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Atmospheric Measurement Techniques Discussions

Interactive comment on "Dimethylamine and ammonia measurements with ion chromatography during the CLOUD4 campaign" *by* A. P. Praplan 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/her helpful and constructive comments. Reviewer comments are portrayed in regular font style, replies in italic.

1) In Figure 3, it appears that only one (or two) calibration standards other than the blank are in the range of the experimental data. Given that many ion chromatography systems are known to have non-linear responses to NH3 (e.g. Ullah et al., 2006), it may improve quantification to have additional standards in the calibration curve.

We agree with the comment of the referee that for a large NH_3 calibration range, a non-linear calibration may have to be used. However, a standard with higher concentration (ca. 240 ng) was also measured, which was not included in the calibration curve. Including this standard and using a quadratic regression curve for the calibration, the authors are able to demonstrate that the calibration is linear in the range of interest (Fig. 1).

2) With regards to the selectivity of the technique, the authors indicate that their chromatography method allows for the resolution of NH3 and DMA, from each other and from Na and K. However later in the manuscript in Section 3.3, it is mentioned that NH3 values could not be obtained due to an interference in the chromatograms. To what do the authors attribute this interference, and how can they be confident that it does not affect the calculated mixing ratios at other times in the experiments? On a related note, what sort of problems would be encountered if other amines were present in the chamber?

The authors did not mention that the resolution of the analytes and the interferences also depends on the concentration of each species. We experienced an instrumental Na^+ contamination at high levels (no contamination of the chamber). It was possible to identify the cause of this contamination: a cation trap column used for the sampling water that had been treated with NaOH. It was then replaced by a new one for the rest of the measurements. For this reason, we are confident that this interference did not occur later again as the Na^+ peak was comparable in intensity with the one of K^+ and NH_4^+ and well separated. The sentence "Only sodium and potassium peaks also appeared in the chromatograms but well resolved from the peaks of interest." is replaced in the manuscript by "Only sodium and potassium peaks also appeared in the chromatograms and were usually well resolved from the peaks of interest. However during the period between 29 June and 7 July, due to an instrumental contamination with sodium, its high and broad peak masked sometimes the small NH_4^+ peak and increased the conductivity background during this period."

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It was not possible to identify other amine peaks during CLOUD4.

3) In Section 3.1, the authors investigate the effect of the liquid-to-air-flow ratio on the sampling efficiency for DMA. The right-hand panel of Figure 4 would be more straightforward to interpret if the y-axis displayed the fractional or normalized signal, rather than the absolute mixing ratio. More importantly, the sensitivity of the sampling efficiency to the flow ratios is only tested for DMA and the results are applied to the scaling of the NH3 data. But as the authors describe in Section 3.1, the solubility and pKa of NH3 is quite different from DMA and this must introduce additional uncertainty to the calculation of the NH3 mixing ratios. This should be addressed in some quantitative way by the authors.

Figure 4 was modified according to the referee's comment and display now the normalized signal. We agree with the referee that the results should not have been applied to both species. According to Bianchi et al. (2012), a liquid to air flow ratio of 0.15 $\times$ *10*$^{-3}$ *is sufficient to achieve a complete sampling of* NH_3*. Therefore, no scaling is applied to* NH_3 *any more as the liquid to air flow ratio was always above this value and Fig. 5 was modified accordingly.*

A fit function of the form $y = ax^b + c$ *was added to Fig. 4 of the manuscript. This fit is now used to correct the DMA data for sampling efficiency and the corresponding text in the manuscript has been modified. The correction factors range from 1 to 1.89 (for a ratio of 0.15* $\times$ *10*$^{-3}$*).*

4) There is an important difference between the delivery of the analyte during calibration (direct injection without pre-concentration) and during sampling of the chamber. During each measurement interval, deionized water containing the soluble analytes is flowed over the concentrator column for a period varying between 70 and 210 minutes. The retention capacity of the concentrator columns can be influenced by injection flow rate and volume (e.g. Markovic et al., 2012). Given the large volumes of liquid passed

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through the concentrator columns in their method, the authors should assess whether there are any potential losses of analytes.

