Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2020-197-AC2, 2020

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.

Anne R. Wecking et al.

arw@wecking-do.de

Received and published: 6 August 2020

We, first of all, like to thank Referee #2. In fact, we were delighted to receive a thoroughly reviewed and thought-through feedback, which is contributing to the quality of our manuscript. Our response to the comments made by Referee #2 is indicated with an Asterix (*) at the beginning and the end of each comment:

In their submission "A novel injection technique: using a field-based quantum cascade laser for the analysis of gas samples derived from static chambers" Wecking et al. report on their experiences with a sampling strategy that analyses both eddy covariance data and chamber measurements on-site sing the same instrument. They calculated

Printer-friendly version

Discussion paper

fluxes of N2O from concentrations measured by GC (conventional) and directly injected into a QCL (novel) in three different fertilisation treatments (+ control). Both concentrations and fluxes were analysed with a variety of statistical methods and found to be practically equivalent, with the exception of near-zero flux conditions. I have thoroughly enjoyed reviewing this manuscript. It is well-structured, well-written, and the figures and tables are polished to a degree that is rarely seen at the preprint stage. It fits the scope of AMT well and should be of value for the community after some clarifications.

Major points: 1) I partially agree with reviewer #1 that the overall idea looks a lot like something that could have been achieved in a simple comparison of concentration measurements. If you assume little error in the sampling itself and that the two analysers work with practically identical samples, there would be no reason to do this in the field, to generate the increased N2O concentrations via fertilisation instead of using standards, or to even calculate the fluxes at all (which are of course identical if the concentrations are identical). For an instrument comparison these would all be unwanted potential sources of error and confounding variables in the analysis. That said, I think I see the authors' reasoning, which is to showcase that their idea actually works well in practice and for its intended purpose (measuring fluxes). It is an unfortunate truth that just because something works well in the laboratory doesn't necessarily mean that it must work well in the field. I think this misconception is something that can be remedied quite easily by explicitly discussing early in the manuscript how and why this is much more than just comparing two instruments' ability to measure concentrations. It left me quite puzzled throughout half of the manuscript, because it only really becomes clear after reading and thinking about it for a while.

*As pointed out by Referee #2, it was our intended purpose to test whether a QCL analyser could be used for the injection of chamber derived N2O samples in the fields. We consciously decided to develop a sampling/analytic approach that would reliably work in the fields, instead, of testing a laboratory approach only. Based on own experiences, we found that an applied approach as such would be very useful for other users

who conduct measurements with static chambers and eddy covariance but are interested in shortening analysis times, receive immediate measurement results and have an interest in reducing costs by accessing the full potential of the QCL analyser. We acknowledge the Referee's comment and are going to add in a specific acknowledgement of the purpose of our work at the end of the introduction in the revised version of the manuscript.*

2) I don't really get the data workflow. What does the QCL output (shouldn't it directly be ppb?), what is QCL peak area in mV supposed to be and how was it translated into concentrations? Figure S1 also doesn't make a lot of sense to me due to this. What is "N2O calculated"? If you did a calibration with standards in glass syringes and those result in higher peak areas, how can you then accurately calculate concentrations for samples that were obtained with plastic syringes which apparently result in lower peak areas...? Obviously it did work in some way or you wouldn't get so similar results to GC, but you have absolutely lost me somewhere on the way there. Expanding section 2.3 would help a lot. I would like to see basically a recipe to get from the QCL output to whatever you did in Fig. S1 (and further)

*For clarification: The injection of 1 mL sample volumes into the QCL resulted in an output of peak area data (i.e. similar to the output as received after GC analysis). In the subsequent data analysis, we calculated the area under each peak for 1) sample injections of unknown N2O concentration, and 2) injected N2O standards of known N2O concentration. We used the results from 2) to generate quadratic models which we then fitted to the data from 1) to translate outputs into N2O concentrations (see Section 2.3 of the manuscript). We agree to the referee that explaining the procedure demands additional clarification, which we will implement to L. 159 of the manuscript. We conducted preliminary tests using glass and insulin syringes in which we applied the above translation from N2O peak areas to N2O concentrations. All data presented in the manuscript were purely based on injections made using glass syringes. This applied to both: 1) the injection of N2O samples and 2) N2O standards. To avoid con-

fusion about the use of different syringe types, we now intend to remove Fig. S1 from the supplementary material. Instead, we will include additional explanations expanding on Section 2.3 and our work-flow procedures as suggested by the referee.*

3) This is in regards to L327-339 - I fully admit I'm not overly familiar with bioequivalence statistics, but I have a strong feeling that you are boldly overstating what it can do. From what you wrote and what I could find in your sources, it's still just frequentist inferential statistics. Don't get me wrong, I applaud that you are willing to do solid statistics and think outside the old t-tests-and-scatterplots box. But to me this honestly just looks like another type of null-hypothesis significance testing, with even more 100 % arbitrary (but hopefully consensus-based) thresholds and ranges. I.e. there is nothing objective and certainly nothing that justifies calling something a "proof" about it. I suggest to word pretty much everything about bioequivalence with a bit less praise. It's a good and interesting approach and it makes sense to apply it to fluxes, but that's about it.

