}$: calculated from which BLM model?

Good point, $3 \mu\text{mol m}^{-2} \text{ s}^{-1}$ from kTE and kHE models, whereas kCC increased to $2 \mu\text{mol m}^{-2} \text{ s}^{-1}$. This will be corrected in the text.

-Page 9, line 25: "The same result. . .": that is, kCC lower than both kTE and kHE?

"The same result..." refers to the previous sentence that compares BLM and EC methods, not the different k models.

-Page 9, lines 28-29: again, what is the impact of using bulk formulas on the calculations of heat fluxes and subsequent kHE and kTE?

Probably not large and the heat flux coverages were quite high in any case and the bulk formulas are well established.

-Page 10, section 3.3. This section is rather confused. If EC is taken as the reference (line 21), then discussion on CO₂ diurnal variation should try to explain why BLM show a diurnal variation which is not expected at the end, as seen from EC measurements.

EC is not taken as a reference, but it is compared to other methods. We do not assume any method being "more correct" than others and different methods may have different diurnal variations.

-Page 10, line 6: ". . .kCC results in a remarkably lower flux than kHE in general": underestimation seems particularly due to underestimation of fluxes when they are at their maximum. Any reason why?

Early morning times are usually a time of lake cooling, which then causes some additional convective mixing in the water column. This is taken into account in kHE model, but not in kCC model.

-Page 10, lines 9-10: is horizontal turbulence assumption consistent with kHE variability given in previous sentence?

Unfortunately it is not completely clear what is meant by 'horizontal turbulence assumption' within this context. Both kCC and kHE are 1-D models considering only the vertical transport. Neither one of them is capable of addressing horizontal processes, and therefore we think that horizontal turbulence is not the cause of differences between the dynamics of these models.

-Page 10, line 15: maximum is rather reached at noon than during the afternoon

Correct, will be corrected in the text.

-Page 10, line 16: " The BLM flux by kTE is thus also larger in the daytime despite the lower $_{[CO_2]}$." $_{[CO_2]}$ is the same for all the BLM models, why adding this element in the discussion, it is somehow confusing. . .

The higher kTE is more dominant than the lower concentration, resulting in a higher BLM flux.

-Pages 10-11, section 3.3.2 Whole section is not convincing. Daytime vs. night time fluxes would need to be calculated to support the discussion. First define precisely hours of the day used to separate the two periods. BLM daytime fluxes do not seem to be significantly higher than night time fluxes. Diurnal variation from EC fluxes not well correlated. No bubbling? Figures not very helpful for comparison and to support discussion. Precise hours will be given in the text and shown in the figures. I would not expect much bubbling from the study area, since the lake is quite deep in the EC footprint area and from the chamber measurements we only saw one or two ebullition events close to the shore (these were removed from the analysis).

-Page 10, lines 26-27: Highest flux value is reached during the late afternoon/evening and during the second part of the night. Not so clear for EC fluxes.

True, also EC fluxes show the late afternoon peak but not the early morning peak. We will rephrase the sentence.

-Page 10, lines 27-28: add wind speed on plot for better comparison.

Wind speed is given in figures 2c, 7b and 9b.

-Page 10, line 29: precise which Fig 9 panel.

Fig 9d, will be specified in the text.

-Page 10, line 31-32: reword sentence: it appears that there is an increase of CH₄ in the afternoon just because of less oxidation. It is both possibly due to that phenomenon and to continuous feeding of CH₄ from underneath.

This has already been stated in line 29, but can be clarified in lines 31-32 as well.

-Page 10, line 32: ". . .enhanced resuspension from sediments". do you mean lateral advection? Suspension of gases? Not clear to me. Any reference to support the assumption

Resuspension in the littoral zone, bringing methane to lake water and then transported further in the lake by lateral advection. This is of course speculation since we do not measure it. Reference given in the text is study by Bussmann, 2005.

-Page 10, line 33: "detached gases. . .": detached does not seem an appropriate word

Will be replaced by "... enhanced transport"

-Page 11, line 6: any reference to support enhanced night time production of CH₄ in sediments?

This is speculation by Podgrajsek et al. (2014), we do not observe higher nighttime CH₄ fluxes. This part of the sentence can also be removed, since there is no other reference and it is not related to our study.

-Page 11, lines 9 and 11: again highest fluxes around noon seems more correct.
Yes, this will be corrected.

-Page 11, lines 13-14: Not clear, are you discussing comparison between day vs. night fluxes, or mixed/stratified periods?
Comparison between day vs. night during the mixing period. We will try to make it clearer.

-Page 11, line 16: " This may be caused by increased convective transport of CO₂ from deep waters to the surface": any other reason possible?
Algal photynthesis may also play a role here although we do not have any direct result on that.

-Page 11, section 4 There is no clear added value of this whole section to the paper. If you have floating chamber measurements and mixing ratio of CO₂ and CH₄ in the water, you should try to calculate a site specific k value and compare it to the one calculated from Cole and Caraco.
We disagree with this and would like to keep the section. Even though we did not find any "hot spots" with the FC measurements, we think it is important to show that. With this analysis we found that EC measurements give higher CO₂ fluxes from the south, shallower side of the lake and the CO₂ EC fluxes did not differ from FC fluxes from the north side of the lake. Site specific k calculation was left out of the analysis for keeping the paper more compact, but we think the reviewer have a good point with suggestion this approach as well. However, there is another manuscript in preparation that is focused on gas transport and includes site specific k calculation from this campaign and we think that adding this calculation to this manuscript would make it more broad and complicated, as we try to focus on flux measurement methods instead of gas transport velocity.

You use 'median' for 'standard diurnal variation' throughout the section.
This will be corrected.

-Page 11, line 28: quote reference(s) that show that anchored chambers can enhance artificially the turbulence and subsequent fluxes.
Lorke et al. (2015) found that anchored chambers create artificial turbulence in *running* waters. This has not been found to be an issue for lakes, as studied in Gålfalk et al. (2013).

-Page 12, line 2: see comment on figure 11.
Yes.

-Page 12, line 19: see comment on page 11 section 4 on calculation of site specific k value
Yes.

-Figures 2 and 3: Variation of parameters are hard to see with original figure dimensions
Will be improved.

-Figure 3b: CH₄ concentration at 11m: mention that it is the blue line.
Yes, good point.

-Figure 4: you should add in the legend, as in Figure 5: ". . . the outliers are represented with the red '+' symbol." A definition need to be given for "outliers" ($>3\sigma$?). Some outliers seems not so different than extremes values kept in the distribution (in Figure 5 particularly), and sometimes fluxes appearing as outliers where not removed (see

CH₄ fluxes on September 22 and 23, panel a, or CO₂ fluxes on September 14 and 15, panel b).

Box plots come from Matlab's box plot function. It determines the extreme values (w , that are not outliers) as approximately $\pm 2.7\sigma$ and 99.3 % coverage and outliers as larger than $q3+w(q3-q1)$ or smaller than $q1-w(q3-q1)$ where $q1$ and $q3$ are the 25th and 75th percentiles, respectively.

-Discussion on Figure 4 and 5 should be supported by statistics on difference/similarity between the different fluxes assessments.

Statistics are already reported in Tables 1 and 2.

-A different Y axis could be given for the stratified period. A dead band corresponding to the detection limit for fluxes could also be added.

While a separate y axis might enhance readability for the stratified period, we think it would make it harder to read the whole figure. A dead band for the detection limit will be added.

-There were no measurements for CH₄ from the automatic system on September 22, 23 and 24?

There were no manual measurements 22-24 Sep (Figs. 4b and 5b), but the automatic system was running.

-Figure 5: There are no negative fluxes from BLM model, when such CO₂ sink is sometime measured with the EC system. Develop to explain this major difference.

Median CO₂ sink was measured with the eddy covariance system only during two days but statistically these measurements were not different from 0 (tested with Mann-Whitney U-test). We can conclude that the fluxes are very small before the lake mixing. It is known that boreal lakes may occasionally act as sinks of CO₂ (e.g. Huotari et al. 2011), but at this time of year it is very unlikely.

-Figure 6: add wind speed.

Wind speed is already given in Fig 7b.

-Figure 6 all through fig 10: add shaded area for day/night time periods or add radiation data to better discriminate the two periods you are commenting.

This is a good idea, a shaded area will be added.

-Figure 8: use same scale for fluxes calculated with kCC (up to 20 nmol m⁻² s⁻¹) It does not appear as evident that daytime fluxes are higher than night time ones. See implication for the discussion.

Same scale can be used, although then the diurnal variation is not that evident.

-Figure 11: Seems that whiskers are showing smaller flux value than what should be error on EC fluxes (see comment on page 8 about errors, precision and detection limit). Add statistics to comment spatial variability on CH₄ FC fluxes

Coefficient of variation or standard deviation will be added.

References:

- Busmann, I. (2005). Methane Release through Resuspension of Littoral Sediment. *Biogeochemistry*, 74(3), 283–302. <http://doi.org/10.1007/s10533-004-2223-2>
- Gålfalk, M., Bastviken, D., Fredriksson, S., & Arneborg, L. (2013). Determination of the piston velocity for water-air interfaces using flux chambers, acoustic Doppler velocimetry, and IR imaging of the water surface. *Journal of Geophysical Research: Biogeosciences*, 118(2), 770–782. <http://doi.org/10.1002/jgrg.20064>
- Huotari, J., Ojala, A., Peltomaa, E., Nordbo, A., Launiainen, S., Pumpanen, J., ... Vesala, T. (2011). Long-term direct CO₂ flux measurements over a boreal lake: Five years of eddy covariance data. *Geophysical Research Letters*, 38(18), n/a-n/a. <http://doi.org/10.1029/2011GL048753>
- Lorke, A., Bodmer, P., Noss, C., Alshboul, Z., Koschorreck, M., Somlai-Haase, C., Premke, K. (2015). Technical note: drifting versus anchored flux chambers for measuring greenhouse gas emissions from running waters. *Biogeosciences*, 12, 7013–7024. <http://doi.org/10.5194/bg-12-7013-2015>
- Mammarella, I., Nordbo, A., Rannik, Ü., Haapanala, S., Levula, J., Laakso, H., ... Vesala, T. (2015). Carbon dioxide and energy fluxes over a small boreal lake in Southern Finland. *Journal of Geophysical Research: Biogeosciences*, 120, 1–19. <http://doi.org/10.1002/2014JG002873>
- Ojala, A., Bellido, J. L., Tulonen, T., Kankaala, P., & Huotari, J. (2011). Carbon gas fluxes from a brown-water and a clear-water lake in the boreal zone during a summer with extreme rain events. *Limnology and Oceanography*, 56(1), 61–76. <http://doi.org/10.4319/lo.2011.56.1.0061>
- Peltola, O., Hensen, A., Helfter, C., Belelli Marchesini, L., Bosveld, F. C., van den Bulk, W. C. M., ... Mammarella, I. (2014). Evaluating the performance of commonly used gas analysers for methane eddy covariance flux measurements: the InGOS inter-comparison field experiment. *Biogeosciences*, 11(12), 3163–3186. <http://doi.org/10.5194/bg-11-3163-2014>
- Podgrajsek, E., Sahlée, E., & Rutgersson, A. (2014). Diurnal cycle of lake methane flux. *Journal of Geophysical Research: Biogeosciences*, 119(3), 236–248. <http://doi.org/10.1002/2013JG002327>
- Rantakari, M., & Kortelainen, P. (2005). Interannual variation and climatic regulation of the CO₂ emission from large boreal lakes. *Global Change Biology*, 11(8), 1368-1380.

Interactive comment on “Methane and carbon dioxide fluxes over a lake: comparison between eddy covariance, floating chambers and boundary layer method” by Kukka-Maaria Erkkilä et al.

Anonymous Referee #2

Received and published: 6 April 2017

This manuscript compares with three widely used methods (Eddy covariance, Floating chamber and Boundary layer method) applied for measuring CH₄ and CO₂ flux over the boreal lake surface, which gives valuable information on measurement technique development needs. Variation of CH₄ and CO₂ flux during stratified and mixing period is both investigated. The results showed there is the deficiency for each method. The main question is as follows: 1) This manuscript compares CH₄ and CO₂ flux estimated with three BLM methods (KTE, KHE and KCC), and the linear fit results has been shown in table1 and table 2. The author considered the BLM methods with slope ratio closer to 1 as the best one method. Usually the (determination coefficient) r² and RMSE are used for statistical criteria. As there is intercept, it's doubted that the slope ratio could be effective. Regarding for the r², the KTE and KHE still have higher r², and KCC has a lower one. However the conclusion is the same.

We thank the anonymous referee #2 for your comment. We will add discussion about the r² value to the text.

