

Answer to anonymous referee #1

>>> *We appreciate the comments and suggestions from the anonymous referee that have helped to improve the manuscript.*

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 >

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.

>>> We agree that the physical basis behind this statement should be taken into consideration. We have used the HITRAN database for absorptions lines of the most important VOCs presented in this study. It can be seen that acetic acid has an absorption line close to ammonia and methanol does also have a line in the measurement range of the CRDS. This is solely from single-wavelength absorption, as line broadening is not taken into account. The following text and Figure 1 has been added to section 1:

The absorptions lines of acetic acid and methanol found in the HITRAN database (Gordon et al., 2017) are in the same range as the ammonia lines used for measurements in the CRDS, see Figure 1. This highlights the importance of the study as the absorption from VOCs can cause similar interference as reported by Rosenstock et al. (2013) and Liu et al. (2018) for PAS.

The following has been added to section 2.2:

The G2103 analyzer measure absorption from 6548.5 to 6549.2 cm⁻¹ (Martin et al., 2016) and Figure 1 shows the absorption of some selected compounds in this range obtained from the HITRAN 2016 database (Gordon et al., 2017). The computed absorption lines in Figure 1 corresponds to 1% H₂O, 400 ppm CO₂, 100

ppb acetic acid, 100 ppb ethanol, and 100 ppb ammonia at 45°C and 140 Torr. Line broadening is not taken into account.

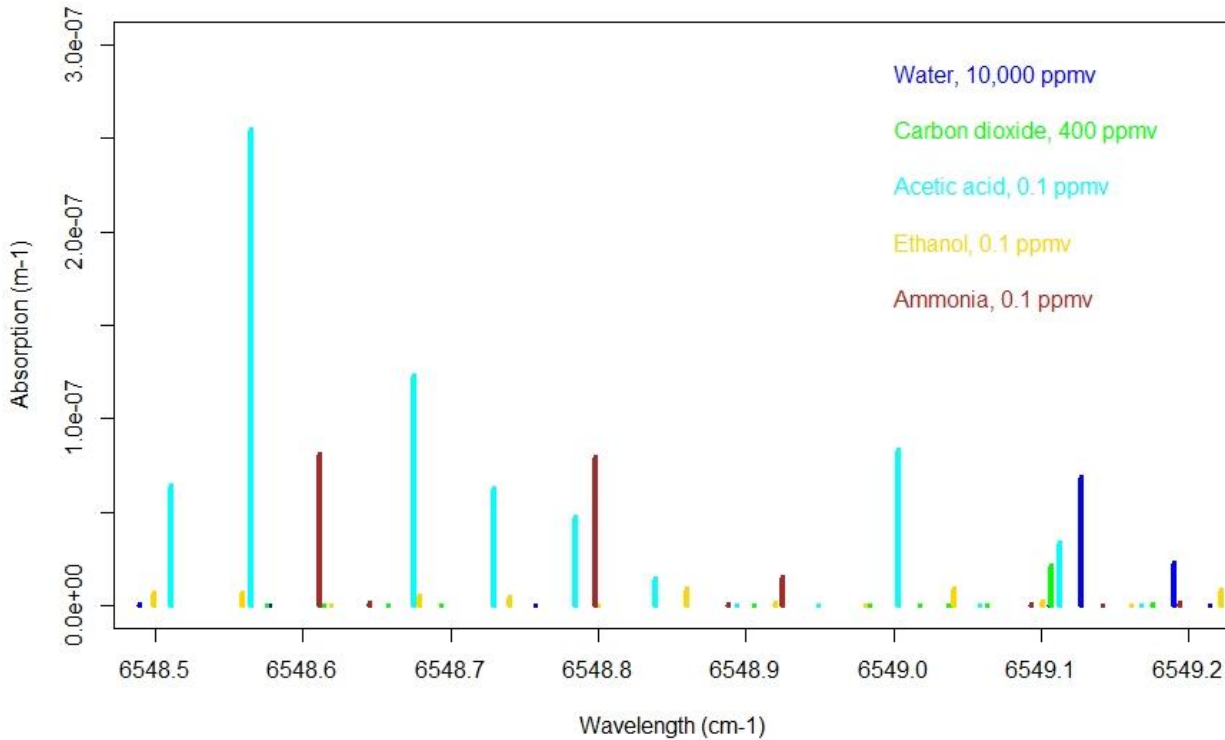


Figure 1 Simulated absorption spectrum from the HITRAN database for 1% H₂O (blue), 400 ppm CO₂ (green), 100 ppb acetic acid, 100 ppb ethanol, and 100 ppb NH₃ at 45°C and 140 Torr.

In addition, we would like to emphasize that the experiences with PAS (and lack of proper validation) has led to a strong need for documenting the limited interferences associated with CRDS. Thus, even if the theoretical contributions of VOC had been low, it would be important to carry out the tests performed in our study in order to convince the scientific community that CRDS is indeed a major improvement.

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 Bobruzki 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?

>>> We have no expectations of a larger bias under higher NH₃ concentrations as the contribution from water is expected to be independent of the ammonia concentration. It is not possible to separate the total measured ammonia concentration into a contribution from water and the pure ammonia signal. We have shown the extreme cases of water interference for this particular model and this is below 5 ppb, which will have negligible influence on ammonia concentrations above e.g. 1 ppm and still have a very low influence down to e.g. 100 ppb.

Regarding the temperature, the cavity temperature and pressure is kept constant at all running times and will not run if these are not stable at the set point. Thus, changing the temperature would only change the equilibration time for absorption/desorption to the tubing and parts before the cavity. The wall absorption has been described by other e.g. (Shah et al., 2006; Vaittinen et al., 2014).

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.

>>> Data from pig houses with finisher pigs can be added to show typical concentrations under different conditions over more than two months. Cycles were Room 1, Room 2, Room 3, Room 4, Background, etc. with 6 minutes measurements at each position (Hansen et al., submitted to Journal of Environmental Quality). Data presented in the figure is hourly mean values with concentrations up to 15 ppm; we suggest that it should be included in the appendix. Data from a dairy cattle barn can also be included, and the figure below shows hourly mean concentration over a week; we suggest that the figure is included in the appendix.

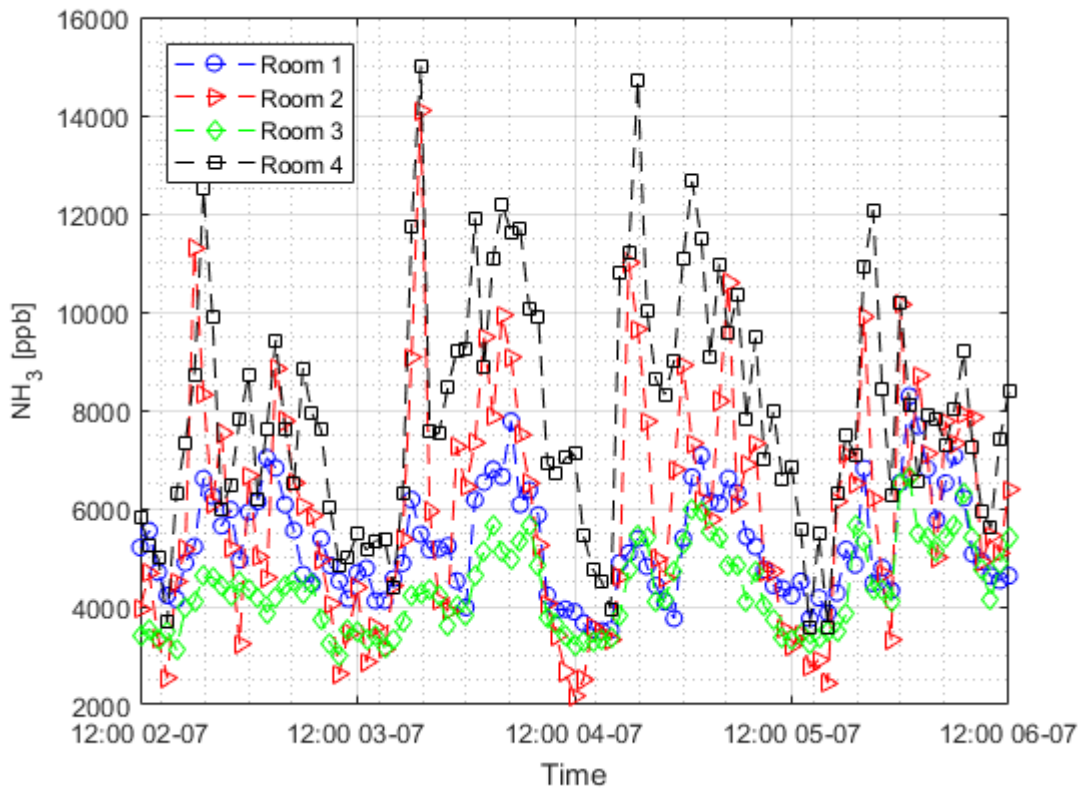


Figure A2 Hourly mean concentrations of NH_3 from four different rooms with finisher pigs, unpublished data.

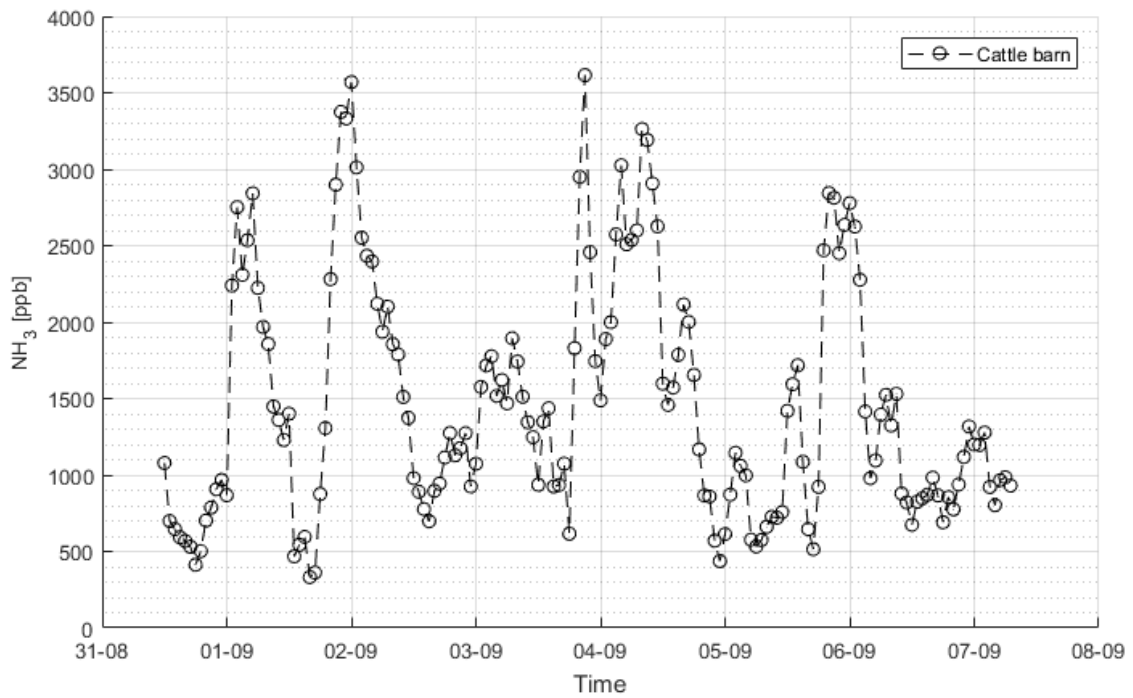


Figure A3 Hourly mean concentrations of NH_3 from a dairy cattle barn, unpublished data.

