

CH₄ exchange at the forest floor of a forestry-drained fen: low flux rates but high temporal variation by Korkiakoski et al.

Response to reviewer #2

The manuscript is based on the continuous two years CH₄ flux dataset obtained by automatic chamber measurement at a forestry-drained fen. The use of high-resolution gas analyzer let the authors to document low and variable fluxes, and continuity of the measurements together with their high temporal resolution allowed to estimate longtime net CH₄ exchange and judge the variability of the fluxes. The site chosen for the study is not an easy one for CH₄ flux measurements: the net result of both methanogenic and methanotrophic activities can change from small negative to small positive flux, being dependent on a combination of different factors. I highly appreciate the value of the obtained dataset, and would really like to see this study eventually published.

Unfortunately, within a number of comments following below, at least one seems to be critical and enforces me to ask for a major revision (followed by an additional review):

Equation 5 (page 6) seems to be incorrect, or, at least, has been presented incorrectly. If the time derivative is expressed in ppm/h, and the resulting flux F is also per hour, why the multiplier 3600 s/h is used? Then, I do not see a reason for a multiplier 273.15 in the numerator of the temperature fraction: the universal gas law with constant R in J mol⁻¹ K⁻¹ in the denominator implies temperature in K (273.15 + T in C) also in the denominator. Another way of expression for this type of flux equations (for example, Koskinen et al., 2014) operates with the standard molar volume of ideal gas instead of the universal gas constant (R), in this case ratios between the standard and the actual temperature and pressure are used. The equation 5 as it is stated in the manuscript is a mixture of these two correct approaches, and is mathematically incorrect. Formally, in the result of these two mistakes, the F values obtained with Eq.5 must be overestimated by six orders of magnitude. However, the reported fluxes seem to be of a realistic order of magnitude, while million times lower fluxes are absolutely undetectable by this type of measurements. Thus, I suppose the authors did not use the Eq.5 as it stated in the manuscript, but I can not exclude a chance that the actually used formula was also somewhat incorrect.

1. Thank you for the important observation, and apologies for this crucial error in the manuscript, which we were not aware of. The error was in the temperature fraction of the equation, which was actually used in the calculation. Also, in the text, the derivative was said to be ppm/h when the actually used derivative was ppm/s. This explains why the reported fluxes were only three times lower, not six orders of magnitude. After the correction, the flux rates are now about three times higher as originally reported. This affected for example the annual balances but did not affect the dynamics of diurnal variation or correlations. Everything in the paper to which this error affected (figures, values, comparisons to other studies) have been updated accordingly.

Talking about flux calculations, I would also ask the authors to describe what software and how was used; I can not imagine such amount of data was processed without some automated scripts/programs. Then, the description of these scripts/programs and their settings might be crucial to evaluate possible weaknesses of the calculations. How, for example, the moment of the chamber closure (t=0, page 5 line 25) was recognized by this program? As I understand from Koskinen et al. (2014), the chambers were controlled from a separate Linux PC, so operated according to its internal clock; the Picarro analyzer recorded the measured concentrations with the time stamp from its own clock – had those two being synchronized, and how often? Was the delay in gas lines between the chamber and the analyzer properly addressed?

2. All the calculations were made with the Python programming language (Python Software Foundation, version 2.7, <https://www.python.org>) using libraries: NumPy (<http://www.numpy.org/>), SciPy (<http://www.scipy.org/>), Pandas (<http://pandas.pydata.org/>) and matplotlib (<http://www.matplotlib.org>). Also, most relevant methods (e.g. fitting) are now explained in more detail in the text.

Unfortunately the Picarro and the PC were synchronized only after September 2012. Therefore we had to manually synchronize the Picarro data afterwards. After September 2012, the Picarro analyzer was connected to and synchronized with the Linux PC, so the problem of different time stamps was avoided. Linux PC acted both as a time (NTP) client fetching time from Finnish Meteorological Institute's time server ca. once a day, and as a time server for the Picarro analyzer.

Example of how the system works during one chamber measurement:

(min:sec)

00:00 chamber lid starts to close, and the valve is switched to the chamber line. Fan has been running all the time.

