Response to interactive comment (Anonymous Referee #2) on 'Gas chromatography vs. quantum cascade laser-based N_2O flux measurements using a novel chamber design'

[R#2.1] The authors have tested the performance of a QCL analyzer connected to a new automated chamber, against a "conventional" GC + automated gas sampling unit system. Data from QCL system were used to observe the non-linearity in the concentration increase during the chamber closure. Based on two short campaigns, the paper gives recommendations how should the measurements, data screening and flux calculations be done. The new chamber design is interesting and the system coupled to QCL seems to be fluently producing nice data. Papers presenting new chamber designs, are always welcome, particularly if they can provide generalizations and recommendations which are useful for other chamber operators. The paper is fluently written, and the observation of different patterns in diurnal cycle is interesting and important. However, there are several deficiencies and pitfalls in the data treatment and the argumentation which need revision. The presentation quality would benefit from separating the results and discussion.

[AC#2.1] We sincerely thank Referee #2 for his/her thorough review. Through the consideration and inclusion of his/her meaningful comments and suggestions, we feel that the manuscript's quality has improved, particularly by shaping the main conclusions and take home messages. We also have streamlined the presentation of the main findings. Below we give our responses to all points raised by the reviewer plus short statements of the actual changes in the manuscript.

<u>Changes to the manuscript</u>:
Main changes are (see specific points below for details):

- Reformulation of the aims of the paper at the end of the Introduction
- Inclusion of a table summarizing main features of the chamber system by providing quantitative measures
- Streamlining the text through splitting up Results and Discussion sections
- Providing a clear story line of investigations (as can be seen by the reformulation of the aims and the newly structured table of contents)
- Shaping up some of the conclusions (see specific points below)
- Few changes to figures (see specific points below)

The restructured aims of the paper now read as follows:

(1) Presentation of a novel chamber design that is connected to both a vial air-sampling setup with subsequent GC analysis and a QCL spectrometer
   - Description of design and setup in Sections 2.1 and 2.2
   - New chamber system is used for the following investigations (aims 2 to 5)

(2) Characterization of the shape of the concentration increase
   - $\rightarrow$ Is the shape rather linear or non-linear?
   - Quantification of the curvature (κ) in concentration increase
   - Using κ to verify chamber density
      - $\rightarrow$ Is κ dependent on wind speed, wind direction, on the flux itself or on closure time?

(3) Comparison of N_2O fluxes and their associated standard errors from linear and non-linear regression models

(4) Testing the novel chamber system under high and low flux conditions and comparing GC vs. QCL-based flux estimates

(5) Investigation of ecosystem and climate-specific flux characteristics such as N_2O uptake and diurnal variation

The single paragraphs of the Results and Discussion section are now as follows:

3. Results
   - 3.1 Shape of concentration increase and curvature (κ) determination
   - 3.2 Comparison of N_2O fluxes and their associated errors from linear and non-linear regression models
   - 3.3 GC vs. QCL-based fluxes under high and low exchange regimes
   - 3.4 N_2O uptake and diurnal variation
4. Discussion
   - 4.1 The parameter κ as a chamber performance criteria
   - 4.2 Closure time and measurement frequency – How long and how often is enough?
   - 4.3 Differences between GC and QCL-based fluxes
   - 4.4 Enabling investigations of flux pattern characteristics

[R#2.2] First, the performance of the GC sampling system makes me wonder whether the comparison of two systems is meaningful. Before making any comparisons, the authors should find out the reason for the bad performance of the GC.

[AC#2.2] Please see detailed response to [R#2.6].

<u>Changes to the manuscript</u>:
Please see detailed response to [R#2.6].

[R#2.3] Secondly, there are several conclusions in the paper which are just qualitative, and as such they are vague and are not supported by the presented data.

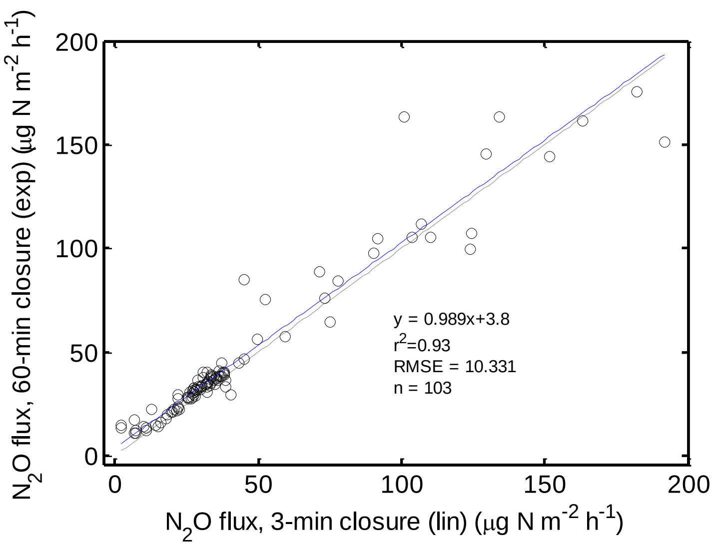
[AC#2.3] We fully agree that some conclusions came a bit out of the blue. We have modified the respective sections as outlined in the specific comments to [R#2.7], [R#2.9], [R#2.11], [R#2.33], [R#2.34], and [R#2.39] below.

<u>Changes to the manuscript</u>:
See responses to comments [R#2.7], [R#2.9], [R#2.11], [R#2.33], [R#2.34], and [R#2.39] below.

[R#2.4] Third, I share the worry of the first reviewer that most of the results shown here are already well known. For example, it has been reported already in numerous papers that the curvature in concentration increase is higher with longer closure time, and that using the linear calculation instead of non-linear can result in great underestimate in flux rate. Instead of reporting curvature, it would be more useful to quantify what is the limit of curvature after which the authors recommend the use of non-linear fitting method.

[AC#2.4] We agree that higher curvature in concentration increase at longer closure time has been hypothesized and shown before. But to our knowledge, it hasn't been quantified and neither its dependency on N_2O fluxes (Fig. 3A) nor on chamber performance criteria like the insensitivity towards wind speed and direction (Fig. 3C and 3D) has been explicitly analyzed like in our study. This is clearly a new investigation alongside presenting a novel chamber design. Also, flux underestimation when using linear instead of non-linear regression may certainly be true for GC measurements when only a limited number of samples are available. But the point in our paper is that we on the hand highlight the advantages of QCL measurements (high time resolution, low standard errors of fluxes; *cf*. Figs. 2, 4, 5, 6) and then recommend to reduce chamber closure time to be able to apply linear regression (see modified Fig. 4D for better visualization of low differences between the application of linear

vs. non-linear regression for flux calculation). We also attach here graphs showing the flux difference, i.e. non-linear–linear, plotted against curvature (Fig. R1). Note that during shorter closure time (10 min; blue circles), relatively small (absolute) differences between the two calculation methods occur, although curvature was highly variable and single κ values up to -1000 μg N m^{-3} h^{-2} were found.
We fully agree that the manuscript would benefit from streamlining the aims, results, and messages towards a more concise overview of useful take home conclusions for the reader. See 'Changes to the manuscripts' at [AC#2.1] for the main modifications. However, regarding curvature in this study, it should not be used to define a threshold after which linear over non-linear flux calculation should be used as it is supposed to demonstrate chamber performance criteria as highlighted in Fig. 3C and 3D. Together with the new Fig. 4D and its slope close 1 in the most common flux range between 0 and 200 μg N m^{-2} h^{-1}, we prefer using the argument throughout the manuscript that reducing chamber closure time and applying linear regression for flux calculation is a valid approach.



New Figure 4D: Linear regression analysis of N_2O fluxes <200 μg N m^{-2} h^{-1} with adapted regression from the exponential vs. the linear model.