List of all relevant changes made in the manuscript:

- Figures are improved:
 - o Figures 2 & 3 have increased font size
 - o Figures 4 & 5 have a deadband showing the eddy covariance flux detection limit and two different y-axis scales for better readability
 - o Figures 6-10 have a shaded area showing the night-time hours
- Former Tables 1 & 2 are merged into one Table 1
- Another Table 2 is added where the daytime and night-time average fluxes and their standard errors are listed for each measurement method separately
- The text has been modified according to reviewer and editor comments
- More description and analysis is added to section *3 Results and Discussion*, especially under subsections *3.3 Diurnal variation of estimated fluxes* and *3.4 Comparison between floating chambers and eddy covariance fluxes*
- The abstract has been made more clear
- Conclusions are more focused on the study objectives

Methane and carbon dioxide fluxes over a lake: comparison between eddy covariance, floating chambers and boundary layer method

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Abstract. Freshwaters bring a notable contribution to the global carbon budget by emitting both carbon dioxide (CO₂) and methane (CH₄) to the atmosphere. Global estimates of freshwater emissions traditionally use a wind speed based gas transfer ~~coefficient~~ velocity, k_{CC} (introduced by Cole and Caraco (1998)), for calculating diffusive flux with the boundary layer method (BLM). We compared CH₄ and CO₂ fluxes from BLM with k_{CC} and two other gas transfer ~~coefficients~~ velocities (k_{TE} and k_{HE}), that include the effects of water-side cooling to the gas transfer besides shear-induced turbulence, with simultaneous eddy covariance (EC) and floating chamber (FC) fluxes during a 16-day measurement campaign in September 2014 at Lake Kuivajärvi in Finland. The measurements included both lake stratification and water column mixing periods. ~~A clear increase in both CH₄ and CO₂ fluxes was detected right after turnover started.~~ Results show that ~~k_{CC} model underestimates both CH₄ and CO₂ fluxes compared to EC measurements and BLM fluxes were mainly lower than EC, with~~ the more recent model k_{TE} gives giving the best fit with EC fluxes. ~~In the stratified period, k_{HE} and, whereas FC measurements resulted in higher fluxes than EC. We highly recommend using up to date gas transfer models, instead of k_{CC} used in BLM calculation have similar diurnal variation for, for better flux estimates.~~

BLM CO₂ flux had clear diurnal variation with all gas transfer models during both stratified and mixing periods, whereas EC measurements did not detect a diurnal behaviour in CO₂ flux, while k_{TE} gives an opposite diurnal cycle. This is probably due to water friction velocity derived from EC measurements in k_{TE} model instead of direct waterside turbulence measurements in this study. In the mixing period all models agree well with each other on diurnal variation. CH₄ flux had a diurnal cycle during lake mixing period according to EC and BLM measurements with highest fluxes detected just before sunset. In addition, we found a clear diurnal cycle in the concentration difference between the air and surface water for both CH₄ and CO₂. We highly recommend using up to date gas transfer models, instead of k_{CC} , for better flux estimates This might lead to biased flux estimates, if only daytime values are used in BLM up-scaling and flux measurements in general.

FC measurements did not detect spatial variation in either CH₄ or CO₂ flux over Lake Kuivajärvi. EC measurements, on the other hand, did not show any spatial variation in CH₄ fluxes, but a clear difference between CO₂ fluxes from shallower and

deeper areas. ~~Fluxes measured with FC were systematically higher than EC fluxes, partly due to deficiencies in the EC method~~
We highlight that while all flux measurement methods have their pros and cons, it is important to carefully think about the chosen method and measurement interval and their effects on the resulting flux.

1 Introduction

5 Freshwaters (rivers, streams, reservoirs and lakes) are found to be a net source of carbon to the atmosphere (Cole et al., 1994) due to supersaturation of especially carbon dioxide (CO₂) but also methane (CH₄). Global estimates of the contribution of lakes to the carbon cycle are highly variable and uncertain (Cole et al. (2007); Tranvik et al. (2009); Bastviken et al. (2011); Raymond et al. (2013)), but significant compared to the terrestrial sources and sinks.

10 Global estimates are usually based on boundary layer method (BLM, also known as boundary layer model) that uses wind speed (via gas transfer ~~coefficient~~velocity k) and concentration gradient between the air and surface water as the only factors driving the gas exchange (Cole and Caraco, 1998). According to recent studies, this up-scaling approach strongly underestimates current emissions from lakes and improved methods are needed (e.g. ~~Schubert et al. (2012); Heiskanen et al. (2014)~~Schubert et al. (2014) and Tedford et al. (2014) suggest k models based also on heat flux and water turbulence measurements for more accurate estimates.

15 A widely used direct flux measurement technique is the floating chamber (FC) method, where the vertical flux at the air-water interface is calculated from the concentration increase within the chamber during the measurement period (Livingston and Hutchinson, 1995). This method has a small source area and is representative ~~only of a small part of a lake~~of the measurement point only. On the other hand, it can be used to quantify the spatial variability of the gas emissions (Natchimuthu et al., 2016). FC method is laborious, but inexpensive, and does not need extensive data post-processing. However, similar to BLM it requires automatic data loggers or access to a gas analyser, such as gas chromatograph, in the case of manual sampling. FC measurements also disturb the air-water interface and might affect to the gas exchange by creating artificial turbulence, especially with anchored chambers in running waters (Lorke et al., 2015). However, these effects are minor for drifting chambers following the water (Lorke et al., 2015)~~and~~. FC measurements on standing water can also correspond well with non-invasive methods for certain chamber types and deployment methods (Gålfalk et al., 2013).

25 Recently, also direct eddy covariance (EC) flux measurements have grown their popularity in lake studies, but still there are only few sites with long data sets (e.g. Mammarella et al. (2015), Huotari et al. (2011)). Instead of measuring just a specific point of the lake, the EC method provides flux estimates over a much larger source area, also known as footprint (Aubinet et al., 2012), and as opposed to chamber measurements, it does not disturb the air-water interface. EC measurements are, however, quite expensive and require extensive data post-processing.

30 In this study, we compared these three flux measurement methods, including three different gas transfer ~~coefficients~~velocities for BLM approach, over a boreal lake in southern Finland for both CH₄ and CO₂ during an intensive field campaign from 11 September to 26 September in 2014. We also studied spatial variation of CH₄ and CO₂ fluxes over the EC footprint area with manual floating chambers, while simultaneously estimating fluxes with EC and BLM methods. Our aim is to compare the three

[methods and make recommendations for future measurements based on our results](#). Because current up-scaling estimates are based on these methods, comparison is needed to reduce the uncertainties in current estimates of the role of [lakes-freshwaters](#) in global carbon cycle. Such a comparison also gives valuable information on measurement technique development needs and so far there is only one comparative study including all three methods for CH₄ in a temperate lake (Schubert et al., 2012). This is, to our knowledge, the first study including the three measurement methods for both CH₄ and CO₂ in a boreal lake, even though the boreal zone harbours a large fraction of the global lakes (Lehner and Döll, 2004; Verpoorter et al., 2014).

2 Materials and Methods

2.1 Site description and measurements

The study site was the humic, oblong Lake Kuivajärvi situated in southern Finland (61°50' N, 24°17' E), in the middle of a managed mixed coniferous forest, close to the SMEAR II station (Station for Measuring Ecosystem Atmosphere Relations, Hari and Kulmala (2005)). The lake has a maximum depth of 13.2 m, mean depth of 6.3 m, length of 2.6 km and surface area of 0.62 km² (Fig. 1a). Due to the oblong shape, the wind ~~blows usually~~ [usually blows](#) along the longest fetch (Mammarella et al., 2015). Lake Kuivajärvi has two separate basins and a measurement raft is mounted on the south basin, near the deepest part of the lake. Lake Kuivajärvi has median light extinction coefficient $K_d=0.59\text{ m}^{-1}$ as estimated in Heiskanen et al. (2015). The low water clarity is mainly due to high dissolved organic carbon (DOC) concentration in the lake. Lake Kuivajärvi is a dimictic lake that mixes thoroughly right after ice out usually in the beginning of May, stratifies for summertime and then mixes again latest in October, until it freezes and stratifies again underneath the ice cover for 5–6 months (Heiskanen et al., 2015). These spring and autumn mixing periods usually bring high amounts of CH₄ and CO₂ from the hypolimnion and bottom sediments of the lake to the atmosphere (Miettinen et al., 2015).

Continuous measurements of carbon exchange between water and air started already in ~~2009-2010~~ and the lake belongs to ICOS (Integrated Carbon Observation System) measuring network. Flux measurement apparatus with the EC system on the raft consists of an ultrasonic anemometer (USA-1, Metek GmgH, Elmshorn, Germany), a closed path infrared gas analyser LI-7200 (LI-COR Inc., Nebraska, USA) for measuring CO₂ and water vapour (H₂O) mixing ratios and a closed path gas analyser Picarro G1301-f (Picarro Inc., California, USA) for measuring CH₄ and H₂O mixing ratios. Measurement frequency was 10 Hz and a 30-min averaging period was used in this study. CO₂ measurements with LI-7200 were stopped on 25 Sept. Air temperature and relative humidity were measured using Rotronic MP102H/HC2-S3 (Rotronic Instrument Corp., NY), while radiation components were measured with Net Radiometer CNR1 (Kipp & Zonen, Delft, Netherlands). These data were collected every 5 s and averaged over 30 min.

Water temperature at depths 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 5.0, 6.0, 7.0, 8.0, 10.0 and 12.0 m was measured with a chain of Pt100 temperature sensors. Water column CO₂ concentration was measured at depths 0.2, 1.5, 2.5 and 7.0 m using semipermeable silicone tubing in the water and circulating air in a closed loop continuously to the analyser (CARBOCAP®GMP343, Vaisala Oyj, Vantaa, Finland). The measurement system is explained in detail in Hari et al. (2008), Heiskanen et al. (2014) and

Mammarella et al. (2015). Water column temperature and CO₂ data were collected at the raft every 5 s and averaged over 30 min periods.

Another gas analyser (Ultraportable Greenhouse Gas Analyzer, Los Gatos Inc., USA) was used for measuring CH₄ and CO₂ concentrations in the air at 1 m height and in the water at depths 0.2 and 11 m. The analyser was connected step-wise to three different intakes; one in air, two in water and a dryer, consisting of a container filled with silica gel. For all levels, air was circulated in closed loop between the gas analyser and the different intakes. The internal pump of the gas analyser was used for this circulation of air at a rate of 1.2 L min⁻¹. The air intake consisted of a ca. 10 cm long diffusive membrane (Accurel S6/2, PP, AKZO NOBEL) that was placed under a protective rain cover. The water intakes at each level consisted of a 4.1 m long, 8 mm diameter silicon tube that was bundled and attached to a metal disc ca. 25 cm in diameter, to give a well-defined measurement depth. The dryer was added to the system to remove excess moisture that could have entered into the tubing system by condensation. The air intake was located 1 m above the lake surface and the water intakes were located at 0.2 m and 11 m depths. A full measurement cycle was completed during two hours. The air intake was connected to the gas analyser for 10 min, while the water intakes were connected during 45 minutes each, but data were averaged only during the last 5 minutes of each connection period in order to allow equilibration to the new concentration after a change of intake. After each measurement cycle for the water intakes, the air was circulated through the dryer. The gas analyser was checked against a standard after the measurement campaign and found to be accurate within the specifications of the standard.

Manual floating chamber measurements of CH₄ and CO₂ fluxes were done with two replicate chambers at eight different spots (Fig. 1b) in the EC footprint area 2–3 times a day (morning, afternoon and night/early morning) during period 11–22 Sept. Unfortunately, measurements were only possible in the first 11 days of the campaign due to high wind and hard weather conditions towards the end. Measurement lines were perpendicular to the shoreline. The line north of the raft was chosen when the wind was blowing from north, and south line was chosen during southerly winds. Measurement spots N2/S2 and N3/S3 were about 10 m deep, and points N1/S1 and N4/S4 were about 3 m deep. They were chosen so that the distance to the measurement raft was about 50 m and the points were marked with buoys.

Chambers used in this study were polyethylene/plexiglas plastic buckets equipped with styrofoam floats and sampling outlets (Gålfalk et al., 2013). Chambers reached approximately 3 cm into the water and their height above water was about 9.6 cm. The closing time for the chambers was 20 min and sampling interval 5 min. Air samples were taken with syringes and injected into 12 ml Labco Exetainer® vials (Labco Ltd., Lampeter, Ceredigion, UK) and analysed with gas chromatograph (GC). The GC system consisted of a Gilson GX-271 Liquid handler (Gilson Inc., Middleton, USA), a 1 ml Valco 10-port valve (VICI Valco Instrument Co. Inc., Houston, USA) and an Agilent 7890A GC system (Agilent Technologies, Santa Clara, USA) equipped with a flame-ionization detector (temperature 210°C).

In addition to automatic water concentration measurements, we took manual water samples for comparison. Two replicate water samples were taken into 60 ml plastic syringes. After sampling, 30 ml of water was pushed out and replaced by 30 ml of N₂ gas. The syringes were placed in a water bath at 20 °C temperature for 30 min. Then the samples were equilibrated by shaking the syringes vigorously for 3 min. The samples of the syringe headspace gas were injected into 12 ml Labco Exetainer® vials (Labco Ltd., Lampeter, Ceredigion, UK) and analysed with the same GC as manual air samples. Final gas concentrations

in the water were calculated using the Henry's Law. Henry's law solubility constants at 298.15 K were for CH₄ 1.4·10⁻³ mol dm⁻³ bar⁻¹ (Warneck and Williams, 2012) and for CO₂ 3.4·10⁻² mol dm⁻³ bar⁻¹ (Seinfeld and Pandis, 2016).

2.2 Data processing and quality criteria

2.2.1 Eddy covariance data

5 EC data were processed using EddyUH software (Mammarella et al., 2016) according to the approaches in Mammarella et al. (2015). Briefly, spikes in the data were removed on the basis of a maximum difference being allowed between two adjacent points, and 2D coordinate rotation was done so that the wind component u is directed parallel to the mean horizontal wind. Linear detrending was used for calculating the turbulent fluctuations. Lag time was determined from the maximum of the cross-covariance function and cross-wind correction was applied to sonic temperature data (Liu et al., 2001). High frequency
10 spectral corrections were calculated according to Mammarella et al. (2009).

