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

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Abstract. Emission of ammonia (NH_3) is a ubiquitous problem due to the adverse effects of NH_3 on environment and human health. The agricultural sector accounts for nearly all NH_3 emissions in Europe. Hence, technologies for abatement of NH_3 emissions from this sector has been in strong demand in recent years. In order to document emissions and evaluate the abatement technologies, there is a strong need for reliable NH_3 measurement methods. Photoacoustic spectroscopy (PAS) is often used to measure NH_3 concentrations, but recent research show interference from compounds typically present in livestock production and during agricultural activities. In this work, the performance of Cavity Ring-Down Spectroscopy (CRDS) from Picarro as an alternative to PAS has been tested with respect to method validation under laboratory and field conditions. Potential interferences of ten volatile organic compounds (VOCs) on CRDS NH_3 measurement were tested with simultaneous VOC analysis performed by Proton-Transfer-Reaction Mass Spectrometry (PTR-MS). Both laboratory and field calibrations show excellent linearity over a large dynamic range of NH_3 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. Apart from the negligible humidity dependency, no interferences of the tested VOCs were observed. Overall, the CRDS system performs satisfactory and is well suited for measurements of NH_3 emissions from livestock production.

1 Introduction

Ammonia (NH_3) 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 NH_3 can lead to eutrophication and acidification, which has negative effects on biodiversity (Sheppard et al., 2011). NH_3 is a precursor of atmospheric aerosols thereby influencing the global radiation budget as well as having a negative influence on human health (Aneja et al., 2001; Baek et al., 2004). In addition, microbial oxidation of NH_3 results in secondary production of nitrous oxide (N_2O) and nitric oxide (NO) (Zhu et al., 2013). N_2O is a very potent greenhouse gas (GHG) and NO is involved in atmospheric reactions producing tropospheric ozone (Aneja et al., 2001). Due to the numerous adverse effect of NH_3 emissions, it is important to measure NH_3 concentrations with high accuracy and precision.

Agricultural activities, mainly manure application and management, accounts for around 94% of NH_3 emissions in Europe (Nielsen et al., 2017)Reliable measurements in the agricultural sector are highly important to give accurate estimates of NH_3 emissions in order to reduce the emissions e.g. by validation of technological improvements within the agricultural sector. In many agricultural emission studies 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. (2019) show high interference on NH_3 measurements from a variety of organic compounds including carboxylic acids and alcohols. Hassouna et al. (2013) reported non-constant bias in the results from PAS measurements on NH_3 and N_2O caused by organic compounds often present at agricultural sites, which makes the PAS measurements unreliable in an agricultural setting. In a few recent studies 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.

It is challenging to measure NH_3 concentrations correctly due to its 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 NH_3 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 NH_3 in livestock buildings, where dust and particles provide large surface areas for its adsorption in particulate filters. NH_3 adsorption can affect response 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 NH_3 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 interferences can introduce errors depending on the instrument used. Proper calibration before and during laboratory and field measurement can reduce the potential errors and improve the accuracy of the measurement system. Quantification of the errors can enhance the quality of the NH_3 measurement data, which is essential to research, emission abatement and policy-making. Bobrutzki et al. (2010) conducted a field inter-comparison of eleven atmospheric NH_3 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 ($R^2 > 0.84$).

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 NH_3 measurements. The scale factor error they discovered is approximately 2% of the absolute water concentration. Our CRDS analyzer has not incorporated this upgraded correction.

We wish to address the interferences from VOCs further as the PAS technique seems to be inadequate for measurements in certain agricultural environments (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 NH_3 measurements as seen for PAS.

In this work, a CRDS NH_3/H_2O analyzer (Picarro Inc., Santa Clara, CA, USA) was used for all measurements of NH_3. 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 NH_3 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 document VOC concentrations in laboratory tests. Due to the major concerns regarding measurements of NH_3 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 emission measurements under dynamic conditions. NH_3 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 monitor temporal variations with only 4-8 measurements per measurements point a day. Thus, the 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 NH_3 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 NH_3 emissions. The focus on reduction of NH_3 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.

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 NH_3 (± 10%) in N_2 calibration gas (AGA A/S, Copenhagen, Denmark), pure (99.99%) CO_2 (AGA), pure (99.99%) CH_4 (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 ± 5%.

2.2 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 NH_3/H_2O analyzer model G2103 (Picarro Inc., Santa Clara, CA, USA) 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.

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 NH_3 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 NH_3 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 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 NH_3 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
5   show 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. The NH_3 standard calibration gas used for all calibrations had an accuracy of ± 10% stated by the manufacturer. The measured NH_3 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. The rise time to
10   1/e of the final concentration level was 8.1 s and 3.6 and the fall time to 1/e of the final concentration level was 3.2 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 8.1 s and 6.3 s (for 0.203 ppm), and 3.1 s and 3.7 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
15   filters, see details in Table A2.

