

Interactive comment on “Chemical ionization mass spectrometer (CIMS) for ambient measurements of ammonia” by D. R. Benson et al.

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The manuscript “Chemical Ionization mass spectrometer (CIMS) for ambient measurements of ammonia by Benson et al. describes an instrument used to measure ammonia over three seasons in Ohio. Since ammonia measurements are challenging, particularly at the sub-ppbv levels reported here, there are few reports of ammonia mixing ratios far removed from concentrated emission sources. As such, these measurements could be valuable for examining the influence of ammonia on particle formation.

Although these measurements represent a considerable long-term effort, this manuscript is not ready for publication. The presented work is an excellent start, but further investigations are needed before the manuscript will likely provide enough new insights to be useful to other researchers. Three primary areas that require further

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work are detailed below.

Response: We are grateful for the reviewer’s useful comments and have revised the manuscript accordingly to address each comment. Below, we show our point by point responses.

Comment 1

There are very many typographical errors, grammar errors, and inconsistencies. While many of the errors are simple omissions of prepositions and noun modifiers, some errors find their way into quantitative parts of the paper.

Response: We have reviewed the manuscript and removed any errors and inconsistencies still present.

For example, in section 2.3, the reaction time in the flow reactor is stated to be 40 s. I suspect the units are wrong here, but I cannot be sure.

Response: The units were changed to “ms”. (Currently, L186).

The year in Figure 4a is 1943. Figure 4b shows an orange trace, and I cannot determine what this represents. The green lines in Figure 4 look to represent different modes, but again they are not explained. What is the difference between ion intensity (Fig 4b) and ion signal (Fig 4a)?

Response: The year in Figure 4a was changed to 2009. 4a and 4b were both changed so that the y- axis was labeled the same (ion signal). As for the green and orange traces, these represented the calibration periods and background periods respectively. For clarity, we have taken these vertical traces out (Figure 4 and its caption).

Mixing ratios are reported as pptv, ppbv, and ppb.

Response: Changed to pptv or ppbv.

The % steady state at t=0 is 105% - this should be explained.

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Response: This was a result from the fitting plot. Changed Figure 3 so highest value was 100%

In section 1, absorption is incorrectly written as “adsorption”. There are so many errors and inconsistencies caused by a lack of attention to detail that the paper is very confusing and unpublishable as it is presented.

Response: We believe adsorption is the proper term as opposed to absorption, since we are talking about NH₃ accumulating on surfaces.

Comment 2

The descriptions of the operation of the instrument and data reduction are unclear, and it would be impossible to repeat this experiment using the provided information. The measured signals are called “mass spectra signals” in section 4 and “mass spectra scanning sequence” in Figure 4. This doesn’t make sense to me, and I don’t understand how the measurements were made. The language suggests that mass spectra were performed repeatedly. But in section 3.1, the data is said to be collected at 1 s resolution. Is a scan performed every second? Is each mass measured for 1 s? Are all the masses measured over 1 s? The duty cycle and measurement sequence needs to be described clearly.

Response: Agree. We added: “Mass scans (Figure 2) were only performed once in a while to make sure the instrument was running properly. During the normal operation, eight ion peaks including the major reagent and product ions indicated above were measured over time. From these measurements, a sequence of the measured data were constructed, including the calibration, background and ambient measurement mode, as shown with ion signals vs. time (Figure 4). With the use of the sensitivity (derived from calibration) and the measured background signals, plots could then be constructed as [NH₃] over time (Figures 6 and 7). Although data were collected every second, they were averaged over one minute and the median values for each minute were used to calculate [NH₃] (Figures 6 and 7).” (L216 – 224).

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The instrument appears to be very unstable, and the causes for the changing response are not discussed. Figure 6 shows that the sensitivity doubled in a few days. Why did this happen? Elsewhere, the sensitivity is reported to vary between 4-25 Hz/ppbv. What determines these changes, and what can be done to make the instrument more stable?

Response: We added: “While we don’t understand which factors affect the stability of sensitivity, it is also clear that even though the sensitivity did vary, this changing sensitivity did not affect the measurements; for example, the calculated [NH₃] did not follow the same pattern as the sensitivity varied and during the fall, [NH₃] were always in the sub-ppbv level (Figure 6)” (L288 – 292).

Perhaps the data reduction technique causes some problems. The ammonia signals are normalized by the sum of the measured reagent signals, but the normalization technique is not justified. The CDC affects the cluster distribution, so these signals may not represent the ions present in the flow tube that react with ammonia. Furthermore, using the sum of the signals assumes that the sensitivity is the same for every cluster. Is there anything to support this assumption? Some tests ought to be performed that examine sensitivity in more detail. If the sensitivity never changed, this wouldn’t be such a concern. But given the large changes in sensitivity that are without explanation, the sensitivity determinations need to be better justified.

