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Atmospheric Measurement Techniques Discussions

Interactive comment on "Characterizing a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) for measurements of atmospheric ammonia" *by* R. A. Ellis et al.

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Page 3312, Line 9: Specify the possible deposition surface, i.e. vegetation, land, etc.

Deposition can occur to land, vegetation or water bodies adjacent to the emission source.

Page 3312, Lines12-13: Reword this sentence. Possibly: Ammonium particulates have a longer atmospheric lifetime than ammonia and therefore, can be transported over

relatively long distances, which increases their potential to affect human health and influence radiative forcing.

Reworded to: “In the presence of these acids, NH3 can contribute to the formation of fine particulate matter with strong implications for human health and radiative forcing. Particulate ammonium (NH4) also has a longer atmospheric lifetime than NH3 and can therefore be transported over relatively long distances.”

Page 3312, Line 16: A quite relevant reference for this sentence is Galloway et al. Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B. and Cosby, B.J., 2003. The nitrogen cascade. Bioscience, 53(4): 341-356. DOI: 10.1641/0006-3568(2003)053.

Inserted reference.

Page 3312, Lines 16-17: Chiefly North American policies have focused on the acidic species. Policies in the EU have traditionally been much more inclusive. For example, the Gothenburg Protocol specifically addresses ammonia. It may be prudent to specify the geopolitical area for the ‘regulatory policies.’

Specified North American policies.

Page 3312, Lines 18-19: So as not to mislead readers, please quantify that the reduction is small, <1 ug/m3 as found by Makar et al.

More information on the studies was included: “Recent modeling studies have explored the effectiveness of NH3 emission reductions on the PM2.5 mass loadings in North America. Pinder et al. (2007) found a 10% reduction in NH3 emission decreased PM2.5 by 1.4% in the summer and 5.7% in the winter in the Eastern U.S., and that NH3 emission reductions are often more cost-effective than SO2 and NOx controls. North America wide reductions of agricultural NH3 emissions by 30% were found to decrease average PM2.5 by 0-7% but decreases in the 95th percentile could be up to a factor of six larger (Makar et al., 2009).”

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Page 3313, Line 19: Add a reference regarding the positive bias introduced by ammonium nitrate and ammonium chloride, possibly Chow et al. 1998. Chow J.C., Watson J.G., Lowenthal D.H., Egami R.T., Solomon P.A., Thuillier R.H., Magliano K., Ranzieri A., 1998. Spatial and temporal variations of particulate precursor gases and photochemical reaction products during SJVAQS/AUSPEX ozone episodes. Atmospheric Environment, 32 (16): 2835-2844.

Inserted reference.

Page 3315, Line 6: Quantify precise spectral ranges for ethylene and methanol.

Ethylene absorbs at 967.33 cm-1 and methanol at 967.36 cm-1.

Page 3315, Line 14: What's a typical flushing period?

The flushing period can be anywhere from 30 seconds to several minutes and is dependant on the environmental conditions (how high NH3 is, humidity) but only the last 1/3 of the measurements made during the flushing period are used for the background. For example, for the field intercomparison in Egbert we used a flushing time of 1 minute initially then switched to 10 minutes to ensure a completely ammonia-free background.

Page 3315, Line 24: Quantify 'moderately high above threshold.'

Approximately 2 V above threshold.

Page 3317, Line 17: How was this 90% quantified with regard to flow separation? More explanation is needed for how flow successfully navigates the 90 degree right turn to enter the optical cell.

The flow separation ranges from 85-93% through the sample path and depends on the pressure drops through each of the paths. It can be confirmed by comparing the total flow to the flow through the optical cell calculated by optical cell volume and residence time of a non surface reactive gas (such as C2H4).

Page 3318, Line 6: State the range of ammonia concentrations used in calibration.

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We use a constant output of 30 ppb from a permeation tube source.

Page 3318, Line 11: What's the average time for stabilization of the signal during calibration? Also, state the frequency of calibration.

The average time is 1 minute. Calibration is usually performed every 2 hours, but depends on the stability of the system.

Page 3319, Line 21: State the degree of accuracy of the difference.