Measurements on zero air over an hour gave a standard deviation on the NH_3 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 levels. Figure 5 shows the effects of the humidity on
20   the NH_3 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 NH_3 measurements from 1.3 to 4.6 ppb over the given RH range.

Figure 6 shows the CRDS signals from CO_2 and CH_4 with random fluctuations in the low ppb level being observed. There are no apparent interferences from these two compounds. All measured NH_3 concentrations for both compounds are below the LOQ.

25   Figure 7 shows the interferences of ten different VOCs with VOC concentration as a function of NH_3 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 NH_3 concentration increased with increased water vapor for all compounds. The observed interferences were in the range from 0.5 to 5 ppb NH_3 equivalents at VOC concentrations from 6 to 8000 ppb. These VOC concentrations range from levels comparable to field conditions up to levels
30   1-2 orders of magnitude higher than 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
35   Figure 9 had an uncertainty of ± 10%.

Figure 10 shows the ammonia concentrations released from 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 m^3 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
40   values are comparable to typical ambient laboratory concentrations ranging from 14-37 ppb; see Table A1.

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; NH_3 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

5 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. This may well explain the small offset (< 4%) from the obtained concentrations seen in Figure 9, 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

10 integration time, as seen in Table 2. 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 NH_3

15 concentrations in animal buildings. Ni and Heber (2008) suggest a response time of less than 2 min to capture temporal NH_3 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 with a tendency towards shorter response time at higher concentration.

20 The manufacturer reports rise- and fall times of approximately 16 seconds, which is as a minimum twice as much as the present results, Table A2 and Figure 2. The response to a change from 0 to 1.02 ppm gave response times of 8.1 s and 3.2 s for the rise- and fall time, respectively. 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 7.3 s, 3.0 s, 8.4 s, and 5.9 s, for SP1, SP2, SP4 and SP5, respectively. Response times are in general faster for higher concentration differences (see Figure 4), which

25 is ascribed to faster surface saturation. The observed concentrations of NH_3 released from particulate filters exposed to air from a livestock house for 2 weeks (Figure 10) suggest that adsorption of NH_3 to the filter material, surfaces and walls is 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 adsorption of NH_3 on the filter material.

30 CO_2 and CH_4 are present in the atmosphere in relatively high concentration compared to other trace gasses, and animals produce CO_2 and CH_4, thus elevated concentrations are normal in animal houses. Over a large concentration range, we observed little scatter and no interference of CO_2 and CH_4 on NH_3 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

35 humid headspace air over a VOC solution gave a correlation between water vapor and VOC concentration. This was also the case for all ten volatile compounds. Martin et al. (2016) observe an interference from water vapor on NH_3 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 expected a small water dependency for NH_3, which is seen in Figure 5. Figure 5 shows the humidity effect on the CRDS signal generated from pure deionized water and

40 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 NH_3 for a nearly water saturated air stream with an absolute H_2O concentration of approximately 1.1%. Thus, in the extreme case of low NH_3 concentrations (e.g. 100 pbb) and very humid air, a water vapor interference of up to 5 % of the NH_3 signal may be present, but under normal conditions, this is negligible.

The ten tested compounds are normally present in sub-ppm levels in agricultural environments (Copeland et al., 2012; Yuan et al., 2017). 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 livestock buildings was used to obtain the potential maximum interference and we only observed very small water induced interferences. 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 NH_3 (Figure 7), except for acetic acid with a difference of nearly 4 ppb. It should be noted that the water to VOC relation differs for the different compounds. With water correction applied, only 1-propanol and acetic acid have increasing tendencies, where NH_3 concentration increase about 0.8 ppb NH_3 for an increase of 7.5 ppm of 1-propanol and 2.9 ppb NH_3 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 3.7 ppb NH_3, 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 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 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 NH_3 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 response times with respect to concentration changes were sufficiently low to measure temporal variations of NH_3 concentrations in livestock emissions. Examinations of external particulate filters lead to no clear recommendations for filter material, but all filters gave acceptable response times and only small amounts of NH_3 adsorption compared to background levels. Potential interferences were tested for ten VOC in known concentrations and the compounds gave negligible interference on CRDS NH_3 measurements.

Code and data availability. Data and code are available upon request to the corresponding author.
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Competing interests. The authors declare no conflict of interest.