Data quality was ensured with tests for flux stationarity ($FST \leq 1$ was approved) and limits for kurtosis ($1 < Ku < 8$) and skewness ($-2 < Sk < 2$) (Vickers and Mahrt, 1997). Wind directions other than along the lake were ignored to ensure that only fluxes from the lake were included. Accepted wind directions were $130^\circ < WD < 180^\circ$ and $320^\circ < WD < 350^\circ$. For gas fluxes, also a criteria for standard deviation of the mixing ratios was used. During night-time, the standard deviation often increased,
15 indicating that there was advection of CH₄ and CO₂ from the forest uphill to the lake causing scatter in the flux measurements. This scatter was found to be small when the standard deviation of CO₂ was less than 3 ppm and thus CO₂ mixing ratio (and flux) data with standard deviation larger than 3 ppm were removed. The same procedure was also done for CH₄, with the threshold value for standard deviation being 0.003 ppm. After all data quality criteria, the data coverage were 27% and 32% of the original data for CO₂ and CH₄ fluxes, ~~respectively.~~ and 83% and 80% for latent and sensible heat fluxes, respectively.
20 Detection limit for the EC gas fluxes was determined according to Finkelstein and Sims (2001) as 3σ of the covariance scaled with \sqrt{N} , where $N = 48$ was the number of observations per day. This estimate for the detection limit takes into account both instrumental noise and one-point sampling random error (Rannik et al., 2016). On average, detection limit of 30 min averaged CH₄ flux was 0.81 nmol m⁻² s⁻¹ and CO₂ flux 0.84 μmol m⁻² s⁻¹. Detection limits scaled for the daily median fluxes were 0.12 nmol m⁻² s⁻¹ and 0.12 μmol m⁻² s⁻¹ for CH₄ and CO₂, respectively. The average source area of the EC system reaches
25 100–300 m from the measurement raft, depending on the stability conditions (Mammarella et al., 2015).

Heat fluxes measured with the EC system were gap-filled using a bulk model depending on water-air temperature difference multiplied by wind speed and vapour pressure difference multiplied by wind speed for sensible and latent heat fluxes, respectively. The coefficients for these relationships were found from a linear fit between measured EC fluxes and the parameters, similar to Mammarella et al. (2015).

2.2.2 Chamber flux calculations

The gas concentration increase inside the chambers was linear over a short closure time (20 min) combined with low flux levels. Flux calculation was conducted according to Duc et al. (2013):

$$F = \frac{d\chi}{dt} \frac{p_a V}{RTA} \quad (1)$$

- 5 where $\frac{d\chi}{dt}$ is the slope of the linear fit to concentration increase inside the chamber during the closure time ($\mu\text{l l}^{-1}\text{s}^{-1}$), p_a ambient pressure (Pa), V chamber volume (m^3), A the area of the surface that the chamber covers (m^2), R universal gas constant ($\text{J mol}^{-1}\text{K}^{-1}$), and T ambient temperature (K). Measurements were accepted when there were no leakages during the chamber closure. If measurements from both replicate chambers (located within 1 m distance from each other) were successful, then an average flux from these two chambers was used.

10 2.3 Boundary layer method

Diffusive gas exchange F between the air and water was determined according to the boundary layer model

$$F = k(c_{aq} - c_{eq}) \quad (2)$$

- where k is the gas transfer velocity (m s^{-1}), c_{aq} the gas concentration (mol m^{-3}) in surface water and c_{eq} the concentration (mol m^{-3}) that the surface water would have if it was in equilibrium with the above air (MacIntyre et al., 1995). Equilibrium
15 gas concentrations were calculated from measurements of mixing ratio χ_c and air pressure p_a and corrected with Henry's constant k_H according to the solubility of the gas in the water

$$c_{eq} = \chi_c p_a k_H \quad (3)$$

- For this study, gas transfer velocity was calculated according to Cole and Caraco (1998), Tedford et al. (2014) and Heiskanen et al. (2014). [Gas concentrations for flux calculations were measured both automatically and by manual sampling.](#) Wind speed,
20 sensible and latent heat fluxes and air friction velocity were measured with the EC system.

2.3.1 Gas transfer velocity

The most simple and the most often used model for gas transfer velocity k is the one proposed by Cole and Caraco (1998)

$$k_{CC} = (2.07 + 0.215U_{10}^{1.7}) \left(\frac{Sc}{600} \right)^{-0.5} \quad (4)$$

- where U_{10} represents the wind speed at 10 m height (in m s^{-1} , approximated by $U_{10} = 1.22U$, where U is the measured wind
25 speed at 1.5 m height) and Sc is the Schmidt number calculated for local conditions. This model considers wind as the only factor causing water turbulence and driving the gas exchange.

A model by Tedford et al. (2014), on the other hand, suggests the importance of the buoyancy flux β driven turbulence during cooling periods, so that the turbulent dissipation rate ε_{TE} becomes

$$\varepsilon_{TE} = \begin{cases} \frac{c_1 u_{*w}^3}{\kappa z} + c_2 |\beta| & \text{if } \beta < 0, \\ \frac{c_3 u_{*w}^3}{\kappa z} & \text{if } \beta \geq 0 \end{cases} \quad (5)$$

where $c_1=0.56$, $c_2=0.77$ and $c_3=0.6$ are dimensionless constants, u_{*w} is the friction velocity in the water, $\kappa=0.41$ is the von Karman constant and depth z is here used as constant 0.15 m (Tedford et al. (2014); Mammarella et al. (2015)). Friction velocity in the water u_{*w} was calculated from direct EC measurements of air friction velocity u_{*a} , so that

$$u_{*w} = u_{*a} \sqrt{\frac{\rho_a}{\rho_w}} \quad (6)$$

where ρ_a is the air density and ρ_w water density. Buoyancy flux β was calculated according to Imberger (1985):

$$\beta = \frac{g \alpha_t H_{eff}}{\rho_w C_p} \quad (7)$$

where g is the gravitational acceleration, α_t coefficient of thermal expansion of water, H_{eff} the effective heat flux (i.e. latent and sensible heat fluxes and portion of shortwave radiation that is not trapped to the mixing layer are subtracted from the net radiation), and C_p the specific heat of water. Buoyancy flux is positive when the effective heat flux is positive and the lake is heating, whereas negative buoyancy ~~flux indicates and effective heat fluxes indicate~~ cooling of the lake. Gas transfer velocity k can then be calculated according to the surface renewal model

$$k_{TE} = c_4 (\varepsilon_{TE} \nu)^{1/4} S c^{-1/2}. \quad (8)$$

where $c_4=0.5$ is a dimensionless constant and ν kinematic viscosity of water ($\text{m}^2 \text{s}^{-1}$).

Another k model that takes heat flux into account as a factor creating turbulence was developed by Heiskanen et al. (2014):

$$k_{HE} = \sqrt{(C_1 U)^2 + (C_2 w_*)^2} S c^{-\frac{1}{2}} \quad (9)$$

Here $C_1 = 0.00015$ and $C_2=0.07$ are dimensionless constants defined for Lake Kuivajärvi (Heiskanen et al., 2014), w_* is the convective velocity defined as

$$w_* = \sqrt[3]{-\beta z_{AML}} \quad (10)$$

and z_{AML} is the depth of the actively mixing layer (m), where temperature varies within 0.25°C of the surface water temperature. This model was developed in Lake Kuivajärvi for CO_2 fluxes but has not been tested for CH_4 before this study.

All these three k models are hereafter referred as they are presented in the formulas.

25 3 Results and Discussion

The results of the measurement campaign are divided into two sub-periods (11 days of stratified period 11–22 Sept and 5 days of lake mixing period 22–26 Sept 2014) according to lake stratification and environmental conditions during the campaign,

since gas transfer processes differ between these two periods. The water column started its autumn turnover on 22 Sept, but the mixing did not yet reach the lake bottom. Continuous measurements of CH₄ and CO₂ fluxes with BLM and EC methods are first compared with each other and the more sporadic FC measurements are then compared to EC measurements by examining the spatial variation and magnitude of the fluxes within the EC footprint area.

5 3.1 Environmental conditions

Weather in the beginning of the measurement campaign in September 2014 was warm with maximum air temperature of 18°C (Fig. 2). Sensible and latent heat fluxes were low, less than 100 W m⁻² and winds were weak, around 2 m s⁻¹ and mostly from south. Air temperature exceeded surface water temperature during the afternoons causing negative sensible heat fluxes. Night-time air temperatures were more than 10°C colder than during daytime.

10 On 22 Sept, a cold front turned winds north bringing cold air and rain (11 mm on 22 Sept). Air temperature dropped to even 0°C on 24 Sept and wind speeds as high as 8 m s⁻¹ were measured at the lake. A drop in the air temperature caused a large temperature difference between air and lake surface water that together with high wind speed caused high, even 200 W m⁻², positive (upward) sensible and latent heat fluxes on 22 Sept and 23 Sept and a large negative (-400 W m⁻²) effective heat flux, resulting in negative buoyancy flux during this cooling period.

15 3.1.1 Water column temperature and gas profiles

In the beginning of the measurement period, the lake was clearly stratified (Fig. 3a). Bottom temperature was around 9 °C, while surface water temperature was about 16 °C. CH₄ concentration according to the automatic measurements at the surface was small, only around 20 nmol m⁻³, while at 11 m depth CH₄ concentration was almost 10 times higher than at the surface (Fig. 3b). Manual measurements, on the other hand, show surface water concentrations ~~up to 0.10~~ of 0.07 mmol m⁻³ on average during the stratified period. Manual CH₄ concentration measurements were always higher than automatic measurements, which might be caused by insufficient equilibration time for CH₄ in the automatic measurement system or by different measurement spots. CO₂ concentration at the surface was around 40 mmol m⁻³ according to the automatic measurements and 10 times higher at 11 m depth (Fig. 3c). Manual measurements show CO₂ concentration of ~~about 80~~ 110 mmol m⁻³ at the water surface -on average. CO₂ is more soluble in water than CH₄ and thus equilibration time of 40 min should be enough for automatic CO₂ measurements. We thereby conclude the difference between automatic and manual CO₂ concentration measurements to be caused by spatial variation rather than the measurement system. We point out, however, that choosing the measurement method as well as the measurement spot has an effect on the observed concentrations. Diel variation of CH₄ and CO₂ concentrations at 11 m could be caused by lake-side cooling and convection or more likely, by internal waves (Stepanenko et al., 2016).

On 14 Sept, the mixing layer of the lake deepened from 5 m to around 6–7 m due to night-time cooling. This mixing brought CO₂ rich water from deeper waters to the surface causing a drop in CO₂ concentration at 7 m depth and a rapid increase in the surface water concentration according to manual samples. Warm daytime air temperature then caused the surface water to stratify again. Similar occasions of night-time cooling on 16 Sept and 17 Sept induced further decrease in CO₂ concentration

at 7 m depth and an increase also in the surface water CO₂ concentration. After 16 Sept, the automatic and manual CO₂ concentration measurements agree better with each other.

On day 22 Sept, a cold front caused the starting of the autumn mixing of the lake. Thermocline reached the depth of 8 m bringing CH₄ and CO₂ rich water to the surface. Thermocline tilting due to high wind speed caused a rapid increase in 11 m CH₄ concentration. CH₄ accumulation near the bottom usually happens in the anoxic conditions in late autumn. CH₄ concentration at 11 m depth was still three times lower than the maximum concentration found in Stepanenko et al. (2016) in late September. A clear increase in CH₄ surface water concentration is seen later, on 23 Sept, and manual measurements show concentrations up to 0.47 mmol m⁻³ on 25 Sept. Decreasing CO₂ concentration at 11 m depth on 23-24 Sept was probably due to up-welling. However, this amount of up-welling was not enough to cause a notable increase in the surface water CO₂ concentration since CO₂ concentration difference between the bottom and the surface is not as drastic as that of CH₄, and the gas gets diluted in a large water volume on its way to the surface. Autumn mixing reached 11 m depth in the end of the measurement campaign on 25 Sept, but did not yet mix the bottom waters.

3.2 Comparison between boundary layer model and eddy covariance flux estimates

3.2.1 CH₄ fluxes

CH₄ fluxes during the stratified period were small (less than 1 nmol m⁻²s⁻¹), estimated both with EC and BLM (Fig. 4). The EC fluxes during the stratified period were below close to the detection limit (approximately 2-0.12 nmol m⁻² s⁻¹)-estimated in Peltola et al. (2014) for daily median flux) and are thus highly uncertain. BLM fluxes calculated using the manual surface water concentration measurements were higher than when using automatic measurements, but still small during the stratified period. The difference between manual and automatic BLM fluxes remained below 0.4 nmol m⁻²s⁻¹ during the stratified period. After the mixing started on 22 Sept, CH₄ fluxes increased rapidly to even 16 nmol m⁻²s⁻¹ due to effective mixing and gas transport from deeper waters to the surface. This increase is clearly visible in both EC and BLM fluxes, although BLM flux calculated with k_{CC} remains lower than other BLM fluxes. CH₄ flux during the stratified period was considerably lower than 4 nmol m⁻²s⁻¹ reported in Miettinen et al. (2015) using BLM with k_{CC} , who used BLM with k calculated from FC measurements, for Lake Kuivajärvi in autumn 2011 and 2012, but 2012. However, the flux peak in the beginning of the mixing period was over 2-fold than to the 6 nmol m⁻²s⁻¹ reported in Miettinen et al. (2015), probably due to rougher weather conditions and more frequent sampling in this study. Ojala et al. (2011). Ojala et al. (2011), on the other hand, report high CH₄ emissions (6 nmol m⁻²s⁻¹) after heavy rain events. Rain on 22 Sept could have also had an effect on lateral CH₄ transport from the catchment (Ojala et al. (2011); Rantakari and Kortelainen (2005).) However, in comparison to the situation described by Ojala et al. (2011), the rain episode in Lake Kuivajärvi was very short in duration.

