

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.

Anonymous Referee #1

Received and published: 24 June 2020

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. 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

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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. The novelty of the method is that the authors get past the inability of the QCL to measure 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. 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 10Hz, and what the noise looks like. 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. 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. 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. 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. 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

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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 required, 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. 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. 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. 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. 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.

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