

Interactive comment on “Field inter-comparison of eleven atmospheric ammonia measurement techniques” by K. von Bobruzki et al.

Anonymous Referee #2

Received and published: 2 October 2009

General Comments

This manuscript describes the results of a field comparison of eleven different NH₃ measurement techniques. Reliable and accurate NH₃ measurements, especially at low concentrations and fast time resolutions, are difficult. This type of experiment under field conditions is necessary to evaluate the current state of NH₃ measurements. The paper attempts to present a general overview of the relative performance of the systems compared to each other. The paper does a fairly good job of this but could be improved and made clearer in some areas. I found the instrument descriptions to be uneven, in particular the level and applicability of citations. One piece of information not provided was an estimated of the accuracy uncertainty for each instrument, i.e., how well does each instrument think it can measure NH₃. For instruments that

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



calibrate using permeation devices, there is an uncertainty associated with the permeation rate that directly ties in with calculating the concentration of the calibration standard. For the absorption techniques, there is an uncertainty associated with the available cross sections. While the manuscript attempts to evaluate instrument A vs. instrument B, it does not address whether either A or B accurately reflects the ambient concentration. I think this is important information in evaluating the overall state of NH₃ measurements. The authors should look at the NASA TAbMEP project (<http://www-air.larc.nasa.gov/TAbMEP.html>) for further examples of comparison analysis. In addition, the abstract ends by stating three factors affecting measurement precision: inlet design, state of inlet filters, and quality of gas-phase standards. Yet, only the inlet filter issues are thoroughly discussed in the text. No place in the text discusses inlet design or gas standards in depth enough to support the conclusion implied in the abstract. There are, also, a number of very general statements concerning certain instruments, in particular in section 4.2, that are not supported with any data presented here. Furthermore, I agree with the other referee that relative humidity could have a significant influence, especially to inlet response. I also agree that describing the quality of the instruments with a correlation coefficient to an ensemble average (NH₃-ref) could mask systematic differences. I think this can be seen in some of the Table 8 correlation plots. Finally, I'm not sure what the take home message of this manuscript is. Is this paper making correction recommendations or is it showing that, compared to trace gas measurements of CO and NO, NH₃ measurements have a long way to go?

Specific Comments

2.1 Site description and Figures 1 and 2 – This section states the inlet heights of all instruments but does not give an indication of the horizontal spacing between inlets. From figure 1 it is difficult to see the actual inlets. At first look one could assume all the inlets are located on the scaffolding but I do not think that is the case. Labeling the location of the inlets in figure 1 or describing the distance between gives stronger support to the claim made later that some difference between instruments is due to

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



natural variability of sampling different air. If they are all at the same location then I question that any instrument is sampling different air. For future experiments the investigators should consider having all the inlets at the same location as in the nitric acid comparison described in Arnold et al., Atmospheric Environment [2007]. The wind panel on Figure 2 does not convey much useful information. There is no scale or direction information. Am I correct in assuming the top of the page is North? There are two typos with the aerosol data. The legend and caption should read NH₄⁺.

2.3 Measurement techniques

P1791 Line 13 – The described inlets were made of what material?

P1793 Line 12 – Starting here and throughout the measurement technique descriptions the authors switch between metric and American units. I find this distracting and confusing and recommend they choose metric throughout.

P1794 Dual-QCLAS – Here the instrumental background is determined by the addition of NH₃ free air generated by a catalyst heated to 300 C. However, not only does this remove NH₃ but changes the RH of the air. Neither here nor in the Whitehead reference given do the authors show that the change in RH has no effect on the inlet characteristics and no impact on the determined background.

P1794 Compact QCLAS – I am intrigued by the use of the virtual impactor but am disappointed that there is no reference or data to support that it works and has no effect on ambient NH₃ concentrations, i.e. possible additional losses. Also, as mentioned in the general comments section, no information about how the permeation rate is determined (i.e., weight loss, optically (see Neuman et al. Environmental Science & Technology [2003]) or its uncertainty is given.

P1796 Nitirolux-100 – During what part of the 6 month calibration cycle was the instrument deployed? What is the uncertainty associated with that calibration?

P1797 CRDS – How often is the manufacturer calibrate the instrument? When was it

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



mostly recently calibrated? What is the uncertainty?

P1797 CIMS – I'm unclear why Marcy et al is referenced in relation to the $\text{H}^+(\text{C}_3\text{H}_6\text{O})_2$ ion chemistry when it describes, as stated in the title of the reference, measurements of HNO_3 , HOI , and ClONO_2 using SF_5^- ion chemistry. The references used to describe the CIMS configuration actually describe some conflicting configurations (i.e., flow tube vs perpendicular ionization configuration, collisional dissociation chamber vs no dissociation). It is difficult to know what was used. The authors should improve their instrument description or more thoroughly vet the references given. Similar to the c-QCLAS no information is given about the permeation device standard.

P1799 Line 22 – More information about the common NH_3 gas cylinder is needed, specifically, its manufacturer, concentration, and uncertainty on the concentration. I think the importance of this test is glossed over in the text. Table 2 shows that only one of the six instruments for which this test was performed was within 13% of 'known' independent standard. If the standard is only believed to be good to 20% this is not bad. If the standard is believed to the 5% level then there may be more problems.

3.1 Time Series and Figure 3 – Figure 3 is difficult to read and discern the different traces. One suggestion is to make two separate larger figures, fig 3 before and fig 4 after fertilisation. The shading is very light on both my computer screen and printout.