Added to section 3.1:

This range is chosen from the expected concentration in a livestock facility as Figure A1 and Figure A2 shows the hourly mean concentration of NH_3 in four rooms with finisher pigs and a dairy cattle barn, respectively. The maximum concentration can exceed 15 ppm in the pig houses and 3 ppm in the cattle barn

Added to section 4:

... as seen in Figure A2 and Figure A3.

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).

>>> Figure A1 is added to the appendix with the caption seen below.

The following text is added to section 2.4:

The length of the sampling lines was approximately 5 m, 15 m, 35 m, 45 m, and 50 m for SP1, SP2, SP3, SP4, and SP5, respectively. See Figure A1 in the appendix.

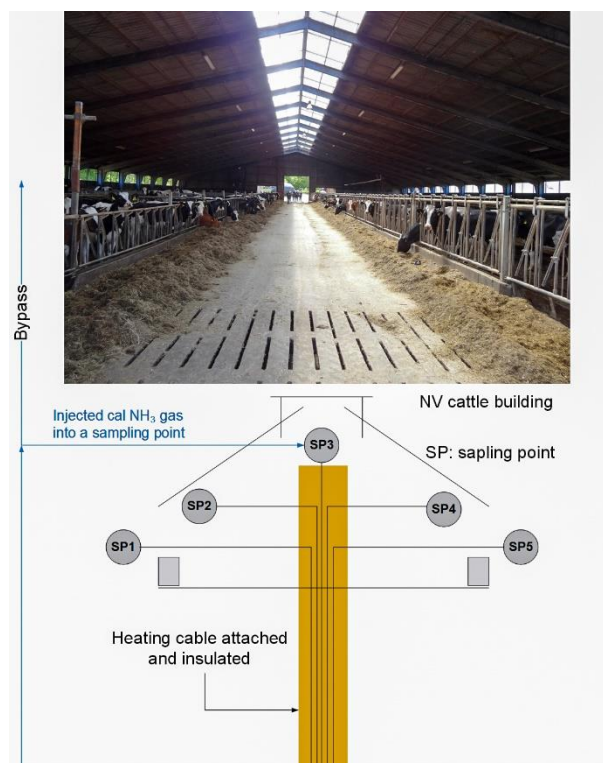


Figure A1 Schematic of the samplings point inside the cattle building. SP1 and SP5 were placed outside for background measurement at 2.5 m height. SP2 and SP4 were on the walls at 2.5 m height. SP3 was placed below the ridge at 9 m height. The lines were approximately 5 m, 15 m, 35 m, 45 m, and 50 m for SP1, SP2, SP3, SP4, and SP5, respectively.

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

>>> Unfortunately, PTRMS data in field conditions are not available, but it would have been the logical next step to measure VOC in field conditions for comparison. We wanted to test for VOC interference in a controlled environment as there are a number of unknown factors and compounds present in the field.

Therefore, this was our priority. Since VOC interferences are documented to be negligible for livestock emissions of NH₃, we do not believe, however, that PTRMS measurements are critical for the conclusions. We have tested the VOC interference well beyond concentrations found in field conditions.

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.

>>> We agree, the bias should be constant as the gas is well mixed in the bottle. The following is added to section 3.1:

... but the bias is considered constant as the gas is well mixed inside the bottle

The following is added to section 4:

... but the system cause minor variations as the bias is considered constant.

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.

>>> We have changed all rise- and fall times to be the e-folding time instead of using this 5% and 95% limits. This is achieved by fitting the rise and fall to an exponential function as suggested, which provides the time constant. All rise and fall times throughout the manuscript has been changed accordingly.

Figure 2 has been changed, see below. Now, the relative concentration is used instead for a more direct comparison visual of the rise and fall time from the two different concentrations. As suggested, the figure has been split into two with focus on the rise and fall time of interest.

The following is added to section 2.3:

The response time for all experiments was found by fitting an exponential function to the step changes, which gave the e-folding time.

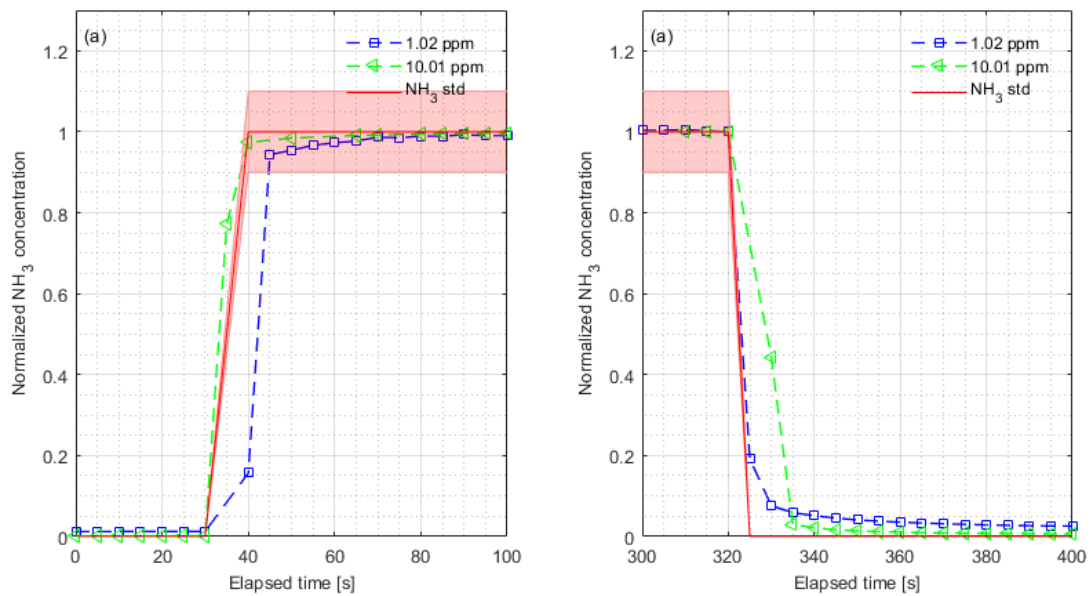


Figure 3. (a) Rise time and (b) fall time for the CRDS measurements normalized to final concentrations during laboratory testing of the response to a step change to 1.02 ppm (blue) and 10.01 ppm (green). The in NH₃ to 1.02 ppm with rise time (1/e) = 8.1 s and fall time (1/e) = 3.2 s; 10.01 ppm with rise time = 3.6 s and fall time = 4.8 s. The red lines and areas represent the NH₃ standard gas

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, I16). 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?

>>> The answer to general comment 4 addresses the lengths of the inlet lines.

The response times have been changed after fitting it to a function to find the e-folding time as proposed, which makes it a bit more difficult to answer this question. Now, the response times are:

SP1: 7.3 s (5 m)

SP2: 3.0 s (15 m)

SP4: 8.4 s (45 m)

SP5: 5.9 s (50 m)

Thus, there are no clear indications of a connection between response time and inlet line length.

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?

>>> It is not completely clear why this was observed in a very few cases. One explanation is that contamination of the filters or tubes with background NH₃ had occurred and that these low concentrations

bled into the system before the addition of a standard gas. However, this does not affect the conclusions regarding the response times.

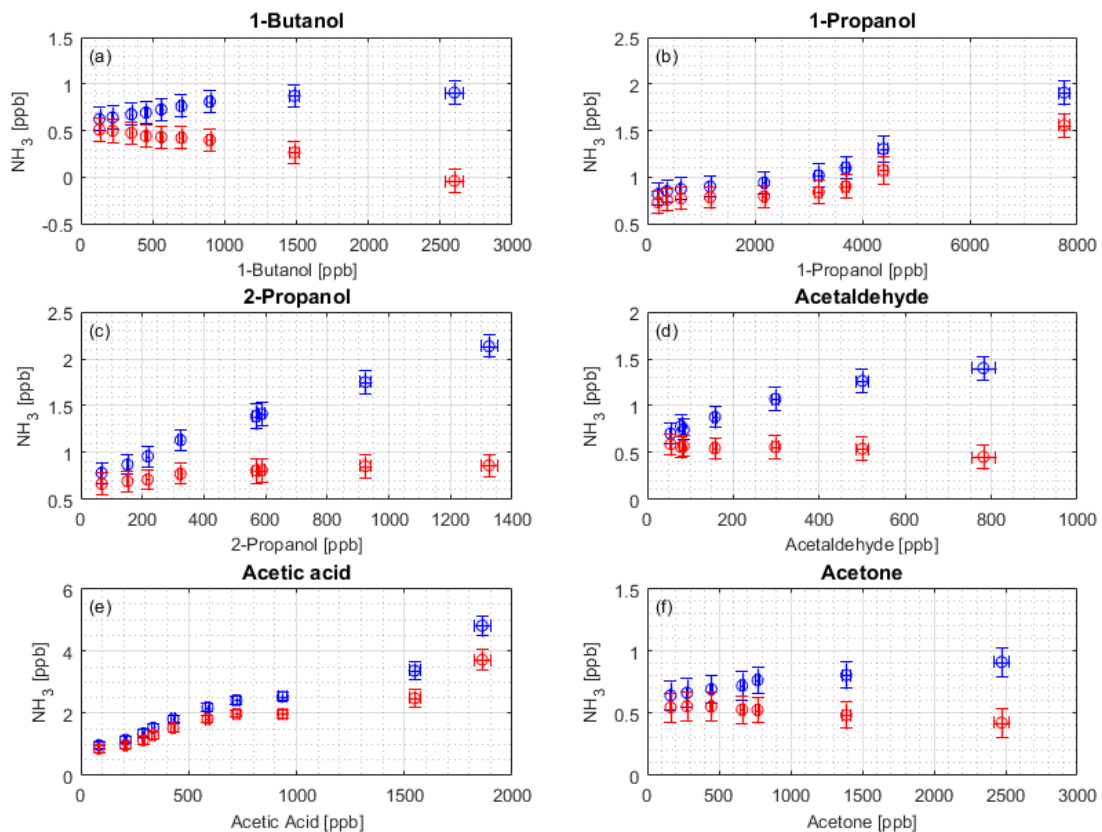
10. Figure 4: What is causing the high variation in the NH₃ bias as a response to the humidity? Is there any possibility that the zero air is not completely zero?

>>> Firstly, it should be noted that these signals are very low, corresponding to a few ppb above the detection limit. Thus, some variation in signals are to be expected. Secondly, the water vapor contributing the signals are created by bubbling air through water and the bursting of bubbles and evaporation of water may be subject to variations contributing to this pattern. If zero air had contained any significant amounts of ammonia, this would not be expected to vary much over the short time of the measurements and would have resulted in a uniform displacement of the regression line but not in more variation.