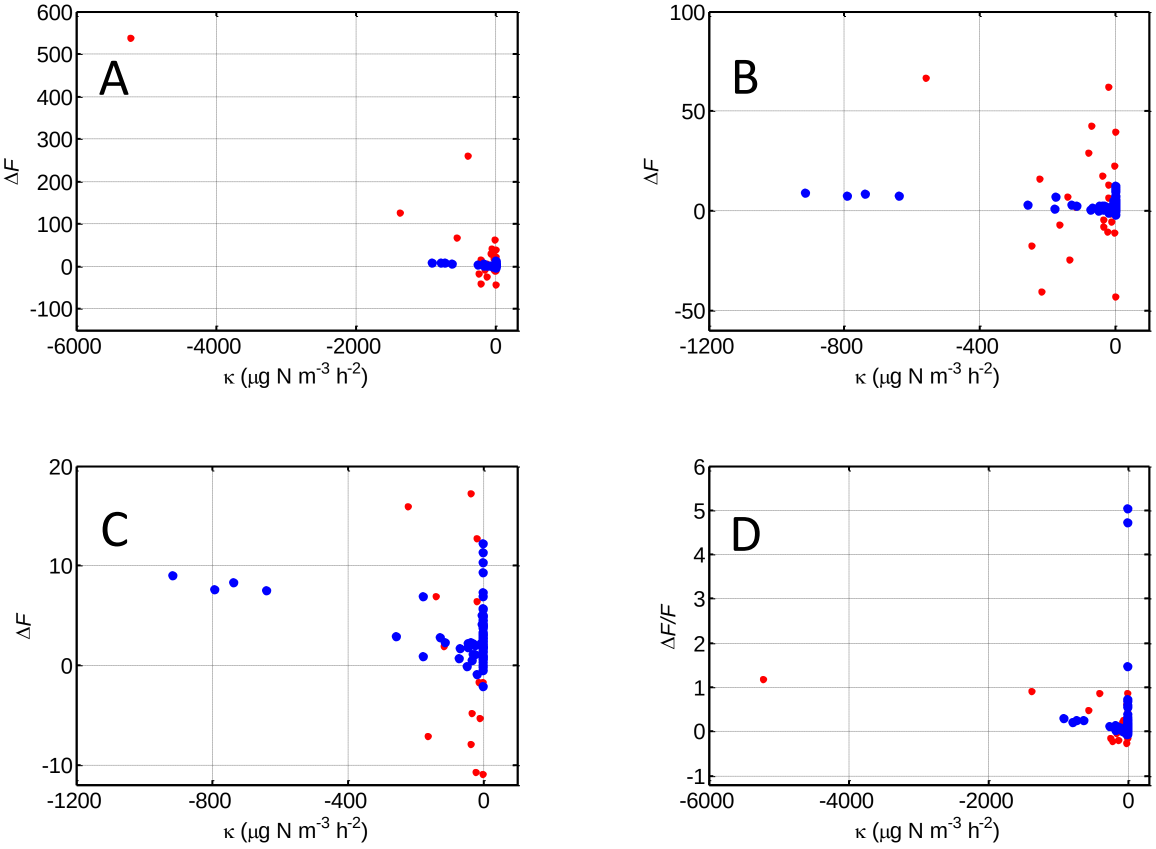


Figure R1 (will not be shown in the manuscript): Panels A, B, and C: Dependency of ΔF, i.e. N_2O fluxes from non-linear regression–linear regression, on κ values for different ranges. Panel D: Dependency of normalized flux difference on κ values.

<u>Changes to the manuscript</u>:
See [AC#2.1] plus revised Fig. 4D and 5.

[R#2.5] Also, it would have been interesting to learn more about the advantages and possible problems in the "novel" chamber design. In general, the paper could be more valuable would it provide more quantitative information and recommend some general tests which each chamber operator should run to ensure adequate data quality. It is also a bit questionable if the paper with such a short piece of data (25 + 6 days) is enough the draw firm conclusions. See more comments below.

[AC#2.5] We highly appreciate this comment and agree that a concise overview of system features will help the reader to get familiar with chamber and instrumentation characteristics. These information including flux detection limit, closure time, number of daily cycles, sampling frequency, etc., are summarized in Table 2. Other more qualitative features are given in Section 2.1. A general test every operator should perform is a (somewhat indirect) density test with a calculation of standard errors of fluxes under different flux magnitudes where the shape of the concentration increase/decrease appears to be valid such as in Fig. 2B at DOY 107.8. The standard errors of these 'good fluxes' should be taken as a reference. Operators should inspect all fluxes that deviate largely from those reference values. However, these absolute numbers predominantly depend on the precision of the analyzers that are used, thus making it difficult to provide specific thresholds of errors after which flux values should generally be discarded. In our study, QCL-based fluxes with a standard error >3 µg N m^{-2} h^{-1} have undergone further double-checking. Only a few of those remained plausible as can be seen in Fig. 4C. Regarding the ‘short piece of data’, we think that the value of a methodological study is not necessarily depending on the length of the observation. In fact moving the same systems to different places instead of measuring longer at one site, increased the range of test conditions, which has added value to the study and made its conclusions more robust. The conditions varied from very low to high fluxes, high external wind speeds (Risø), moderate wind speeds (Braunschweig), lower and higher temperatures. The effects were clear and thus we feel that performing longer tests would not have considerably increased the information with respect to the objectives of the study.

Changes to the manuscript:
Inclusion of Table 2 with quantitative features; we also add some rather qualitative characteristics in Section 2.1 such as the fact that the size of the chamber allows for investigations including plants of considerable size (even up to rape seed; publication in preparation) and that lifting the chamber diagonally away from the soil frame reduces shading for radiation and precipitation, thereby keeping the measurement spots as natural as possible.

Table 2: Features of the chamber-analyzer system used in this study.

	GC* (model: Shimadzu GC-2014)	QCL* (model: Aerodyne Research Inc. mini-QCLAS)
No. of chambers	3	3
Chamber closure time	60 min	60 min 10 min (recommended)
Sampling frequency	every 20 min	0.1 sec (max) 5 sec (recommended)
No. of concentration records per chamber run	4	36000 in 60 min 6000 in 10 min
No. of chamber cycles per day	24 (max)	72 (recommended) 144 (max)
Maximum number of samples	168 (depending on autosampler size)	Limited only by data storage capacity of QCL's computer or external hard drive
Lag time	(~10 sec)	~10 sec
N_2O flux detection limit ($\mu g\ N\ m^{-2}\ h^{-1}$)	13.0	2.6
Mean campaign N_2O flux ($\mu g\ N\ m^{-2}\ h^{-1}$)	BS (pref.[1]): 6.42 Risø (pref.[1]): 77.40	BS (lin.): 7.77 Risø (lin.[2]): 122.95
Mean campaign SE of N_2O fluxes ($\mu g\ N\ m^{-2}\ h^{-1}$)	BS (pref.[1]): 5.98 Risø (pref.[1]): 8.17	BS (lin.): 0.13 Risø (lin.[2]): 0.21
Median campaign N_2O flux ($\mu g\ N\ m^{-2}\ h^{-1}$)	BS (pref.[1]): 5.15 Risø (pref.[1]): 64.80	BS (lin.): 7.38 Risø (lin.[2]): 105.43
Median campaign SE of N_2O fluxes ($\mu g\ N\ m^{-2}\ h^{-1}$)	BS (pref.[1]): 5.04 Risø (pref.[1]): 4.72	BS (lin.): 0.10 Risø (lin.[2]): 0.17
Percentage of flux estimates where HMR could be fitted	BS: 8.5 % Risø: 37.9 %	BS: 100 % Risø: 100 %

GC – Gas chromatograph, QCL – Quantum cascade laser spectrometer, [1]preferred means non-linear HMR model was used if applicable, otherwise robust linear regression was taken, [2]mean/median of DOY 105.5 to 108.5 to make it comparable to GC data set

MORE DETAILED COMMENTS:

[R#2.6] What is the reason for the very bad performance of the GC system? On p5 lines 7-10 it is said that the system was checked against ten samples of ambient air, and only if the CV falls <3%, the data is acceptable. Is this CV limit of 3% really acceptable for a GC system? From Figs. 2a and 7a it seems clear that the GC is not able to resolve concentration increases for fluxes < 20 µgN m-2 h-1. At least to my knowledge, much lower fluxes analyzed with the GC have been reliably reported. I think that a comparison between QCL and GC is not really meaningful if GC is not able to measure these "small" fluxes of N2O. However, Fig. 2a makes me doubt, whether the problem is in the autosampler, and not in the GC detection limit? In some cases the GC can quite perfectly detect a concentration increase of about 12 ppb's similarly to the QCL (second measurement of DOY 339), but during many other closures the data seems arbitrary. What is the reason for that?

[AC#2.6] We appreciate the reviewer's concerns, but do not agree with the premise that a CV below 3 % (it was mainly close to 2 % in our study) at ambient concentrations is a 'very bad performance'. Inter-laboratory comparisons within Germany have shown that GC systems commonly exhibit CVs in this range during routine operations (publication in preparation). Also compare with Parkin et al. (2012), who show a CV of 4.4 % as an example in their Fig. 2. Based on this they calculated a detection limit of about 35 ppb h^{-1} for the linear flux model (see their Fig. 6, corresponds to about 40 µg N h^{-1}) and even higher detection limits for non-linear flux calculation schemes (which however reduce bias). Furthermore, detection limits should be determined based on statistics and not based on single flux measurements (e.g., on DOY 339). The median standard error of GC based flux measurements in our campaigns was SE = 6.5 µg N m^{-2} h^{-1}, thus the detection limit is approximately DL = 2 * SE = 13.0 µg N m^{-2} h^{-1}. See also response to Short Comment 3 for details.