The 42CTL instrument has a detection limit of approximately 50 ppt (2min) on each channel so NH3 by difference should have a detection limit on the order of 100 ppt. In terms of the accuracy of the difference it is complicated by several factors. 1) Instrument measures both NOy and NOy + NH3 at different times. Instrument cycles 10s on each of three channels NOy, Nt (NOy+ NH3), and background correction. Time lag in the measurements affects the determined difference under varying concentrations. 2) The accuracy of a 1 ppb difference in the two channels can be affected by the amount of NOy. That is we are much more confident in a 1 ppb measurement under conditions of low NOy (<10 ppb) as opposed to a 1 ppb difference measurement under high NOy circumstances ($\sim$100 ppb) 3) Given that ammonia is a 'sticky' gas, there are slight sample inlet surface effects that are dependent on factors such as temperature and humidity. Rapid changes in these or the ambient concentration of ammonia could temporarily offset the equilibrium (see Fig. 7a). 4) The possibility exists that other atmospheric constituents (such as amines) may be converted to NO across the stainless steel converter. Therefore the presented ammonia measurements for this instrument are represented as an 'upper-limit'. However, during this intercomparison the measured NOy in this rural environment was typically less than 10 ppb and under stable conditions it is estimated that measured ammonia is with + 10%

Page 3319, Line 25: While daily replacement of the filter was probably sufficient, this reviewer wonders if any effects of such frequent changes were observed in the data. Is daily replacement recommended by the manufacturer or a practice adopted by the

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authors based on previous experience?

Other than a short conditioning period of approximately 15 min. after changing the filter, no effects were noticed in the data. The implementation of a daily filter change was done more to minimize any possible effect of ammonium nitrate volatilization as opposed to trying to fix an apparent problem.

Page 3320, Line 3: This reviewer assumes that met data were collected as hourly averages. Explicitly state if this is the case.

The met data was indeed collected as hourly averages.

Page 3322, Line 12: Are more concentrations available for comparison? Perhaps, stepwise changes of _50 ppb versus several hundred would be preferable. Even in agricultural systems, lower concentrations, especially with ammonia fluxes, can be present.

The only mixing ratios we investigated were 30, 100, 350, 700 and 1000 ppb. These were chosen to span the range of values found in areas of intensive agricultural activity.

Page 3322, Lines 14-16: A short paper by Mukhtar et al. addresses some of the physics and physical parameters influencing ammonia adsorption. It may provide some supporting information for this statement. Mukhtar, S., Rose, A., Capareda, S., Boriack, C., Lacey, R., Shaw, B. and Parnell, C., 2003. Assessment of ammonia adsorption onto Teflon and LDPE tubing used in pollutant stream conveyance. Agricultural Engineering International: The CIGR Journal of Scientific Research and Development: BC03012.

Inserted reference.

Page 3322, Lines 24-26: Some reference to the physics involved, i.e. polarity, should be included.

A reference was made on line 20 about ammonia's ability to form strong hydrogen bonds with water.

Page 3323, Line10: What about ammonia adsorption/desorption especially consider-

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ing that the discrepancies occur at lower concentrations? It seems you address these later in the text when referring to Fig. 7b. This reviewer suggests the authors renumber figures so that Fig. 6 and Fig. 7b are Fig. 6a and Fig. 6b.

A sentence has been added to draw a stronger connection between the time periods in Figure 7a and 7b and the outliers in Figure 6. Because Figures 7a-c are all time series we prefer to keep them together.

Page 3323, Line 12: What's the evidence, anecdotal or otherwise, that fertilization caused these increased mixing ratios?

We do not have any direct evidence, but we believe that since our site was in an agricultural region there may have been some late fertilization occurring in May. We did not see higher mixing ratios for the remainder of the study and there was no other known nearby source expect for fertilization to explain the increase.

Page 3323, Lines 19-20: This reviewer is not totally confident that your data fully support this statement. Based on simple statistical degrees of freedom, it is difficult to draw this conclusion. If other inlet-equipped devices were included in the study, then stronger evidence may have been possible.