Linear fit parameters for the EC and BLM flux comparison for CH₄ show that k_{TE} ($r^2=0.53$) and k_{HE} were similar ($r^2=0.50$) were similar and comparable to EC measurements, but k_{CC} ($r^2=0.48$) differed from the two others (Table ??1). According to the fitting parameters, we can deduce that k_{TE} model gives CH₄ fluxes which are almost the same as EC, whereas k_{CC} has the worst agreement with EC measurements (only 50% of the EC measured flux). Ebullition is not an important gas transport

mechanism in the EC footprint area as found in Stepanenko et al. (2016) and thus BLM including only diffusive gas flux is expected to give results close to EC. A similar result with k_{CC} giving the lowest flux estimate was also found in Schubert et al. (2012), where EC and FC methods gave 8 and 7 times higher cumulative fluxes than BLM with k_{CC} . Also Blees et al. (2015) report seasonal changes in CH_4 flux due to cooling and changes in buoyancy flux. This further encourages to prefer up to date k models instead of k_{CC} in CH_4 flux estimates.

3.2.2 CO_2 fluxes

CO_2 flux was also small (below $1 \mu\text{mol m}^{-2}\text{s}^{-1}$) in the beginning of the measurement campaign due to low wind speeds and thermal stratification of the lake (Fig. 5). Increased surface water concentration in manual samples caused also high BLM fluxes flux on 14 and 15 Sept (Fig. 5b). However, this higher flux was not visible in EC measurements or BLM with automatic concentration measurements. On other days, the BLM fluxes calculated using manual samples are slightly higher than the ones calculated using automatic measurements. The difference still remains within $0.2 \mu\text{mol m}^{-2}\text{s}^{-1}$ throughout the measurement period, excluding days 14–15 Sept. The flux increased to almost 3-fold when the lake started mixing with higher wind speeds. Both EC and BLM fluxes show this increase, but k_{CC} model gives clearly lower fluxes than other k models after mixing started. BLM by k_{TE} and k_{HE} on the other hand, agree well with each other during the mixing period. Fluxes before mixing are very similar in magnitude to those reported in Miettinen et al. (2015), Mammarella et al. (2015) and Heiskanen et al. (2014), although the CO_2 flux peak measured by BLM with k_{TE} and k_{HE} models in the beginning of the mixing period was larger ($3 \mu\text{mol m}^{-2}\text{s}^{-1}$) was larger than reported in other studies from Lake Kuivajärvi (less than $2 \mu\text{mol m}^{-2}\text{s}^{-1}$, Miettinen et al. (2015); Mammarella et al. (2015)). EC on the other hand, measured daily median CO_2 flux less than $2 \mu\text{mol m}^{-2}\text{s}^{-1}$, as reported in other studies. Negative daily median EC flux on 11 Sept and 14 Sept was not statistically different from zero (tested with Mann-Whitney U-test) and denotes a very small flux close to the detection limit of the system ($0.12 \mu\text{mol m}^{-2}\text{s}^{-1}$), rather than uptake which would be very unlikely in September in a boreal lake.

Linear fit parameters for the EC and BLM comparison (Table ??1) show that k_{TE} ($r^2=0.26$) and k_{HE} ($r^2=0.27$) give the best results when compared with EC (about 60%). BLM CO_2 flux based on k_{CC} was clearly underestimated, being only about 30% of the measured EC flux ($r^2=0.20$). The same result of k_{CC} giving lower fluxes than EC was found also in other studies (e.g. Heiskanen et al. (2014); Mammarella et al. (2015); Podgrajsek et al. (2015)) and the use of this model in global carbon budget estimates may therefore be questionable (e.g. Raymond et al. (2013)). During lake stratification k_{CC} gives the general flux level quite well, while during lake mixing and rain events it is clearly lower than the other modelled fluxes. However, on annual scale, these special occasions might contribute significantly to the CH_4 and CO_2 budgets (Ojala et al., 2011; Miettinen et al., 2015) and should be noted in up-scaled flux estimates.

Including the effect of lake cooling clearly improves the flux estimate both for CH_4 and CO_2 , albeit these models are not as simple to use as wind speed based models. In the absence of an extensive measurement system, the use of e.g. bulk formulas for estimating latent and sensible heat fluxes for k_{HE} and k_{TE} would result in better flux estimates than the use of k_{CC} . Calculating the buoyancy flux (Eq. 7) for k_{HE} and k_{TE} models using bulk formulas for heat fluxes requires an estimate for the depth of the actively mixing layer z_{AML} , light extinction coefficient, radiation data, wind speed, as well as temperature

and moisture differences between the air and water surface. First, latent and sensible heat fluxes may be calculated from moisture and temperature differences multiplied with wind speed and water vapour or heat transfer coefficients, respectively (Xiao et al., 2013). Net shortwave radiation, z_{AML} and k_d are used to calculate the portion of shortwave radiation that is not trapped to the mixing layer by subtracting entrained shortwave radiation from the radiation remaining at mixing layer depth.

- 5 With these information, it is possible to calculate the effective heat flux and buoyancy flux, after which estimating k_{HE} and k_{TE} is straightforward, keeping in mind that the water-side friction velocity for k_{TE} model may be estimated from wind speed measurements by scaling it with an appropriate drag coefficient.

3.3 Diurnal variation of estimated fluxes

3.3.1 Stratified period

- 10 In order to deepen the comparison between the methods, diurnal variation of CH_4 and CO_2 fluxes are analysed for the two study periods separately. Diurnal variation of CH_4 flux during the stratified period was negligible (results not shown), but CO_2 flux variation was separately studied for the two periods: stratified and lake mixing periods. The sun rose at 5:45 and set at 18:45 during the stratified period whereas during the mixing period sunrise was at 6:15 and sunset at 18:15.

3.3.1 Stratified period

- 15 BLM CO_2 fluxes had clear diurnal variation before mixing (Fig. 6). BLM fluxes by k_{HE} and k_{CC} show similar diurnal pattern with lowest flux in late afternoon, although k_{CC} results in a remarkably lower flux than k_{HE} in general. ~~Lower-Low~~ BLM fluxes in the daytime (0.305 ± 0.009 and $0.201 \pm 0.004 \mu\text{mol m}^{-2}\text{s}^{-1}$ on average with k_{HE} and k_{CC} models, respectively) are probably caused by photosynthetic activity of algae in the lake that reduces the CO_2 concentration difference between air and water ~~CO_2 concentrations~~ ($\Delta[CO_2]$) right after sunrise (Fig. 7d, Table 2). Also the convective term (C_2w_*) in k_{HE} is
- 20 negligible during daytime when the lake is heating due to higher air temperature, resulting in a lower k_{HE} (Fig. 7a). Higher ~~fluxes flux~~ during night-time are (0.410 ± 0.008 on average with k_{HE} model) is probably caused by turbulence created by waterside cooling. This is seen in Fig. 7a as the convective term in k_{HE} increases towards night-time causing higher total k_{HE} . Podgrajsek et al. (2015) argued that the main driver for enhanced night-time gas exchange is convection, and they did not find a correlation with the concentration difference $\Delta[CO_2]$. However, we find that also $\Delta[CO_2]$ increases during night-time in the
- 25 lack of algal photosynthesis, ~~which makes also BLM by k_{CC} fluxes slightly higher during night-time, even when it lacks the convective term.~~ The magnitude of the BLM fluxes with k_{HE} and k_{CC} are ~~however, however,~~ quite different, and k_{CC} gives lower fluxes throughout the day and no clear difference in average daytime and night-time fluxes (Figs. 6a and 6b), ~~Table 2). CO_2 flux is especially underestimated during night-time by k_{CC} , when night-time cooling and convective mixing are more important, because it lacks the convective term.~~
- 30 BLM by k_{TE} gives highest fluxes ~~in the afternoon at noon~~ when also friction velocity gains its maximum value (Fig. 7c). The BLM flux by k_{TE} is thus also larger in the daytime ($0.545 \pm 0.014 \mu\text{mol m}^{-2}\text{s}^{-1}$ on average, Table 2) despite the lower $\Delta[CO_2]$, and night-time flux ($0.396 \pm 0.010 \mu\text{mol m}^{-2}\text{s}^{-1}$) is 27% smaller than the daytime flux. Water friction velocity, that

was used in k_{TE} , was calculated from direct EC measurements in the air (Eq. 6). Friction velocity calculated from wind speed measurements (with a drag coefficient 0.001 for a water surface) instead of direct u_{*a} measurements gave similar diurnal variation as models k_{HE} and k_{CC} (data not shown), but resulted in a lower u_{*w} . BLM with k_{TE} could give better results with direct turbulence measurements in the water. The buoyancy term (β) in k_{TE} is low compared to the shear term ($u_*^3/(\kappa z)$) throughout the day (Fig. 7c). EC flux does not show any diurnal variation for CO₂ exchange over the lake when the lake is stratified (Fig. 6d). Vesala et al. (2006) found the same result in CO₂ EC flux in September over a small humic lake in Finland with fluxes usually under 1 $\mu\text{mol m}^{-2}\text{s}^{-1}$ during the stratified period. Overall, k_{TE} , k_{HE} and EC measurements agree well on the magnitude of CO₂ flux during ~~night-time, but daytime~~ daytime, but night-time values differ.

3.3.2 Mixing period

During the mixing period all BLM as well as EC fluxes show similar diurnal pattern in CH₄ flux, so that the highest flux value is reached in the afternoon/~~evening, just before sunset~~ (Fig. 8). ~~Because this EC measurements, however, miss the early morning flux peak detected with BLM models just before sunrise. Because the afternoon flux peak~~ is also seen in the BLM by k_{CC} , we can deduce that it is due to higher wind speed and enhanced shear during the afternoon as well as higher CH₄ concentration difference ($\Delta[\text{CH}_4]$) between the ~~air and surface water~~ surface water and air, that is also partly due to enhanced mixing bringing CH₄ from deeper waters (Fig. 9d). The larger concentration difference $\Delta[\text{CH}_4]$ towards the afternoon may be caused by higher oxidation rate in dark that lowers CH₄ concentration in the water during night (Mitchell et al., 2005). During daytime solar radiation, the oxidation rate would then be lower resulting in an increase of water CH₄ concentration towards the afternoon. Another possibility for larger concentration difference $\Delta[\text{CH}_4]$ in the afternoon, in addition to CH₄ feeding from the deeper waters and lower oxidation rate, is enhanced resuspension from the sediments in the littoral zone during periods of high wind speed (Bussmann, 2005). Rain on 22 Sept could have also ~~detached-gases~~ enhanced transport from the catchment to the lake (Ojala et al., 2011). EC and BLM fluxes by k_{HE} and k_{TE} are also similar in magnitude ~~-(5.9±0.3, 7.1±0.6 and 7.7±0.6 nmol m⁻²s⁻¹ daytime averages, respectively),~~ whereas k_{CC} gives clearly lower fluxes (3.7±0.3 nmol m⁻²s⁻¹ daytime average, Table 2). All the models give similar diurnal patterns of CH₄ flux, only the magnitudes are different. Night-time minimum flux values were 90%, 95% and 91% smaller than the daytime maximum for k_{HE} , k_{CC} and k_{TE} fluxes, respectively. Models k_{HE} and k_{TE} show CH₄ flux variation quite similar to EC also in magnitude (Table 2). Keller and Stallard (1994), Bastviken et al. (2004) and Bastviken et al. (2010) also report highest daytime fluxes for CH₄ probably caused by more effective turbulent transfer during daytime, while Podgrajsek et al. (2014b) report higher night-time fluxes and suggest it to be caused by water-side convection ~~and CH₄ formation in the sediments during night~~. However, we find that both surface water concentration changes and more effective daytime gas transfer are likely explanations to the higher daytime CH₄ fluxes in Lake Kuivajärvi.

After mixing started, all models agreed well on diurnal variation of CO₂ flux with higher fluxes during daytime and lower during night (Fig. 10). Average daytime CO₂ fluxes were 1.3±0.2, 2.15±0.06, 2.37±0.06 and 1.11±0.04 $\mu\text{mol m}^{-2}\text{s}^{-1}$ with EC method and BLM by k_{HE} , k_{TE} and k_{CC} , respectively and night-time average fluxes notably smaller, as 0.88±0.14, 1.43±0.05, 1.54±0.05 and 0.58±0.02 $\mu\text{mol m}^{-2}\text{s}^{-1}$ with EC method and BLM by k_{HE} , k_{TE} and k_{CC} , respectively (Table

2). Night-time lowest fluxes were 60%, 76% and 68% lower than the daytime maximum BLM fluxes with k_{HE} , k_{CC} and k_{TE} models, respectively. Highest flux according to BLM with all three k models is gained in the late afternoon at noon when wind speeds are highest, even though $\Delta[\text{CO}_2]$ is at minimum (Fig. 9d). Shear terms C_1U and $u_*^3/(\kappa z)$ in k_{HE} and k_{TE} models, respectively, have diurnal variations with highest values in late afternoon at noon as well (Figs. 9a and 9c), which is then visible in the diurnal variations of fluxes (Figs. 10a and 10c). BLM by k_{CC} , however, shows considerably lower fluxes than k_{HE} and k_{TE} both during daytime and night-time (Fig. 10b, Table 2). Higher fluxes during daytime than night-time in the mixing period are expected due to enhanced gas transfer during stronger winds in the daytime. The buoyancy term β in k_{TE} is still almost a magnitude smaller than the shear term and does not influence the k_{TE} much, even during lake mixing (Fig. 9c).