<u>Changes to the manuscript</u>:
None.

[R#2.7] There are conclusions in the paper which are not supported by the presented data. For example: p.1 line 30: "new chamber design reduces the disturbance of the soil". There was nothing on that in the results. What are the possible disturbances? How can you detect that those can be omitted by your system?

[AC#2.7] This statement is simply related to the way the chamber is lifted and dragged away from the collar spot in a 45° angle. In comparison to many other chamber designs, soil and vegetation inside the soil collar are thereby kept under as natural conditions as possible, because the positions of the chambers when they are not operating largely prevent unintended shading and do not disturb throughfall, which is important when the chamber system is supposed to run for a longer time. This information was already given at the end of Section 2.1. We will slightly rephrase the sentence in the Abstract.

<u>Changes to the manuscript</u>:
Sentence modified to: 'Our new chamber design prevents the measurement spot from unintended shading and minimizes disturbance of throughfall, thereby complying with high quality requirements of long-term observation studies and research infrastructures.'

[R#2.8] Or: lines 25-26: GC was found to be a useful method to determine N2O fluxes at longer time scale". Where is the data to prove such a conclusion? There were no budgets

calculated. What happens with the low fluxes, how can you reliably determine budget if you cannot detect the flux?

[AC#2.8] See response to [AC#2.39].

<u>Changes to the manuscript</u>:
See response to [AC#2.39].

[R#2.9] Or p.8 line 31 forward: how do you justify the recommendation of removing the first 2 minutes of data?

[AC#2.9] We agree that the reader must have been puzzled by this sudden recommendation without showing any data. This statement arises from an observation we made in the increase pattern of the concentrations. In ~5 % of the cases, a somewhat irregular pattern as shown in the figure below was observed. It only happened right after setting the chamber onto the soil collar so maybe it was caused pressure fluctuations. We could not identify any correlations to either environmental or internal system conditions when this pattern was found. We therefore think it is a reasonable security procedure to remove the first two minutes (because it never exceeded this initial period) of data from a chamber cycle to ensure natural steady state soil efflux.

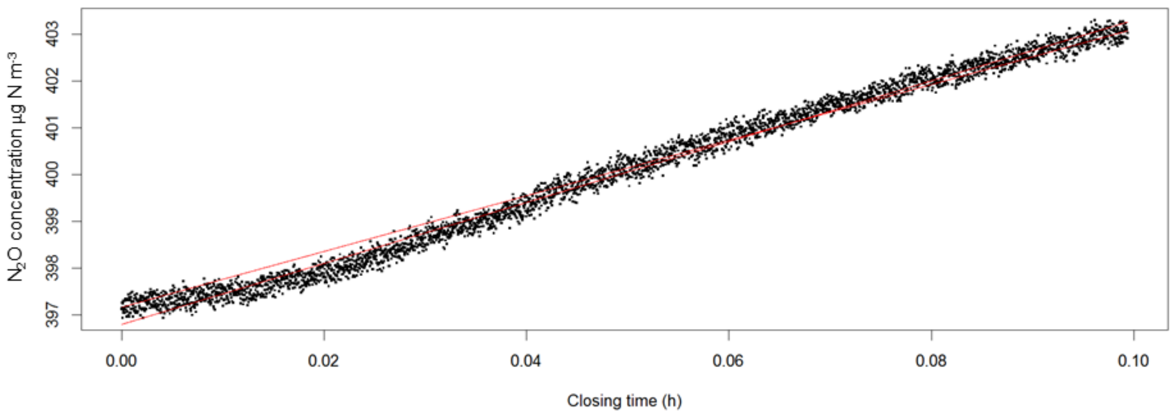


Fig. S1: Example of N_2O concentrations right after chamber closure up to 0.1 h (=6 minutes). Note the small dent at the beginning up to 0.03 h (=108 seconds).

<u>Changes to the manuscript</u>:
Inclusion of Fig. S1 into the supplementary material and reference to the figure on Page 9, Line 1.

[R#2.10] Or "1 to 5 s frequency was sufficient to keep SE on much lower level than in fluxes determined by the GC method" (p. 9). "sufficient" was not defined here.

[AC#2.10] See detailed responses to [AC#2.33] and [AC#2.34].

<u>Changes to the manuscript</u>:
See modified Fig. 5 detailed responses to [AC#2.33] and [AC#2.34].

[R#2.11] How do you justify the limit of using only the first 10 min of the data? Please give some argument based on the data, not just the feeling that this is good.

[AC#2.11] In [AC#2.9] we now point out that the first two minutes of data after chamber closure should be discarded and not used for the regressions. One of the main conclusions of the paper is that applying linear regression to only a short piece of QCL data is fully sufficient to reliably calculate the flux. We show this for periods of three minutes. Chamber operators can decide on their own whether they want to use 3 or 5 or 10 minutes for flux calculation or even extend the initial data that is discarded. Our point is that we clearly found that it does not take a long chamber deployment time to calculate robust fluxes. A period of 10 minutes gives the user enough tolerance for setting its own schedule. We will clarify this in the respective paragraphs of the manuscript.

<u>Changes to the manuscript</u>:
See [AC#2.9] and analyses of fluxes from 3-min linear regressions (Figs. 4, 5, 6, 7). Clarification will be provided in the newly arranged Section 4.2.

[R#2.12] Many of the conclusions of the paper follow those observed in previous studies and are already well known. The one exception is the data in Fig. 8 showing the diurnal variation in N2O flux, as this phenomenon is not much studied. In addition to such data providing information on GHG formation processes, the value of the paper could have been in showing how exactly this chamber system works and what are the special and quantified conditions needed to run the system and to screen the data in order to provide reliable flux data.

[AC#2.12] See responses to [RC#2.4] and [RC#2.5].

<u>Changes to the manuscript</u>:
See responses to [RC#2.4] and [RC#2.5].

[R#2.13] I strongly recommend to separate the results and discussion parts; presently it is difficult to follow the storyline.

[AC#2.13] We agree that splitting results and discussion into two parts may improve the readability of the paper.

<u>Changes to the manuscript</u>:
See [AC#2.1] for the newly structured results and discussion sections.

METHODS

[R#2.14] P.4 L.3 Why "semi-automatic"?

[AC#2.14] The term 'semi-automatic' refers to the operation mode when the system is connected to vial air-sampling, i.e. collecting air in the autosampler. It describes the fact that the sampling is automatic, but the actual gas analysis is done later in the lab. The term is explained in the Introduction, P.2, L.24.

<u>Changes to the manuscript</u>:
None.

[R#2.15] P.4 L.6-7 A volume of L x W x H does not result in 0.33 m3

[AC#2.15] It is true that the interior dimension we have given on Page 4, Line 6 would result in ~0.341 m^{-3}; however, the number 0.33 m^{-3} describes the real conditions as we needed to subtract volume of some items inside the chamber such as the fan, different bigger screws and supporting racks and tubes. We clarify this in the manuscript.

Changes to the manuscript:
Sentence modified to: 'Subtracting inside items such as an axial fan, screws, supporting racks and tubes, the chambers have a headspace volume of 0.33 m^{-3} and covered a surface area of 0.56 m^{-2}.'

Chapter 2.3:

[R#2.16] p.5 L. 26: what are the conditions when HMR function cannot be fitted? ; L27, what is Akaike information criterion, please open this a bit, although there is the reference, the reader should get some kind of an idea just by reading the text here.

[AC#2.16] For clarification, we slightly rephrase this paragraph and provide some additional information as given below.

Changes to the manuscript:
The paragraph on Page 5, Lines 24 ff. has been modified to: 'Briefly, non-linear flux estimation with the HMR method (R Core Team, 2012; HMR package version 0.3.1) was performed when four data points were available and all of the following criteria were met, i.e. (1) the HMR function could be fitted, (2) Akaike information criterion (AIC; Burnham and Anderson, 2004), which is a measure of (relative) model quality, i.e., gives fit quality penalized by the model's degrees of freedom, and can be used to compare the quality of different model fits to the same dataset, was lower for HMR fit than for linear fit, (3) p value of flux calculated using HMR was lower than that from robust linear fit, and (4) the HMR flux was less than four times larger than the robust linear flux. Otherwise, robust linear regression or ordinary linear regression was used when four or three data points were available, respectively.'