Unfortunately in this specific study we only compared with the Thermo 42CTL. However, during the intercomparison between eleven different NH3 analyzers described in the von Bobrutzki paper we also found our inlet to have the fastest time response when compared to other systems. In the earlier part of our manuscript we presented results from the QC-TILDAS and TDLAS which were both equipped with the quartz inlet and found similar time responses.

Page 3323, Line28: Was condensation visible in the lines? Were these sample lines heated to 40C as mentioned for the QC-TILDAS in Section 3.2? Norman et al. postulated that heated samples lines should have minimized this effect.

A visual inspection of the filter and sampling lines of the Thermo 42CTL for condensa-

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tion was not performed. The sample lines for the Thermo 42CTL were not heated.

Page 3324, Line 10: Again, Norman et al. only saw condensation during periods of precipitation, not during periods of high RH, even near 100%. Considering those findings, more weight should be placed on precipitation as the mitigating factor instead of RH.

Changed wording to: "One of the reasons for this instrumental offset may be that the prolonged high humidity following rainfall on the previous day prevented evaporation of condensed water on the sampling intake of the Thermo 42CTL. However a visual inspection of the filter and sampling lines of the Thermo 42CTL for condensation was not performed. If condensation was present, when the temperature rose the following morning and the Thermo 42CTL inlet was dried, it may have released NH3 trapped on the surface, leading to a delayed increase in mixing ratio. Norman et al. (2009) also observed losses due to condensation and uptake of NH3 in the inlet during and after rainfall."

Page 3324, Line 21: Specify how the background spectrum was assessed.

The background spectrum may be variable in time because changing instrument conditions lead to variations in absorbance that the software integrates as a mixing ratio of NH3. We have observed this even when the system has been exposed to NH3-free air for a prolonged period of time when we are confident there is no NH3 left in the optical cell.

Page 3334, Fig. 5: It would be helpful to have some quantifiable error associated with each D-factor shown as error bars.

We used the standard deviation calculated from the double exponential fit and propagated the errors in A1 and A2 to calculate the error in the D-factor. We have added the error bars to the graph.

Technical Corrections

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Throughout the manuscript, the authors use both the term ‘ammonia’ and the symbol NH3. Select one for consistency.

We selected to use NH3 and made the necessary changes in the manuscript.

Ensure that vendor names, cities, and countries (if applicable) are listed after the first mention of specific equipment used in the study.

Done

Page 3311, Line 5: Add a hyphen between ‘thermoelectrically’ and ‘cooled.’

Done

Page 3311, Line 7: Id.

Following convention of previous papers, we identified the source of equipment used in the study starting with the introduction not the abstract.

Page 3312, Line 7: Add a comma after ‘plants.’

Done

Page 3312, Line 9: Make ‘reaction’ plural.

Done

Page 3312, Line 14: Add the chemical symbol in parenthesis after ‘ammonium.’

Done

Page 3312, Line 21: Add ‘in-situ’ after ‘accurate.’

Done

Page 3313, Line 2: Replace ‘often suffers from’ with ‘is prone to.’

Done

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Page 3313, Line 6: Add ‘in field conditions’ after ‘deploy.’

Done

Page 3313, Line 9: Delete ‘both.’

Done

Page 3313, Lines13-14: Make ‘surface’ singular. Replace ‘involved in the sampling intake’ with ‘in contact with the sample air flow.’

Done

Page 3313, Line 14: Make ‘wall’ plural. Delete ‘in contact with the air flow.’

Done

Page 3313, Line 22: Add a comma after ‘Research.’ Add a period after ‘Inc.’

Done

Page 3313, Line 27: Add ‘and’ after ‘humidity.’

Done

Page 3314, Line 19: Add the chemical symbol for ethylene and delete later occurrence (Pg. 3315).

Done

Page 3315, Line 3: Define the acronym ‘HITRAN.’

Done

Page 3315, Line 22: Change ‘underestimates’ to ‘underestimation.’

Done

Page 3317, Line 15: Utilize consist units for pressure (kPa or Torr).

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Changed Torr to kPa.

Page 3318, Line 1: Replace ‘experience’ with ‘encounter.’

Done

Page 3319, Line 19: Give full name of chemical, nitrogen oxide, in addition to symbol.

Done

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 3309, 2009.