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Atmospheric Measurement Techniques Discussions

Interactive comment on "Open-path, quantum cascade laser-based sensor for high resolution atmospheric ammonia measurements" *by* D. J. Miller et al.

D. Griffith (Editor)

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I agree with the two referees that the paper is well written, clear, and suitable for publication in AMT after minor revisions (including mine below). Please go ahead and address the referees' comments and submit a response to these comments and revised manuscript with changes highlighted.

I would like to add a couple of editor comments to those of the two referees: - Please be consistent in the correct use of "mixing ratio" (more correctly "mole fraction") and "concentration". A quantity measured in ppb is the former, the latter is either a generic

term in the appropriate context, or specifically an amount per unit volume.

- Throughout the typeset manuscript, "double f" appears as a script ff, presumably a typesetting error by the journal (it is correct in the submitted manuscript. I will bring it to their attention and suggest the authors do as well.

- In the introduction pages 7007-7008, the authors completely neglect to mention open path measurements of NH3 by FTIR spectroscopy, which has been around for some time in biomass burning and agricultural measurements. I append examples (not an exhaustive bibliography) from work I have been involved in (and declare my own background in FTIR). In the context of this paper, I think FTIR should be included in the introductory literature survey of existing techniques.

- On p 7013 L26 et seq. and the discussion of calibration accuracy, it is incorrect to claim that the accuracy is comparable to existing sensors. For example open path FTIR is actually significantly more accurate than that claimed in this paper. See for example Smith et al below.

- Section 3.1 Calibration. The method described and illustrated in Fig 4 is NOT calibration. Fig 4 is a comparison between direct and second harmonic detection. It is only calibration if one or the other result is proven and accepted to be an accurate measure of the true mole fraction of NH3 in the sampled air (I add that it should be also then plotted on the X axis as the independent variable). Calibration is the relationship between the sensor response and an independent value of the mole fraction measured by a reference method. In this case the reference method hinges on the 25ppm stock mixture of NH3 in N2, and the quantitative dilution with N2. The sensor response (either direct or 2f) should be plotted and regressed against the mole fractions calculated from this dilution series to derive the calibration equation. The errors in the reference values (starting mixture and propagated dilution accuracy) should be quantified. Why was N2 used as the diluent, rather than air, when it was well known and recognised by the authors that this involves a significant line-width error? It sounds somewhat weak to

say you didn't bother because it was within the accuracy limits of the technique (10%). In general, I find the approach to calibration is rather superficial and could have been improved with little effort.

Examples of FTIR references Burling, I. R., R. J. Yokelson, et al. (2010). "Laboratory measurements of trace gas emissions from biomass burning of fuel types from the southeastern and southwestern United States." Atmospheric Chemistry and Physics 10: 11115-11130. Galle, B., L. Klemedtsson, et al. (2000). "Measurements of ammonia emissions from spreading of manure using gradient FTIR techniques." Atmospheric Environment 34(28): 4907-4915. Smith, T. E. L., M. J. Wooster, et al. (2011). "Absolute accuracy evaluation and sensitivity analysis of OP-FTIR NLS retrievals of CO2, CH4 and CO over concentrations ranging from those of ambient atmospheres to highly polluted plumes." Atmospheric Measurement Techniques 4: 97-116. Griffith, D. W. T. and B. Galle (2000). "Flux measurements of NH3, N2O and CO2 using dual beam FTIR spectroscopy and the flux-gradient technique." Atmospheric Environment 34(7): 1087-1098.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 7005, 2013.