[R#2.17] Equations 1-3 and the text related to them: add units.

[AC#2.17] To keep fluent readability, we will add units in a single sentence at the end of Section 2.3.

Changes to the manuscript:
Sentence added: 'Units for concentrations $c(t)$, c_{max}, and c_0 are g m^{-3}, units for k are g m^{-2} s^{-1}, and units for κ are g m^{-3} s^{-2}.'

RESULTS

[R#2.18] P.7 L.7: "low negative k values": care should be taken to express the relations between negative and more negative values. Perhaps more clear to speak about absolute values when comparing these.

[AC#2.18] We agree that this expression may lead to confusion and will refer to absolute values as suggested.

Changes to the manuscript:
Sentence changed to: 'Extremely low absolute κ values between -10^{-4} and -10^{0} – indicating quasi-linearity in $\partial c/\partial t$ – were almost exclusively found under low flux conditions, whereas…'

[R#2.19] P.7. L 10-11 "Near zero fluxes indicate no considerable changes in N2O concentration". Isn't this self-evident without any measurements? Also, what is "considerable change in N2O concentration"? Do you mean significant? If there's no significant increase in concentration, there is no flux, true? Remove or reword the sentence. The whole chapter (Lines 7-14) seem quite self-evident, as the authors hint in the last sentence of the chapter. From Line 15 onwards you say that application of linear model is acceptable in some cases. However, no quantification, i.e. limit below which this is acceptable, is given. I also do not understand how do you draw this conclusion from the results on Lines 7-14.

[AC#2.19] We agree that it would be self-evident when only taking the cited part as given above. In the manuscript, however, the sentence is clearly written in the context of the kappa discussion. Also, if there is no significant (with regard to being lower than the flux detection limit) increase in concentration, i.e. the flux is (close to) zero, which depicts a very important state of the ecosystem and should definitely be taken into account, the corresponding curvature is also marginal. In our opinion, this should at least be stated once. Again, a quantification of kappa hasn't been shown many times before and is used in our paper as a chamber performance criterion (*cf*. Fig. 3C and 3D; [AC#2.4]). We definitely like to stick with the description in Lines 7-14 as it is. Regarding the statement about the acceptance of linear regression at low fluxes, we will include the newly found relationship of Fig. 4D and rephrase the statement accordingly (see below).

<u>Changes to the manuscript</u>:
Sentence starting on Page 7, Line 15 modified to: 'Our results imply that at low to moderately high flux rates <200 µg N m^{-2} h^{-1} (*cf*. Fig. 4D) and/or short chamber closure, the slight non-linearity in concentration change when calculating fluxes is of minor importance and the application of linear models is acceptable, particularly with regard to other commonly observed errors such as those originating from soil disturbance, chamber placement (Christiansen et al., 2011), temperature, pressure and humidity perturbations, etc. (Parkin and Venterea, 2010).'

[R#2.20] P.7. L.23: what is meant with dispersion here?

[AC#2.20] The soil surface basically releases a dispersion plume to the chamber headspace, which eventually is being transported through tubing to the analyzer. If the dispersion of the elevated gas concentration is initially not uniformly mixed with the air inside the tubing, then a lagged concentration increase in the form of exponential analyzer readings (up to a certain point in time) may be observed.

<u>Changes to the manuscript</u>:
Additional information to the sentence starting on Page 7, Line 22: 'These are exponentially increasing N_2O concentrations after chamber closure due to possible dispersion effects leading to biased analyzer readings when the elevated gas concentration is initially not uniformly mixed with the air inside the tubing, placement of…'

[R#2.21] P.7 L. 29-30 "…outside the chamber and inside chamber conditions…" please reword

[AC#2.21] Sentence rephrased.

<u>Changes to the manuscript</u>:
Changed to: 'We also investigated the possible effect of ambient wind speed and direction on concentration build up characteristics (Figure 3C and 3D, respectively) as differences between the turbulence conditions outside the chamber may possibly vary from those conditions inside the chamber under changing wind speed.'

[R#2.22] P.7 L. 30-31 "…coupling of the flux under ambient conditions…" I do not understand this sentence, please reword

[AC#2.22] It means that placing a chamber on soil is a substantial interference with the local wind regime, particularly when wind speed is high and soil pores in the uppermost soil layer may have been ventilated under ambient conditions (i.e. conditions without a chamber) and it thus would take a while until a steady state flux is established. Sentence rephrased.

Changes to the manuscript:
Sentence(s) changed to: 'Theoretically, pores in the uppermost soil layer might be ventilated under high wind speed when no chamber is in place, thus a close coupling of the flux to the atmosphere exists. Consequently, the establishment of a steady state flux may be more postponed under these high wind speed conditions once the chamber is put onto the soil frame.'

[R#2.23] P.7 L.28 → What about the impact of the fan speed on curvature? Soil pores may be ventilated also by the fan (see for example Lai et al. 2012, BG).

[AC#2.23] Lai et al. (2012) found that 13 min of closure were needed before their fluxes (concentration increase) became constant and therefore they extended the deployment period to 30 min. In our study, we found in most cases clear linear or slightly saturating concentration increases right from the beginning. The few cases with 'irregular start patterns' are discussed under [AC#2.9] and in Section 4.1.
Not only fan speed, but also orientation may affect natural efflux from soil. Information on our fan operation is added to Section 2.1.

Changes to the manuscript:
Sentence on Page 4, Line 13 is modified to: 'Chambers were ventilated during measurements using an axial fan, which was mounted to produce a horizontally oriented airflow alongside chamber walls to minimize interference with the natural steady-state soil efflux, but to maximize proper mixing of the chamber headspace as was described in Drösler (2005).' See also [AC#2.9] with regard to the removal of the initial 2-min period.

Chapter 3.2

[R#2.24] Might be good to start with your own results, not with the literature review. For clarity, I strongly recommend separating results and discussion.

[AC#2.24] Results and discussion will be split up.

Changes to the manuscript:
See [AC#2.1] for newly arranged Results and Discussion section.

[R#2.25] P.8 L. 15 onwards: Figure 4B indicates that actually the 3-min/lin method produces higher fluxes than the 60 min/exp method in the lower flux regime (below 200 µg N m-2h-1). When taking into account also the higher fluxes (n=6), the relationship changes so that these 6 data points make a very strong impact, as the authors already discuss. Even though this is the case, the discussion here emphasizes continuously how the linear fluxes are smaller than exponential, although the results shown support this observation only for the few high flux points. This makes me to doubt how one can make generalizations about the validity of these two methods. I am missing discussion which tries to find explanation for the higher

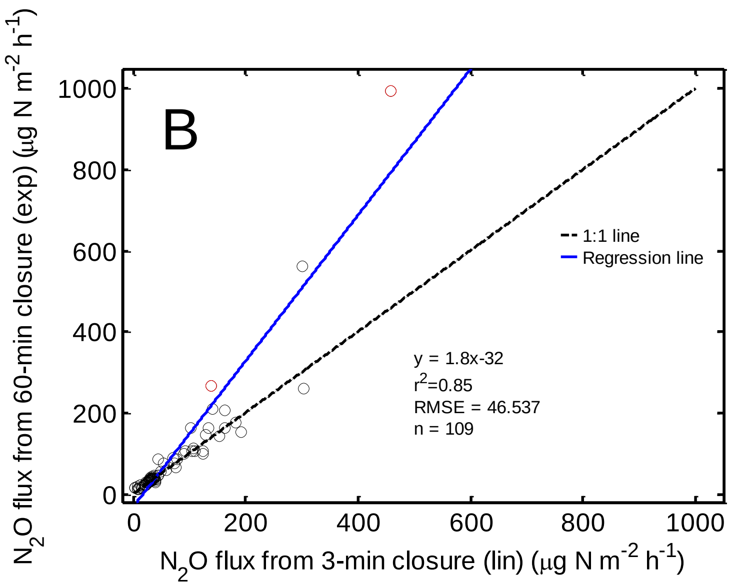
fluxes with 3-min/lin method. Is it so that the data set should be split, or is it far too small to make generalizations?

[AC#2.25] Looking at the newly arranged Fig. 4D (see under [AC#2.4] and [AC#2.44]), there is no indication that 3-min-lin fluxes result in systematically higher values than 60-min-exp fluxes. Only few data points are under the 1:1 line and the slope is 0.989. It is true that we discuss flux underestimation by using linear methods, but that is exactly what is mainly found in the literature (and caused the regression in Fig. 4B). We do not follow the quest of trying to explain why the 3-min-lin method produces higher numbers than the HMR method, because it is just simply not the case, neither in literature nor in the data shown in Fig. 4. We will, however, give a more detailed discussion why HMR-based fluxes are sometimes higher under high flux conditions.

