Atmospheric
Measurement
Techniques
Discussions

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comment

Interactive comment on "Negligible influence of livestock contaminants and sampling system on ammonia measurements with cavity ring-down spectroscopy" *by* J. N. Kamp et al.

Anonymous Referee #1

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The manuscript describes field and laboratory experiment to test the influence of livestock contaminants (VOCS) and parts of the sampling system on Picarro-CRDS ammonia concentration measurements. The manuscript is well-written and the conclusions are clear. While the experiments are well described, I think that one or two important steps are missing which would strengthen the conclusions and show that the Picarro is the instrument to use under conditions with extremely high ammonia concentrations (>1 ppm). After some major corrections, (major as another test is needed, minor as I think it should not take too much time to perform and add to the manuscript).

< General comments and suggestions >

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Discussion paper

Main comments: 1. The authors mention that the VOC's can potentially interfere with Picarro-CRDS NH3 measurements, but what is the actual physical basis behind this statement? Does any of the VOC's have an absorption line near the two NH3 lines used in the Picarro instrument? (Such as the H2O lines that we can see in the water vapour case, shown in Martin et al., 2016) Why would any of the VOC's have an influence on NH3? Looking at the results in Figure 6, the bias in the NH3 concentrations follow directly from H2O, which was shown in the past by Martin et al., 2016. If we would remove the VOC sections from the manuscript, what remains is a non-conclusive test of the different filters and a response time test under extremely high concentrations with long inlet lines, which I think in itself and in its current form, is not original enough to warrant publication.

2. I would like to see the humidity test (and in extension the CO2/CH4 and VOC.. tests) under extremely high ammonia conditions. The author states the intent to use the Picarro to measure NH3 concentrations in animal production buildings. Concentrations inside such facilities are up to 4 orders higher than the usual atmospheric concentrations found in most (outside) field experiments (1-20 ppb, for example see Bobrutzki et al., 2010, where the range is 0.07 – 25 ppb for the CRDS). While the current tests show that one should definitely not use this Picarro-CRDS under normal atmospheric conditions (with a bias of the order of a few ppb) without an H2O correction, this does not have to be true inside the animal productions facility, where concentrations are of the order of a few ppm. The current results however do not show if the instrument bias changes under extremely high concentrations. If the authors can reproduce the few ppb bias even under extremely high nh3 concentrations (>1ppm) I would with confidence use this instrument inside such a facility. Furthermore, does temperature not influence the measurements? All lab experiments seem to have been done under a fixed temperature of 22 degrees, maybe vary this if possible?

General comments: 3. The manuscript describes conditions with concentrations up to an order or 3 higher than the usual atmospheric concentrations reported in other field

experiments. It might be good to add a plot/figure showing one or more time series of the typical concentrations and variations from hour to hour / day to day. This will give the reader a better grasp on the expected concentrations. It will also show if the 1.02-ppm and 10.01 ppm experimental air mixtures are sensible amplitudes to test the instrument responses for.

4. While the field and lab setups are well described it will be helpful for the reader to have a picture or schematic of the setup with the relevant parameters shown. (filter locations / inlet lines / inlet height).

5. What is the main reason that the PTR-MS was not used under field conditions? (p3, l20-21)

6. While the NH3 calibration gas is stated to have a concentration of 101ppm +-10%, I assume that the gas is still well mixed inside one bottle. If the same bottle was used for all tests, one can assume a constant bias. Looking at Figure 2 I would argue that the mixture is biased slightly high (as each of the response curves ends up at the fixed mixture value). Any variations in the signal follow from the Picarro system and local conditions.

7. Response time is defined as the time it takes to go from 100 – 5% and 0 to 95%. Is this 95% of the final level or of the expected concentration of the mixture? Why not fit an exponential function to the rise and fall sections of the graph? From those fits one can derive the e-folding time of the instrument instead of the to me less informative 95% check.

If possible adjust the figures to show the 20 or so seconds of interest. Split figure 2 into 4 sections. (a) and (b) covering the Rise and fall time of the 1.02 (more like 1.05) mixture, and (c) and (d) the rise and fall time of the 10.01 ppm (more like 10.25 ppm) mixture. 8. The response times of SP1 – SP5 seems to mostly to be related to the length of the inlet line and the height that the inlet is positioned at (P7, l16). What are the actual lengths of the inlet lines? The longest fall response time was

found to be ~70s under lab conditions. What is the maximum instrument response time found under field conditions? 9. Figure 3 shows a variety of starting and final NH3 concentrations for each of the filters. What is causing the higher initial and final concentrations of PTFE 0.2 (or GA200) and the lower step change? 10. Figure 4: What is causing the high variation in the NH3 bias as a response to the humidity? Is there any possibility that the zero air is not completely zero? 11. Figure 6. While interesting to see NH3 to VOC, H2O and H2O to VOC I think you can show all of this in one figure. The authors show in figure 4 that NH3 has a relation to H2O. If possible, normalize the figure by diving NH3 over the fitted value. Show that the VOC's indeed have no effect. Furthermore, similarly as mentioned in point 2, test the bias under extremely high NH3 concentrations. 12. Table A1 shows a range of 0.1 – 5.5 ppb for NH3, what is causing these variations? Does the humidity change? And even if it does, why do we find 5.5 ppb for NH3 when the max bias was shown to be ~5ppb under 100% humidity conditions. 13. I am missing a description of the measurement principle of the Picarro-CRDS. If possible add a description to section 2.2.

< technical corrections >

Throughout the manuscript, there are a number of grammatical errors. If possible, let someone with English as the mother tongue edit the document before final submission.

P2,l22 : Quantify, good is objective. Also Bobrutzki et al., 2010, showed an inter-comparison between instruments for concentrations around 1-25 ppb, not ppm's. P3,l16 : "The CRDS", change throughout the document