The maximum and minimum concentration differences $\Delta[\text{CO}_2]$ are/were 1.4 to 1.6 times higher during the mixing period than in the stratified period. This may be caused by increased convective transport up-welling of CO_2 from deep waters to the surface and algal photosynthesis at the surface. This indicates that using selectively only daytime gas concentration measurements in flux measurements and global budgets already makes a biased assumption. The EC measured CO_2 flux does not show a clear diurnal variation during this period either.

3.4 Floating chamber measurements Comparison between floating chambers and spatial variation of gas eddy covariance fluxes

Spatial In addition to comparison between FC and EC measurements, spatial variation of CH_4 and CO_2 fluxes was within the EC footprint area was also studied with floating chambers at different parts of the lake within the EC footprint area during the stratified period 11–22 Sept 2014. The measurement spots were chosen upwind from the measurement raft to ensure being within the EC footprint area. Results are shown in Fig. 11, where the median of FC measurements at different spots are compared with the median of simultaneous EC measurements.

3.4.1 Spatial variation of CH_4 fluxes

During the stratified period, CH_4 fluxes measured with the FC method were very small, mainly less than $2 \text{ nmol m}^{-2}\text{s}^{-1}$ (Fig. 11a). Measurement points N3 and N4 produced slightly higher FC fluxes than elsewhere The average of all FC CH_4 flux measurements was $1.67 \text{ nmol m}^{-2}\text{s}^{-1}$ and the coefficient of variation was 1.25. FC CH_4 fluxes were systematically higher than EC fluxes ;(statistical significance tested with Mann-Whitney U-test, $p < 0.01$), as also observed in Eugster et al. (2011). One Daytime average FC CH_4 flux was $2.4 \pm 0.3 \text{ nmol m}^{-2}\text{s}^{-1}$ whereas daytime EC flux was only $0.41 \pm 0.04 \text{ nmol m}^{-2}\text{s}^{-1}$. Night-time average FC CH_4 flux was $1.1 \pm 0.2 \text{ nmol m}^{-2}\text{s}^{-1}$ and EC flux $0.34 \pm 0.04 \text{ nmol m}^{-2}\text{s}^{-1}$ (Table 2). There is a clear difference between these methods during both day and night, although daytime difference is more remarkable. Partly this difference is of course due to FC fluxes averaged over the different measurement spots, and measurement points N3 and N4 showed slightly higher FC fluxes than elsewhere.

Other possible reason for this the difference could be that the chambers were anchored to the boat during flux measurements, which might create artificial turbulence, although Gålfalk et al. (2013) did not find a significant difference between anchored and drifting chambers with this particular chamber design. A more probable reason behind the result is that these low fluxes

are very difficult to detect with the EC method, since the FC-CH₄ fluxes were ~~lower than very close to~~ the detection limit of the gas analyser used in EC measurements. ~~Probably higher~~ Higher fluxes during the mixing period could have ~~probably~~ produced a better comparison. Podgrajsek et al. (2014a) did not find systematically higher fluxes with EC or FC and found quite good agreement between these two methods ~~for CH₄ fluxes~~. In this study EC and FC CH₄ fluxes did not compare well
5 with each other and the difference in fluxes is statistically significant(~~tested with Mann-Whitney U-test, $p < 0.01$~~), mainly due to too low CH₄ fluxes for the EC method to detect reliably. ~~EC method has a larger source area than FC method, which might also affect the flux. Windy conditions during the mixing period could have made the comparison better, but manual FC measurements are difficult to do during high wind and rough weather conditions.~~

3.4.2 Spatial variation of CO₂ fluxes

10 ~~During the stratified period, CO₂ flux varied around 0.2–0.6 $\mu\text{mol m}^{-2}\text{s}^{-1}$ when measured with FC, whereas EC measured fluxes varied between 0.3–0.4 $\mu\text{mol m}^{-2}\text{s}^{-1}$ (Fig. 11). The average FC CO₂ flux was 0.40 $\mu\text{mol m}^{-2}\text{s}^{-1}$ and the coefficient of variation was 0.63 (Fig. 11b). Daytime average FC CO₂ flux was $0.62 \pm 0.08 \mu\text{mol m}^{-2}\text{s}^{-1}$ and differed from daytime EC CO₂ flux ($0.31 \pm 0.04 \mu\text{mol m}^{-2}\text{s}^{-1}$). Night-time fluxes, however, are not different between FC and EC methods ($0.29 \pm 0.04 \mu\text{mol m}^{-2}\text{s}^{-1}$ when measured with FC and $0.28 \pm 0.08 \mu\text{mol m}^{-2}\text{s}^{-1}$ with EC, Table 2). CO₂ fluxes were almost always
15 higher when measured with FC than EC method (statistical significance tested with Mann-Whitney U-test, $p < 0.01$) and the FC measurements did not show spatial variation(~~Fig. 11b~~). Eugster et al. (2003) also report higher CO₂ flux when measured with FC compared to EC. However, from the north side of the measurement raft (measurement spots N1–N4), FC fluxes do not differ statistically from EC CO₂ fluxes. ~~During the stratified period, CO₂ flux varied around 0.2–0.6 $\mu\text{mol m}^{-2}\text{s}^{-1}$ when measured with FC, whereas EC measured fluxes of 0.3–0.4 $\mu\text{mol m}^{-2}\text{s}^{-1}$.~~~~

20 There is a clear difference between EC measurements from the south and north sides of the lake (tested with Mann-Whitney U-test, $p < 0.01$) with approximately 0.1 $\mu\text{mol m}^{-2}\text{s}^{-1}$ higher CO₂ fluxes measured from the south than from north (Fig. 11b). South side of the raft is shallower than the north side (Fig. 1a) and thus more prone for the mixing to reach bottom even during the stratified period. The EC footprint area of 100–300 m (Mammarella et al., 2015) from the raft reaches further to the shallow areas than the FC measurements that were done approximately 50 m south from the raft. EC is thus more likely to catch the
25 higher gas fluxes resulting from up-welling of gas-rich waters from the bottom. Higher CH₄ flux from the south side is not detected probably due to CH₄ oxidation in the water column into CO₂. ~~This oxidation would not increase the CO₂ efflux, as CH₄ flux is so much smaller than that of CO₂~~. Footprint area north from the raft is over significantly deeper water and mixing from the deeper waters during stratified period is unlikely.

~~EC measurement systems are set up in one place, often on the shore or on a raft near the deepest parts of the lake to have
30 a large footprint area for measurements. This is due to limitations in the EC method, because it requires a homogeneous surface and favourable wind conditions, but leads to possibly biased flux estimations, especially if flux is only measured over a particularly deep or shallow area. FC method is good for detecting spatial variation, but has its limitations regarding temporal and spatial data coverage and challenging measurement conditions.~~

4 Conclusions

We found that all gas transfer velocity, k , models used in BLM calculation gave mainly lower flux estimates of both CH₄ and CO₂ compared to EC, while FC measurements were higher than EC. For CH₄ fluxes, this difference between FC and EC methods is probably caused by the EC system ~~being incapable of reliably detecting fluxes lower than 2 nmol m⁻² s⁻¹~~ detection limit that was very close to the measured fluxes during lake stratification. For CO₂, there was no statistical difference between FC and EC methods over the north side of the lake and night-time average fluxes were almost the same with these two methods. Gas transfer velocity models by Tedford et al. (2014) (k_{TE}) and Heiskanen et al. (2014) (k_{HE}) showed very similar fluxes both for CH₄ and CO₂, and the k model by Cole and Caraco (1998) (k_{CC}) resulted in clearly lower gas fluxes especially during the lake mixing period. A comparison between BLM and EC fluxes showed that, on average, the k_{TE} model is the most similar and the k_{CC} model the lowest, when compared to EC fluxes. For global up-scaling, it would be preferable to use up to date k models instead of k_{CC} to reduce the risk of systematic biases. The simple k_{CC} model underestimates the flux especially during special occasions of e.g. lake mixing and rain events, which may vastly contribute to the annual flux estimate.

Diurnal variation of CH₄ and CO₂ fluxes was examined by BLM and EC measurements. During the mixing period the BLM with different k models agreed well with ~~EC measurements each other~~ on the shape of the variation both for CH₄ and CO₂ fluxes, but the magnitudes differed between the models. During the stratified period, CO₂ flux by k_{TE} showed an opposite diurnal pattern than other models ~~and EC measurements~~ due to higher air friction velocity during daytime. This model could work better with direct friction velocity measurements in the water. The buoyancy term included in k_{TE} model was not significant compared to the shear term and does not affect the diurnal variation of the flux. CO₂ concentration difference between the surface water and air was found to have a diurnal cycle with lower values during daytime, probably due to algal photosynthesis reducing surface water concentration of CO₂. An opposite diurnal cycle was found for CH₄ concentration difference with highest values reached in the afternoon. This might be due to CH₄ feeding from the deeper waters, lower oxidation rate in daylight in the water column, or due to more effective lateral transport from the littoral zone during higher wind speeds in the daytime. As we observe a clear diurnal cycle in the concentration difference for both CH₄ and CO₂, it is important to note that using only daytime concentration (and wind speed) measurements for up-scaling with BLM affects the resulting flux estimate.

FC measurements did not show a spatial variation in either CH₄ or CO₂ flux. CO₂ EC flux was clearly higher from the south side of the measurement raft than north, due to shallower lake area within the EC footprint on the south side. This was not detected with CH₄, probably due to oxidation in the water column.

FC measurements are generally used for studying spatial variation, but our results suggest that also EC measurements are able to detect differences between different wind sectors. As we find clear differences between night-time and daytime flux measurements as well as between stratified and lake mixing periods, it is advisable to prefer frequent and diverse sampling over daytime-only measurements, that can lead to biases in greenhouse gas budget estimates.

5 Data availability

Eddy covariance, water column temperature and CO₂ concentration and meteorological data are available in AVAA - Open research data publishing platform (<http://openscience.fi/avaa>). The metadata of the observations are available via ETSIN-service. Data from manual measurements are available upon request from the first author.

- 5 *Author contributions.* IM, DB, JH, MR and TV designed the field experiments. KME, MR, AO and JH carried out manual field measurements. KME, IM and OP participated in eddy covariance data processing and analysis. TB and AL carried out automatic gas concentration measurements in the water column. All authors participated in analysing the results and KME prepared the manuscript with contributions from all co-authors.

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

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References

- Aubinet, M., Vesala, T., and Papale (eds.), D.: Eddy covariance: a practical guide to measurement and data analysis, Springer Science & Business Media, 2012.
- Bastviken, D., Cole, J., Pace, M., and Tranvik, L.: Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate, *Global Biogeochemical Cycles*, 18, 2004.
- Bastviken, D., Santoro, A. L., Marotta, H., Pinho, L. Q., Calheiros, D. F., Crill, P., and Enrich-Prast, A.: Methane emissions from Pantanal, South America, during the low water season: toward more comprehensive sampling, *Environmental Science & Technology*, 44, 5450–5455, 2010.
- Bastviken, D., Tranvik, L. J., Downing, J. A., Crill, P. M., and Enrich-Prast, A.: Freshwater methane emissions offset the continental carbon sink, *Science*, 331, 50–50, 2011.
- Blees, J., Niemann, H., Erne, M., Zopfi, J., Schubert, C. J., and Lehmann, M. F.: Spatial variations in surface water methane super-saturation and emission in Lake Lugano, southern Switzerland, *Aquatic Sciences*, 77, doi:10.1007/s00027-015-0401-z, 2015.
- Bussmann, I.: Methane release through resuspension of littoral sediment, *Biogeochemistry*, 74, 283–302, doi:10.1007/s10533-004-2223-2, 2005.
- Cole, J. J. and Caraco, N. F.: Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF₆, *Limnology and Oceanography*, 43, 647–656, 1998.
- Cole, J. J., Caraco, N. F., Kling, G. W., and Kratz, T. K.: Carbon dioxide supersaturation in the surface waters of lakes, *Science (New York, N.Y.)*, 265, 1568–1570, 1994.
- Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., and Middelburg, J. J.: Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget, *Ecosystems*, 10, 172–185, 2007.
- Duc, N. T., Silverstein, S., Lundmark, L., Reyier, H., Crill, P., and Bastviken, D.: Automated flux chamber for investigating gas flux at water–air interfaces, *Environmental Science & Technology*, 47, 968–975, 2013.
- Eugster, W., Kling, G., Jonas, T., McFadden, J. P., Wüest, A., MacIntyre, S., and Chapin, F. S.: CO₂ exchange between air and water in an Arctic Alaskan and midlatitude Swiss lake: Importance of convective mixing, *Journal of Geophysical Research: Atmospheres* (1984–2012), 108, 2003.
- Eugster, W., DelSontro, T., and Sobek, S.: Eddy covariance flux measurements confirm extreme CH₄ emissions from a Swiss hydropower reservoir and resolve their short-term variability, *Biogeosciences*, 8, 2815–2831, 2011.
- Finkelstein, P. L. and Sims, P. F.: Sampling error in eddy correlation flux measurements, *Journal of Geophysical Research: Atmospheres*, 106, 3503–3509, 2001.
- Gålfalk, M., Bastviken, D., Fredriksson, S., and Arneborg, L.: Determination of the piston velocity for water-air interfaces using flux chambers, acoustic Doppler velocimetry, and IR imaging of the water surface, *Journal of Geophysical Research: Biogeosciences*, 118, 770–782, doi:10.1002/jgrg.20064, 2013.
- Hari, P. and Kulmala, M.: Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II), *Boreal Environment Research*, 10, 315–322, 2005.
- Hari, P., Pumpanen, J., Huotari, J., Kolari, P., Grace, J., Vesala, T., and Ojala, A.: High-frequency measurements of productivity of planktonic algae using rugged nondispersive infrared carbon dioxide probes, *Limnology and Oceanography: Methods*, 6, 347–354, 2008.