The authors have evidence that these long concentrating times and the large volume passed through the concentrator column did not influence the DMA measurements. A sample acquired on 13 and 14 July was concentrated for almost 10 hours (0.48 pptv) and is consistent with the previous (0.57 pptv, 3.51 hours) and the following (0.33 pptv, 4.10 hours) samples (within uncertainties).

The NH_3 *concentration for this long sampling time was lower due to losses and a too large blank correction (blank correction is proportional to the volume passed through the concentrator column). However, data from 14 and 15 July showed that a similar (blank corrected) mixing ratio was obtained for a sample with 4.5 hours sampling time (5.9 pptv) as the previous and next samples (5.3 pptv and 7.0pptv, both sampled for 3.5 hours). Therefore, the authors are confident that a sampling time of 210 minutes (which was used most of the time) does not result in losses of* NH_3*. This discussion was also included in the manuscript.*

References

F. Bianchi, J. Dommen, S. Mathot, and U. Baltensperger, Atmospheric Measurement Techniques Discussion, 5, 2111–2130, doi:10.5194/amtd-5-2111-2012, 2012.

M.Z. Markovic., T.C. Vandenboer, J.G. Murphy, Journal of Environmental Monitoring, 72, 1156-1162, doi: 10.1039/c2em00004k, 2012.

S. M. R. Ullah, M. Takeuchi, and P. K. Dasgupta, Environmental Science and Technology, 40, 962–968, doi:10.1021/es051722z, 2006.

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 2395, 2012.

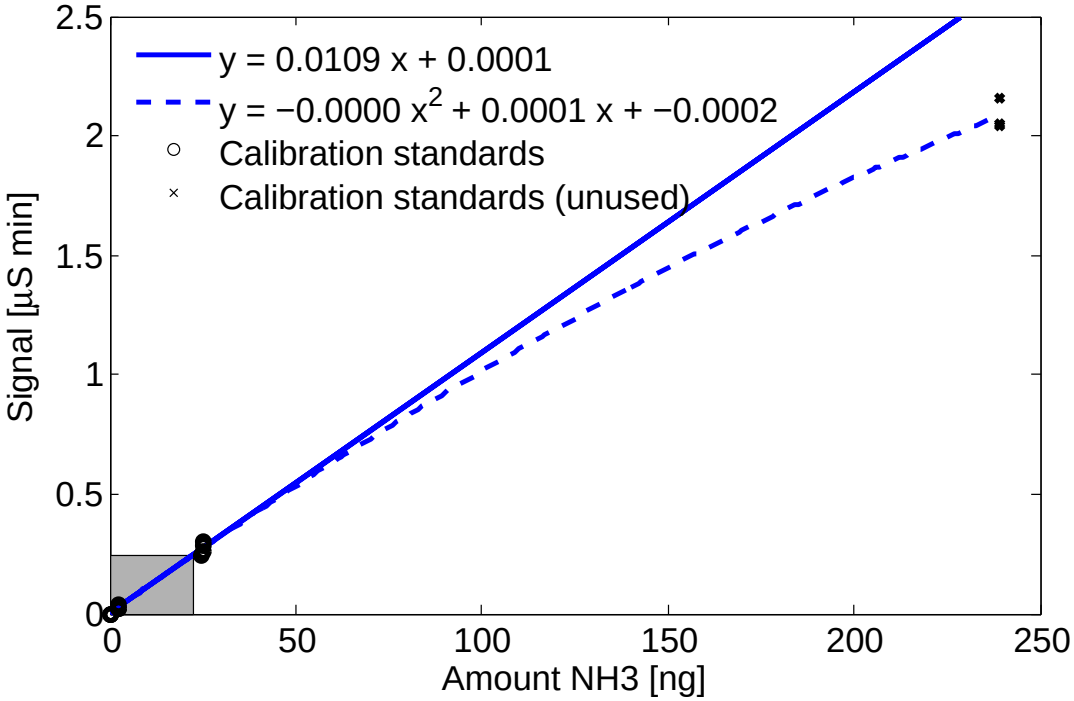

Fig. 1. Comparison of calibrations. The quadratic fit takes into account the highest standard concentration, while the linear one does not. The gray area represents the range of data measured during CLOUD4.

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