*The reviewer is correct that the bioequivalence test performed in our study (as described in Section 3.4.1) is a frequentist hypothesis test. However, what is vitally important here is that the test is designed to assess (e.g. that two products are the same) . In our experiment, we were interested in whether calculated N2O concentrations/fluxes from QCL (FN2O_QCL) are effectively the same as those determined by a standard method, i.e. in our case laboratory-based GC (FN2O_GC). The bioequivalence test allowed us to assess this. The equivalence range (i.e. maximum acceptable difference) does need to be specified, and this perhaps could be seen as arbitrary. However, here it is important to be aware of the following: that 1) this is set a-priori to analysis and 2) this explicitly defines what is meant by bioequivalent (as explained in Section 2.5). We have endeavoured to make very clear in the paper what the equivalence range is (e.g. L210, L334, L338, L342, L350, Figure 6) and how this determines the definition of "bioequivalence" (e.g. L205-215). Following the reviewer's advice, we are going to rephrase all sentences regarding bioequivalence so that we don't overstate what the methodology can do. This includes changing "proof of bioequivalence" to "evidence of

bioequivalence" (lines 334, 336, 340, 345, 351).*

4) In section 3.4.2 you write about "using a QCL [...] without much disruption of other measurements". I respectfully disagree with that, considering that in section 3.3 you say that you already need an initial lag time of 10 to 30 mins, so I assume you lose at least two half-hourly EC measurements for a single sample (How much is it actually? Please state it in the manuscript!). This is something that I, as someone working at an EC station, would not want to sacrifice at least during daytime and/or after significant management events (but I wouldn't want to inject gas samples the whole night either). You mention postponing analysis later in section 3.4.2. I would like to ask you to elaborate on this idea. Would it make sense to collect multiple samples and analyse them in one batch? Is this feasible in the field? In Tab. 1 you state that you can inject 200 samples per hour. For how long can the samples be stored on site (e.g. could it wait until the next maintenance of the EC system excl. the QCL)? I would like to see some of your ideas on this and maybe an actual example for a sampling plan that minimises EC downtime. This disruption is a core issue for anyone doing EC, so it should play a much more central role in the discussion.

*We acknowledge the Referee's interest in the capability of the QCL device to provide rapid analysis of chamber derived N2O samples. As pointed out in L. 133, Section 2.2.3, the conversion of the EC QCL system to the injection mode took less than 30 min. This time comprised the establishment of an operational set-up including: to assemble and mount tubes, gas bottles etc. to the QCL, adjust the flow of N2 carrier gas and let the temperature-controlled enclosure system of the QCL housing adjust and recover from the disruptions made (e.g. lid-opening, flow-rate change). Afterwards and as identified by the referee, it is recommended to inject as many samples as available and avoid EC down-time. In L. 378, we have already indicated (see quotation of Faust and Liebig, 2018) that storing gas samples in Exetainer vials is possible and allows to minimise disruptions to EC measurements. We will add a couple of sentences to the end of Section 3.4.2 to provide further clarification about the advantages of our

injection technique – as indicated by the referee.*

Minor points: - L97: Please give a justification for the very high application rates somewhere around here. - Check typographical rules for formulae, etc. Variables should be cursive (but _descriptive_ indices upright). - L163: "Since the quadratic fit suited lower C_N2O better than a linear fit, quadratic models were preferred [...]" The fit will naturally be better (in terms of R2) if you throw more parameters at your model. Am I missing something here? - L203: Power depends on (among other things) the sample size. You can't just say a 90 % CI corresponds to 80 % statistical power. - L268: I think here you can replace "might explain" with "explains". At least to my understanding it's somewhat trivial that you calculate a larger flux if you measure higher concentrations with the QCL, no? - L314-315: Have you tested injecting blanks and see what happens? - L520: Typo "TAylor" - Figure 3: Panel c and d should have equal scaling on their respective x and y axes (i.e. the 1:1 line should be the diagonal). - Table S3: Where were the soil samples taken?

We are going to acknowledge these minor comments in the revised version of our manuscript. A detailed description of changes made will be provided to the associated editor with re-submission of the manuscript. This description will reiterate a detailed reasoning for changes made and indicate where (line number), how and to what degree the comments from Referee #1 and Referee #2 were implemented.

Kind regards in the name of all authors from Hamilton, New Zealand – 06/08/2020 Anne Wecking

FAUST, D. R., and LIEBIG, M. A.: Effects of storage time and temperature on greenhouse gas samples in Exetainer vials with chlorobutyl septa caps, MethodsX, 5, 857-864, https://doi.org/10.1016/j.mex.2018.06.016, 2018.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2020-197, 2020.