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.

>>> We agree. The relationship between NH₃ and H₂O has been used to correct the NH₃ concentrations by subtraction the contribution from H₂O. Thus, Figure 6 (changed to Figure 7) has been changed to contain only a single plot per compound with both uncorrected and corrected NH₃ concentrations.

The new Figure 7 is seen below with the caption.



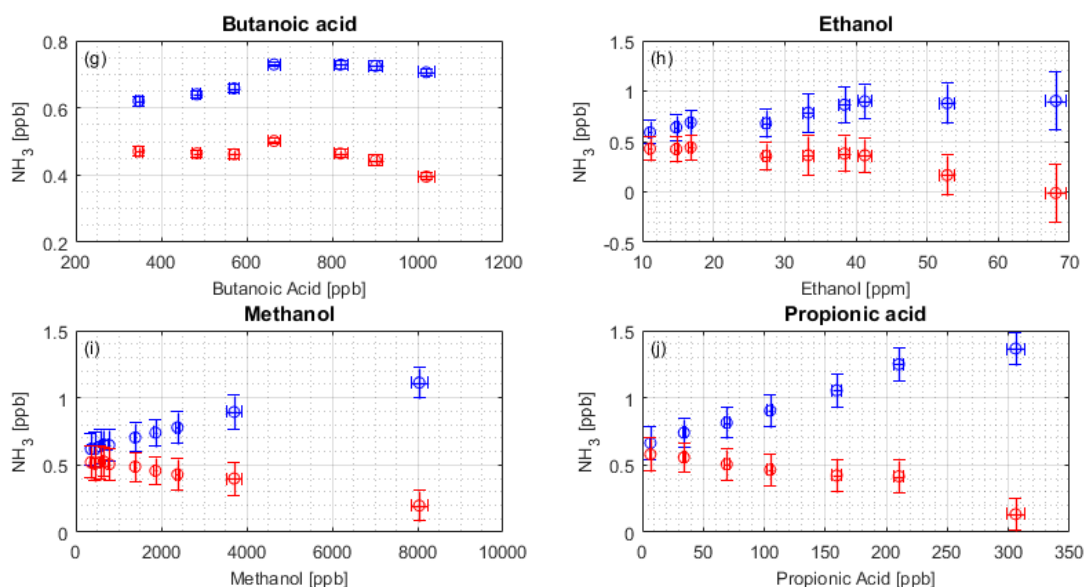


Figure 7. Interference of different organic compounds on the CRDS NH₃ measurement. Blue markers indicate the original data and red markers indicate water corrected data from the regression showed in Figure 5. The compounds are (a) 1-butanol; (b) 1-propanol; (c) 2-propanol; (d) acetaldehyde; (e) acetic acid; (f) acetone; (g) butanoic acid; (h) ethanol; (i) methanol; (j) propionic acid.

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.

>>> We do observe some variation in the background signal fluctuating around an average of 1 ppb, which may be due to variable levels of residual ammonia in tubes etc. It is difficult to prove that the charcoal-filtered and dried air does not contain any ammonia above the detection limit, but the average level is close to the detection limit and some variation (reported as 43% in Table A1) can be expected. The value of 5.5 ppb is highest extreme and not representative. For this reason, we suggest removing the “Range” column in Table A1 as the CV% and mean better represents typical levels and variation.

13. I am missing a description of the measurement principle of the Picarro-CRDS. If possible add a description to section 2.2.

>>> Description of the measurement principle is added in section 2.2.

“The operational principle of CRDS relies on ring down time laser light. An air sample enters a cavity at low pressure (140 Torr) and laser light is pulsed into the cavity, where almost all light it is reflected by mirrors, which gives an effective path length of kilometers. A small fraction of the light penetrates the mirrors to reach the detector and the intensity of the light is proportional to the concentration of target gas, as the target gas will absorb to light.”

< 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.

>>> We agree that the text needed a revision. Several of the authors have helped in the thorough proofreading of the manuscript.

P2,I22 : Quantify, good is objective. Also Bobruzki et al., 2010, showed an intercomparison between instruments for concentrations around 1-25 ppb, not ppm's.

>>> Added to line 22: *up to 120 ppb*. Added to line 22: $(R^2>0.84)$

P3,I16 : "The CRDS", change throughout the document

>>> Changed throughout the manuscript.

Answer to anonymous referee #2

>>> *We appreciate the comments and suggestions from the anonymous referee that have helped to improve the manuscript.*

General comment

According to the manuscript, the CDRS was calibrated under laboratory and field conditions. Due to possible interference of other compounds (water, dust, temperature) or between compounds (NH₃, CH₄, CO₂,...), it is important to compare the specifications and performance of the instrument under field conditions by comparing results of simultaneous measurements performed by using this instrument and a reference method (e.g. gas washing for NH₃, gas chromatographie for CH₄, N₂O and CO₂). This information is missing. Please add to the manuscript whether these measurements were performed (or not). If so, please report the results of the comparison. If not, please comment in the manuscript why this was not performed, and how this is going to be checked before using the instrument for real under field conditions.

>>> We hypothesize that there are no interferences in the CRDS, which we test for and validate with laboratory tests of potential VOCs interference, CO₂, CH₄ and calibration with standard gas. We have not used a reference method as impingers or gas washing of ammonia as there are large variations in the concentration determination e.g. Misselbrook et al. (2005) report a coefficient of variance for absorptions flask of 21%. Furthermore, these methods are offline and rely on accumulation of ammonia over a long time span whereas the CRDS is running on a very different time scale, thus we do not find it suitable to use this as a reference method for the time-resolved concentration. The calibrations were conducted with a certified ammonia standard gas under a variety of conditions resembling realistic conditions, thus we find it sufficient as validation. Water, dust and temperature are mentioned as possible interfering compounds, and we have actually shown that water has a small interference in the model we are using, but this has been changed by water correction after the discoveries by Martin et al., (2016). The temperature is kept very stable at 45°C in the cavity, so temperature can only affect the sampling, which is also discussed in the introduction with the absorption of ammonia the walls and tubing. A filter removes dust mechanically, so it will never reach the cavity, and filter tests show a very small contribution from ammonia absorbed in the filter compared to the accumulated amount of ammonia flowing through the filter over a 2-week period.

Other comments:

In general, for a number of compounds the subscripts are not as subscript in the manuscript. Page 3, lines 12-15. These are results, not part or an introduction.

>>> All subscript are corrected to the right form throughout the manuscript.

We think these results from other studies highlight the importance of response times, which was addressed in previous comments from the editor.

Negligible influence of livestock contaminants and sampling system on ammonia measurements with cavity ring-down spectroscopy

Jesper Nørlem Kamp^{1,2}, Md Albarune Chowdhury¹, Anders Peter S. ~~Adamsen~~³Adamsen^{1,3} and Anders Feilberg¹

¹Department of Engineering, Aarhus University, Aarhus, 8000, Denmark

²Arctic Research Centre, Aarhus University, 8000 Aarhus, Denmark

³~~SEGES, 8200 Aarhus-N~~³Present APSA, 8800 Viborg, Denmark

Correspondence to: Anders Feilberg (AF@eng.au.dk)

Abstract. ~~Pollution from~~Emission of ammonia (NH₃) is a ~~widespreadubiquitous~~ problem due to the ~~adverse~~ effects of NH₃ on the environment and human health. The agricultural sector accounts for nearly all NH₃ emissions in Europe; ~~thus, focus has especially been on~~. Hence, technologies for abatement of NH₃ emissions from this sector has been in strong demand in recent years. ~~We need abatement techniques to reduce NH₃~~In order to document emissions, and ~~in order to~~ evaluate the ~~techniques~~abatement technologies, there is a strong need for reliable NH₃ measurement methods. Photoacoustic spectroscopy (PAS) is often used to measure NH₃ concentrations, but recent ~~discoveries~~research show interference from compounds typically present in livestock production and during agricultural activities. ~~We tested~~In this work, the performance of the Cavity Ring-Down Spectroscopy (CRDS) from Picarro as an alternative to PAS ~~for filter effects and~~has been tested with respect to method validation under laboratory and field ~~calibrations with standard gasses~~. Furthermore, concentrations~~conditions~~. Potential interferences of ten volatile organic compounds (VOCs) ~~where determined on~~CRDS NH₃ measurement were tested with simultaneous VOC analysis performed by Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) ~~to test the potential interference of these VOCs~~. Both laboratory and field calibrations show excellent linearity over a large dynamic range of NH₃ concentrations. The analyzer shows a small humidity effect of up to a few ppb in the extreme case of a nearly water saturated air stream. ~~Besides~~Apart from the negligible humidity ~~dependence~~, there is ~~dependency~~, no interference from interferences of the tested VOCs; ~~were observed~~. Overall, the CRDS system performs satisfactory and is well with only negligible influences from other compoundssuitable for measurements of NH₃ emissions from livestock production.

1 Introduction

Ammonia (NH₃) is an important atmospheric pollutant as it has negative effects on ecosystems and human and animal health (Aneja et al., 2001; Davidson et al., 2005). Deposition of NH₃ can lead to eutrophication and acidification, which has negative effects on biodiversity (Sheppard et al., 2011). ~~NH₃ is not a greenhouse gas (GHG), but it is a precursor for aerosol formation thereby influencing the global warming, furthermore different oxidation pathways of NH₃ produce~~NH₃ is a precursor of

~~atmospheric aerosols thereby influencing the global radiation budget as well as having a negative influence~~ nitrous oxide (N₂O) and nitric oxide (NO) (Zhu et al., 2013). ~~N₂O is a very potent GHG and NO is involved in atmospheric reactions producing tropospheric ozone (Aneja et al., 2001). As a precursor for aerosols and thereby formation of particles in the atmosphere, NH₃ has harmful effects on human health (Aneja et al., 2001; Baek et al., 2004). In addition, microbial oxidation of NH₃ results in secondary production of nitrous oxide (N₂O) and nitric oxide (NO) (Zhu et al., 2013). N₂O is a very potent greenhouse gas (GHG) and NO is involved in atmospheric reactions producing tropospheric ozone (Aneja et al., 2001). Emissions of NH₃ have an impact on ecosystems, global warming and human health, thus it is important to measure NH₃ concentrations correctly. Due to the numerous adverse effect of NH₃ emissions, it is important to measure NH₃ concentrations with high accuracy and precision.~~