<u>Changes to the manuscript</u>:
Discussion added in Section 4.2. Beside any form of unintended interferences to the 'natural steady-state flux' like for example disturbances through macrofauna, fluctuating pump performance or analyzer malfunctions due to internal re-calibration during chamber deployment, much higher 60-min-based HMR fluxes compared to 3-min-based linear fluxes may be observed when one of two following concentration increase patterns are observed.

1) Slow initial increase of concentrations followed by steeper rise after some minutes. Slope of the linear fit will then be much lower than the one from the HMR fit (lin fit at t_0).
2) Steady linear start of concentration increase followed by sudden relatively sharp bend with lower linear increase afterwards. HMR fit will also have a much steeper slope at t_0 than the linear fit, which will be on top of the data points for the first few minutes.

Red dots in Fig. 4B indicate situations similar to those described under (2) above.



Panel B of Figure 4: Linear regression analysis of N_2O fluxes from the exponential vs. the linear model. Red dots in Fig. 4B indicate situations where a steady linear start of concentration increase was followed by a sudden relatively sharp bend with lower linear increase afterwards.

[R#2.26] Would be also interesting to see, what happens to the SE/RMSE or similar, when apparently low fluxes are calculated with the exponential method. Is there perhaps a risk of

higher error /noisy flux data? Would it be possible to find a flux rate below which the linear method is working more reliably than the exponential?

[AC#2.26] See discussion above. For fluxes <200 µg N m^{-2} h^{-1} there is no significant deviation between the two methods. Even for the few high flux rates, standard errors are still on an acceptable level around 3 µg N m^{-2} h^{-1}.

Changes to the manuscript:
None in particular for this comment, but see also responses [AC#2.4] and [AC#2.25].

[R#2.27] L. 25 I do not understand this sentence

[AC#2.27] What sentence and what is unclear? In the study by Kroon et al. (2008), linear flux rates were underestimated by 60 % compared to those from an exponential function. This was the same order as the flux uncertainty due to temporal variation. Or was the following sentence meant? A simple description of mean and median values of standard errors of fluxes from both the linear and the non-linear model is given.

Changes to the manuscript:
As it is unclear to us what is meant, we stick with the given formulation as we feel the description is very clear.

[R#2.28] P.8 L.31 onwards, continuing on P.9: Here you give important recommendations, but show no data. Also the reference to Section 3.1 is strange, as I do not find anything about the delayed concentration increase in 3.1. This data should be definitely shown if such recommendations are given. You should justify the removal of the first 2 minutes of data: why exactly 2 minutes?

[AC#2.28] See [AC#2.9] for the reason of the removal of the initial 2-min period. The reference to Section 3.1 is indeed strange, because it is a relic from a former version when the kappa analysis looked slightly different than in the submitted version and will be removed.

Changes to the manuscript:
Inclusion of a graph showing delayed concentration increase for the justification to remove the first two minutes of data. Reference to Section 3.1 removed.

[R#2.29] P.8 L3. "…we also compared HMR-based fluxes from QCL? with robust linearly calculated…". How does this vary from that in Fig 7 upper right panel?

[AC#2.29] We assume the reviewer refers to Page 9, Line 3. The difference between the comparison described in Lines 3-10 and Fig. 7 (upper right panel) is that in Fig. 7 linear fluxes are based on 3 minutes of data (as everywhere else in the manuscript), whereas in the described comparison in Lines 3-10 (data not shown), the linear fluxes are – as mentioned in Line 4 – based on the full 60-min cycle of data. To avoid misunderstanding, we add information to the caption of Fig. 7. Please note that in the entire manuscript linear fluxes always refer to 3 minutes of data and HMR fluxes always refer to the full available data set (60 min in Braunschweig and in Risø from DOY 105.5 to DOY 108.5 and 10 min in Risø before DOY 105.5 and after DOY 108.5). This information is explicitly mentioned on Page 5, Lines 30-33.

Changes to the manuscript:

Modified Fig. 7 caption (other changes to Figure 7 are given in [AC#2.46]: ‘Panels A and B: GC vs. QCL-based N_2O fluxes. Panels C and D: Relationships between standard errors (SE) of N_2O fluxes and the respective flux values. Blue markers indicate QCL data, which are all based on the 3-min linear calculation method. Red markers indicate GC data, which are based on the full 60-min data set. Crosses are plotted for GC data when all criteria for flux calculation using the exponential HMR model were met (see text for details), otherwise circles are plotted indicating the usage of a linear model for flux calculation.’

[R#2.30] A general comment/hint: there are many different comparisons with different analyzers, calculation methods and closure times, in which partly different data sets have been used (low and/or high flux) and it is not easy to follow how do all these small experiments differ from each other or support each other. A separate result section with subsections dedicated to each of these questions might help in that. Now there is lot of text (e.g. Chapter 3.2) and it is difficult to follow the argumentation on logics of the text. Also a clearer division into paragraphs would help the reader. And, as already pointed out, division into results and discussion is needed.

[AC#2.30] We fully agree and split Section 3 into two parts as outlined under [AC#2.1].

Changes to the manuscript:
Results and discussion will be split up.

[R#2.31] P.9 L. 3-10: In which figure are these shown? Are the slope of 0.97 (lin fluxes are independent) and the HMR fluxes being 22% higher in conflict with each other? How is it possible that now the linear and HMR based fluxes estimated from 60-min data are almost identical (slope=0.97), while earlier you have stated that linear method underestimates the fluxes?

[AC#2.31] See [AC#2.29]. The analysis described in Lines 3-10 is not shown in a figure as mentioned in Line 4. The whole idea of this paragraph is to make these values, i.e. linear fluxes from 60-min closure comparable to other results presented in literature as for example Kroon et al. (2008) or Forbrich et al. (2010), which have been included in the discussion on Page 8, Line 19 ff.

Changes to the manuscript:
See [AC#2.29].

[R#2.32] P.9 L 11-18: How were the standard errors calculated?

[AC#2.32] In the whole manuscript, we deal with the standard error of the flux, not of individual concentrations. As the flux is a parameter in Equation (1), SE is the standard error of the parameter in the respective regression model (not of the residuals of the concentrations). The regression algorithm used is based on the Levenberg-Marquardt method and was taken from the R package ‘minpack.lm’ (https://cran.r-project.org/web/packages/minpack.lm/minpack.lm.pdf), function ‘nlsLM’. The parameter errors are provided by the algorithm. Further details can be found in:

- https://www.rdocumentation.org/packages/minpack.lm/versions/1.2-0/topics/nlsLM
- Equation 22 in http://people.duke.edu/~hpgavin/ce281/lm.pdf
- Bates, D.M. and Watts, D.G.: Nonlinear Regression Analysis and Its Applications, Wiley, 1988.
- Moré, J.J.: The Levenberg-Marquardt algorithm: implementation and theory, in Lecture Notes in Mathematics 630: Numerical Analysis, G.A. Watson (Ed.), Springer: Berlin, 1978, pp.105-116.

Changes to the manuscript:
Additional information added at the end of Section 2.3: ‘Standard errors in this study were calculated as the parameter errors from the respective regression model with the algorithm being based on the Levenberg-Marquardt method (‘nlsLM function in R package ‘minpack.lm’, R Core Team, 2012).’

[R#2.33] This section and Figure 5: I think that SE is not an appropriate quantity when estimating the “sufficient” frequency of concentration data. By definition, SE is related to (the root square of) the number of observations. It is therefore evident that if you decrease the frequency and the number of data, you increase the SE. In a case where the random error of the concentration measurement during the chamber closure is constant, the SE will anyway increase in case the number of observations decreases, whereas the NRMSE, or the error in the flux will not increase. Therefore a better quantity to estimate the error related to the frequency of concentration data is RMSE (or NRMSE).

[AC#2.33] We sincerely thank the reviewer for this catch and fully agree that reducing sample size automatically leads to an increase in the error estimate when using the method given in [AC#2.32]. However, instead of taking RMSE – which wouldn’t work, because we deal with the SE of a parameter and not of residuals – we normalized the SE by multiplication with $\sqrt{n}$. This is now shown in the newly arranged Fig. 5 (see below). The result is fascinating: mean and median for both 3-min-lin and 60-min-exp fluxes are basically invariant with changing sampling time even up to a frequency of 0.03. Note that only 6 data points are left in that latter frequency class for the 3-min-lin fluxes. We rephrase our conclusions accordingly.

