Response to interactive comment (SC1) on ‘Gas chromatography vs. quantum cascade laser-based N_2O flux measurements using a novel chamber design’

[SC] The manuscript “Gas chromatography vs. quantum cascade laser-based N2O flux measurements using a novel chamber design” by C. Brümmer et al,. is a methodical and well written study. The results show that modern quantum cascade lasers are able to out-perform aging GC methodology when it comes to N2O flux measurements from soils. The paper highlights some strengths of the new methodology and I believe that it should be published.

However, I do have some concerns with the cited literature. This is not the first study of its kind and the novelty of the setup could be questioned. An almost identical experiment was carried out in:

Cowan, N. J., Famulari, D., Levy, P. E., Anderson, M., Bell, M. J., Rees, R. M., Reay, D. S. and Skiba, U. M.: An improved method for measuring soil N2O fluxes using a quantum cascade laser with a dynamic chamber, Eur. J. Soil Sci., 65(5), 643–652, doi:10.1111/ejss.12168, 2014.

Both of these studies conclude very similar points and I believe that this paper should be cited in both the introduction and discussion part of the manuscript before publication.

[AC] We highly appreciate the advice to cite the Cowan et al. (2014) paper, which in fact deals with very similar points and we fully agree to mention it in both introduction and discussion. We will add an extra line on Page 3, Line 10 stressing that first examples of high-resolution chamber measurements have been successfully carried out by Cowan et al. (2014a; 2014b) as well as by other teams like Hensen et al. (2006), Laville et al. (2011), Savage et al. (2014) or Sakabe et al. (2015). Further, we will compare findings of standard error calculation from our manuscript to the Cowan et al. (2014) paper in the discussion section (Page 8, Line 28). For differences in the uncertainty estimation between the two studies, please see respective comment below.

Regarding the comment ‘…the novelty of the setup could be questioned.’, we like to clarify that at no point in our manuscript we claim that the measurement setup or any of the flux calculation methodologies have not been shown elsewhere before. The term ‘novelty’ (or ‘novel’) exclusively refers to the chamber design, which has so far not been presented in peer-reviewed literature. The aim of our paper is to highlight differences between GC and QCL setup using a ‘novel’ chamber system and to determine associated differences when applying linear vs. non-linear models to these datasets.

[SC] Further examples of this closed loop chamber methodology include:

Hensen, A., Groot, T.T., van den Bulk, W.C.M., Vermeulen, A.T., Olesen, J.E. & Schelde, K. 2006. Dairy farm CH4 and N2O emissions, from one square metre to the full farm scale. Agriculture, Ecosystems & Environment, 112, 146-152.
Laville, P., Lehuger, S., Loubet, B., Chaumartin, F. & Cellier, P. 2011. Effect of management, climate and soil conditions on N2O and NO emissions from an arable crop rotation using high temporal resolution measurements. Agricultural & Forest Meteorology, 151, 228-240.

I believe it would improve the manuscript to mention some of these papers, at least in the introduction section, if not also the discussion when comparing results.

[AC] We agree that it would be helpful to refer to some earlier studies where high-resolution measurements were used. We will include Hensen et al. (2006) and Laville et al. (2011) in the introduction section (see comment above).

[SC] Another reference that is very relevant when investigating negative fluxes/instrumental detection limits is:

Cowan, N. J., Famulari, D., Levy, P. E., Anderson, M., Reay, D. S. and Skiba, U. M.: Investigating uptake of N2O in agricultural soils using a high-precision dynamic chamber method, Atmospheric Meas. Tech., 7(12), 4455–4462, doi:10.5194/amt-7-4455-2014, 2014.

[AC] This is a very good hint and an excellent paper regarding the discussion about N_2O uptake by soils. We will add a few lines on Page 11, Line 3 highlighting their observation of approx. 10 % negative fluxes with only 4 out of 115 measured flux rates being above the limit of detection (LOD) and will compare these findings to our results.
Regarding the detection limit of our QCL and GC setups, LOD could be estimated using our campaign data assuming stationary conditions during the low flux campaign in Braunschweig. Taking the whole campaign into account, the calculated standard deviations were 2.5 µg m^{-2} h^{-1} and 7.5 µg m^{-2} h^{-1} for QCL and GC measurements, respectively. Thus, the resulting 2-σ uncertainty range for QCL was 5.0 µg m^{-2} h^{-1} and for GC 15.0 µg m^{-2} h^{-1}. If only the first quarter of the Braunschweig campaign data are taken, i.e. a period where environmental conditions were less variable than over the whole campaign, the calculated standard deviations were 1.3 µg m^{-2} h^{-1} and 6.5 µg m^{-2} h^{-1} for QCL and GC measurements, respectively. Thus, the resulting 2-σ uncertainty range for QCL was 2.6 µg m^{-2} h^{-1} and for GC 13.0 µg m^{-2} h^{-1}. These estimates can be regarded as an upper flux detection limit. A supposable lower flux detection limit solely depends on the sensitivity of the analyzers. Precision of the QCL is 0.03 and 0.01 ppb when averaging over 1 and 60 s, respectively. We will add a few lines at the end of chapter 2.2 on Page 5, Line 20 to provide this information.