00:30 chamber is fully closed

00:50 a flag is added to data stream indicating the source of gas (e.g. 'Chamber1'). There was a certain lag time (up to 20 sec, depending on the flow rate) between the chamber closure and the observable analyzer response, and to ensure that all the data having the flag was usable for flux calculation this higher lag was used. In addition, during the post-processing four Picarro data points, representing about 20 s, were removed from the beginning.

More about the setup: was it the same as described by Koskinen et al. (2014), just with the Picarro analyzer connected in parallel to the Licor CO₂ analyzer? In the current manuscript it is stated (page 4 line 25): "The polycarbonate chamber was attached to a stainless steel frame (see description in Koskinen et al., 2014)." – not clear for the reader, is the reference about the frame, or the whole chamber, or the whole setup. Then some setup features are described, almost exactly in the same words as in the 2014 publication, but others (like valves, fan, etc.) are skipped. As the result, the description looks somewhat

sleazy: for example (page 4 line 20), “A gas inlet tube made of polyurethane (FESTO, OD = 6 mm, ID = 4 mm)” – but wasn’t the outlet tube made of the same material and size? I would strongly suggest the authors to completely rethink section 2.2 – clearly state in the beginning, that the setup was described in details by Koskinen et al. (2014), repeat only key elements of that description without details, then clearly state what in the described measurement system is different from 2014 publication (here with all the details).

3. Thanks for this comment. It is true, that the chapter was in some parts copied from Koskinen et al., but it was not clearly stated that the system is exactly the same. Now, the whole chapter 2.2. has been rewritten with these suggestions taken into account.

My next group of comments is related to the fact that the majority of the fluxes reported in the current study have a really low value (Fig.3). According to my back-of-the-envelope calculations, a net uptake of $20 \mu\text{g CH}_4 \text{m}^{-2} \text{h}^{-1}$ equals to CH_4 concentration change in the chamber of about 3 ppb over 2 minutes! Being amazed by the quality of the study, which made possible to justify such small fluxes, I have to stress the authors about the extra precaution with such data processing, interpretation and discussion.

For example, was the effect of water vapor dilution properly addressed? In CO_2 study (Koskinen et al., 2014) it was stated “The CO_2 concentration values were not corrected for water vapor dilution as the change in air humidity during measurement was small (data not shown)”. In the current study, when CH_4 concentration in the chamber changes so tiny ($3/1850=0.16\%$), even a small change of humidity inside the chamber during the measurement can strongly influence the result. Was H_2O concentration in the gas sample measured by the same Picarro G1130 analyzer (page 4, line 24 – unfortunately, I was unable to find any information about this model in the Internet)? Was the wet or the dry mixing ratio used in the calculations? I think the water vapor dilution should be both addressed in the calculations, and discussed in the manuscript.

4. Picarro G1130 gas analyzer measures also H_2O concentration, so the dilution correction is possible and it is also automatically made by the analyzer. By the referee’s suggestion, we are now using the dilution corrected data, which in some cases had a very small impact on fluxes, but in some cases even the sign of the flux was changed. The correction changed the annual balances a little and some correlations with CH_4 flux and meteorological and soil quantities. However, its impact to the diurnal variations was in some cases very significant. For example, we cannot see diurnal variation showing higher CH_4 uptake during the daytime any more as observed in June 2012 (Fig.8 in the original manuscript). The diurnal variation did not vanish, but it is now similar to the ones observed in spring and summer 2011. This phenomena came, as the referee suggested, purely from the concurrent variation in H_2O concentration. So now all the diurnal variation we see, shows lower uptake during the midday. As a whole, this was a very important comment by the referee and crucial for the quality of this study and we thank him for that, and apologize for neglecting it in the original manuscript.

In opposite, with such small change in the chamber headspace CH₄ concentration, I think the discussion about “distortion of the vertical concentration gradient” between the soil and the headspace (mentioned many times throughout the whole manuscript) and the concentration feedback on the microbial oxidation rate (page 11 line 29) is virtually not applicable to the current study. Undoubtedly, both can be discussed, but with a clear note, that the change in the headspace concentration from 1850 to 1847 ppb CH₄ should practically not affect either gradient or methanotrophic activity.