Response: The data reduction method is correct. “Primary reagent ions seen in CIMS spectra, in the order of decreasing ion intensity, were protonated ethanol dimer (C₂H₅OH)₂H⁺ (93 amu), trimer (C₂H₅OH)₃H⁺, (139 amu) and monomer (C₂H₅OH)H⁺ (47 amu). Primary product ions were (C₂H₅OH)NH₄⁺ (64 amu), NH₄⁺ (18 amu) and (C₂H₅OH)₂NH₄⁺ (110 amu). Only the product ion signal at 64 amu was used for [NH₃] calculations, since this was the most prominent ion peak (Figure 2) and gave the best sensitivity. To account for the possible fluctuations in reagent ion signals which were caused by the fluctuation of pressure in the ion-molecule reaction region (<10%), we also monitored these primary reagent ions and normalized them to calculate [NH₃].” (L202-L209) For normalization, the mean value of the sum of the three

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major reagent ion signals for a day was taken as a standard value for that day. Then the sum of the three major reagent ions at each time was compared with this mean value and the ratio of the each sum value to the mean value was taken into account into for ammonia mixing ratios. If the ratio is 1 then the normalization factor would be 1 for ammonia mixing ratio calculations; if the ratio is 1.1 then the normalization factor would be 1/1.1. For proton-transfer chemical ionization reactions, clusters are commonly exist and in order to avoid the complexity of ion clusters, a CDC is used to make spectra much cleaner. Using the sum of the three reagent ions does not need any assumption of the same sensitivities, because theoretically the reaction rates of these proton transfer ion molecule reactions (for example, the three reagent ions with ammonia) are very similar to each other ($\sim 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), as they are collision limited ion-molecule reactions.

The importance of temperature control is noted, but the stability of the temperature control is never stated ("constant temperature of about 35 °C" in section 2.2 is vague).

Response: The temperature was 35 °C ($\pm 1.5^\circ\text{C}$) (L162).

Are the calibration tank, regulator, and lines temperature controlled?

Response: The calibration line from the MFC to the calibration tee was temperature controlled, but the calibration tank, the regulator and the line from the regulator to the MFC were not. Revised to: "Heating was done by wrapping all the tubing and valves (except for the tubing from the regulator on the ammonia tank to the mass flow controller) in aluminum foil that was heated using heating tape." (L163-166)

How is the calibration magnitude known to 5%? How is it determined to be constant over the course of a year?

Response: "The standard gas supplied from a source cylinder (Linde, mixing ratio 4.5 ppmv, $\pm 5\%$) was added to the system with the flow between 1 – 10 sccm via a mass flow controller (MKS, $\pm 0.6\%$), which was regularly calibrated with a DryCal (Bios)."

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(L171–L173); so 5% was not the calibration magnitude. We have not experimentally determined whether this magnitude was constant over a year.

Why can't ammonium nitrate decompose to form ammonia in the CIMS?

Response: "Ammonium nitrate volatilization was found to be negligible for temperatures under 50 °C (Neuman et al., 2003)". (L113–L115) This decomposition is also expected to be temperature dependent. But since there was no dependence of measurements on temperature (including background, sensitivity and calculated ammonia mixing ratios), this also proves that desorption/decomposition of ammonium to ammonia was typically negligible under our measurement conditions (L265–L266, L287–L288).

The new measurements presented here are not directly compared with any other technique. The introduction notes that citric acid denuders are simple and low cost and have "served as the standard method to which the other techniques are judged." It would be useful to assess the long-term stability of the CIMS by comparing it with denuder measurements.

Response: "In the present study, we did not make an intercomparison with other ammonia instruments." (L374-L375) We also do not plan to acquire any other ammonia instruments such as citric acid denuder for the intercomparison purpose. "In this context, however, during the summer of 2009, ammonia measurements were performed in the Michigan forest using our CIMS and a wet scrubbing method coupled with long-path absorbance photometry (employed by Professor Xianliang Zhou from State University of New York - Albany). The ammonia data showed similar results (930 ± 670 pptv for the CIMS and 1200 ± 550 pptv for the wet scrubbing method coupled with long-path absorbance photometry over an 8 day period), and the trends of these ammonia measured from these two instruments were also the same. However, the denuder/spectrophotometer method had a poorer time resolution (data collected every 5 minutes in CIMS vs. averaged every hour in the denuder/spectrophotometer) and a

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higher detection limit (170 pptv). A detailed description of these comparison results will be shown in (Kanawade et al., in preparation)." (L375-L384)

Comparisons of instrument performance shown in Table 1 demonstrate that the instrument described here appears to be nearly identical to Nowak et al 2006(b), and has a much slower time response than Nowak et al 2007 (c). What new advances have been made?

Response: "The purpose of the following discussion is to improve our understanding of the system and to make technical evaluations, using various approaches including the comparison with the preexisting techniques. . ." (L337-L341) "Overall, our CIMS had a lower background than the (Nowak et al., 2006)'s low pressure version and a higher sensitivity than the (Nowak et al., 2007) version (Table 1)." (L359-L361)

Comment 3

The context and interpretation of the results are unclear. The introduction is thorough and provides a good motivation for developing a sensitive ammonia detector. Yet these motivations are not adequately addressed in the study. No ancillary measurements, other than standard meteorological parameters, are presented. Hence, the influence of ammonia on aerosol abundance cannot be investigated. While it is interesting to know that ammonia levels in this rural region are consistently low, the measurements presented here will be hard to place in context with other studies without some indication of the abundance of other pollutants.