3.2 Instrument inter-comparison – the term NH_3 -ref is somewhat misleading. I initially thought this referred to the calibration standard briefly mentioned in section 2.4. The use of the term 'ref' also implies that this is independent and it is not. NH_3 -ref is actually an ensemble average of NH_3 observations made. This type analysis is similar to that used to evaluate regional air quality models, i.e. McKeen, S., et al. J. Geophys. Res., 110, D21307, doi:10.1029/2005JD005858 [2005]. How was this average calculated? Was there any weighting? Was there a minimum number of data points required from the faster time resolution measurements to be include in the average? Based on the individual instrument uncertainties, what is the estimated precision and total uncer-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



tainty for this NH₃ average value? As discussed earlier, comparison to this ensemble can mask important systematic differences. The fitting is presented as simple linear regression not taking into account the uncertainty in the measurements. This does not seem realistic. Each instrument does have associated errors. These should be taken into account when performing the fits. If this was taken into account it should be stated more clearly in the text. On this same note all scatter plots in figure 4 and in figure 5 should show at least one low and high point with the associated error bars to give the reader a feeling of the uncertainty range.

The rest of the section and tables 4 through 8 are very dense with many numbers. It is very hard put into context what these numbers means. This goes back to my earlier comment concerning the take home message of this comparison. For example, what significance is there for relations with noticeable high intercepts? What is the definition of a high intercept? In table 4 CIMS vs CRDS yields an intercept 1.6 and is considered high; while RBD vs AMANDA yields an intercept of 1.41 and is not considered high. Whether or no an intercept is high depends on how well an instrument can determine zero and this is not clearly discussed in the text. In short, I'm not sure what to do with all these regression statistics.

I found the 'dual' nature of these tables difficult to discern. The explanation is that the regression provided is the row against the column. For example, in table 4 RBD against AMANDA yields an intercept of 1.41 ppb but according to the text AMANDA against RBD does not yield a slope of 0.86. I think for the top half of the table the regression provided is the row against the column but for the bottom half it switches to the column against row.

Table 8 is completely useless due to the size of the plots, even when blown up on the computer screen. No scale is given on either axis. I agree that there is quite a bit of important information in these plots but in the current format is not being presented to the reader in a clear fashion. Therefore, each should be prepared as in figure 4 but with at least one low and high point showing the associated error bars. This complete set

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



of plots should be submitted as supplemental material to the text. Table 8 then should be stricken from the manuscript.

3.3 Characterisation of instrument time response – This section should be renamed ‘Characterisation of instrument time response relative to the c-QCLAS’. Why was the c-QCLAS chosen? I find it more curious why the same time response analysis using exponential decays performed in the references, Whitehead et al., ES&T [2008] and Nowak et al. JGR [2007] was not performed for those instruments with the data available here. This analysis constrains the known slower instruments but does nothing to evaluate the time response of the perceived fast time response instruments.

4.1 Overall measurement accuracy – This section should be renamed ‘overall measurement agreement’. This paper focuses on the agreement between instruments relative to each and not the absolute accuracy of the measurements, though I think an attempt to address the accuracy uncertainty of each instrument should be made.

4.2 Instrument specific issues – I like the discussion of the issues with inlet filters. However, I think much of the rest of this section is unclear and not well supported. There is not enough evidence presented here to justify the statement on page 1809 line 17 ‘Three instruments deployed here (DUAL-QCLAS, c-QCLAS and CIMS) have the potential to provide a fast NH₃ spot measurement, of particular interest for aircraft applications and eddy-covariance flux measurements.’ As mentioned earlier this paper presents no independent analysis of the time response for these instruments.

Another example page 1808 line 26 ‘CIMS preferentially extracts charged ions into the drift tube and thus favours gas molecules over the aerosol’. There is no data presented here or reference(s) given to support this. In fact, none of the references given to describe the CIMS set-up describe instruments that use a drift tube. All references that can be associated with the Georgia Tech CIMS team (table 1) describe systems that use low-pressure flow tubes for the ion-molecule reaction region. According to section 2.3.5 the CIMS in this study samples air through a pinhole, size not given, into

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



the ionization region. How much aerosol does get through the pinhole? What effect does the pressure change have on gas-phase/aerosol partitioning of ammonium nitrate aerosol? This further emphasizes my earlier comment of the uneven and inconsistent instrument descriptions.

Page 1810 line 6-7. It is stated here that the c-QCLAS was one of the better performing instruments. What criteria are used to support this statement and is it relative to the ensemble NH₃ average?

Page 1810 line 9. I disagree with the statement that c-QCLAS and the CIMS require continuous gas-phase calibration in the field. I am not sure how a continuous calibration would work with a spectroscopic measurement. Again there is no evidence presented that the calibration frequency stated in the instrument descriptions is inadequate.

Page 1810 line 20. According to the references Nowak et al. 2007 is the paper describing the airborne instrument not 2006. This paper seems to emphasize taking frequent instrument backgrounds not doing frequent calibrations, from paragraph 28 in Nowak et al 2007 “The area in need of most improvement is understanding and controlling the background signal from the instrument. Both the absolute level and the variability in the background need to be reduced in order to measure ambient levels from 10 to 100 pptv”. This leads to another question for this CIMS instrument not addressed in the instrument description how is the instrument background determined and how often is a background performed?

4.3 Time responses – This section should be renamed ‘time response relative to the c-QCLAS instrument’. Again, this paper does not present any time response analysis for the ‘faster’ instruments.

5 Conclusions – This section presents more vague generalities than conclusions. There seems to be conclusions, in particular about the CIMS and c-QCLAS instruments, made in section 4.2. And, as discussed earlier, those statements are not well

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



supported in the text.

Table 1 – Time resolution in the heading is two words. I think a column stating the estimated accuracy or total uncertainty of each instrument should be added, whether that comes from a manufacturer or is determined by in-situ calibration.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 1783, 2009.

AMTD

2, C567–C574, 2009

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

