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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: Page 2113, line 10. Ambient NH3 levels in the atmosphere range over many orders of magnitude depending on proximity to sources. Therefore, it is important to clearly define here what concentrations constitute 'low NH3' as applied to this study early in the manuscript.

A: The sentence has been clarified.

Q: Page 2113, line 11 – page 2114, line 8. NH3 measurements at low concentrations are difficult not only because the absolute background level can be high but also due to variability in the background. Since for many of the instruments described here the background can only be determined periodically, variability between background determinations greatly influences the limit of detection. Also, many of the papers discussed here are describing the detection limits of ambient measurements. The background levels and, therefore, the detection limits of these instruments will be influenced by changes in ambient NH3 levels and ambient conditions, e.g. temperature and relative humidity. The study described in this paper at CERN is essentially a laboratory study under much more controlled conditions than ambient measurements. Whether detection limits of any of these instruments would be improved under the conditions of this study is unknown. Conversely, whether the technique described here would have similar limits of detection under ambient conditions is also unknown. Thus, the comparison implied here is not exactly fair.

A: We do not say that our technique is superior. This section just gives an overview of the techniques developed and used so far. A difficulty related to the CLOUD chamber is that the standard sampling line is quite long implying large losses of ammonia. With our sampling system we overcome this problem. We are aware of the fact that our sampling could not be used as such in the ambient.

Q: Page 2114, lines 16 – 18. The inlets used in the papers cited here vary considerably in length, flow rate, and materials. What is meant by slow response time? I find it curious that Hanson et al., 2011 and Nowak et al. 2007 are not cited here. Hanson et al. 2011 claim time response on the order of 1 minute. Nowak et al., 2007 present data showing a 5 s time response determined from the signal decay after removal of a standard addition calibration value. They also claim in a more recent paper not cited here, Nowak et al. Airborne observations of ammonia and ammonium nitrate formation over Houston, Texas, J. Geophys. Res., 115, D22304, doi:10.1029/2010JD014195, 2010, to have made improvements reducing the time response to 1-2 s. These appear to be fast compared to the time scales discussed in the experimental section here.

Because of the difficulty sampling and quantifying NH3, it is difficult to make general statements regarding time response and detection limits. These quantities need to be justified at the levels appropriate for the analysis presented for every study performed.

A: The slow time response is related to the CLOUD sampling line where we have a stainless steel tube that cannot be shorter than 130 cm and where the flow rate may not be higher than 10L/min. The instruments cited above have clearly a fast response time. However, to obtain this, heated teflon sampling lines are used. Sampling with those instruments through a stainless steel tube would seriously deteriorate the overall time response. As the reviewer points out, these issues are special for each application and need to be considered in the analysis. We say now specifically that due to the material requirements of the sampling line at the CLOUD chamber there is an additional time response problem. It was not the intention to make a general statement here. We rephrased this section pointing out that special care needs also to be taken to the inlet design even when the time response of the instrument is low. We also included the citations mentioned by the reviewer at appropriate places in the manuscript.

Experimental

Q: There is no description or definition of what constitutes a background measurement. Section 3.1 refers to a blank signal. Is the blank signal taken as the instrument background? How is the blank signal determined? Where in relation to Fig 1 is the blank added?

A: The instrument background was obtained by bypassing the stripping solution of the sampling line entering directly the instrument. This pathway was added to Figure 1.

Q: Though the manuscript states early (page2115, line1) that this is a high time resolution technique, the time resolution is not explicitly stated. What is the time resolution of the measurement? How is it defined or determined? Section 2.2 states that the residence time in the reaction coil is 540 s. Section 2.4 states that data is provided every 2 s but, also, that due to the reaction time and the detection time there is an 18 minute time delay for the concentration of ammonia. Is the reaction time in 2.4 the same as the residence time stated in 2.2? What is meant by the detection time? With a 540 s residence time how meaningful is the data reported at 2 s? Also, as a follow-up on my earlier comment on detection limits, averaging over longer measurement periods can lower the detection limit of many instruments. Therefore, the measurement period should be noted when comparing detection limits. The liquid and gas flow rates seem to be important, in particular for controlling the residence time between sampling and the de-bubbler. How are these quantities measured? Where are they measured in Fig. 1?

