

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

Anonymous Referee #1

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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 work are detailed below.

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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. 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. 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)? Mixing ratios are reported as pptv, ppbv, and ppb. The % steady state at $t=0$ is 105% - this should be explained. 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.

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.

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/pptv. What determines these changes, and what can be done to make the instrument more stable? 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

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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. 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). Are the calibration tank, regulator, and lines temperature controlled? How is the calibration magnitude known to 5%? How is it determined to be constant over the course of a year? Why can't ammonium nitrate decompose to form ammonia in the CIMS?

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. 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?

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.

The interpretation of the ambient ammonia mixing ratios is inaccurate. The end of the

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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?

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