5
10 Agricultural activities, mainly manure application and management, accounts for around 94% of NH₃ emissions in Europe (Nielsen et al., 2017), ~~and much control in the agricultural sector intend to limit these emissions.~~ Reliable measurements in the agricultural sector are highly important to give accurate estimates of NH₃ emissions in order to reduce the emissions e.g. by validation of technological improvements within the agricultural sector. ~~Many~~In many agricultural ~~emission studies use~~ photoacoustic spectroscopy (PAS) (Poissant et al., 2005; Rom and Zhang, 2010; Saha et al., 2010; Wu et al., 2012; Zhang et al., 2005; Zong et al., 2014), ~~has been used,~~ but findings by Rosenstock et al. (2013) ~~and Liu et al. (2018) show high interference on NH₃ measurements from a variety of organic compounds including carboxylic acids and alcohols.~~ and Liu et al. (2019) ~~show high interference on NH₃ measurements from a variety of organic compounds including carboxylic acids and alcohols.~~ Hassouna et al. (2013) ~~report~~reported non-constant bias in the results from PAS measurements on NH₃ and N₂O caused by organic compounds often present at agricultural sites, which ~~make~~makes the PAS measurements ~~uncertain~~unreliable in an agricultural setting. ~~Other agricultural~~In a few recent studies ~~use~~CRDS ~~has been used~~ to measure ammonia concentrations (Maasikmets et al., 2015; Sintermann et al., 2011). ~~The absorptions lines of acetic acid and methanol found in the HITRAN database (Gordon et al., 2017) are in the same range as the ammonia lines used for measurements in the CRDS, see Figure 1. This highlights the importance of the study as the absorption from VOCs can cause similar interference as reported by Rosenstock et al. (2013) and Liu et al. (2019) for PAS.~~

15
20
25 It is challenging to measure NH₃ concentrations correctly due to its ~~properties of~~ high water solubility and polarity, which cause adsorption on surfaces in the sampling system and within the instrument (Rom and Zhang, 2010; Shah et al., 2006; Vaittinen et al., 2014). This “sticky nature” of NH₃ causes delays in the measurements, giving longer response times (Rom and Zhang, 2010; Shah et al., 2006; Vaittinen et al., 2014). Furthermore, it is a challenge to measure NH₃ in livestock buildings, where dust and particles provide large surface areas for its adsorption in particulate filters. NH₃ adsorption can affect response
30 time and accuracy of the analyzers, causing a time delay and measuring errors.

The air inside animal production buildings contains a variety of chemical compounds, relatively high water content and high densities of particulate matter. Several NH₃ analyzers are sensitive to water vapor and other gasses (Bobrutzki et al., 2010; Huszár et al., 2008; Ni and Heber, 2008; Rom and Zhang, 2010; Rosenstock et al., 2013). Such ~~interference~~interferences can introduce errors depending on the instrument used. Proper calibration before and during laboratory and field measurement can

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reduce the potential errors and improve the accuracy of the measurement system. Quantification of the errors can enhance the quality of the NH₃ measurement data, which is essential to research, emission abatement and policy-making. ~~There are varieties of NH₃ measurements methods~~, Bobruzki et al. (2010) ~~conduet~~conducted a field inter-comparison of eleven atmospheric NH₃ measurement techniques at concentrations up to 120 ppb including Cavity Ring-Down Spectroscopy (CRDS), and the results show a good overall agreement between the instruments on an hourly basis. ~~(R²>0.84)~~.

The CRDS provides measurements in real time with high sensitivity, high selectivity and a fast response time. The CRDS analyzer maintains high linearity, precision and accuracy over changing environmental conditions without the need for frequent calibration. The work of Martin et al. (2016) led to an improvement of water vapor interference calculations on Picarro's CRDS for NH₃ measurements. The scale factor error they discovered is approximately 2% of the absolute water concentration.

~~Unfortunately, our Picarro~~Our CRDS analyzer has not incorporated this upgraded correction, ~~but the analyzer still corrects for H₂O interference; thus, we expect this to have insignificant effect on the results.~~

We wish to address the interferences from VOCs further as the PAS technique seems to be inadequate for measurements in ~~somecertain~~ agricultural environments (Hassouna et al., 2013; Liu et al., 2018; Zhao et al., 2012)(Hassouna et al., 2013; Liu et al., 2019; Zhao et al., 2012). A great number of VOCs are emitted in agricultural buildings from e.g. silage, manure and the animals (Feilberg et al., 2010; Hafner et al., 2013; Hansen et al., 2012; Ngwabie et al., 2008; Shaw et al., 2007; Yuan et al., 2017). The VOCs can potentially interfere with NH₃ measurements as seen for PAS.

~~Our focus is on~~In this work, a CRDS ~~and we use the Picarro~~NH₃/H₂O analyzer (Picarro Inc., Santa Clara, CA, USA) ~~was used~~ for all measurements of NH₃. The manufacturer states a lower detection limit below 0.5 ppb + 0.1% of reading (1s, 1σ) and below 0.03 ppb 0.1% of reading (5 min, 1σ) (Picarro, 2017). The response time is stated to be less than 30 seconds for 0 to 3 ppm and a recovery time from 10 to 0.2 ppb of less than 1 hour (Picarro, 2017). Our aim is to demonstrate the performance of the CRDS analyzer for measurements of NH₃ gas concentration under laboratory and field conditions. Furthermore, to identify and quantify potential interfering compounds present in livestock buildings with state of the art Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) ~~to measure VOC concentration. To our knowledge no studies has focused on the interference from VOCs on CRDS measurements, which cause major concerns for measurements with PAS techniques (Hassouna et al., 2013; Liu et al., 2018; Zhao et al., 2012).~~ Due to the interferences present in PAS measurement, there is a need for a better alternative, ~~which is debated in the scientific society document VOC concentrations in laboratory tests. Due to the major concerns regarding measurements of NH₃ with PAS (Hassouna et al., 2013; Liu et al., 2019; Zhao et al., 2012), it is pertinent that any influence of VOC on CRDS is thoroughly documented, which to our knowledge has not been done previously.~~ Another issue with PAS measurements is the long response time of up to 25 minutes (Rom and Zhang, 2010), which lowers the time resolution of ~~a study~~emission measurements under dynamic conditions. NH₃ is underestimated by approximately 14% and 2% after 12.5 and 25 minutes, respectively (Rom and Zhang, 2010). Typical measurements in cattle barns takes places at multiple points, e.g. Rong et al. (2014) measure at 7 points in a dairy cow building and Ngwabie et al., (2009) measure at 11 points in a dairy cow barn. The cycle time for a typical setup in a barn would be in the order of 3-5 hours, which makes it impossible to ~~see most~~monitor temporal variations with only 4-8 measurements per measurements point a day. Thus, the

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response time is a key parameter for equipment measuring at multiple points as done in livestock buildings. The CRDS has a potential to be a more accurate, precise and faster responding alternative to PAS.

This study aims to validate CRDS for measurements in the agricultural industry, thus we test for interference with a number of compounds typically present in pig houses and cattle farms where NH₃ concentration measurements are routine. Laboratory tests include determination of the response parameters linearity, response time, influence of particulate filters and chemical interference. Field tests include determination of the response parameters linearity, response time and particulate filter effect. To test for the effects of VOC, we used PTR-MS, a powerful tool to measure selected VOCs and trace gasses in real time. Protonated water is a soft ionization source that protonates VOCs in a non-dissociative manner (de Gouw and Warneke, 2007; Lindinger et al., 1998). High selectivity and sensitivity are key characteristics of the method along with short response time (de Gouw and Warneke, 2007). PTR-MS is ideal to quantify low concentrations of potentially interfering compounds in real time.

In this paper, we address the accuracy of CRDS in terms of interference from a range of VOCs normally present during livestock production and manure handling. The CRDS is one of the online and not labor-intensive methods with the potential to measure NH₃ emissions. The focus on reduction of NH₃ emissions (e.g. Directive on the reduction of national emissions of certain atmospheric pollutants (EU 2016-2284) (EC, 2016)) makes reliable and accurate measurement techniques essential.

Field Code Changed

2 Materials and Methods

2.1 Chemicals, reagents and gasses

We used the following chemicals during the experiments: 70 mM acetic acid (VWR int. S.A.S., Fontenay-sous-Bois, France), 27 mM 1-propanol (Merck KGaA, Darmstadt, Germany), 1.3 mM 2-propanol (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), 0.7 mM acetaldehyde (Sigma-Aldrich), 4 mM propionic acid (Alfa Aesar GmbH & Co KG, Karlsruhe, Germany), 0.8 mM acetone (Merck), 10 mM methanol (VWR), 2.2 mM 1-butanol (Merck), 69 mM ethanol (CCS Healthcare AB, Borlänge, Sweden) and 44 mM butanoic acid (Alfa Aesar). Deionized water dissolved the chemicals to the wanted concentrations.

We used the following gasses during the experiments: 101 ppm NH₃ (\pm 10%) in N₂ calibration gas (AGA A/S, Copenhagen, Denmark), pure (99.99%) CO₂ (AGA), pure (99.99%) CH₄ (AGA) and as zero air compressed air passed through a bed of silica gel and charcoal to remove water, ozone, hydrocarbons and other common contaminants. Mass flow controllers (MFCs) from the EL-FLOW (Bronkhorst High-Tech B.V., Ruurlo, Netherlands) series regulated all gas flows with an accuracy of \pm 5%.

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2.2 Interference Instrumentation

The operational principle of CRDS relies on ring down time laser light. An air sample enters a cavity at low pressure (140 Torr) and laser light is pulsed into the cavity, where almost all light it is reflected by mirrors, which gives an effective path

length of kilometers. A small fraction of the light penetrates the mirrors to reach the detector and the intensity of the light is proportional to the concentration of target gas, as the target gas will absorb to light. The G2103 analyzer measure absorption from 6548.5 to 6549.2 cm^{-1} (Martin et al., 2016) and Figure 1 shows the absorption of some selected compounds in this range obtained from the HITRAN 2016 database (Gordon et al., 2017). The computed absorption lines in Figure 1 corresponds to 1% H_2O , 400 ppm CO_2 , 100 ppb acetic acid, 100 ppb ethanol, and 100 ppb ammonia at 45°C and 140 Torr. Line broadening is not taken into account.

For the determination of interference, we used a Picarro $\text{NH}_3/\text{H}_2\text{O}$ analyzer model G2103 (Picarro Inc., Santa Clara, CA, USA) measured to measure the NH_3 concentration continuously and a high sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) measured concentrations of different VOCs for the interference tests. The drift tube setting was 600 V, 2.1-2.2 mbar and 60°C, which yield an E/N of approximately 130 Td. Fragmentation of alcohols are normal in PTR-MS and we use the fragmentation of alcohols as described by Brown et al. (2010) to calculate the final concentration with all fragments taken into consideration.

One stream of clean air passed through the headspace air over an aqueous solution containing a single compound. Another stream diluted the outflow from the headspace. We changed the airflows to get different concentrations of the compound in the gas phase. The CRDS and PTR-MS received the diluted air streams.

2.3 Linearity, calibration and filter effect

We used a flow dilution system with zero air and NH_3 calibration gas (101 ppm) to test the linearity of the CRDS measurements. NH_3 gas concentrations for the calibration were in the range from 0.20 to 16.8 ppm in the laboratory and from 0.27 to 20.0 ppm under field conditions. We performed the calibrations in the laboratory without external filters. Introduction of all gasses in the field was through a multi-position rotary valve (MPV, Cheminert low-pressure valve, model C25, VICI AG International, Schenkon, Switzerland) for 6 min while the CRDS was in normal sampling mode. We performed a single point calibration in the field to test the system integrity and analyzer response time by introducing 7.8 ppm NH_3 calibration gas directly into the sampling lines manually removed from their position. The response time for all experiments was found by fitting an exponential function to the step changes, which gave the e-folding time. We tested the PTFE filters in the laboratory for NH_3 signals by connecting filters used for 2 weeks to a clean air supply under heating to maximum 75°C. Monitoring of the NH_3 signals continued until the concentration went below 5 ppb; see Table 1 for abbreviations and specifications of the used filters.