In this context, I do not agree with the reasoning (for example, page 11 line 20) that the distortion of the vertical concentration gradient is the main reason for non-linearity of the concentration change in the closed chamber and the difference between the linear and exponential flux estimations. In my opinion much more important reasons are water vapor dilution (see above) and leakages (both through chamber construction and through the soil). The possible leakages are not discussed at all in the manuscript; even the fact that “when the wind speed increased, the uptake of CH₄ decreased” (page 15 line 8) does not seem suspicious for the authors. However, such fact often can be very clearly explained by small leaks in the chamber – see for example Pirk et al., 2016 (doi:10.5194/bg-13-903-2016), where the non-linearity of detected fluxes is directly related to the wind speed and the material of chamber sealing.

5. We agree with the referee in this subject. After performing the dilution correction as suggested by the referee, the closures where the H₂O concentration changed significantly, became more linear. We considered and examined the wind speed impact on fluxes, and found that the observed diurnal variation was mainly explained by the wind speed (see also answer #4 for referee 1). However, as pointed out in the answer #4, the wind speed dependency is not necessarily fully attributed to leakage, but can be related to the distortion of the soil concentration gradient by wind before the chamber closure. We also studied the curvature parameter *c* in relation to wind speed and found that the curvature was typically smaller with higher wind speeds (see also answer #4 for referee 1). The discussion has now been modified accordingly.

Another point I do not agree with, is an intransigent statement that “use of linear regression systematically underestimated CH₄ flux rates” (page 1 line 14, and many times later in the manuscripts). Such statement implies that one knows the “true” flux values, and compares them to the ones obtained by a linear regression. This is not the case in the current study (but is the case for example in Pihlatie et al., 2013, where the flux was pre-set). Instead, the fluxes were estimated with two different mathematical methods (linear and exponential), and the results were somewhat different (Fig.2). Then the authors propose, that the linear estimation is more correct for low fluxes, and exponential – for high fluxes. This should be phrased as a proposal, as an assumption, supported by theoretical arguments and other studies, but still not as a statement, proven by this study.

6. We agree with the referee that it was wrong to use the statement “underestimation” in case of linear regression and this is now corrected in the text (see also the answer #26 for referee 1). Our intention was not to prove that the linear estimation is more correct for low fluxes, but to find a method by which the high noise in the small fluxes produced by exponential fitting could be reduced. Therefore we are suggesting, that for our data a flux limit of $2.5 \mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ would be an appropriate limit, and that in the forthcoming studies a similar approach could be applied, but the limit need to be estimated individually for each case. By referring to comment #2 for referee1, we think that using this limit provides a more accurate and robust estimate of very low CH_4 fluxes. Below this limit the concentration variations from which the flux is derived become increasingly affected by measurement noise and the exponential fitting becomes more prone to random perturbations to individual concentration data points and does not result in realistic flux estimates anymore.

Still having in mind very low magnitude of the fluxes, I would ask the authors to add, either in the main paper or in the supplementary material, a figure with two typical examples of concentration data during flux measurements – one with a high flux (over $3.5 \mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$), and one with a low flux – with lines for the linear and the exponential approximation over each. That will be a very sensible for the reader illustration of the measurement precision, signal-to-noise ratios, etc.

7. Figures of concentration data of ‘high’ and ‘low’ flux cases have been added to the revised version of the manuscript (see also answer #25 for referee 1).

