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Atmospheric Measurement Techniques Discussions

Interactive comment on "A novel injection technique: using a field-based quantum cascade laser for the analysis of gas samples derived from static chambers" *by* Anne R. Wecking et al.

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The study "A novel injection technique: using a field-based quantum cascade laser for the analysis of gas samples derived from static chambers" by Wecking et al. describes an experiment in which samples of N2O measured using the static chamber method are then analysed on a QCL and GC instrument for comparison. The study is well written and presented, but there are some over simplifications that should be addressed, in how the complexity of the system is described and the way the data is handled in the study. I advise quite a significant re-write focussing on the actual focus of the study, which is how the instruments compare.

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Discussion paper

* We like to thank Referee #1 for her/his extensive comments. Our response to these comments is indicated with an asterix (*) at the beginning and the end:

For clarification, the interest of our study was not only to compare two different analytic devices but to further the suitability of a field-based quantum cascade laser (QCL) and associated sampling/measurement procedures to measure chamber derived samples of nitrous oxide (N2O). Of particular interest for us was to develop a technique that is applicable and easy to conduct in field environments, and that can be used in conjunction with eddy covariance (EC). Furthermore, we compared resource efficiency of the whole operation which is critical for decisions that will be made by researchers when considering actual costs of different research approaches and analytical devices. *

My first comment is that this study is essentially a comparison of concentrations measured using two instruments. This work could have been carried out with gas standards without the need for any chamber measurements. The real point of the study here is whether gas injected through a QCL following this setup is a valid way to measure gas concentrations. If so, then fluxes calculated from the sample will compare well regardless.

* Using gas standards would have allowed for a comparison between GC and QCL. However, this would not have included the whole sampling/analysis approach. Initial lab-based comparisons of QCL to other analytic devices have already been provided in the literature and shown that the suitability of a QCL device to quantify N2O standards is without doubt (Zellweger et al. (2019); Rosenstock et al. (2013)). We were, therefore, highly interested in whether the lab-based accuracy and precision of a QCL could also be achieved in a field-based “mini-lab” – and under realistic sampling procedures that included N2O sampling from static chambers, sample separation to inject identical sample volumes and concentrations into either of the two analysers, sample storage, sample and data processing. *

The novelty of the method is that the authors get past the inability of the QCL to mea-

sure actual concentrations of a sample by using standards to integrate peak areas, similar to the way the GC reports measurements, thus reducing the sample volume required.

* Agreed, this is one advantage of using the QCL in the field setting. Further benefits were 1) the process of getting to the point of receiving these peak area data (e.g. developing sampling procedures and the injection set-up in a field environment); and 2) to test whether the QCL could reliably process samples of low, medium and high N2O concentration (that were derived from static chambers in a real scenario including method specific uncertainties). *

I'd like to see some examples of the QCL concentration output at 10Hz while measuring low, medium and high concentrations of N2O in the standards to observe the shape of the peaks that are integrated. I think the presentation of the integration of these peaks far outweighs the flux work. By the authors own numbers, I believe a flush rate of the cell is greater than 1 second, so I'd be interested to see how the laser reports concentrations while measuring at 10 Hz, and what the noise looks like.

* L. 150: All our injections were conducted at a 10 Hz frequency, which means that all QCL concentration data reported in the manuscript were consistently determined at this particular frequency. Examples of how low to high N2O concentrations were reported by the QCL were provided in the supplementary material of the work, i.e. Figure S1 a) and b). Raw data can also be found in the data repository associated with the manuscript. However, we are in line with the Referee that including a raw 10 Hz time series of injection peaks might be a useful addition to the manuscript/the supplementary material and will be considered. *

As this is the real novelty in the manuscript, much more emphasis should be on the outputs of the instrument itself, and less on the flux measurements.

* The focus of our manuscript is on the concentration output of the QCL and GC analysers as represented by the majority of section 2 and section 3.2, 3.3, 3.4. Calculating

the resulting N2O fluxes was a necessary exercise in addition to the emphasis on N2O concentrations. We like to point the Referee to the objective of the bioequivalence analysis applied to both N2O concentration and flux data (see Section 3.4.1). Determining the suitability of a measurement device for a particular purpose has to be evaluated. However, a simple comparison of concentration data based on linear regression does not satisfy this purpose. Consequently, we were led by the intention to not only assess the degree to which the two methods (GC and QCL) would agree (orthogonal regression, Bland Altman). But to further determine whether N2O concentration and flux data, in fact, were statistically speaking "the same" (i.e. bioequivalent). Receiving reliable N2O fluxes when using the QCL injection technique was the ultimate goal of our study. We like to acknowledge that applying statistical tests like bioequivalence describes a concept most N2O flux researchers might be unfamiliar with. However, to assess the comparability of data derived from two different methods these tests are essential as was our evaluation of N2O flux data to discuss the relevance of our results in a real world scenario. *

I agree with many of the points the authors make, and I feel the study has value as a reference for people who may want to use the method presented in future studies; however, I don't see it being popular. Most Eddy C sites will value the collection of uninterrupted data over the ability to run the instrument as a makeshift GC.

* It is good that we have general agreement about the value of the work. One of the key purposes of this work was to provide information for operators to make informed decisions about how they might operate their eddy covariance sites and consider trade-offs of data loss for short periods of time. How popular this approach becomes remains to be seen but was not really a focus of the current study. Thus, even if not prominent at present, we are convinced that using a QCL in the most cost- and time-efficient way to suit multiple research purposes provides a promising future application. *

Choosing manual injections over the more common auto injection systems used by the GC also introduce a bit of a time cost and add room for human error.