We performed laboratory tests on the response time by switching between ambient air and 1.02 ppm NH_3 with the MPV without external filters attached. We also tested response time to a step change in NH_3 concentration with different external particulate filters attached. The concentrations were 0.203 and 10.01 ppm NH_3 with filters of different pore size made of PTFE, glass fiber and quartz. Table 1 shows the specifications of the filters.

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2.4 Field testing

We conducted field tests in a cattle barn with natural ventilation located in central Jutland outside Viborg, Denmark. The cattle barn is 9 m high, 60 m long and 36 m wide and naturally ventilated. We measured NH₃ concentrations in the cattle building with the CRDS combined with a 10 port (P1-P10) MPV (C25-61800, VICI Valco Inst. Co. Inc., Texas, USA). Measurements were set up according to Rong et al (2014) and Wu et al. (2012). We considered the division into three 20 m sections inside the cattle barn to be representative of the animal-occupied zone of the barn. We sampled NH₃ concentrations from the three sections using PTFE tubes (inner diameter 6 mm, 20 m long) with 20 uniformly distributed sampling openings. The sampling points (SP) SP2, SP3 and SP4 were inside the building, with SP2 and SP4 on each of the end walls adjacent to the windows, i.e. sidewall openings, placed 2.5 m above the floor. SP3 was just below the ridge opening in the middle of the building placed 9 m above the floor. SP1 and SP5 were outside ~~as~~-background measurements from two single points placed 5 m from the building sidewalls at 2.5 m height. The sample tubes were between 5 and 50 m long with heating cables attached to avoid condensation inside the tubing. The length of the sampling lines was approximately 5 m, 15 m, 35 m, 45 m, and 50 m for SP1, SP2, SP3, SP4, and SP5, respectively. See Figure A1 in the appendix. Each sampling line had a secondary suction pump (flow rate of 6-7 L min⁻¹) with a PTFE membrane to generate a constant flow through the lines. A PTFE filter (0.20 µm pore size) removed airborne particulate matter from the sample air before the sampling ports of the MPV. Replacement of filters was at last fortnightly. Measurement lasted 6 min for each sampling port with automatic switching, i.e. a measurement cycle was 30 min.

3 Results

3.1 Laboratory tests

The CRDS had a highly linear response ($R^2=0.99998$) to NH₃ concentrations over the dynamic range 0.20-16.8 ppm (Figure 2). This range is chosen from the expected concentration in a livestock facility as seen in Figure A2 and Figure A3, which show the hourly mean concentration of NH₃ in four rooms with finisher pigs and a dairy cattle barn, respectively. The maximum concentration can exceed 15 ppm in the pig houses and 3 ppm in the cattle barn. The NH₃ standard calibration gas used for all calibrations had an accuracy of ± 10% stated by the manufacturer. The measured NH₃ concentrations in Figure 2 are averages of several hundred measurements and the standard deviations are indicators of stability. Figure 3a) and b) shows the result of a step change in concentration from clean air to 1.02 ppm and 10.01 ppm, respectively, and back to clean air, where the. The rise time to 95%1/e of the final concentration level was 438.1 s and 3.6 and the fall time to 5%1/e of the final concentration level was 493.2 s and 4.8 s for 1.02 and 10 ppm, respectively. Furthermore, Figure 4 shows response times to step changes to two concentrations (0.203 and 10.01 ppm) with different types of external particulate filters. The response times varied for the different filter types with an average rise and fall time of 388.1 s and 526.3 s (for 0.203 ppm), and 143.1 s and 123.7 s (for

10.01 ppm), respectively (Figure 4). Across all filter types, the response time was fastest for changes to the highest concentration expect for the fall time for three filters, see details in Table A2.

Measurements on zero air over an hour gave a standard deviation on the NH₃ concentration of 0.115 ppb. This gives a limit of detection (LOD) of 0.35 ppb for three standard deviations and a limit of quantification (LOQ) of 1.15 ppb for ten standard deviations, see Table 2.

We used pure deionized water to produce a range of different humidity without any contaminating compounds levels. Figure 5 shows the effects of the humidity changes on the NH₃ signal from relative humidity (RH) ranging from 6.3% to 98.6%. The response to the change in humidity is linear ($R^2 = 0.83$) with NH₃ measurements from 1.3 to 4.6 ppb over the given RH range. Figure 6 shows the CRDS signals from CO₂ and CH₄, where with random fluctuations in the low ppb level are present being observed. There are no apparent interferences from these two compounds. All measured NH₃ concentrations for both compounds are below the LOQ.

Figure 7 shows the interferences of ten different VOCs, where each row represent one compound. The third column shows with VOC concentration as a function of NH₃ concentration corrected for water contribution and the uncorrected concentration as well. This correction was due to a clear pattern for increased water vapor with VOC concentration as water is introduced with the VOCs, and NH₃ concentration increased with increased water vapor for all compounds. The observed interferences were in the range from 0.5 to 5 ppb NH₃ equivalents at VOC concentrations from 6 to 8000 ppb. These VOC concentrations range from levels comparable to field conditions up to levels 1-2 orders of magnitude higher than at maximum field conditions.

3.2 Field Tests

In the field, the CRDS also has a highly linear response ($R^2=0.9995$) in the concentration range 0.27-20.04 ppm, see Figure 8. Figure 9 shows the results of a single point field calibration of the system integrity and response time to a sudden change to 7.8 ppm with response times varying from 6 to 25 s. The calibration gas used in the measurements showed in Figure 8 and Figure 9 had an uncertainty of $\pm 10\%$.

Figure 10 shows the signals ammonia concentrations released from 2-weeks-old external particulate filters having been exposed to ammonia in a livestock house for 2 weeks. Vacuum pumps applied a gas flow rate of minimum 6 L min⁻¹ through the filter over the two-week period, thus a minimum volume of 120 m³ of air went through each filter. The pre-exposed filters were flushed with zero air and ammonia release was monitored by CRDS. The concentration maximum varied between 25 and 38 ppb. The peak values are comparable to typical ambient laboratory concentrations ranging from 14-37 ppb; see Table A1. Vacuum pumps applied a gas flow rate of minimum 6 L min⁻¹ through the filter over the two-week period, thus minimum 120 m³ of air went through each filter.

4 Discussion

The CRDS analyzer had a linear response during both laboratory test and field validation (Figure 2 and Figure 8) in the range from approximately 0.2 to 20 ppm; NH₃ concentrations in livestock buildings are normally within this range (Heber et al., 2006; Koerkamp et al., 1998), as seen in Figure A1 and Figure A2. This is in agreement with the manufacturer specifications that guarantees the range from 0 to 500 ppb, and with operational and optional expanded range up to 10 and 50 ppm, respectively (Picarro, 2017). The field calibrations show excellent agreement with the standard gas concentrations. The standard gas had an uncertainty of ± 10% according to the data sheet from the manufacturer, which, This may well explain the small offset (< 4%) from the obtained concentrations seen in Figure 9. The LOD, but the system cause minor variations as the bias is considered constant. The LOD (0.35 ppb) found in the present study is comparable to the manufacturer's specifications for 1 seconds integration time, as seen in Table 2. The charcoal filter used might not clean the zero air generated completely compared to analytical standard gasses, thus we expect even lower LOD and LOQ by the use of analytical gas standards instead of air filtered by activated charcoal. The performance of a single point field calibration showed very good agreement with the expected concentrations as seen in Figure 9. The potential bias from the zero might also influence the other laboratory experiments, which can explain some of the variations we see in e.g. filter response (Figure 4) or water dependency (Figure 5).

It is a requirement to have fast responding analyzers to understand the dynamic behavior and diurnal variations of NH₃ concentrations in animal buildings. Ni and Heber (2008) suggest a response time of less than 2 min to capture temporal NH₃ concentration variations. The CRDS shows sufficiently low response times under laboratory (Figure 3 and Table A2) and field conditions (Figure 9). These times are also comparable to < 30 s for responses to 3 ppm as reported by the manufacturer (Picarro, 2017). Furthermore, there are no clear changes in response time without the use of an external particulate matter filter. The tested filters vary by < 10 s in response time, but it is clear that the concentration difference in the step change was important where increasing concentration differences gave decreasing with a tendency towards shorter response times. The manufacturer reports rise- and fall times of approximately 16 seconds, which, compared to is as a minimum twice as much as the present results, are very similar with some variations. Table A2 and Figure 2. The response to a change from 0 to 1.02 ppm gave response times of 8.1 s and 193.2 s for the rise- and fall time, respectively (Figure 3). Rise. A change from 0 to 10.02 gave response times of 3.6 s and 4.8 s for the rise- and fall time, respectively (Figure 3). The rise times with external particulate filters connected were 167.3 s, 63.0 s, 138.4 s, and 255.9 s, for SP1, SP2, SP3 and SP4 and SP5, respectively. Adsorption to sampling material including filters explains the differences in response time. Response times are in general faster for higher concentration differences; (see Figure 4, as Figure 4), which is ascribed to faster surface saturation is faster. The observed concentrations of NH₃ released from 2-weeks-old particulate filters (Figure 6) exposed to air from a livestock house for 2 weeks (Figure 10) suggest that adsorption of NH₃ to the filter material, surfaces and walls were negligible. The levels released over 1 minute (< 50 ppb) should be compared to a filter exposure of ammonia of >100 ppb (ranging in to low

ppm levels) over 2 weeks. These results indicate that the use of external filters gives satisfying response times and no problems with ~~long-term~~ adsorption of NH₃ on the filter material.

~~The gasses~~ CO₂ and CH₄ are present in the atmosphere in relatively high concentration compared to other trace gasses, and animals produce CO₂ and CH₄, thus elevated concentrations are normal in animal houses. Over a large ~~dynamic area~~ concentration range, we observed little scatter and no interference ~~for of~~ CO₂ and CH₄ on NH₃ measurements as seen in Figure 6. The mean concentration of both compounds are below the LOQ.

For the interference of single VOCs, it was as expected that the different dilutions prepared from clean dry air mixed with humid headspace air over a VOC solution gave a correlation between water vapor and VOC concentration. This was also the case ~~as seen in the subplots in the third column of Figure 6~~ for all ten volatile compounds. Martin et al. (2016) observe an

interference from water vapor on NH₃ measurements due to spectral line broadening, which the manufacturer corrects for in all models produced after the publication. Our Picarro analyzer from December 2014 does not make this extra correction, ~~and we~~ thus ~~we~~ expected a small water dependency for NH₃, which ~~we indeed see is seen~~ in Figure 5 ~~and Figure 6~~. Figure 4 Figure 5 shows the humidity effect on the CRDS signal generated from pure deionized water and reveals a small dependency for water vapor, which the improvements ~~suggested~~ by Martin et al. (2016) potentially remove. Nonetheless, our results show up to 4.5 ppb NH₃ for a nearly water saturated air stream with an absolute H₂O concentration of approximately 1.1%. Thus, in the extreme case of low NH₃ concentrations (e.g. 100 ppb) and very humid air, a water vapor interference of up to 5 % of the NH₃ signal may be present, but under normal conditions, this is negligible.