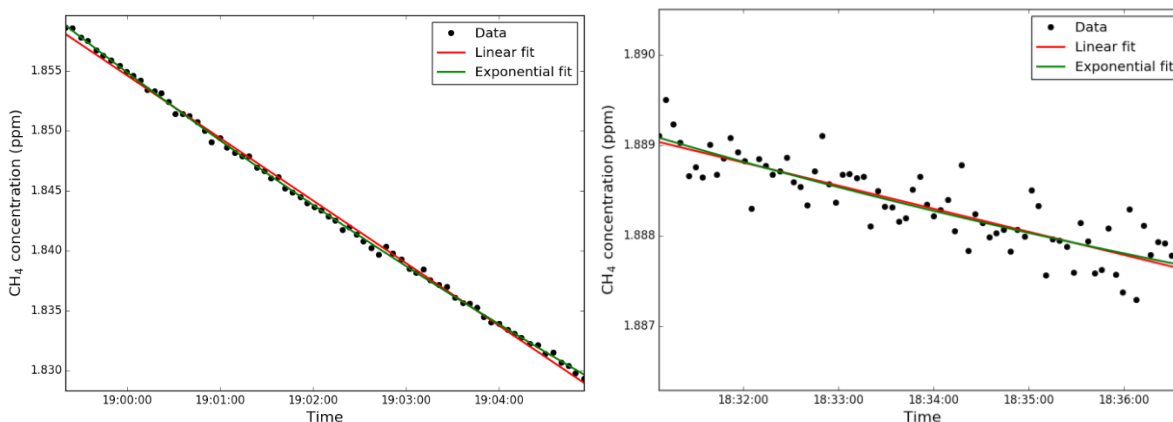


Figure 2A. Concentration data during one chamber closure for a case with a higher (left: linear and exponential: -90 and $104 \mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$, respectively) and lower (right: lin -3.5 , exp $-4.3 \mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$) flux.

And the last general comment. Unfortunately, I have to mention somewhat careless formulations and citations in the introduction:

Page 2 line 10: “In peatlands, the net CH_4 flux between the soil and atmosphere is the sum of CH_4 production and oxidation (Dunfield et al., 1993)” – the word “sum” is never used in this publication; it was a great detailed study of both processes, but the authors never stated that they sum up to the flux. There are more processes – lateral transport (applicable to the

current study with drainage ditches), subsurface storage – which affect the net fluxes as well.

Page 2 line 20: “...a lack of electron acceptors other than acetate and hydrogen are a precondition for the production of CH₄ (Segers, 1998; Kotsyurbenko et al., 2004).” Acetate and hydrogen are not electron acceptors! Hydrogen is the donor (in reaction with CO₂), acetate decays formally without donor-acceptor interaction. The publication by Segers is mentioning “alternative electron acceptors” a lot, but never stated that acetate and hydrogen are electron acceptors; the publication by Kotsyurbenko et al. does not contain the words “electron” or “acceptor” in any form.

Page 2, lines 22-23: “The rate is mainly controlled by oxygen concentration, temperature and soil moisture (Boeckx and Van Cleemput, 1996).” The study by Boeckx and Van Cleemput was focused on experimental evaluation of three factors affecting methane oxidation: soil moisture, soil temperature and nitrogen (NH₄⁺, NO₃⁻) addition. Neither oxygen concentration nor CH₄ concentration were examined (were set the same in all samples); their importance for the methanotrophic oxidation was supposed to be obvious because they are reagents. Boeckx and Van Cleemput have never stated which factors are “main”, but mentioned soil compaction and pH as well. So this citation is also incorrect and misleading: oxygen concentration, as well as methane concentration (as stated at page 11 line 29) and methanotrophic potential (amount and oxidation capacity of bacteria) are the factors, directly influencing CH₄ oxidation; temperature, moisture etc. are the factors of indirect action.

Page 2, line 25: “Closed chambers are commonly used in the measurement of greenhouse gas exchange between the forest floor and the atmosphere (e.g. Livingston and Hutchinson, 1995; Christensen et al., 1995; van Huissteden et al., 2005; Alm et al., 2007; Denmead, 2008; Forbrich et al., 2009, Koskinen et al., 2014).” The publication by Livingston and Hutchinson has only one mentioning of a forest floor (an example of study in Brazilian rain forest), but does not say how common such studies are; the publications by Christensen et al. and by van Huissteden et al. are focused on tundra and never mention “forest”.

I do not clearly remember all the publications cited in the current manuscript, and do not have enough time to check every reference. The four examples above warn me that the authors are not careful enough in their citations, so I really suggest them to check meticulously every citation in the manuscript: did the publication really state or show that? It is a big work, indeed, but it had to be done much earlier in the manuscript preparation stage.

8. We apologize for our carelessness. We went through the citations and either corrected the text or removed the references.

At this stage I will not go for more specific comments and technical corrections related to the current manuscript text, as I imagine the text will be strongly changed before the

resubmission. Still wish the authors to continue their work and bring their study to publication in a more carefully written form.

9. As a general comment we want to notice that due to the recalculations and other changes and corrections in the manuscript the discussion part was in most parts rewritten. For example, the comparison to other studies will be changed, since the fluxes in the new version will be three times as high as previously. We also included two additional coauthors in the paper.