Changes to the manuscript:
Inclusion of newly arranged Fig. 5 and reformulation of the paragraph on Page 9, Lines 11-19: ‘A further intriguing analysis shows that standard errors were found to be invariant on QCL sampling frequency (Figure 5). We simulated different sampling times ranging from one tenth of a second to 25.6 sec, which corresponds to a frequency of 0.0390625 Hz, by excluding the respective intervals from the original 10-Hz dataset. Results show that the median of the standard error of the fluxes remains stable over a wide range of measurement frequencies. At a frequency class of 0.15 and lower (3 boxes on the right-hand side of Fig.5), which corresponds to a sampling time of ~5 sec and higher, lower and upper quartile values begin to deviate and the median changes slightly.’ (can now be found at the end of Section 3.2). Further, we add at the end of Section 4.2: ‘The conclusion we can draw from this finding is that chamber operators – in case an analyzer with a precision like the QCL presented in this study is available – can reduce their sampling time down to 5 seconds without risking an increase of the standard error of the flux, which would still be on a much lower level than those obtained from GC measurements.’

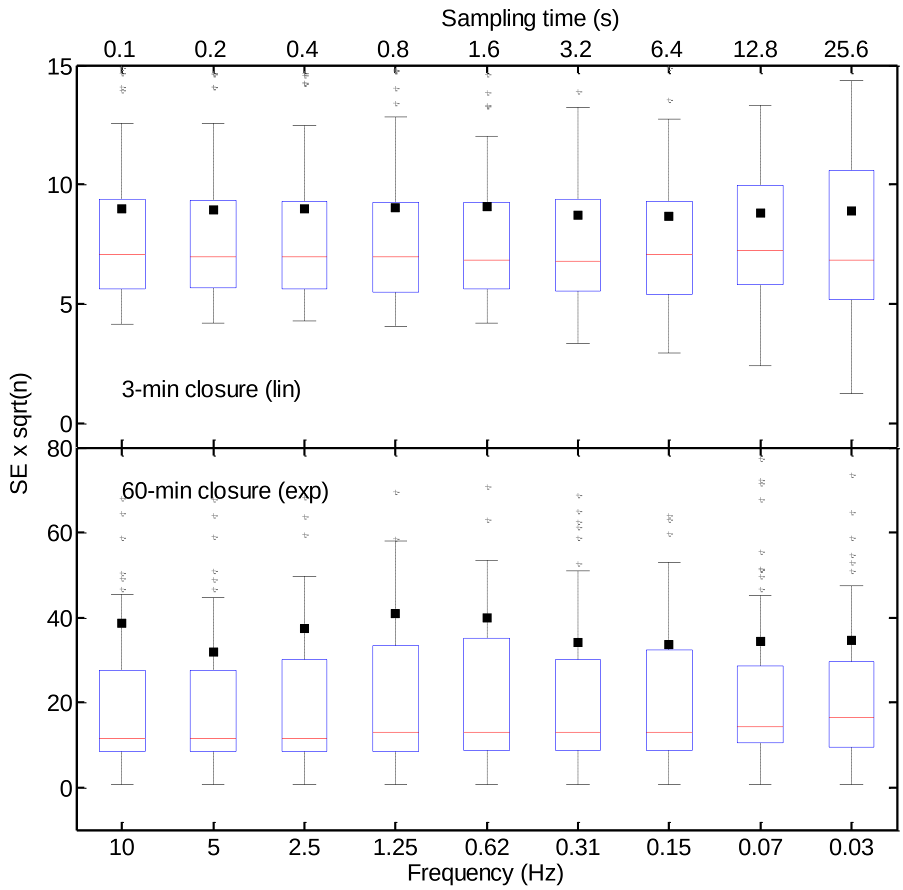


Figure 5. Boxplots of standard errors of N_2O fluxes for different frequency classes and regression models used, i.e. linear regression with 3 minutes of data (upper panel) and the exponential HMR model with 60 minutes of data (lower panel). To avoid a pseudo-dependency on sample size, the standard errors were normalized by multiplication with $\sqrt{n}$. Black squares represent the arithmetic mean, red horizontal lines indicate the median, blue horizontal lines indicate lower and upper quartile values, black whiskers represent the interquartile range and outliers from this range are plotted as grey crosses.

[R#2.34] Your argument "..sampling times between 1 and 5 sec are sufficient to keep SE of fluxes on a much lower level…" is vague. How do you justify that exactly the 1-5 sec limit is sufficient? What means sufficient? How much is "much lower level"? Please quantify and justify this with an appropriate and objective criteria.

[AC#2.34] See [AC#2.33]. The threshold will be set to 5 seconds.

<u>Changes to the manuscript</u>:
See [AC#2.33]. Rephrasing of occurrences where the threshold is given; now set to 5 seconds.

[R#2.35] P.9 L.12: "..to approx.. one minute,…" isn't it approx. half a minute (25.6 sec)?

[AC#2.35] Correct, but the paragraph has been rephrased anyway as mentioned under [AC#2.33].

<u>Changes to the manuscript</u>:
Rephrased as mentioned under [AC#2.33].

Chapter 3.3

[R#2.36] P.9 L. 23 To be exact, QCL fluxes are not explained by GC fluxes. They are correlated with GC fluxes.

[AC#2.36] We agree. The expression would fit better if we would look at a controlling factor (x-axis) of some dependent variable (y-axis). Sentence rephrased.

<u>Changes to the manuscript</u>:
Sentence rephrased to: 'A linear regression revealed no significant relationship between GC and QCL fluxes with a very low coefficient of determination of 0.036 (Figure 7A).' We also rephrased the sentence on Page 9, Lines 31-32 '48 % of the variance in QCL-based fluxes could be explained by fluxes from the GC method.'. It now reads 'A linear regression between GC and QCL fluxes revealed a coefficient of determination of 0.48 (Figure 7B).' as it deals with the same topic as the one above.

[R#2.37] P.10 L4 What does mean "…no dependency on flux value was observed…" Why should SE depend on flux value? Again, how was SE defined?

[AC#2.37] The standard error of a flux may depend on the flux itself for example when at very low fluxes (low concentration increases) the slope fit may be prone to much higher uncertainty than at larger fluxes when an analyzer with moderate or low precision is used. On the other hand high fluxes may show high standard errors for example when an analyzer is not well calibrated or not able to properly resolve certain concentration ranges. This is something we needed to investigate and a dependency that might explain faulty QCL calibration could not be found. See [AC#2.32] for SE calculation method.

<u>Changes to the manuscript</u>:
None.

[R#2.38] P.10 L 14 indicates → indicating

[AC#2.38] No, we don't change that. The word 'indicates' refers to 'The fact that…'. We think changing this to 'indicating' would lead to incorrect grammar (and/or different meaning).

<u>Changes to the manuscript</u>:
None.

[R#2.39] P.10 L 15 forward: "…GC is still useful method to determine soil-atmosphere exchange… at longer time scales.." What is your argument based on? There are no budget calculations in the paper. Averages were reported to be similar, particularly for the small flux regime, but at the same time the fluxes were hardly detected with the GC. Is it correct to say that GC fits for budget studies? How big errors are acceptable in budget studies?