The ten tested compounds are normally present ~~during agricultural activities~~ in sub-ppm levels ~~in agricultural environments~~ (Copeland et al., 2012; Yuan et al., 2017). ~~We choose a~~ ~~As seen in Figure 1, acetic acid and methanol have absorption lines in~~

~~the wavelength area used for the Picarro CRDS measurements. A~~ concentration range that covers a large dynamic area and exceeds the normal maximum concentration in ~~e.g.~~ livestock buildings ~~was used~~ to obtain the potential maximum interference and we only observed very small water induced interferences. ~~E.g., a 1-butanol concentration of 1.5 ppm gave a CRDS-NH₃ concentration of 0.9 ppb, i.e. less than 0.06% of a 1:1 interference, which Liu et al. (2018) observe for several organic compounds when using photoacoustic NH₃ analysis. Figure 7 shows the contribution from the single VOCs corrected for water~~

~~and uncorrected, and as can be seen, the interferences is in general insignificant.~~ Overall, the difference between high and low concentration for a single VOC was approximately 1-2 ppb, ~~NH₃~~ (Figure 7), except ~~for~~ acetic acid with a difference of nearly 4 ppb, ~~but. It should be noted that the differences in water vapor was different to VOC relation differs~~ for the different compounds. ~~With water correction applied, only 1-propanol and acetic acid have increasing tendencies, where NH₃ concentration increase about 0.8 ppb NH₃ for an increase of 7.5 ppm of 1-propanol and 2.9 ppb NH₃ for an increase of nearly~~

~~1.8 ppm of acetic acid.~~ Acetic acid, 2-propanol and propionic acids were the only compounds with absolute humidity above 1% as we used higher flow rates over the headspace to obtain the targeted concentrations. The very moist sample of acetic acid had a ~~corrected~~ maximum of ~~4.63.7~~ ppb NH₃, which is very low compared to e.g. concentrations in animal buildings, which typically range from < 1 to 20 ppm, but in extreme cases up to 50 ppm (Heber et al., 2006; Koerkamp et al., 1998). Thus, errors on few ppb introduced by humidity effects would have overall impact on the results. For the given setup, the interferences

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from water vapor were in the same order of magnitude as the LOQ of 1.15 ppb. For more than half of the VOCs, the NH₃ concentration falls below the LOQ for all or most measurement. This demonstrates a very low interference from the investigated VOCs.

The results of this study clearly demonstrate the advantage of CRDS compared to the performance of the photoacoustic analyzers studied by Liu et al. (2019) for which severe VOC interferences on ammonia were observed.

Our tests of the Picarro CRDS showed great linearity during both laboratory and fieldwork. The ~~rise and fall~~ response times with respect to ~~e~~ concentration changes were sufficiently low to measure temporal variations of NH₃ concentrations in NH₃ ~~e~~ livestock emissions. Examinations of external particulate filters lead to no clear recommendations for filter material, but all ~~filter~~ filters gave acceptable response times and only small amounts of NH₃ adsorption compared to background levels. ~~We used PTR-MS to determine accurate VOC concentration for ten compounds~~ Potential interferences were tested for ten VOC in known concentrations and the compounds gave negligible interference on CRDS NH₃ measurements.

Code and data availability. Data and code are available upon request to the corresponding author.

Author contributions. Conceptualization, A.F., A.C. and J.K.; Methodology, A.F., A.C. and A.P.A.; Validation, J.K., A.F. and A.C.; Formal Analysis, J.K. and A.C.; Investigation, J.K. and A.C.; Resources, A.F. and A.P.A.; Data Curation, J.K. and A.C.; Writing-Original Draft Preparation, J.K. and A.C.; Writing-Review & Editing, A.F., and A.P.A.; Visualization, J.K.; Supervision, A.F. and A.P.A.; Project Administration, A.F. and A.P.A.; Funding Acquisition, A.F. and A.P.A.

Competing interests. The authors declare no conflict of interest.

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5 Tables

Table 1. Specifications of tested particulate filters with abbreviations.

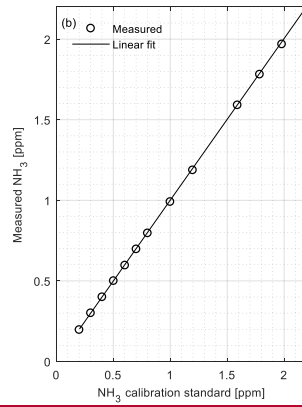
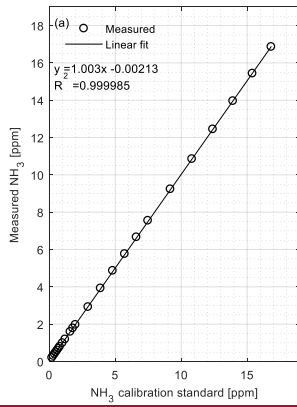
Filter material	Pore size (μm)	Thickness (mm)	Diameter (mm)	Porosity (%)	Filter code
PTFE ¹	0.2	0.08	25	74	PTFE 0.2
PTFE ¹	0.5	0.08	25	78	PTFE 0.5
PTFE ¹	1.0	0.08	25	79	PTFE 1.0
PTFE ¹	3.0	0.08	25	83	PTFE 3.0
PTFE ¹	5.0	0.08	25	-	PTFE 5.0
Glass fiber	0.6	0.21	25	-	GA 55
Glass fiber	0.4	0.56	25	-	GB 140
Glass fiber	0.8	0.74	25	-	GA 200
Quartz fiber	-	0.38	25	-	QR 100

¹ Polytetrafluoroethylene

Table 2. Limit of detection and limit of quantification from a one-hour stable measurements on zero air.

	N	Mean	SD	LOD (3 x SD)	LOQ (10 x SD)
H ₂ O [%]	2065	0.082	0.0019	0.006	0.019
NH ₃ [ppb]	2065	0.636	0.115	0.345	1.151

Figures



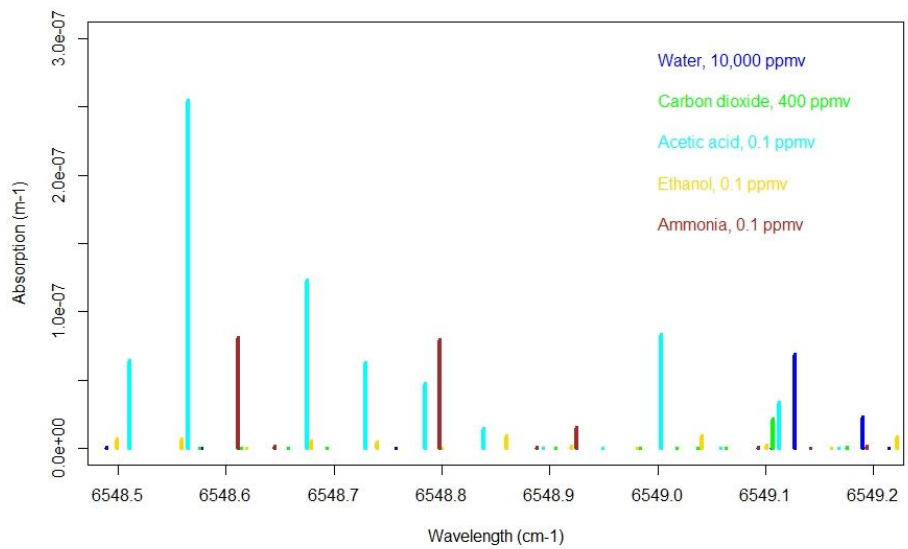


Figure 1. Simulated absorption spectrum from the HITRAN database for 1% H₂O (blue), 400 ppm CO₂ (green), 100 ppb acetic acid, 100 ppb ethanol, and 100 ppb NH₃ at 45°C and 187 mbar.

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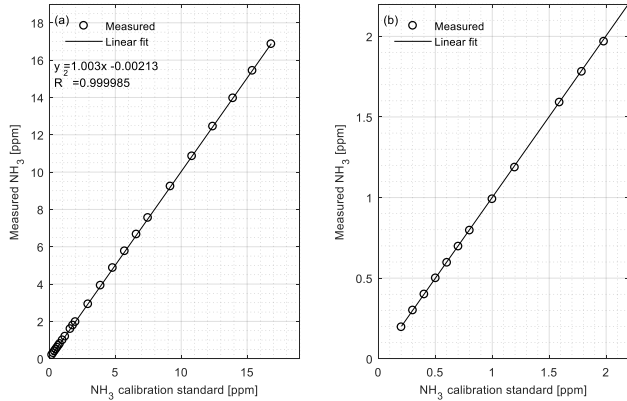
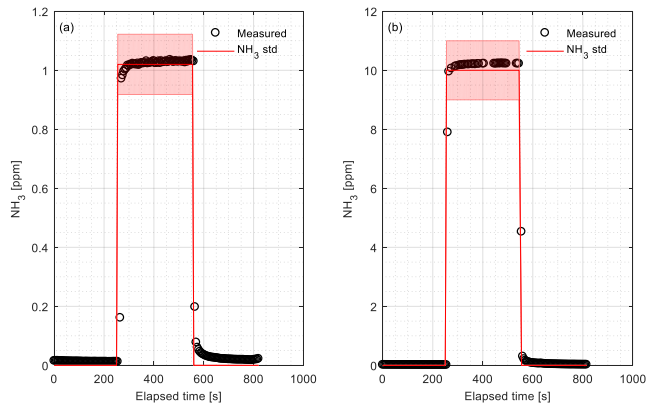


Figure 2. (a) Calibration curve of the CRDS from 0.20 to 16.8 ppm NH₃ conducted under laboratory conditions; (b) Calibration curve limited to 0 to 2 ppm. Symbols represent measured values, error bars the standard deviation, and the line is the fitted regression model.

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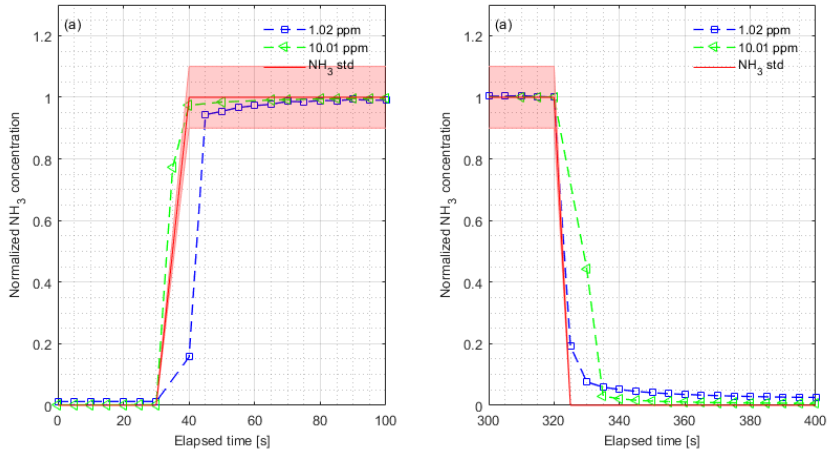


Figure 3. (a) Rise time and (b) fall time for the CRDS measurements normalized to final concentrations during laboratory testing of the response to a step change in NH₃ to (a) 1.02 ppm (blue) and 10.01 ppm (green). The in NH₃ to 1.02 ppm with rise time (0% to 95% response) = $131(e) = 8.1$ s and fall time (100% to 5% response) = $191(e) = 3.2$ s; (b) 10.01 ppm with rise time = 83.6 s and fall time = 144.8 s. The red lines and areas represent the NH₃ standard gas concentration with 10% accuracy, the blue markers show the normalized concentration from 1.02 ppm, and the green markers show the normalized concentration from 10.01 ppm.