- Heiskanen, J. J., Mammarella, I., Haapanala, S., Pumpanen, J., Vesala, T., MacIntyre, S., and Ojala, A.: Effects of cooling and internal wave motions on gas transfer coefficients in a boreal lake, *Tellus B*, 66, doi:10.3402/tellusb.v66.22827, 2014.
- Heiskanen, J. J., Mammarella, I., Ojala, A., Stepanenko, V., Erkkilä, K.-M., Miettinen, H., Sandström, H., Eugster, W., Leppäranta, M., Järvinen, H., Vesala, T., and Nordbo, A.: Effects of water clarity on lake stratification and lake-atmosphere heat exchange, *Journal of Geophysical Research: Atmospheres*, 120, 7412–7428, doi:10.1002/2014JD022938, 2015.
- Huotari, J., Ojala, A., Peltomaa, E., Nordbo, A., Launiainen, S., Pumpanen, J., Rasilo, T., Hari, P., and Vesala, T.: Long term direct CO₂ flux measurements over a boreal lake: Five years of eddy covariance data, *Geophysical Research Letters*, 38, doi:10.1029/2011GL048753, 2011.
- Imberger, J.: The diurnal mixed layer, *Limnology and Oceanography*, 30, 737–770, 1985.
- 10 Keller, M. and Stallard, R. F.: Methane emission by bubbling from Gatun Lake, Panama, *Journal of Geophysical Research: Atmospheres*, 99, 8307–8319, doi:10.1029/92JD02170, 1994.
- Lehner, B. and Döll, P.: Development and validation of a global database of lakes, reservoirs and wetlands, *Journal of Hydrology*, 296, 1–22, doi:10.1016/j.jhydrol.2004.03.028, 2004.
- Liu, H., Peters, G., and Foken, T.: New equations for sonic temperature variance and buoyancy heat flux with an omnidirectional sonic anemometer, *Boundary-Layer Meteorology*, 100, 459–468, doi:10.1175/JHM-D-12-020.1, 2001.
- 15 Livingston, G. P. and Hutchinson, G. L.: Enclosure-based measurement of trace gas exchange: applications and sources of error, in: *Biogenic trace gases: measuring emissions from soil and water*, edited by Matson, P. and Harriss, R., pp. 14–51, Blackwell Science Ltd, 1995.
- Lorke, A., Bodmer, P., Noss, C., Alshboul, Z., Koschorreck, M., Somlai-Haase, C., Bastviken, D., Flury, S., McGinnis, D. F., Maeck, A., Müller, D., and Premke, K.: Technical note: drifting versus anchored flux chambers for measuring greenhouse gas emissions from running waters, *Biogeosciences*, 12, 7013–7024, doi:10.5194/bg-12-7013-2015, 2015.
- 20 MacIntyre, S., Wanninkhof, R., and Chanton, J. P.: Trace gas exchange across the air-water interface in freshwater and coastal marine environments, in: *Biogenic trace gases: measuring emissions from soil and water*, edited by Matson, P. and Harriss, R., pp. 52–97, Blackwell Science Ltd, 1995.
- Mammarella, I., Launiainen, S., Grönholm, T., Keronen, P., Pumpanen, J., Rannik, Ü., and Vesala, T.: Relative humidity effect on the high-frequency attenuation of water vapor flux measured by a closed-path eddy covariance system, *Journal of Atmospheric and Oceanic Technology*, 26, 1856–1866, doi:10.1175/2009JTECHA1179.1, 2009.
- 25 Mammarella, I., Nordbo, A., Rannik, Ü., Haapanala, S., Levula, J., Laakso, H., Ojala, A., Peltola, O., Heiskanen, J., Pumpanen, J., and Vesala, T.: Carbon dioxide and energy fluxes over a small boreal lake in Southern Finland, *Journal of Geophysical Research: Biogeosciences*, 120, 1296–1314, doi:10.1002/2014JG002873, 2015.
- 30 Mammarella, I., Peltola, O., Nordbo, A., Järvi, L., and Rannik, Ü.: Quantifying the uncertainty of eddy covariance fluxes due to the use of different software packages and combinations of processing steps in two contrasting ecosystems, *Atmospheric Measurement Techniques*, 9, 4915–4933, doi:10.5194/amt-9-4915-2016, 2016.
- Miettinen, H., Pumpanen, J., Heiskanen, J. J., H., A., Mammarella, I., Ojala, A., Levula, J., and Rantakari, M.: Towards a more comprehensive understanding of lacustrine greenhouse gas dynamics — two-year measurements of concentrations and fluxes of CO₂, CH₄ and N₂O in a typical boreal lake surrounded by managed forests, *Boreal Environment Research*, 20, 75–89, 2015.
- 35 Mitchell, B. G., Broody, E. A., Holm-Hansen, O., and McClain, C.: Inhibitory effect of light on methane oxidation in the pelagic water column of a mesotrophic lake (Lake Biwa, Japan), *Limnol. Oceanogr.*, 36, 1662–1677, 2005.

- Natchimuthu, S., Sundgren, I., Gålfalk, M., Klemedtsson, L., Crill, P., Danielsson, Å., and Bastviken, D.: Spatio-temporal variability of lake CH₄ fluxes and its influence on annual whole lake emission estimates, *Limnology and Oceanography*, 61, S13–S26, doi:10.1002/lno.10222, 2016.
- Ojala, A., Lopez Bellido, J., Tulonen, T., Kankaala, P., and Huotari, J.: Carbon gas fluxes from a brown-water and a clear-water lake in the boreal zone during a summer with extreme rain events, *Limnology and Oceanography*, 56, 61–76, doi:10.4319/lo.2011.56.1.0061, 2011.
- Peltola, O., Hensen, A., Helfter, C., Belelli Marchesini, L., Bosveld, F. C., Van Den Bulk, W. C. M., Elbers, J. A., Haapanala, S., Holst, J., Laurila, T., Lindroth, A., Nemitz, E., Röckmann, T., Vermeulen, A. T., and Mammarella, I.: Evaluating the performance of commonly used gas analysers for methane eddy covariance flux measurements: the InGOS inter-comparison field experiment, *Biogeosciences*, 11, 3163–3186, doi:10.5194/bg-11-3163-2014, 2014.
- Podgrajsek, E., Sahlée, E., Bastviken, D., Holst, J., Lindroth, A., Tranvik, L., and Rutgersson, A.: Comparison of floating chamber and eddy covariance measurements of lake greenhouse gas fluxes, *Biogeosciences*, 11, 4225–4233, doi:10.5194/bg-11-4225-2014, 2014a.
- Podgrajsek, E., Sahlée, E., and Rutgersson, A.: Diurnal cycle of lake methane flux, *Journal of Geophysical Research: Biogeosciences*, 119, 236–248, doi:10.1002/2013JG002327, 2014b.
- Podgrajsek, E., Sahlée, E., and Rutgersson, A.: Diel cycle of lake-air CO₂ flux from a shallow lake and the impact of waterside convection on the transfer velocity, *Journal of Geophysical Research: Biogeosciences*, 120, 29–38, doi:10.1002/2014JG002781, 2015.
- Rannik, Ü., Peltola, O., and Mammarella, I.: Random uncertainties of flux measurements by the eddy covariance technique, *Atmospheric Measurement Techniques*, 9, 5163–5181, doi:10.5194/amt-9-5163-2016, 2016.
- Rantakari, M. and Kortelainen, P.: Interannual variation and climatic regulation of the CO₂ emission from large boreal lakes, *Global Change Biology*, 11, 1368–1380, 2005.
- Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., and Humborg, C.: Global carbon dioxide emissions from inland waters, *Nature*, 503, 355–359, doi:10.1038/nature12760, 2013.
- Schubert, C. J., Diem, T., and Eugster, W.: Methane emissions from a small wind shielded lake determined by eddy covariance, flux chambers, anchored funnels, and boundary model calculations: a comparison, *Environmental Science & Technology*, 46, 4515–4522, 2012.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric chemistry and physics: from air pollution to climate change*, John Wiley & Sons, 2016.
- Stepanenko, V., Mammarella, I., Ojala, A., Miettinen, H., Lykosov, V., and Vesala, T.: LAKE 2.0: a model for temperature, methane, carbon dioxide and oxygen dynamics in lakes, *Geoscientific Model Development*, 9, 1977–2006, 2016.
- Tedford, E. W., MacIntyre, S., Miller, S. D., and Czikowsky, M. J.: Similarity scaling of turbulence in a temperate lake during fall cooling, *Journal of Geophysical Research: Oceans*, 119, 4689–4713, doi:10.1002/2014JC010135, 2014.
- Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon, P., Finlay, K., Fortino, K., and Knoll, L. B.: Lakes and reservoirs as regulators of carbon cycling and climate, *Limnology and Oceanography*, 54, 2298–2314, doi:10.4319/lo.2009.54.6_part_2.2298, 2009.
- Verpoorter, C., Kutser, T., Seekell, D. A., and Tranvik, L. J.: A global inventory of lakes based on high-resolution satellite imagery, *Geophysical Research Letters*, 41, 6396–6402, doi:10.1002/2014GL060641, 2014.
- Vesala, T., Huotari, J., Rannik, U., Suni, T., Smolander, S., Sogachev, A., Launiainen, S., and Ojala, A.: Eddy covariance measurements of carbon exchange and latent and sensible heat fluxes over a boreal lake for a full open water period, *Journal of Geophysical Research: Atmospheres*, 111, 2006.
- Vickers, D. and Mahrt, L.: Quality control and flux sampling problems for tower and aircraft data, *Journal of Atmospheric and Oceanic Technology*, 14, 512–526, 1997.

Warneck, P. and Williams, J.: The atmospheric Chemist's companion: numerical data for use in the atmospheric sciences, Springer Science & Business Media, 2012.

Xiao, W., Liu, S., Wang, W., Yang, D., Xu, J., Cao, C., Li, H., and Lee, X.: Transfer coefficients of momentum, heat and water vapour in the atmospheric surface layer of a large freshwater lake, *Boundary-layer meteorology*, 148, 479–494, 2013.

Table 1. Linear fit $y = ax + b$ parameters for comparison between EC and BLM fluxes according to different models for k , when EC flux estimates were on the x-axis. Uncertainties are given by the standard errors of the parameters. The comparison was made using daily median fluxes calculated from 1/2 h averages.

	Model	a	b [nmol m ⁻² s ⁻¹]	r ²	RMSE [nmol m ⁻² s ⁻¹]
CH ₄	k_{HE}	0.9±0.2	-0.3±0.8	0.50	2.62
	k_{TE}	1.0±0.2	-0.3±0.8	0.53	2.58
	k_{CC}	0.5±0.1	-0.2±0.4	0.48	1.38
	Model	a	b [μmol m ⁻² s ⁻¹]	r ²	RMSE [μmol m ⁻² s ⁻¹]
CO ₂	k_{HE}	0.6±0.3	0.3±0.2	0.27	0.58
	k_{TE}	0.6±0.3	0.4±0.2	0.26	0.59
	k_{CC}	0.3±0.1	0.2±0.1	0.20	0.30

Table 2. Average daytime and night-time CH₄ and CO₂ fluxes during lake stratification and mixing periods using different measurement methods. Note that FC fluxes are averaged also over different measurement spots. Mixing period did not include enough FC measurements for this analysis. Uncertainties are given by the standard errors of the flux averages.