* This is correct and this human error is captured within the error reported in the paper. Sample loops could be included in our proposed setup to further reduce the error, if desired. The time taken for one injection was less than 10 seconds and accounted for in our time analysis (Table S2) which shows overall a large time saving of, in our case, multiple days (considering transport of samples to the lab and analysis time, see Table 1). We could show that at a given flow rate of 1 L min-1 the delay time between single injections of 1 mL sample volumes was generally short (5 to 8 sec). The return of the N2O concentration in the QCL sample cell to basically zero (= background level of the N2 carrier gas) was straight forward when using visual examination of the real-time curve in TDL-Wintel. Suitable delay times were, thus, easily adjustable if the sample concentration would have exceeded 20 ppm N2O (line 312). In our study, field samples did not exceed a N2O concentration greater 10 ppm. This supported the applicability of our approach. It is to consider that using an auto-injection system would have to account for different delay times after sample injection and, therefore, would likely include longer sample delay and overall sample analysis times. *

In terms of running costs, a QCL requires an air conditioned site with mains power to operate in EC mode, which is essentially a lab in itself. This system is expensive to run in terms of power and replacement of parts (pump maintenance, laser lifetime of approx. 7 years etc.). The author's point is that this system is already up and running, so the additional ability to do chamber measurements doesn't add cost.

* We agree. *

This is true, and although it's also true to say you don't need to take samples off-site, you will still likely have to travel some distance as plot experiments really shouldn't be setup within the footprint range of an eddy C system (ideally more than 1 km away due to the exponential rise in fluxes observed after N fertiliser application and the potential for advection effects which nullify the assumptions made by the eddy c method). The air conditioned site thus becomes a mini-lab, in some cases closer to a field site where chamber measurements are made. Some discussion on the limitations of use is re-

quired, as the study seems to suggest N fertiliser plots could be setup next to an EC tower which would be very unwise unless the plots were to mimic the exact conditions of the field of interest to the EC measurements.

* We positioned and aligned all static chamber measurements with overall site management conditions and associated research goals. Chambers were placed outside the immediate footprint of the eddy flux tower as determined by Wall et al. (2020). This meant that the chamber trial area was about 100 m (walking distance from the tower) to avoid the Referee′s concerns. Our previous work (Wecking et al., 2020), provided an example of how to conduct chamber measurements near to an EC tower. We demonstrated that the flux signal originating from the chamber plots was not strong enough to impact our EC measurements. To address the reviewers concern, we are going to add in a sentence recommending that care has to be taken when locating chambers near an EC tower to avoid cross-contamination. *

In terms of the flux experiment, I find the application of fertilisers to be far larger than is common practice. 300 Kg N ha-1 is very large, and 600 and 900 is beyond realistic. In these cases I assume some kind of saturation of N in the soil and N2O in the chamber during a 45 minute enclosure which would also affect the magnitude of the fluxes observed. In any case, the fluxes reported are of little use other than to compare the instruments.

* Applications rates of ammonium nitrate fertiliser were chosen intentionally to trigger different low, medium and high N2O fluxes (line 18, line 95 f.). In this study, we did not intend to mimic realistic fertiliser application scenarios. Having said this, however, the N deposited in a single urine patch of dairy cattle (i.e. a major source of N2O emissions) are comparable to N loading commonly observed at 600 kg N2O-N ha-1 (Selbie et al., 2015, p. 238 and references therein). *

In this case, there is no reason to take means from plots. Due to the log-normal nature of N2O emissions, the (arithmetically derived) mean values reported from a small n size

(less than 25 chambers) is going to be fairly uncertain. Without accounting for the log-normal nature of these fluxes in both time and space, any uncertainties in cumulative flux estimates are not statistically meaningful.

* The study's intention was not to discuss the effect of different applications rates of ammonium nitrate fertiliser on N2O fluxes. Treatment effects were only of secondary interest. Different rates of fertiliser were only applied to result in a wide range of N2O fluxes (low to high), and thereby to allow for a methodological comparison of GC and QCL data. *

I return to my original point that this comparison is of gas concentrations and not of plots. The fluxes derived from both instruments are valuable on a 1:1 basis as presented in Figs 3a and 3b. That's all the paper requires and it's a great result in terms of showing the system works as well as the GC.

* Our study is a comparison of two methods, GC and QCL. Validation of this comparison is retrieved from different statistical tests (orthogonal regression, Bland Altman and bioequivalence) that enabled us to use a QCL for the purpose of analysing static chamber derived N2O samples under real field conditions. N2O concentration and flux data were determined and used to verify this objective. *

In conclusion, I think the work presented is a well carried out and valid study, but it needs a bit of a re-write to focus on the actual message, and not get distracted by flux comparisons and methods of comparing significance.

* Perhaps this is where we disagree, we are focussed on comparing the whole process required to quantify fluxes from a chamber trial using a field-based QCL rather than a laboratory based GC. Even a field based GC would give a very different outcome because of the longer time needed for separating and analysing samples. Our study will provide a broader assessment for researchers considering using QCLs in the field including quantifying precision and accuracy of the approach coupled to time and resource needs. In addition, testing the suitability of a new method (QCL) compared with

a standard method (GC) requires suitable statistical tests that do not only compare the significance but let us evaluate the agreement and bioequivalence of these methods (line 198, we also recommend reading the references quoted in Section 2.5 – Bland and Altman, 1986 and Giavarina, 2015 – that provide powerful insights into the warrant of applying these statistical tests to both N2O concentrations and fluxes in our study). *

Yours sincerely, A. Wecking in the name of all associated Co-Authors Hamilton, New Zealand – 30-06-2020

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