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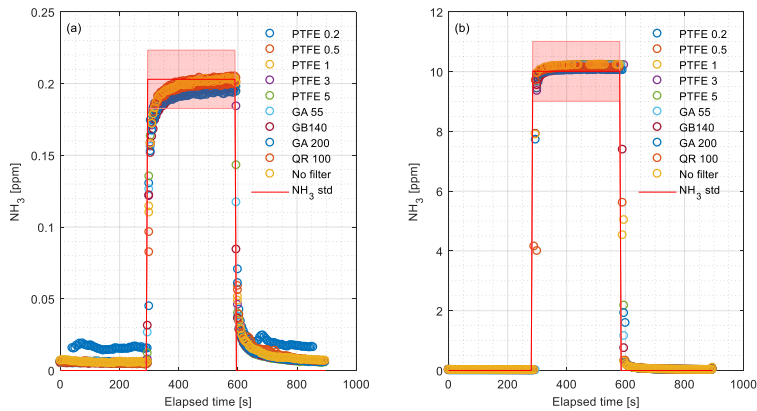
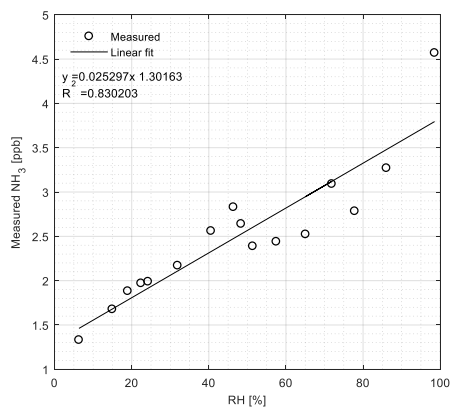
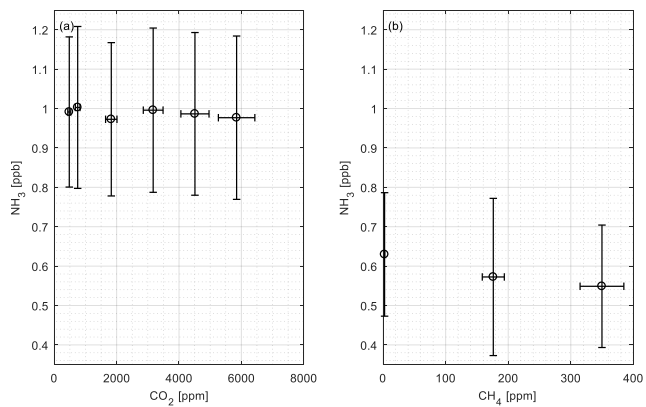


Figure 4. The response to a step change in NH₃ at (a) 0.203 ppm and (b) 10.01 ppm with and without external inlet filters during laboratory testing. The red line and area represent the NH₃ standard gas concentration with ~~with~~ 10% accuracy. See the legend abbreviations in Table 1.



5

Figure 5. The CRDS signals of NH₃ (ppb) in zero air at different concentrations of water vapor, ranging from 6 to 99 % relative humidity (RH) at 22°C under laboratory conditions. Symbols represent measured values and the line is the fitted linear regression model.

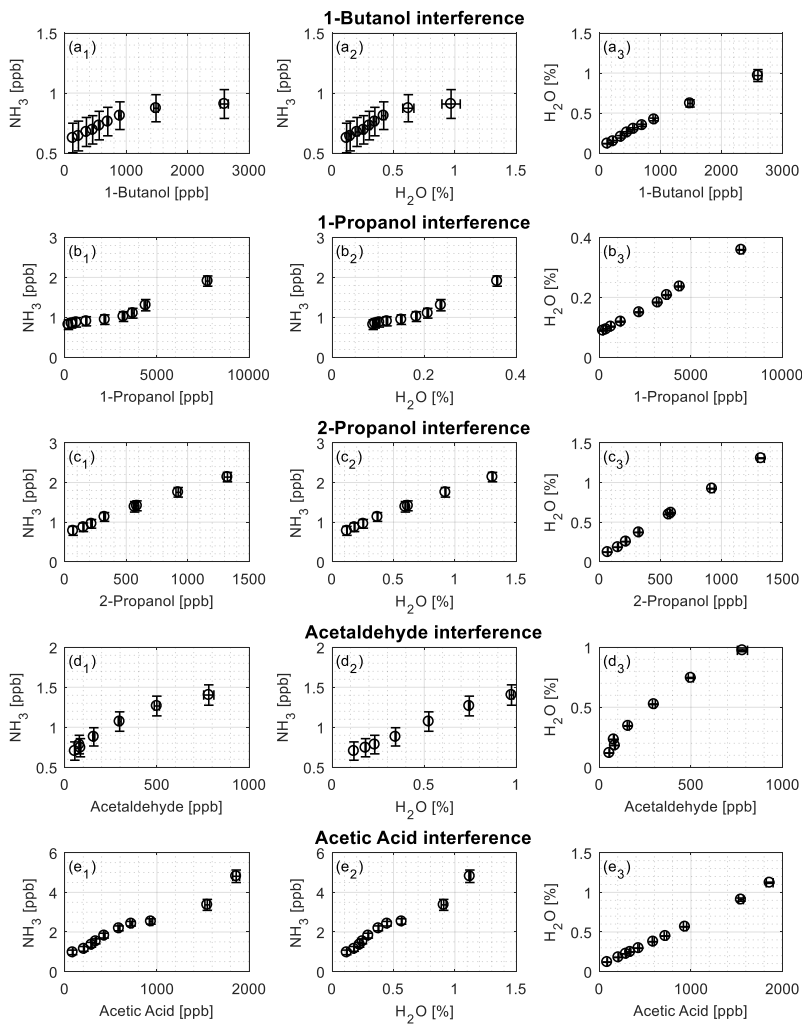


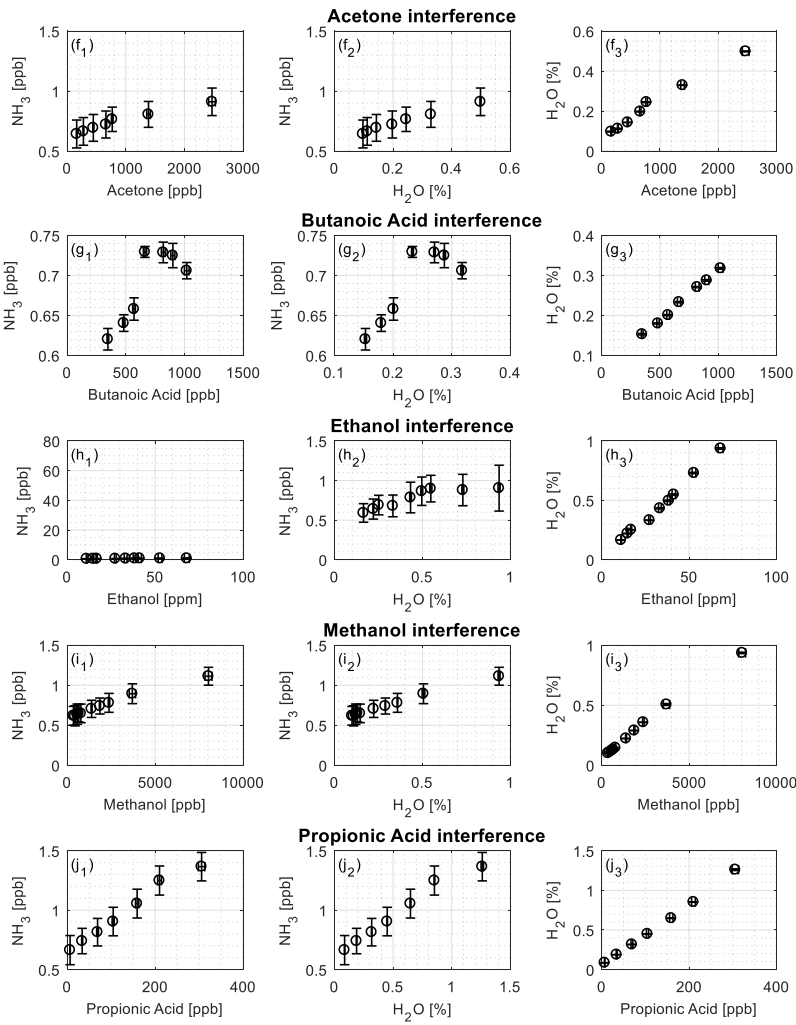
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Figure 6. The CRDS signals of NH_3 in zero air response to various concentrations of (a) CO_2 (480-5848 ppm) and (b) CH_4 (2.42-350 ppm) under laboratory conditions. Symbols represent measured values and vertical and horizontal bars the standard deviation of the measurements.