[SC] The uncertainty cited in the manuscript for the fluxes measured using the QCL chamber method in the abstract was ~0.1%; however, how can the authors be so sure of chamber volume? The uncertainty in flux is not the same as uncertainty in dc/dt. In the flux equation the uncertainty in the volume of the chamber is relative to the height measurement, which on a uniform flat surface is negligible, but on a soil surface is more difficult to measure. Surely this uncertainty is at least 1% if not an order of magnitude greater, and so when propagated with uncertainty in dc/dt the flux uncertainty must also rise. See above references for examples.

[AC] This must be a misunderstanding and will be clarified in the manuscript. We do not investigate uncertainty that is directly related to observational errors or any kind of measurement or setup issues, e.g. changes in flow rate, temperature sensitivity of the QCL, pump performance, changes in chamber volume due to rough soil surfaces or plants in the chamber, etc. As it is one of the main aims of the paper, we just simply look at a comparison of standard errors associated with the flux calculation method for GC and QCL. This approach ensures quantitative comparability between linear vs. non-linear regression models on the one hand and GC and QCL on the other hand. (Surely the regression uncertainties are indirectly influenced by observational errors). Further, if we would include the error of the effective chamber height, the uncertainty for both (GC and QCL) would be affected in the same way. We appreciate the comment that the reader might be misled. We will add a sentence at the end of Section 2.3, Page 6, Line 17 for clarification.

[SC] There is no mention of a lag time between the instrument and chamber. It is suggested the first two minutes of measurement data are removed to avoid artifacts from soil disturbance. Does this also cover the time it takes for the gas to circulate fully between chamber to instrument and back to chamber again. If not then this “dead time” should be extended until the closed loop completes one full circulation to ensure mixing of the air within the tubing and chamber.

[AC] Good point. It wasn't mentioned that the 'dead time' is already included in our suggestion to remove the first two minutes of data to avoid artifacts from soil disturbance. 'Dead time' within the QCL setup was ~10 s given a tube length of 10 m, a flow rate of 1 L min^{-1}, and an inner diameter of 4.6 mm (note that ID of the sample tube within the QCL setup was different from ID of the sample tube within the GC setup; cf. Page 4, Line 16). We will add 'In our case, the 'dead time' of the QCL measurement system, i.e. the time that passed between an air sample leaving the chamber and entering the analyzer, was ~10 s given a tube length of 10 m, a flow rate of 1 L min^{-1}, and an inner diameter of 4.6 mm.' on Page 9, Line 2.

[SC] Uncertainties in comparisons of fluxes seem relatively low. Have you used standard errors in these comparisons? Would 95 % confidence intervals not be more relevant when comparing measurements known to have such large spatial and temporal variability?

[AC] Yes, we used standard errors of the regression model as mentioned several times in the text and as shown in Figures 4 to 7. Although in general N_2O flux measurements are known to feature large spatial and temporal variability, we compare in our study fluxes measured simultaneously in the same chamber. The aim is a quantitative comparison of different flux calculation methods and not the investigation of temporal or spatial heterogeneities. Therefore we explicitly want to point out the statistical error associated with the linear or non-linear regression model. For sparse GC sample data the standard error of the regression is more meaningful. A rough estimation of the 95 % confidence intervals is two times the standard error. Any other more complex statistics do not make much sense for only 4 data points.

[SC] A mobile field scale experiment was carried out using a similar methodology. It may not fit with this specific manuscript, but I include it for the author's interest.

Cowan, N. J., Norman, P., Famulari, D., Levy, P. E., Reay, D. S. and Skiba, U. M.: Spatial variability and hotspots of soil N2O fluxes from intensively grazed grassland, Biogeosciences, 12(5), 1585–1596, doi:10.5194/bg-12-1585-2015, 2015.

[AC] Thank you for mentioning this paper. However, as the same analytical devices are used as in Cowan et al. (2014a; 2014b) and it mainly deals with spatial variability, we will not include it in our manuscript.

<u>References</u>:

Sakabe, A., Kosugi, Y., Takahashi, K., Itoh, M., Kanazawa, A., Makita, N., Ataka, M.: One year of continuous measurements of soil CH_4 and CO_2 fluxes in a Japanese cypress forest: Temporal and spatial variations associated with Asian monsoon rainfall, J. Geophys. Res. – Biogeosciences, 120(4), 585–599, 2015.

Savage, K., Phillips, R., and Davidson, E.: High temporal frequency measurements of greenhouse gas emissions from soils, Biogeosciences, 11, 2709–2720, 2014.