<u>Stratified period</u>	<u>CH₄ flux [nmol m⁻²s⁻¹]</u>		<u>CO₂ flux [μmol m⁻²s⁻¹]</u>	
	<u>day</u>	<u>night</u>	<u>day</u>	<u>night</u>
<u>BLM k_{HE}</u>	<u>0.177 (\pm 0.005)</u>	<u>0.431 (\pm 0.008)</u>	<u>0.305 (\pm 0.009)</u>	<u>0.410 (\pm 0.008)</u>
<u>BLM k_{TE}</u>	<u>0.370 (\pm 0.011)</u>	<u>0.439 (\pm 0.007)</u>	<u>0.545 (\pm 0.014)</u>	<u>0.396 (\pm 0.010)</u>
<u>BLM k_{CC}</u>	<u>0.128 (\pm 0.003)</u>	<u>0.186 (\pm 0.004)</u>	<u>0.201 (\pm 0.004)</u>	<u>0.180 (\pm 0.004)</u>
<u>EC</u>	<u>0.41 (\pm 0.04)</u>	<u>0.34 (\pm 0.04)</u>	<u>0.31 (\pm 0.04)</u>	<u>0.28 (\pm 0.08)</u>
<u>FC</u>	<u>2.4 (\pm 0.3)</u>	<u>1.1 (\pm 0.2)</u>	<u>0.62 (\pm 0.08)</u>	<u>0.29 (\pm 0.04)</u>
<u>Mixing period</u>	<u>CH₄ flux [nmol m⁻²s⁻¹]</u>		<u>CO₂ flux [μmol m⁻²s⁻¹]</u>	
	<u>day</u>	<u>night</u>	<u>day</u>	<u>night</u>
<u>BLM k_{HE}</u>	<u>7.1 (\pm 0.6)</u>	<u>6.6 (\pm 0.5)</u>	<u>2.15 (\pm 0.06)</u>	<u>1.43 (\pm 0.05)</u>
<u>BLM k_{TE}</u>	<u>7.7 (\pm 0.6)</u>	<u>7.1 (\pm 0.5)</u>	<u>2.37 (\pm 0.06)</u>	<u>1.54 (\pm 0.05)</u>
<u>BLM k_{CC}</u>	<u>3.7 (\pm 0.3)</u>	<u>2.8 (\pm 0.2)</u>	<u>1.11 (\pm 0.04)</u>	<u>0.58 (\pm 0.02)</u>
<u>EC</u>	<u>5.9 (\pm 0.3)</u>	<u>5.0 (\pm 0.4)</u>	<u>1.3 (\pm 0.2)</u>	<u>0.88 (\pm 0.14)</u>

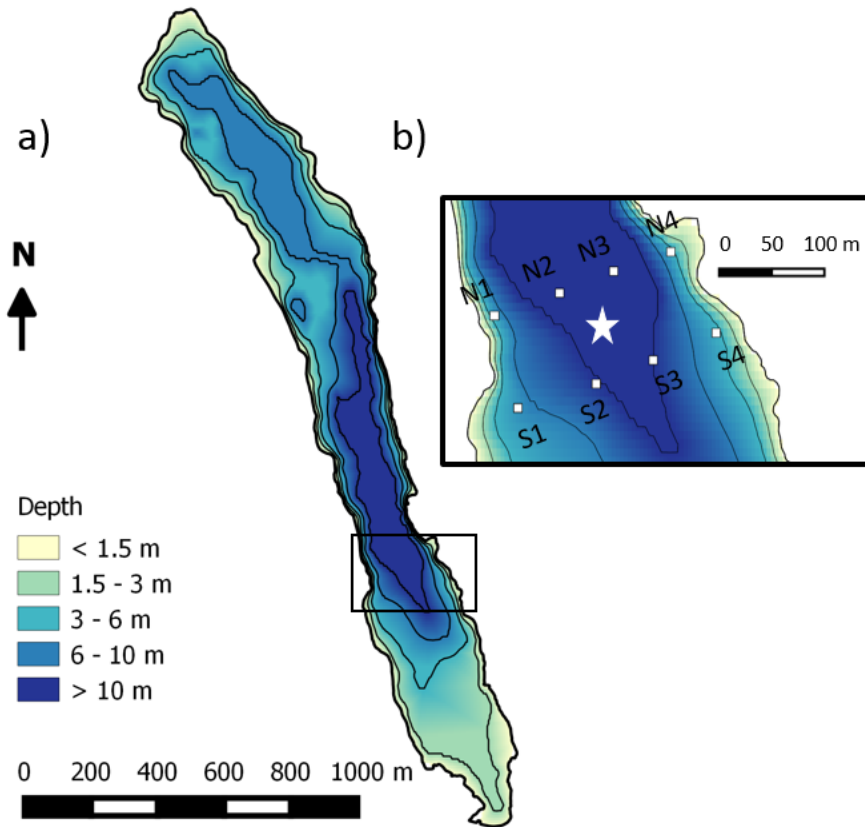


Figure 1. (a) Bathymetry of Lake Kuivajärvi and (b) floating chamber measurement spots (white squares) around the eddy-covariance measurement raft (white star).

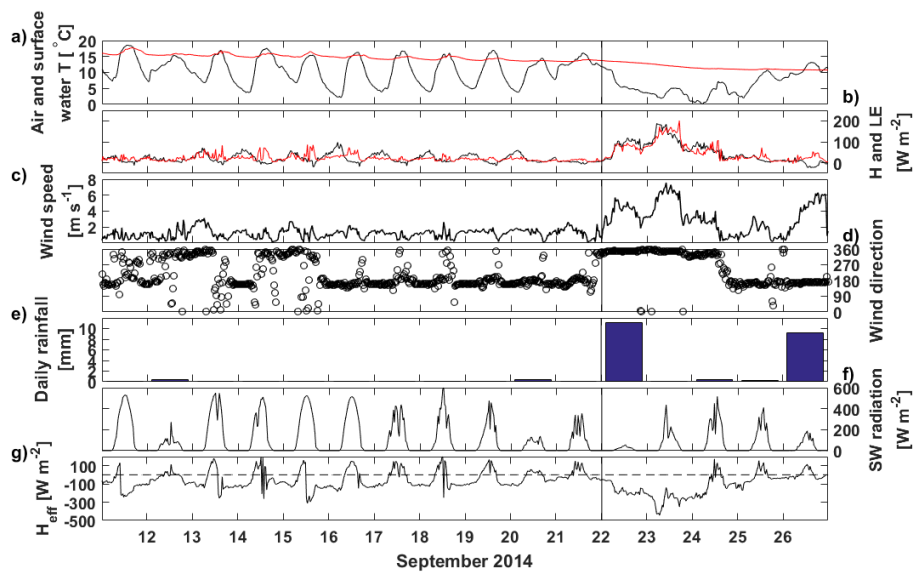


Figure 2. Half hour averages of (a) measured air temperature (black) and lake surface water temperature (red), (b) sensible (black) and latent (red) heat fluxes measured with the EC system and gap-filled using a bulk formula (see Sect. 2.2.1 and Mammarella et al. (2015) for details), (c) wind speed, (d) wind direction, (e) daily rainfall, (f) incoming shortwave radiation and (g) effective heat flux measured at the measurement raft. Time ticks represent midnight and the vertical black line the start of the lake mixing period.

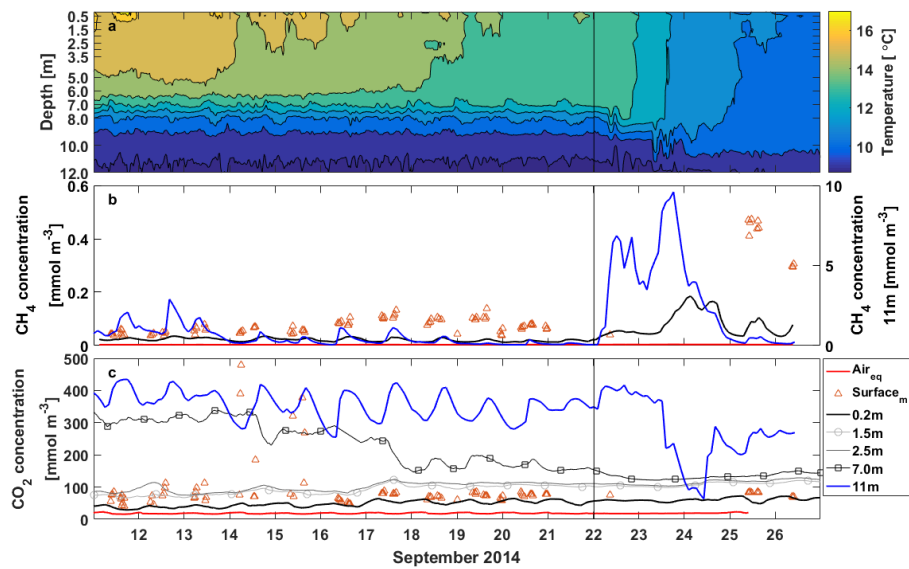


Figure 3. Half hour averages of (a) temperature, (b) CH₄ concentration and (c) CO₂ concentration in the water column at different depths. The red line is the equilibrium concentration of CH₄ and CO₂ at the surface in subplots b and c, respectively. The orange triangles are manual headspace samples taken from the surface water at chamber measurement locations. Time ticks represent midnight and the vertical black line the start of the lake mixing period. Note that CH₄ concentration at 11 m depth (blue line) is read from the right y-axis.

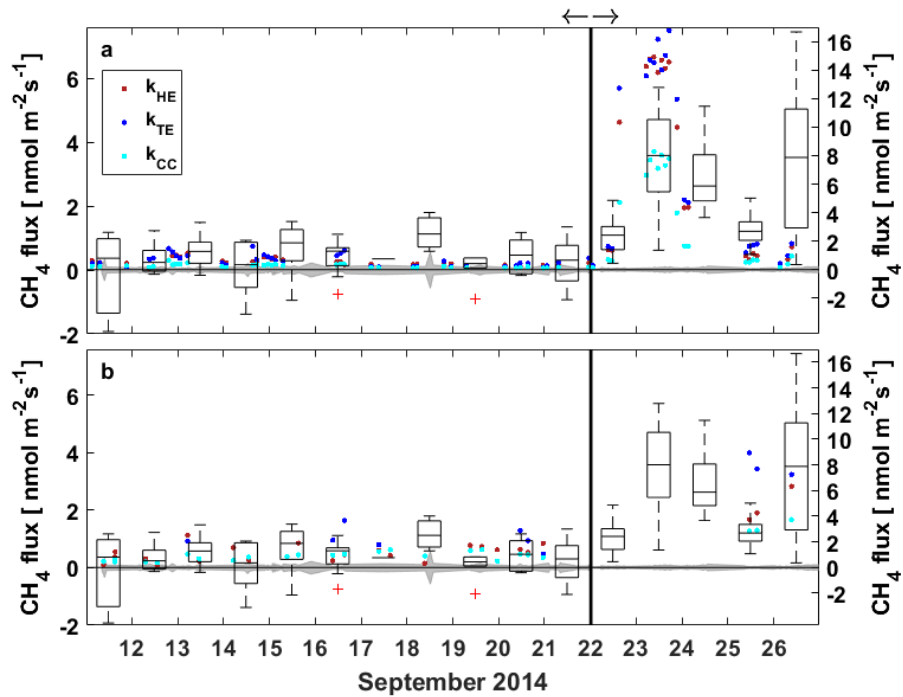


Figure 4. Daily median EC CH₄ flux (boxplot) and BLM CH₄ fluxes with different models for gas transfer coefficient-velocity k using surface water CH₄ concentration from (a) automatic measurements and (b) manual water samples. In the boxes, the middle black line is the daily median flux while the bottom and top edges of the boxes indicate the 25th and 75th percentiles, respectively. The black whiskers show the most extreme data points that are not considered as outliers ($\pm 2.7\sigma$) and the outliers are represented with the red '+' symbol. Gray shadowed area shows the flux detection limit (3σ of the covariance). Time ticks represent midnight and the vertical black line the start of the lake mixing period. Fluxes during the stratified period (11-22 Sept) are read from the left and mixing period fluxes (22-26 Sept) from the right axis.

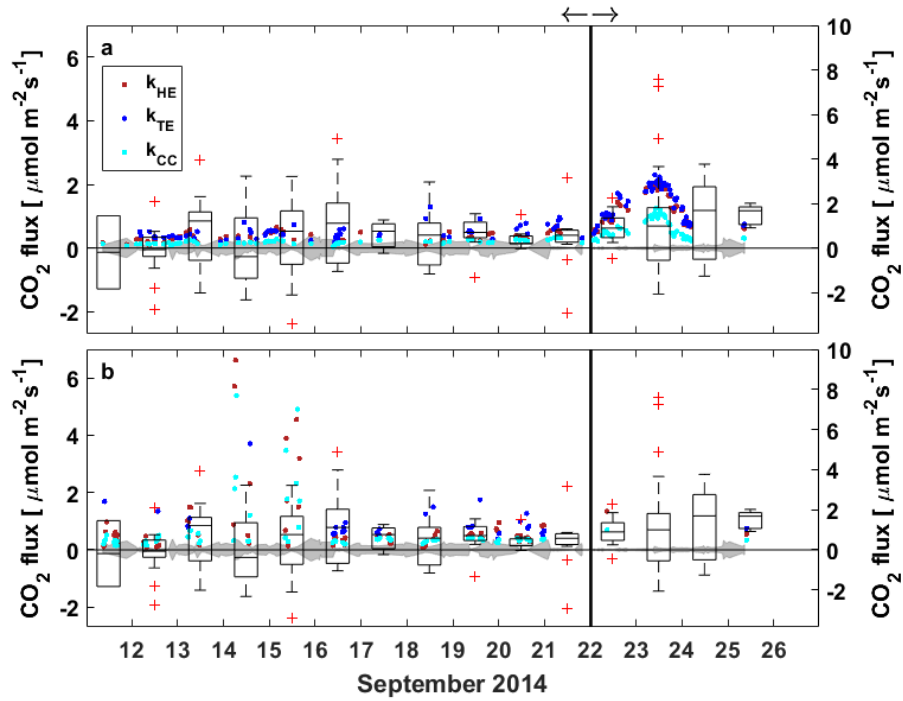


Figure 5. Daily median EC CO₂ flux (boxplot) and BLM CO₂ fluxes with different models for gas transfer coefficient-velocity k using surface water CO₂ concentration from (a) automatic measurements and (b) manual water samples. In the boxes, the middle black line is the daily median flux while the bottom and top edges of the boxes indicate the 25th and 75th percentiles, respectively. The black whiskers show the most extreme data points that are not considered as outliers ($\pm 2.7\sigma$), and the outliers are represented with the red '+' symbol. Gray shadowed area shows the flux detection limit (3σ of the covariance). Time ticks represent midnight and the vertical black line the start of the lake mixing period. Fluxes during the stratified period (11-22 Sept) are read from the left and mixing period fluxes (22-26 Sept) from the right axis.