A: The residence time of 540 s in the reaction coil leads to a time shift of the appearance of the signal. However, this long reaction time also leads to mixing and therefore a smearing out of the signal. In addition, the filling of the waveguide also leads to a damping and averaging of the signal. We define the time response as the rise time of the signal (from 10% to 90% of its final value) after a step concentration change. This was determined to be about 10 minutes. The data of the UV-Vis spectrometer were collected every 2 seconds (this is the integration time of the light). The ratio of the gas to liquid flow is important for the stripping efficiency. It needs a thorough turbulent mixing. The residence time in the sampling line is very short and does not affect the response time. All this information was added in the manuscript to make it clear and avoid any misunderstanding.

Results

Q: Page 2118 section 3.1 Where is the NH4Cl solution added when the calibration curve determined? Is it between the I.E. column and sampling line or after the sampling line in Fig 1? What is the uncertainty in the standard NH4Cl solutions used to calibrate?

A: The text and the figure were adapted to show where the standard solutions were injected. The uncertainty of liquid standard solutions was always lower than 5%.

Q: Page 2119, lines 4 – 8. The stripping efficiency was checked by adjusting the water flow rate until there was no change in NH3 signal. Does this measured NH3 level agree with the estimated concentration added to the chamber? Does the water flow rate needed to strip 100% of the NH3 from ambient air change as a function of ambient NH3 concentration, i.e., is more or less water flow needed to strip 10 ppbv than 100 pptv? How many times was the stripping efficiency checked? What do the error bars in Fig. 4 represent?

A: Generally, the ammonia level measured was lower than expected from the estimated addition to the chamber. We think that this is a problem of the ammonia injection system. The stripping efficiency will decrease with high ammonia concentrations because the pH of the stripping solution will increase. This will decrease the effective Henry constant and less ammonia will partition into the liquid phase. At the high end of our ammonia mixing ratios (between 1 and 2 ppb) such an effect is less than 10%. In case of even higher ammonia concentrations one needs to add an acid to the stripping solution or adapt the flow rates (low air flow rate or high liquid flow rate). The stripping efficiency was checked once.

Q: P 2120 lines 4 -13. I agree that the behavior observed in the CLOUD chamber is a function of the properties of NH3. However, the chamber characteristics, such as, total surface area, residence time, and materials used, are quite different than any of the inlets used in papers cited in the introduction. Therefore, a blanket comparison of the CLOUD chamber behavior to all inlets in general is not valid.

A: Yes, the conditions of the CLOUD chamber are special and that is why we emphasize the importance of a carefully designed inlet. We do not generalize with respect to other studies. However, we believe that the stickiness of ammonia needs to be addressed carefully in every measurement system. It might be easier to tackle in many cases due to less restrictions in choice of materials and sampling designs.

Minor Editorial Comments:

Q: Page 2112, line 7. Here the campaign name appears as CLOUD3 not CLOUD-3 as in page 2114, line 23.

A: corrected

Q: Page 2116, line 21 Change shown to discussed because this point is not shown by any data presented here.

A: done

Q: Figure 2. Section 2.3 gives dimensions in the description of the sample line. They should be added to Figure 2, even if the figure is not to scale.

A: done

Q: Figure 5. Remove the single quote from the legend labels. Change left y-axis and legend label to Observe NH3 mixing ratio for consistency with the figure caption. Change units of left y-axis to pptv to agree with x-axis of figure 6.

A: done

Q: Figure 6. Change the x-axis label to Ammonia Mixing Ratio since that is what is plotted, not concentration.

Q: done

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