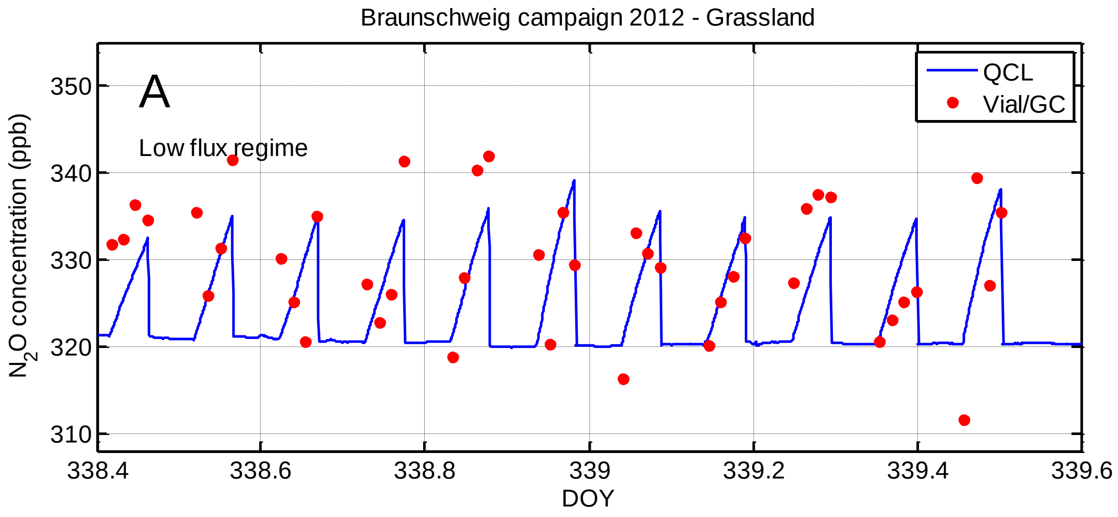
[AC#2.39] We agree that 'at longer time scales' is a bit strong given the fact that we only show a few weeks of data. Nevertheless we need to point out that mean and median of the whole BS campaign where fluxes were on average quite low match pretty well. In Risø – although single flux values were closer to each other – deviation between GC and QCL mainly occurred at high fluxes (Fig. 7B) under the influence of fertilization. But this also indicates that using a GC is still useful for a wide range of periods over an entire year. However, taking into account that the bulk of the annual efflux occurs after management events at a relatively short time scale, usage of a GC-based system will be prone to large uncertainties. Paragraph on Page 10, Lines 15-21 will be adjusted.

Changes to the manuscript:
Page 10, Lines 15-21 adjusted to: 'In summary, our comparison of GC vs. QCL fluxes revealed that despite much higher precision, robustness, and temporal resolution in QCL measurements, GC is still a useful method to determine the average campaign N_2O soil efflux. Although single flux values particularly under low exchange regimes did not match well, campaign means and medians were similar to those obtained by the QCL method. Under high exchange regimes, however, flux patterns matched considerably better, but resulted in larger absolute errors when comparing the campaign average, thereby leading to systematic errors (in our case an underestimation) when using the GC method at high N_2O fluxes for the assessment of N balances. However, given the fact that the bulk of the annual efflux occurs after management events at a relatively short time scale (Flechard et al., 2007; Skiba et al., 2013), usage of a GC-based system will be prone to large uncertainties (cf. Fig.7).'

[R#2.40] FIG 2 add A) and B) to panels and refer to them in the legend

[AC#2.40] Labels were added and were referred to in the text.

Changes to the manuscript:
Modified Figure 2 with modified caption:



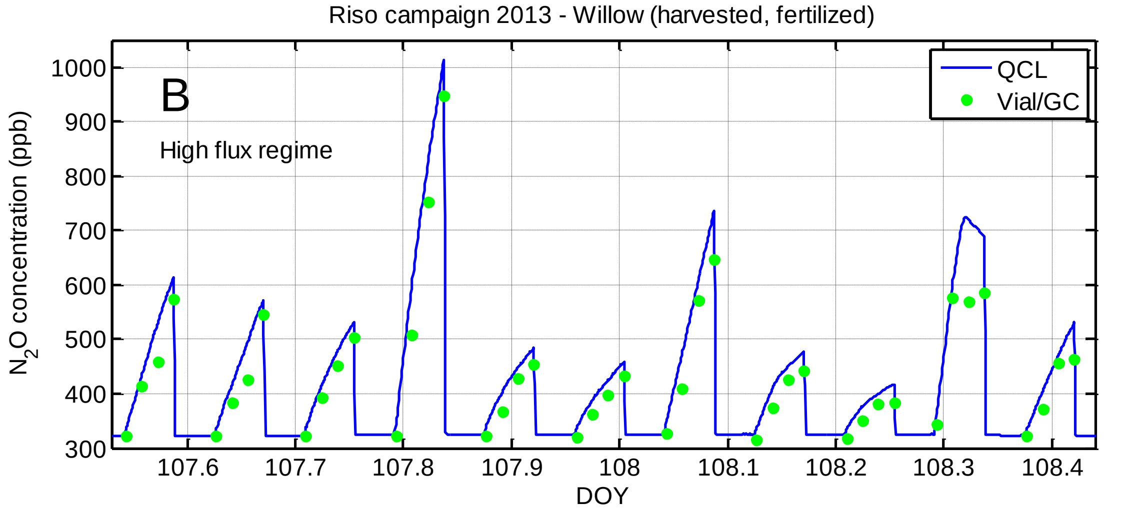


Figure 2. Examples of time series of N_2O chamber concentrations during the Braunschweig (Panel A) and Risø campaign (Panel B). Chambers were periodically closed for 60 minutes. Vials were filled with sample air at t_0, t_{20}, t_{40}, and t_{60}. The QCL system was operated at a sampling frequency of 10 Hz; plotted are 1-min means.

FIG 4

[R#2.41] - Refer to "A, B, C and D" before each legend text parts; "Figure 4. a) Comparison of N2O fluxes… b) Linear regression…"

[AC#2.41] Modified as suggested. Please also notice that Panel D has been changed for a better visualization of lower fluxes and its regression as a result to comment [R#2.26].

<u>Changes to the manuscript</u>:
Modified Figure 4 caption reads:

Figure 4. Panel A: Comparison of N_2O fluxes measured on a harvested willow field during the Risø campaign by the QCL system based on a linear model using only the first three minutes of data after chamber closure (filled blue circles) and an exponential model (open red circles) (see text) using either the full 60 minutes (DOY 105.5 to DOY 108.5) or the full 10 minutes of data (DOY <105.5 and DOY >108.5). Panel B: Linear regression analysis of N_2O fluxes from

the exponential vs. the linear model. Panel C: Standard errors of fluxes shown in Panel A. Panel D: Same as Panel B, but only for fluxes <200 μg N m^{-2} h^{-1} with adapted regression.

[R#2.42] - The legend text should be shortened. Remove phrases such as "Also shown is…" Figure 4b is showing 60-min fluxes plotted against 3 min fluxes.

[AC#2.42] Modified as suggested.

Changes to the manuscript:
See [AC#2.41].

[R#2.43] - Please remove the text "Riso campaign 2013, Willow…" from the top of each separate panel and add that part of information into the legend text which is not already there.

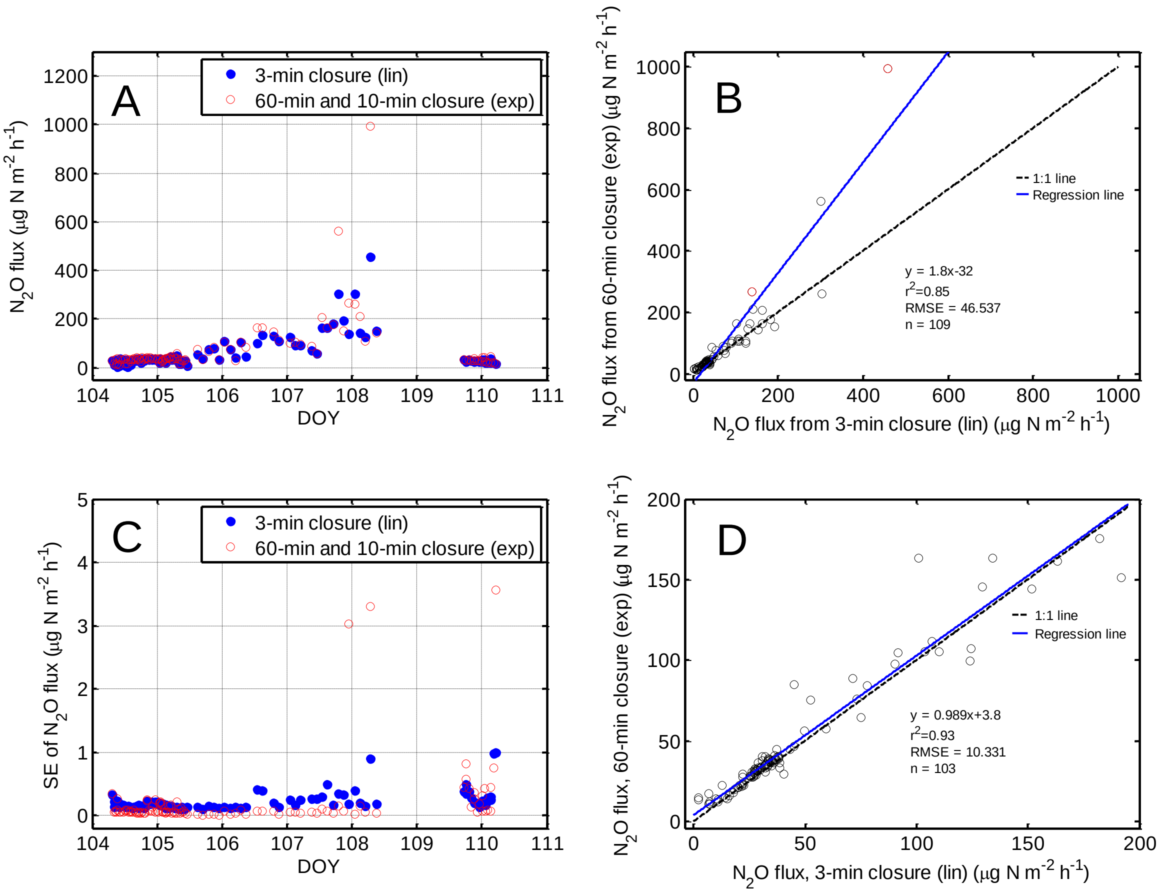
[AC#2.43] Modified as suggested.