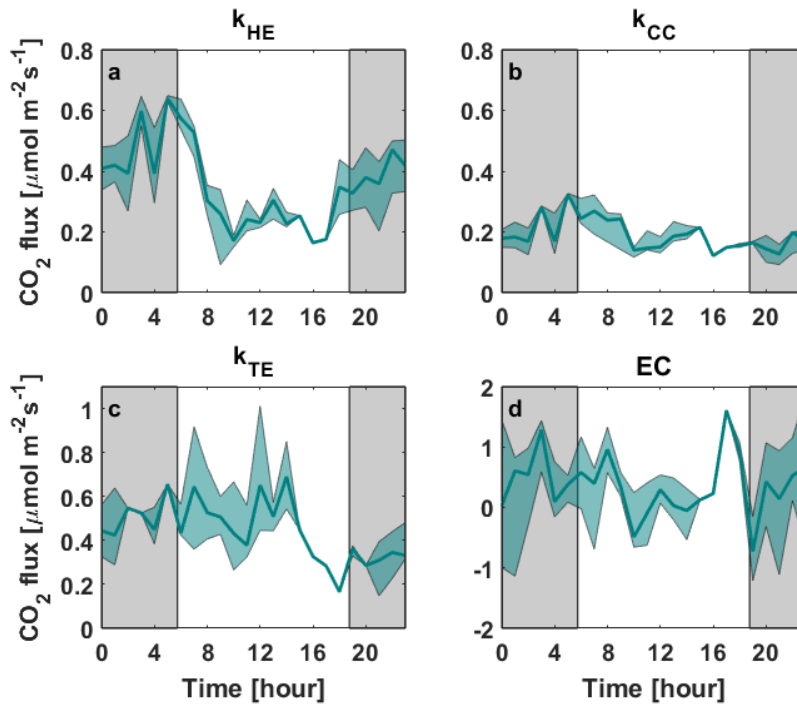


Figure 6. Median-diurnal variation of CO₂ flux ($\mu\text{mol m}^{-2}\text{s}^{-1}$) using the BLM method with gas transfer velocity calculated according to (a) k_{HE} , (b) k_{CC} and (c) k_{TE} , and (d) the measured EC flux during the stratified period 11 –22 September 2014. Thick gray line is the median value and the shadowed light blue area shows the 25th and 75th percentiles. Gray areas represent night-time. Note the change in y-axis scale in subplots c and d.

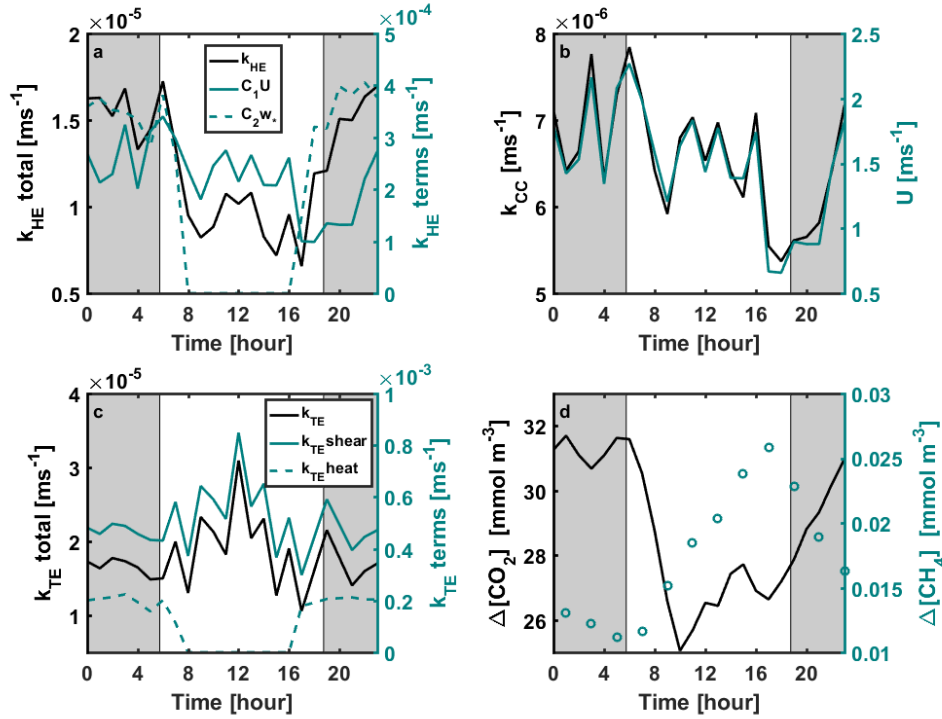


Figure 7. Median-diurnal-Diurnal variation of (a) k_{HE} and its shear and convective terms (Eq. 9), (b) k_{CC} and wind speed, (c) k_{TE} and its shear ($k_{TE}^{shear} = \frac{c_1 u_{*w}^3}{\kappa z}$ or $k_{TE}^{shear} = \frac{c_3 u_{*w}^3}{\kappa z}$) and convective ($k_{TE}^{heat} = c_2 |\beta|$ or $k_{TE}^{heat} = 0$) terms (Eq. 8) and (d) CO_2 and CH_4 concentration differences between air and surface water during the stratified period 11–22 September 2014. Shear and convective terms in subplots a and c are not corrected with the Schmidt number. Gray areas represent night-time.

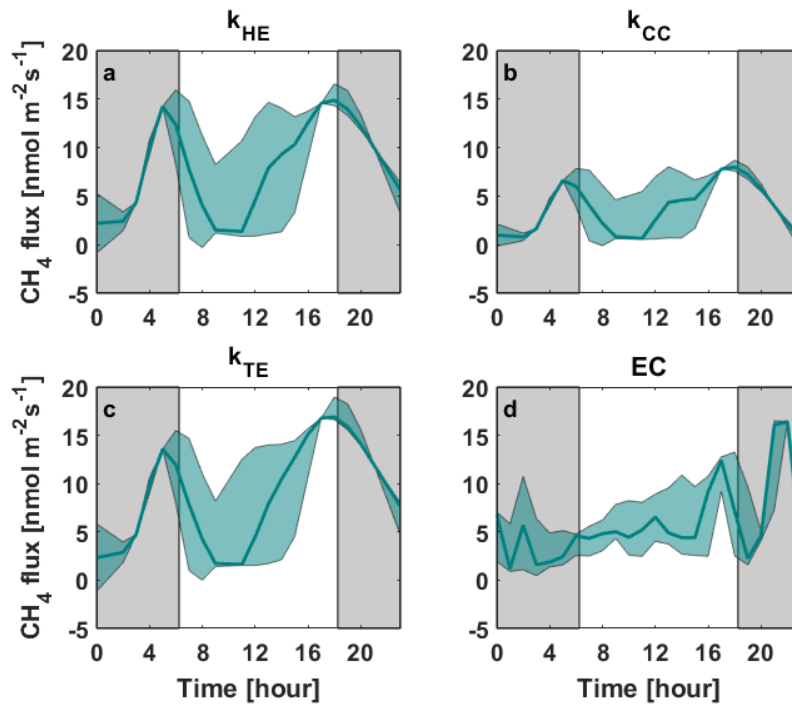


Figure 8. ~~Median-diurnal~~ Diurnal variation of CH_4 flux ($\mu\text{mol-nmol m}^{-2}\text{s}^{-1}$) using the BLM method with gas transfer velocity calculated according to (a) k_{HE} , (b) k_{CC} and (c) k_{TE} , and (d) the measured EC flux during the mixing period 22–26 September 2014. Thick ~~gray-blue~~ gray-blue line is the median value and the ~~shadowed-light blue~~ shaded-light blue area shows the 25th and 75th percentiles. Gray areas represent night-time.

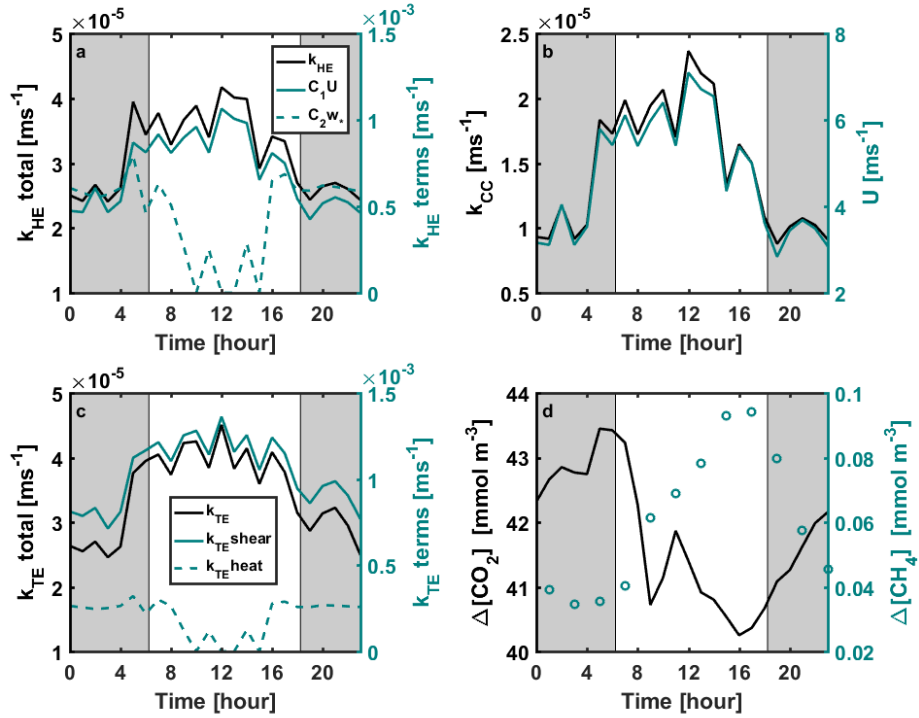


Figure 9. Median-diurnal-Diurnal variation of (a) k_{HE} and its shear and convective terms, (b) k_{CC} and wind speed, (c) k_{TE} and its shear ($k_{TEshear} = \frac{c_1 u_{*w}^3}{\kappa z}$ or $k_{TEshear} = \frac{c_3 u_{*w}^3}{\kappa z}$) and convective ($k_{TEheat} = c_2 |\beta|$ or $k_{TEheat} = 0$) terms (Eq. 8) and (d) CO_2 and CH_4 concentration differences between air and surface water during the mixing period 22–26 September 2014. Shear and convective terms in subplots a and c are not corrected with the Schmidt number. Gray areas represent night-time.

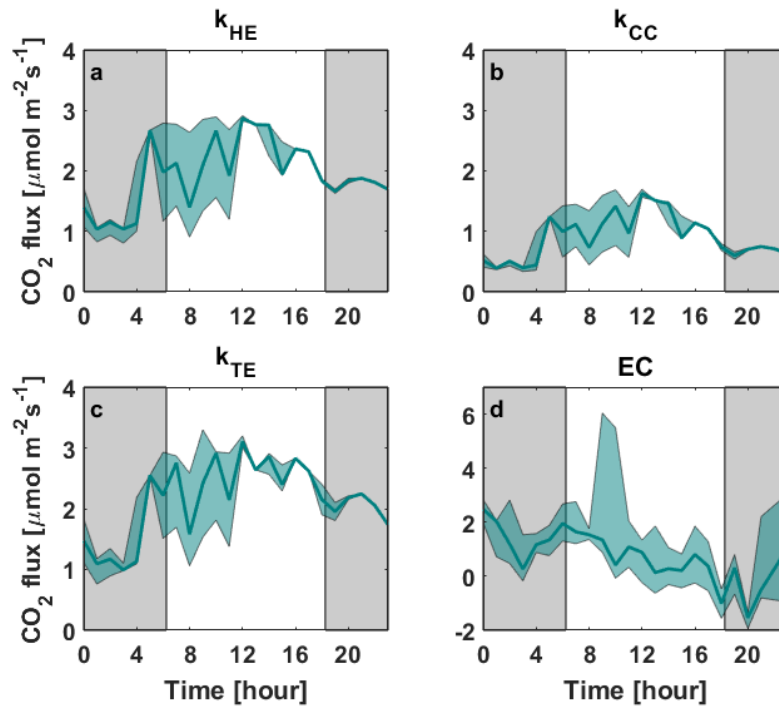


Figure 10. Median-diurnal-Diurnal variation of CO₂ flux ($\mu\text{mol m}^{-2}\text{s}^{-1}$) using the BLM method with gas transfer velocity calculated according to (a) k_{HE} , (b) k_{CC} and (c) k_{TE} , and (d) the measured EC flux during the mixing period 22–26 September 2014. Thick gray blue line is the median value and the shadowed-light blue area shows the 25th and 75th percentiles. Gray areas represent night-time. Note the change in y-axis scale in subplot d.

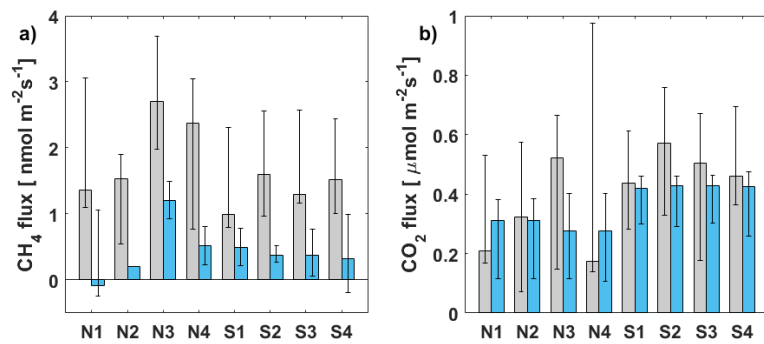


Figure 11. Median (a) CH₄ and (b) CO₂ FC fluxes (grey bars) at different measurement spots and median of simultaneous EC measurements (blue bars) during lake stratification. Black whiskers represent the 25th and 75th percentiles.