Atmospheric Measurement Techniques Discussions

Interactive comment on "On-line determination of ammonia at low pptv mixing ratios in the CLOUD chamber" *by* F. Bianchi et al.

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We would like to thank the referee for taking the time to read and comment on this manuscript and for his helpful and constructive comments.

Q: Overall, this is a clear, well-written paper describing the methodology for measuring gas phase ammonia in the CERN CLOUD chamber. While the specifics of the technical implementation (e.g. lack of discrimination against particles) mean that the approach is not universally applicable, the details are important to describe for interpretation of experiments regarding the ammonia dependence of nucleation rates. Given that there is strong motivation to reduce the detection limit below 35 ppt, I wonder if the authors considered using an acid to reduce the pH of the scrubbing solution? This may allow

for the efficient capture of NH3 at a lower liquid flow rate, potentially improving the sensitivity.

A: At these low NH3 concentrations the pH does not increase that much under our flow conditions. The uptake is rather kinetically limited as shown in Figure 4. We can not reduce the liquid flow rate further. Otherwise the ratio between air flow rate and water flow rate would be too high.

Q: Abstract and later - The detection limit is reported for what measurement interval?

A: The detection limit given here is for an averaging time of 10 minutes. We mention this in the revised text.

Q: P 2113, L 1-10 The authors are providing background literature on the NH3 concentration dependence of nucleation rates, however they do not explain at what NH3 levels the Benson et al. experiments were carried out. Also, might it not be expected that the ratio of NH3/SO4 rather than the absolute value of NH3, would be important in determining the dependence of nucleation rates on NH3?

A: This is an important note of the referee and we agree that it should be more highlighted in the manuscript. The NH3 level reported by Benson et al. was between 0.08 and 20 ppbv and the sulphuric acid concentration was 106-107 cm-3. Thus, their lower end of the ammonia concentration was at the upper end of our concentration range while their H2SO4 concentrations were in the lower range of ours. The ratio between ammonia and sulphuric acid was therefore much higher in the study of Benson et al. and according to our finding (this manuscript and Kirkby et al. 2011) the nucleation rate is virtually saturated with respect to a further increase in ammonia levels. This explains that Benson et al. did not see a strong enhancement in the nucleation rate with an increase in ammonia concentrations. This discussion is added to the revised manuscript.

Q: P 2114, L 3-7 I think the high detection limit with many techniques, including the

CIMS instruments described in this section, can be attributed to variability in background levels, rather than simply high backgrounds.

A: We agree, and the sentence has been changed accordingly.

Q: P 2114, L 9-18 This paragraph reads a little awkwardly. Initially two reasons are mentioned (particles and hydrophilicity), then a third (diffusion coefficient). In the last sentence, it's not clear which 'two properties' are being referred to.

A: The paragraph has been rephrased.

Q: P 2114, L 18 In the text, the publication year of Bae et al. is 2009, but in the references it is listed as 2007

A: The publication year has been corrected.

Q: P 2116, L 23 Which flow has a rate of 10 L/min? This doesn't seem to match anything mentioned later in the text.

A: 10 L/min was taken as an example to show that even at high flow rates the losses are big. The sentence has been changed to make it easier to understand.

Q: P 2117, L 1 Which dimension is 34 mm?

A: The outer diameter of the sampling tube is 34 mm. The sentence has been clarified.

Q: P 2117, L 16 Data are provided every 2 seconds, but considering the residence time and volume in the coil, there is a lot of opportunity for mixing, which would smooth out the instrument response. Have any tests been done to assess the true time response of the system?

A: This is a good point. The rise time of the signal (from 10% to 90% of its final value) after a step concentration change was determined to be around 10 minutes. This information has been added in the manuscript.

Q: Equation 1 – The authors should clarify if the fit is forced through the origin.

A: The fit was forced through the origin. This clarification has been added.

Q: P 2119, L 4-8, I find the terminology 'stripping efficiency' a little unclear in this context. Presumably, by efficiency, the authors mean the fraction of gas phase ammonia collected per unit air sampled. However because there is also a liquid flow, one could interpret the meaning as the efficiency per unit liquid flow. This would obviously have a very different relationship than the data presented in Figure 4. I recommend clarifying the mean of 'efficiency'. More broadly, does the plateau at 0.3 mL/min hold over a large range of gas phase concentrations? Since ammonia is a weak base, it will become more difficult to collect the same fraction into solution at higher levels of $NH_4^+(aq)$. This should be considered by the authors.

A: By stripping efficiency we mean the fraction of gas phase ammonia collected per unit air sampled. This is now clarified in the manuscript. It is true that the pH in the stripping solution increases which lowers the gas/liquid equilibrium (effective Henry constant) with increasing ammonia concentrations. However, calculations show that the efficiency is not more than 10% reduced at 1ppbv. At higher ammonia concentrations one would need to acidify the stripping solution.

Q: P 2119, L 7, add a comma: '...further, indicating...'

A: Comma added.

Q: Figure 5 – it would be interesting to know what the theoretical ammonia mixing ratio in the chamber is (based on the rate at which air is exchanged) in addition to the MFC setting. How far off are the measured values from what would be theoretically calculated, even after significant time for equilibration?

A: The factors determining the concentration in the chamber are the rate of injection, loss to the chamber walls and evaporation from them, air exchange in the chamber. We calculated the steady state concentration of ammonia assuming a wall loss life time of 10-15 min (this is similar to the measured lifetime of sulfuric acid). It was found that the

calculated concentration of ammonia was within a factor two of those measured values, which had enough time (many hours) to reach the equilibrium This is now mentioned in the text.