Changes to the manuscript:
See [AC#2.41].

[R#2.44] - Panel B: indicate what are the two lines in the figure? Why are they not direct lines, but show some tiny variation?

[AC#2.44] The dashed black line is the 1:1 line and the blue solid line is the linear regression fit line. Line labels have been added to Panel B and D. They probably didn't appear as straight lines in the former version, because of the graphical resolution of the figure. This has now been improved.

Changes to the manuscript:
Modified Figure 4 (for caption see [AC#2.41]):



[R#2.45] - In Fig. 4 and Fig 5, what is the reason to compare 3-min linear and 60-min exponential fluxes? Why not to compare separately the lin vs exp AND 3-min vs 60 min closure times?

[AC#2.45] In Figures 4 and 5 we explicitly deal with high-resolution measurements of the QCL, which gives us the opportunity to use robust and precise data to compare the application of a linear model simulating short closure time (here 3 minutes) with a non-linear model representing long closure time (here 60 minutes). One of the main aims of the paper is to investigate whether it is suitable to reduce chamber closure time and to apply simple linear regression to calculate the N_2O flux. Through Figure 4 (particularly Panels A and D) and Figure R1 (see above), we demonstrate that the bulk of the flux differences between linear and non-linear models is in an acceptable range, keeping in mind that shorter closure times also have the advantage that plants and soil in the measurement plots are less affected in the long term. Hence, comparing fluxes from a linear model using 3 minutes of data with fluxes from a non-linear model using 60 minutes of data clearly supports our specific aim of the study, while for example applying a linear model to a 60-min data set that reveals obvious curvature (see κ values in Figure 3) or applying a non-linear model to only 3 minutes of data that are quasi linear would not give any further insights when investigating whether reducing chamber closure is acceptable or not.

Changes to the manuscript:
None.

FIG 7
[R#2.46] - Please use A-D notations, not left/right/upper/lower explanations

[AC#2.46] We added Labels A to D and included them in the figure caption to keep it consistent with Figure 4.

<u>Changes to the manuscript</u>:
Modified Figure 7 with modified caption:

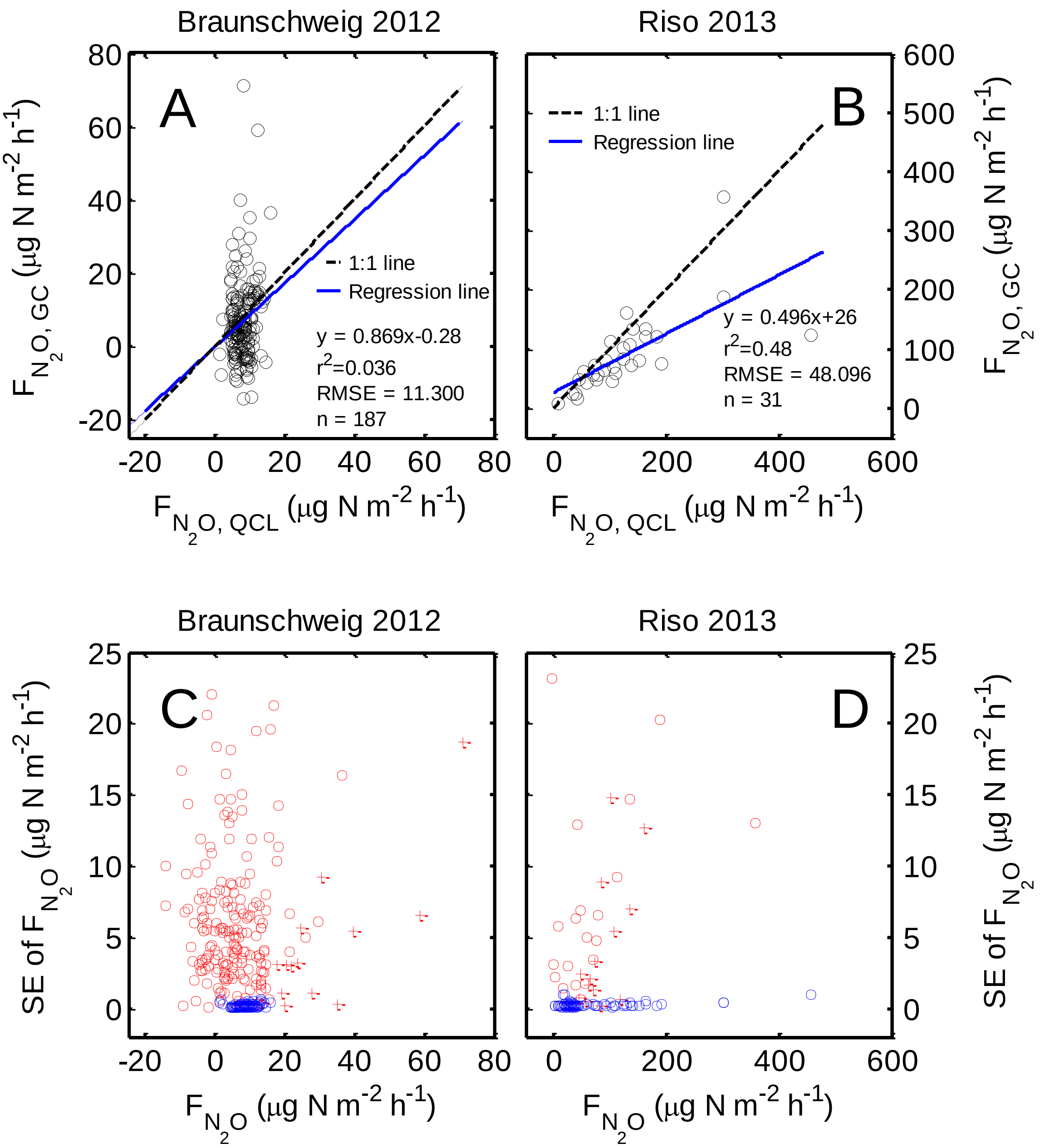


Figure 7. Panels A and B: GC vs. QCL-based N_2O fluxes. Panels C and D: Relationships between standard errors (SE) of N_2O fluxes and the respective flux values. Blue markers indicate QCL data, which are all based on the 3-min linear calculation method. Red markers indicate GC data, which are based on the full 60-min data set. Crosses are plotted for GC data when all criteria for flux calculation using the exponential HMR model were met (see text for details), otherwise circles are plotted indicating the usage of a linear model for flux calculation.

[R#2.47] - Upper panel: define the lines

[AC#2.47] Line labels added.

Changes to the manuscript:
See [AC#2.46].

FIG 8
[R#2.48] - An interesting Figure. What does the error bar denote? Is the diurnal variation significant? Why is the hourly data not shown? Are the points averages from many hours? What was actually the frequency of measurements in both campaigns, I did not find it, but I assumed you measured hourly?

[AC#2.48] The error bar indicates the standard error of the mean from all flux values in each bin. Each bin contains fluxes from 3-hour periods, i.e. from 00:00 to 03:00, 03:00 to 06:00, 06:00 to 09:00 and so on. The mean values in Figure 8 are plotted in the center of each bin. Fluxes were binned due to irregular starting times of new chamber cycles. In general, a new chamber cycle could be started each full hour, but to get a more robust diurnal pattern, we decided to bin data in the above-mentioned 3-hour containers. While the diurnal variation of N_2O fluxes from the Risø campaign is significant (*p*-value = 0.0059), the diurnal variation found during the Braunschweig campaign is not as the difference between mean minimum and maximum values is lower than the upper flux detection limit of ~2.6 μg N m^{-2} s^{-1} (*cf.* response to SC3).

Changes to the manuscript:
Information on data handling and significance of the diurnal variation is added to Section 3.4.

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