Response: "The present study describes our CIMS instrument for in-situ NH₃ detection. Since the key technical issues for NH₃ detection are the instrument background, calibration and time response, our focus is to address these key technical issues. We also include the seasonal variation of the NH₃ in Kent, Ohio (a relatively less polluted U.S. Midwestern town) to demonstrate the instrument capability for atmospheric observations. The purpose of measuring NH₃ in this site was to see the NH₃ effects on aerosol nucleation. And, the influence of NH₃ and sulfuric acid (H₂SO₄) on aerosol

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abundance is discussed in another manuscript (Erupe et al., Correlation of Aerosol Nucleation Rate with Sulfuric Acid and Ammonia in Kent, Ohio: An Atmospheric Observation, under review; hereinafter referred to as Erupe et al., in preparation). In another second paper (V. Kanawade et al., Observations of ultrafine particle sizes, sulfuric acid, and ammonia in the Michigan Forest during the PROPHET 2009 CABINEX mission, in preparation; hereinafter referred to as Kanawade et al., in preparation), we also show the inter-comparison results of NH₃ instruments in the Michigan forest, with a large number of gas phase species and aerosol measurements together." (L79-L92)

The interpretation of the ambient ammonia mixing ratios is inaccurate. The end of the discussion highlights the many reports of very high ammonia mixing ratios measured in automobile tunnels, and concludes that the lower levels found at Kent "suggest that Kent has much less emissions of NH₃ year around". Mixing ratios are affected not only by emissions, but also by proximity to the emission source and ventilation, which explains the high values in tunnels. The primary purpose of the tunnel measurements was to determine emission factors and not mixing ratios, and it isn't particularly useful to compare the mixing ratios in tunnels to those in a rural region. And it certainly isn't correct to conclude that emissions are lower in the rural region. It would have been much more meaningful to elaborate on the comparison to measurements from other rural regions, and discuss if these values are important to particle abundance. The discussion should justify the conclusion that nucleation theories ought to be revised. Are ammonia mixing ratios from 0-100 pptv used this because values over 100 pptv aren't important, or because they aren't expected to exist?

Response: We agree that an extended discussion on emission measurements from tunnels is not valid to discussion of concentration measurements so we revised the discussion accordingly: "Our measurements made in Kent show that the NH₃ mixing ratios were lowest in the winter (60 ± 75 pptv) and higher in the spring (200 ± 120 pptv) and fall (150 ± 80 pptv) (Figure 7). In comparison, NH₃ mixing ratios in the remote marine atmosphere were 86 pptv on average (Schlesinger and Hartley 1992) and as

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low as 20 pptv in some remote areas (Dentener and Crutzen 1994). Rural regions in the eastern United States have shown mixing ratios of 100 – 500 pptv (Dentener and Crutzen 1994) with a mean mixing ratio of 300 pptv (Langford et al., 1992). On the other hand, polluted areas have shown mixing ratios as high as 30 ppbv (Dentener and Crutzen 1994) and mixing ratios up to 430 ppbv have been seen in strong point source locations (Schlesinger and Hartley 1992). For example, in New York City, an average NH₃ mixing ratio of 800 pptv was measured during one winter month (Li et al., 2006). Emission measurements made in different automobile tunnels have shown NH₃ mixing ratios of 50 – 400 ppbv (Fraser and Cass 1998; Kean et al., 2000; Moeckli et al., 2004). NH₃ mixing ratios of 20-70 ppbv have been reported from smoke plumes (Yokelson et al., 1999; Goode et al., 2000) as well as mixing ratio as high as 100-200 ppbv in plumes from biomass burning (Hurst et al., 1994; Yokelson et al., 2003; Li et al., 2006). These comparisons suggest that Kent falls into the range of a typical rural region.” (L385-L400) We don’t know what is the reason for the ammonia-ternary nucleation theories to include the ammonia range only from 0-100 pptv, but it is clear that this range does not reflect the real atmospheric conditions. “Our atmospheric observations, together with other observations discussed in this study, suggest that these nucleation theories should be revised to include larger concentrations of NH₃ mixing ratios in their parameterizations to represent all atmospheric conditions. As discussed in (Erupe et al., in preparation), when we did ternary homogeneous nucleation simulations using the measured sulfuric acid and ammonia conditions and using (Merikanto et al., 2007), we could not reproduce the atmospherically observed nucleation rates. Therefore, we believe that this parameterization needs to be constrained by the observations.” (L404 – 410).

References added:

Erupe M. et al., Correlation of Aerosol Nucleation Rate with Sulfuric Acid and Ammonia in Kent, Ohio: An Atmospheric Observation, under review.

Kanawade V. et al., Observations of ultrafine particle sizes, sulfuric acid, and ammonia

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in the Michigan Forest during the PROPHET 2009 CABINEX mission, in preparation.

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