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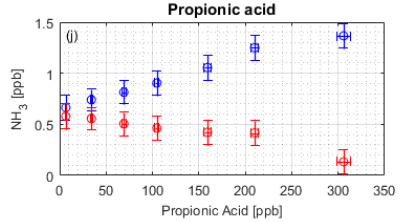
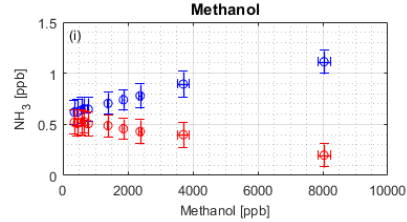
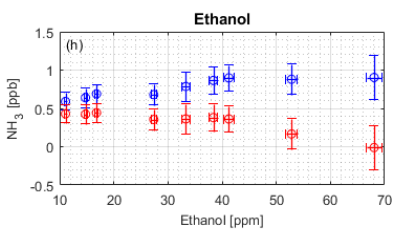
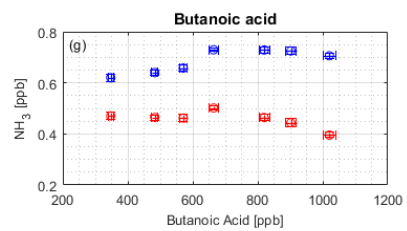
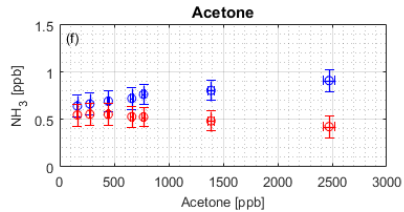
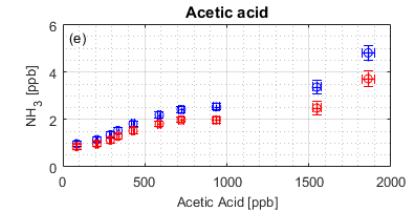
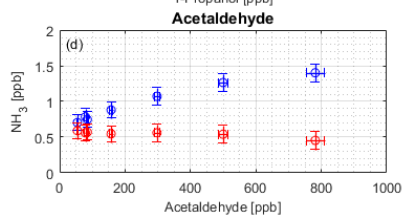
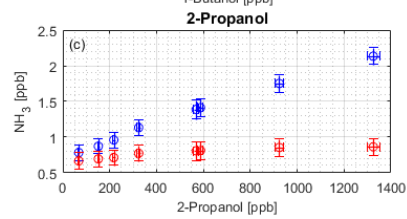
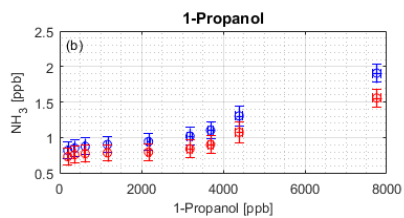
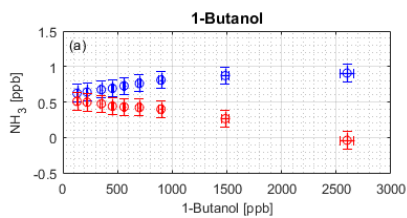


Figure 7. Interference of different organic compounds. Panels with subscript 1 show on the CRDS signal to NH_3 measurement. Blue markers indicate the compound. Panels with subscript 2 show CRDS signal to the absolute original data and red markers indicate water content. Panels with subscript 3 show absolute water content and the concentration of the compound corrected data from the regression showed in Figure 5. The compounds are (a) 1-butanol; (b) 1-propanol; (c) 2-propanol; (d) acetaldehyde; (e) acetic acid; (f) acetone; (g) butanoic acid; (h) ethanol; (i) methanol; (j) propanoic acid.

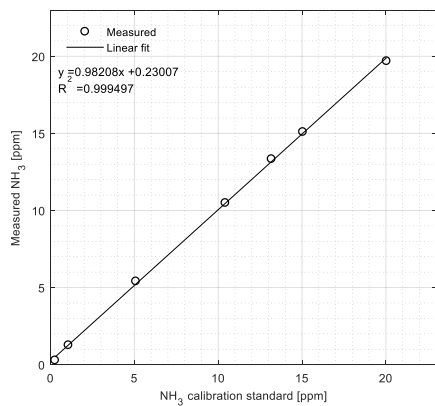


Figure 8. Calibration curve of the CRDS from 0.27 to 20.04 ppm NH_3 conducted under field conditions. Symbols represent measured values and the line is the fitted linear regression model.

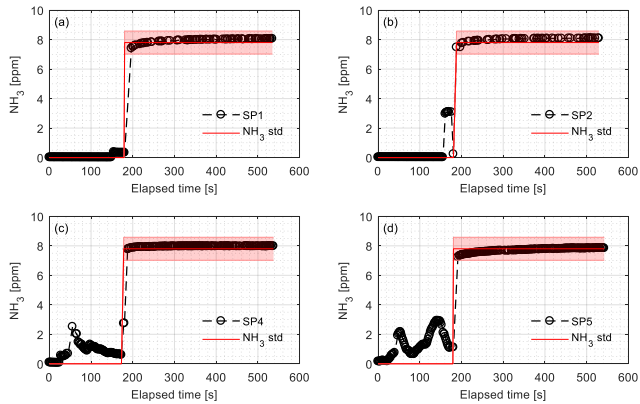


Figure 9. Calibration of the NH_3 sampling and measurement system and associated response times of the CRDS during field-testing. Introduction of 7.8 ppm NH_3 gas was at (a) SP1; (b) SP2; (c) SP4 and (d) SP5 while monitoring the NH_3 concentration at the outlet port connected to the analyzer. SP denotes sampling point. The rise times were **167.3 s**, **63.0 s**, **138.4 s**, and **255.9 s**, for SP1, SP2, **SP3**SP4 and SP5, respectively. The red line and area represent the NH_3 standard concentration with uncertainty.

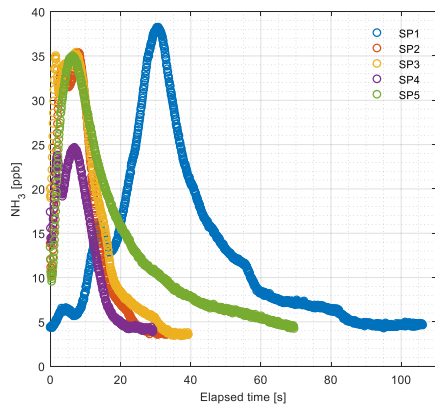


Figure 10. Levels of NH_3 concentration in the 2-week old external particulate filters (PTFE, 0.20 μm pore size) measured by the CRDS in the laboratory. Filters collected from the field were installed before each sampling port. SP denotes sampling port.

Appendix A

Table A1. Measured concentrations of NH₃, CO₂ and CH₄ in laboratory zero air (n = number of data points; CV = coefficient of variation).

Gas	Concentration	Mean	CV (%)	Range (min-max)	Measurement duration (h)
NH ₃	ppb	1	43	0.1-5.5	19
CO ₂	ppm	480	5	460-545	19
CH ₄	ppm	2.4	10	1.7-3.2	19

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5 Table A2. ~~This Rise (0% to 95%)~~The rise (1/e response time) and fall (~~100% to 5%~~1/e response time) times (s) of the CRDS analyzer for measurements of NH₃ concentrations (0.203 and 10.01 ppm) with or without external inlet particulate filters during laboratory testing. For filters detail, see Table 1.

Filter code	0.203 ppm NH ₃		10.01 ppm NH ₃	
	Rise (s)	Fall (s)	Rise (s)	Fall (s)
No filter	307.3	554.7	83.3	144.9
PTFE 0.2	154.8	507.1	102.0	172.7
PTFE 0.5	258.0	505.3	186.0	131.5
PTFE 1.0	356.9	504.9	1.8	135.3
PTFE 3.0	356.3	504.5	152.1	1.4
PTFE 5.0	405.3	459.5	271.2	133.2
GA 55	5012.4	458.5	131.8	112.3
GB 140	6512.7	507.0	93.3	167.0
GA 200	559.3	505.6	183.3	63.0
QR 100	308.0	705.5	135.9	135.7
Min	154.8	454.5	81.2	1.4
Max	6512.7	709.5	276.0	177.0
Mean	388.1	526.3	143.1	123.7

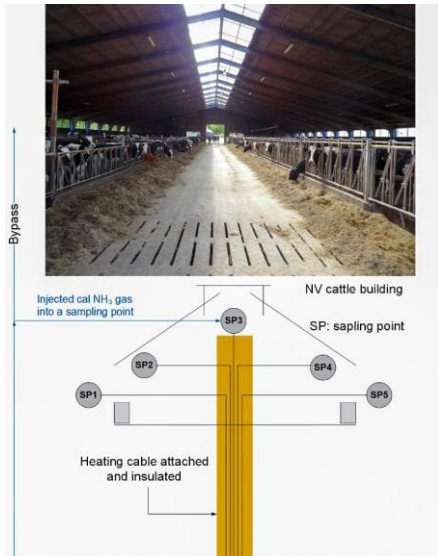


Figure A1 Schematic of the samplings point inside the cattle building. SP1 and SP5 were placed outside for background measurement at 2.5 m height. SP2 and SP4 were on the walls at 2.5 m height. SP3 was placed below the ridge at 9 m height. The lines were approximately 5 m, 15 m, 35 m, 45 m, and 50 m for SP1, SP2, SP3, SP4, and SP5, respectively.

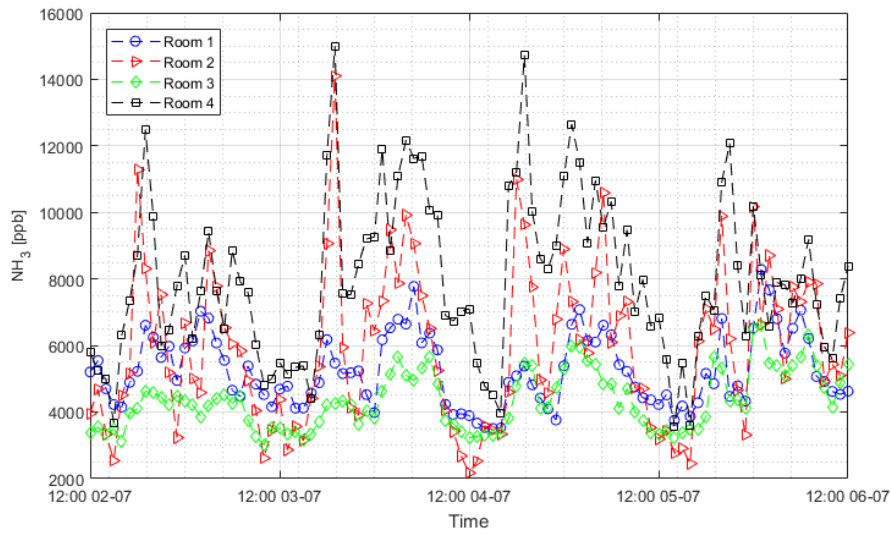


Figure A2 Hourly mean concentrations of NH₃ from four different rooms with finisher pigs.

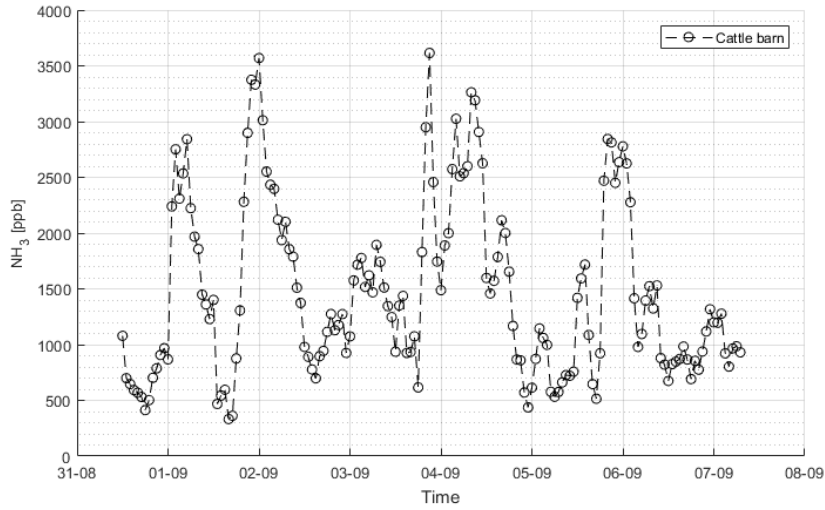


Figure A3 Hourly mean concentrations of NH₃ from a dairy cattle barn, unpublished data.

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