

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

### **Anonymous Referee #2**

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This manuscript describes the deployment of a CIMS for the measurement of atmospheric ammonia in three different seasons. The technique appears promising for the provision of high time response data, with sufficient sensitivity to make measurements at sub-ppb mixing ratios. The value of the season-to-season comparisons is questionable, because the configuration of the sampling assembly seems to have been altered for each period of deployment, which may introduce biases. Additionally, there appears to be a large degree of variability in the accuracy and precision of the technique, which the authors have not adequately explained.

In order to be publishable in AMT, this manuscript must present the characterization of the instrument performance in a more consistent and understandable way. For example, the analysis of the time response provides some parameters from a single fit, but

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presumably several experiments were carried out. The authors should more clearly address whether the presence of volatile ammonium aerosol could bias their signal. The interpretation of the ambient measurements is limited by the lack of supporting measurements (e.g. aerosol composition or at least mass loading, SO<sub>2</sub>, HNO<sub>3</sub>), but nevertheless the implication that mixing ratios are low because emissions are low is overly simplistic. Have past aerosol composition measurements been made in the region that could at least suggest whether aerosol is generally acidic?

I provide more specific comments below: Abstract – the discussion of the sensitivity, uncertainty and detection limits is a bit ambiguous. What averaging time is used to calculate a detection limit of 60 pptv and is that for a 3sigma detection limit?

Introduction – is citric acid denuder really a technique on its own? Don't you need to specify the analysis technique used after the denuder collection? For what sampling period and analysis technique is the 25 pptv detection limit given?

There are many more recent discussions of ammonia measurement techniques (in AMT alone: Wolff et al., 2010; von Bobruzki et al., 2010; Ellis et al., 2010; and in ACP Norman et al., 2009) Given that you heated the inlet to 35 °C (at least during the fall), how confident are you that no ammonium-containing particles volatilized prior to the ion-molecule reaction region? P1135 L 27, Sentence should start ' Amongst these' P1137 L7, The sentence "Below, we only describe the inlet and flow tube regions (Sects. 2.2 and 2.3)." should be moved to the end of the paragraph it is part of.

P1137 L23 – km and miles in same sentence

Figure 1b – Was any attempt made to characterize sampling losses of ambient ammonia in the inlet before PFA tee 1?

Figure 2 – It's extremely difficult for the reader to see the various colours meant to differentiate between the ambient, cal, and zero.

Section 2.3 – How constant were the relative proportions of the reagent ion? Did you

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perform any tests to confirm that normalizing to their sum was the most appropriate approach? Is there evidence that they all react with ammonia to produce  $m/z = 64$  amu with the same efficiency?

The authors state that the use of the CDC prevents them from detecting clusters of water and reagent ion, but can they be sure they don't exist in the ion-molecule reaction region. Could the humidity-dependence of calibrations offer any indication as to whether this might be significant?

Section 3 P1141 – Equation 1 – this looks like an equation for a bi-exponential fit, and the  $1/e^2$  time depends both on the time constants and each terms pre-factors. Why does Equation 1 provide parameters for one specific fit, when the time decay experiments were carried out several times – as shown in Figure 3? The authors should present a more representative value with some indication of uncertainties. Given that the shorter time constant is on the order of 2 sec, a data collection rate of 1 Hz may not be sufficient to describe the decay rate of the signal.

Figure 4a – why was the time response so much worse in calibration addition C4 than for addition C3, which both had the same nitrogen flow? P1141 – L25 why was the instrument response to the addition of 400 pptv as expected for the addition of 800 pptv?

Section 3.2 P1142 If some of the signal during the background is from desorbing ammonia from the inlet, wouldn't it be most appropriate to normalize the signal to the reagent ions (i.e. use the sensitivity to calculate it as a mixing ratio)?

Fig 5a: If the inlet design and time response were optimized for the fall measurements, why are the counts so much higher during the background in this season?

Fig 5b – I don't think this is the appropriate use of 'calibration curve' in the caption. Section 3.3 What accounted for the wide range in sensitivity? Was the concentration of the NH<sub>3</sub> cylinder confirmed by another method?

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P1145 L 11 – extra period before reference

Discussion In your comparison of the different CIMS ionization schemes, you indicate that the different reagent ions lead to different background measurements. Can you be sure that this difference wouldn't be more appropriately attributed to the inlet configuration used by each instrument?

Why would a curved inlet lead to the loss of a gas phase species?

P 1146 L26 – The lower levels in Kent may be attributed to lower vehicle emissions, but one should also consider the role of aerosol uptake. Could the presence of high levels of aerosol sulphate act as a strong condensational sink where your measurements are made?

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Interactive comment on Atmos. Meas. Tech. Discuss., 3, 1133, 2010.

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