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Comment

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

**D. J. Miller et al.**

mzondlo@princeton.edu

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Responses to D. Griffith, Editor:

Comment: 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.

Response: We are grateful for the constructive comments of the Editor. We have improved the existing manuscript and submitted a revised manuscript based on the

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comments of the Editor and two anonymous referees. Below are detailed responses and improvements to originally submitted manuscript in response to all comments and suggestions.

Comment: 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.

Response: Ammonia is measured in ppbv as mole fraction (uncorrected for water vapor dilution effects). We have corrected the revised manuscript accordingly. As noted in the revised manuscript (section 4), all field measurements presented are corrected for water vapor dilution and expressed as mixing ratios in dry air.

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.

Response: We will bring this typesetting error to the attention of the journal.

Comment: In the introduction pages 7007-7008, the authors completely neglect to mention open path measurements of NH<sub>3</sub> 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.

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. Klemetsson, et al. (2000). "Measurements of ammonia emissions from spreading of manure using gradient FTIR techniques." *Atmospheric*

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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 CO<sub>2</sub>, CH<sub>4</sub> 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 NH<sub>3</sub>, N<sub>2</sub>O and CO<sub>2</sub> using dual beam FTIR spectroscopy and the flux-gradient technique." Atmospheric Environment 34(7): 1087-1098.

Response: We agree that open-path FTIR NH<sub>3</sub> sensors should be explicitly included as an existing technique for in-situ NH<sub>3</sub> measurements. The focus of our manuscript is on compact, in-situ NH<sub>3</sub> point sensors. However, we include remote measurements to show the advantages of open-path detection approaches. Thus, we add the following on FTIR techniques to our review of existing measurement techniques in the introduction (and citations added to the references section as necessary): "Open-path remote systems employing Fourier transform infrared (FTIR) spectroscopy techniques have been demonstrated for path-integrated field NH<sub>3</sub> measurements, including agricultural flux measurements with single ppbv sensitivity [Griffith and Galle, 2000; Galle et al., 2000]. Open-path TDLAS and differential optical absorption spectroscopy (DOAS) systems in remote measurement configurations have been used to measure NH<sub>3</sub> with ppbv detection limits [Thoma et al., 2005; Volten et al., 2012]. Mount et al. (2002) demonstrated open-path NH<sub>3</sub> measurements with a mid-ultraviolet DOAS system and achieved 1 ppbv NH<sub>3</sub> sensitivity in 1 s. The high time resolution (>1 Hz) of this approach illustrated the value of an open-path configuration. However, all of these sensors require long paths rather than compact sensor footprints."

We do not include the reference for Burling et al. (2010) because this paper describes laboratory measurements, while the focus of our literature review is on in-situ NH<sub>3</sub> sensing techniques. We refer to the reference Smith et al. (2011) in the response below on calibration accuracy of FTIR techniques, but do not include it here as Smith et al. (2011) did not discuss NH<sub>3</sub> measurements.

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Comment: 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.

Response: We modify this sentence to clarify our comparison. We are claiming that the stated accuracy ( $0.2 \text{ ppbv} \pm 10\%$ ) is comparable to currently existing, state-of-the-art  $\text{NH}_3$  sensors (not for all trace gas sensors) as follows: “The pulsed QC laser-based  $\text{NH}_3$  instrument demonstrated by McManus et al. (2008) has a typical concentration uncertainty of 5-20%. Nowak et al. (2007) found uncertainties in CIMS  $\text{NH}_3$  measurements to be  $\pm 25\text{-}30\%$  during field operation. Sintermann et al. (2011) found calibration accuracy of  $\sim 5\%$  for a CIMS  $\text{NH}_3$  instrument.”

We note that Smith et al. (2011) have not reported accuracies for  $\text{NH}_3$  measurements. As explained in our introduction and references therein, the surface adsorption and partitioning artifacts associated with  $\text{NH}_3$  calibrations present unique challenges (compared with other trace gases such as  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{CO}$ ) that limit accuracy, especially for low mole fractions.

Comment: 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  $\text{NH}_3$  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  $\text{NH}_3$  in  $\text{N}_2$ , and the quantitative dilution with  $\text{N}_2$ . 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.

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Response: We agree with the stated definition of calibration. Our calibration is based on a spectroscopic reference method, which is independent of our WMS retrieval. We note that many gas standard mixing ratios are validated using spectroscopic methods. Direct absorption is an accepted method to measure trace gas concentrations as long as the uncertainties, including absorption lineshapes (HITRAN parameters) and path length, are quantified and acknowledged. The standard NH<sub>3</sub> mole fractions for calibration of our WMS retrieval are calculated based on a direct absorption fitting using these calibrated HITRAN parameters. In previous work, we have characterized uncertainties in the HITRAN parameters for the NH<sub>3</sub> absorption lines utilized [Sun et al., 2013]. Owen et al. (2013) also studied these NH<sub>3</sub> absorption transitions and reported an uncertainty of <10%. Our calibration method has an uncertainty of  $\pm 10\%$ , constrained by spectroscopic calibration uncertainties for the relevant HITRAN parameters. Details are explained in Sun et al. (2013). We add a new section 2.4 to the revised manuscript to describe the calibration method.

The uncertainties associated with the standard dilutions method for NH<sub>3</sub> calibration are much more challenging to constrain due to surface adsorption and partitioning artifacts in the dilution system and calibration chamber as well as residual NH<sub>3</sub> in the dry air used for dilution. These uncertainties are likely much larger than our method using known uncertainties in HITRAN parameters. The uncertainty increases at lower mole fractions, when dilution of typical NH<sub>3</sub> standards by a factor of 1000 or larger is necessary. We acknowledge that for low mole fractions, the direct absorption reference method also presents larger uncertainties. However, we discuss zero calibration and associated uncertainties of the 2f retrieval in our response to Anonymous Referee #1 below and in the revised manuscript in section 3.1.

Finally, we modify Fig. 4 so that the reference mole fractions, based on direct absorption, are plotted on the horizontal axis.

Comment: Why was N<sub>2</sub> 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

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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.

We made an error in the original manuscript in describing our diluent for calibrations. To clarify, we used dry air (rather than dry N<sub>2</sub> as stated originally) as the diluent, consistent with the zero NH<sub>3</sub> background experiment described in section 3.3. In addition, the spectroscopic correction due to line-widths in dry N<sub>2</sub> is removed, as it is not relevant for our discussion. Section 3.1 is modified as follows: "This 25 ppmv NH<sub>3</sub> standard mixing ratio is decreased incrementally by dilution with dry air and each calibration point is recorded in both 2f and direct absorption as shown in Fig. 4. The horizontal axis is the NH<sub>3</sub> standard mole fraction derived from direct absorption measurements. The vertical axis displays the retrieved NH<sub>3</sub> mole fraction based on 2f spectral fitting with the online spectroscopic calibration method described in section 2.3. We note that the calibration is performed at mole fractions much less than that of the original 25 ppmv NH<sub>3</sub> standard. Therefore, we use HITRAN parameters appropriate for NH<sub>3</sub> in dry air."

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

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