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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_2O [%]	2065	0.082	0.0019	0.006	0.019

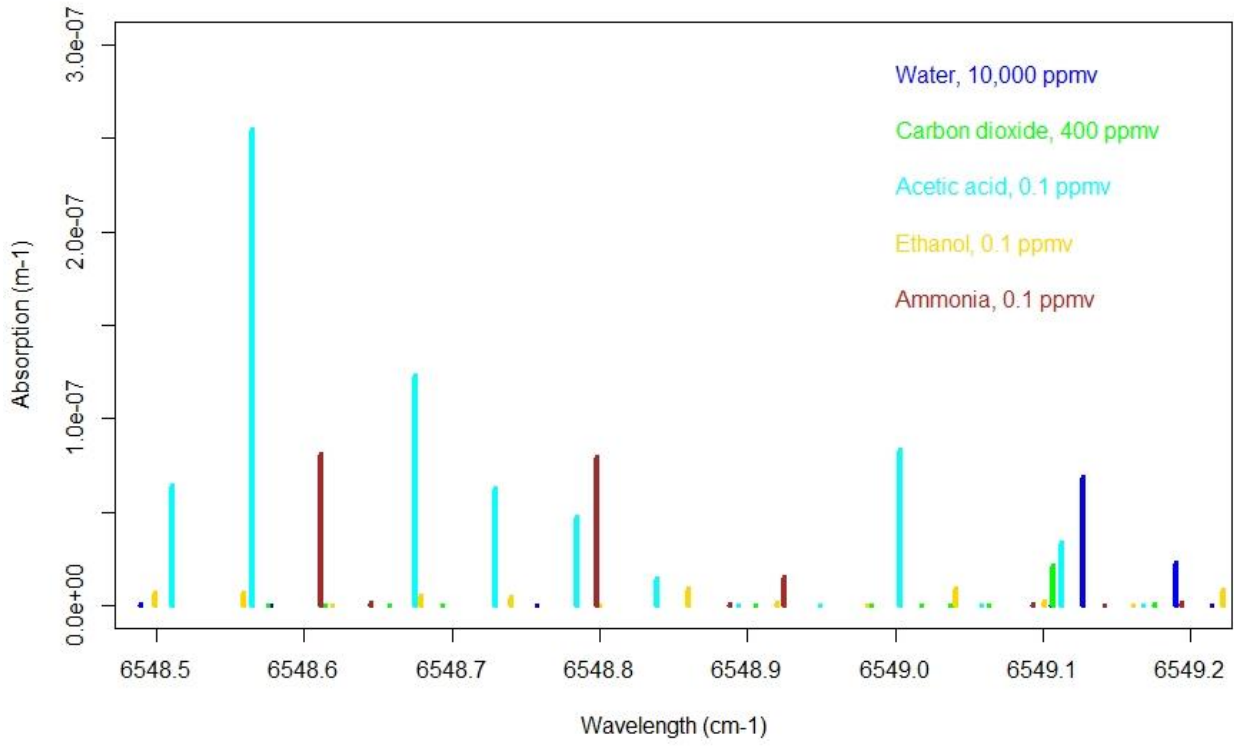
NH₃ [ppb]	2065	0.636	0.115	0.345	1.151

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.

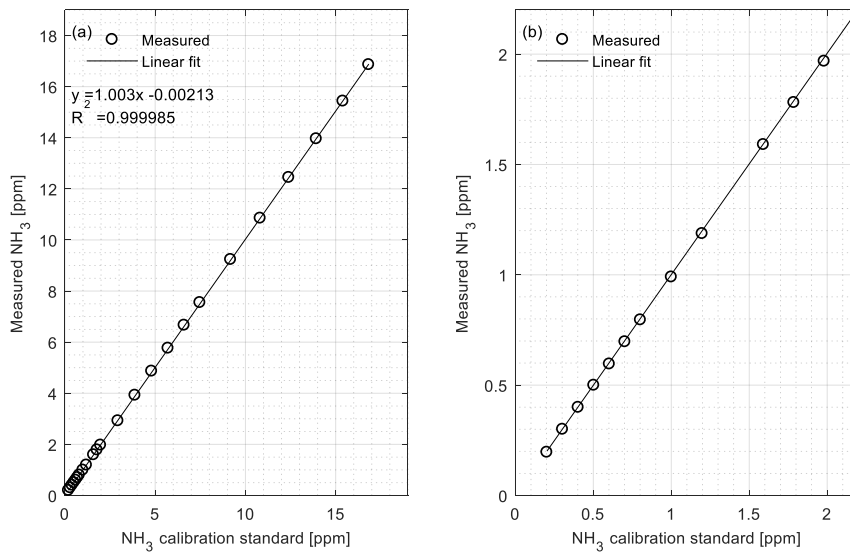



Figure 2. (a) Calibration curve of the CRDS from 0.20 to 16.8 ppm NH₃ conducted under laboratory conditions; (b) Calibration curve limited to 0 to 2 ppm. Symbols represent measured values, error bars the standard deviation, and the line is the fitted regression model.

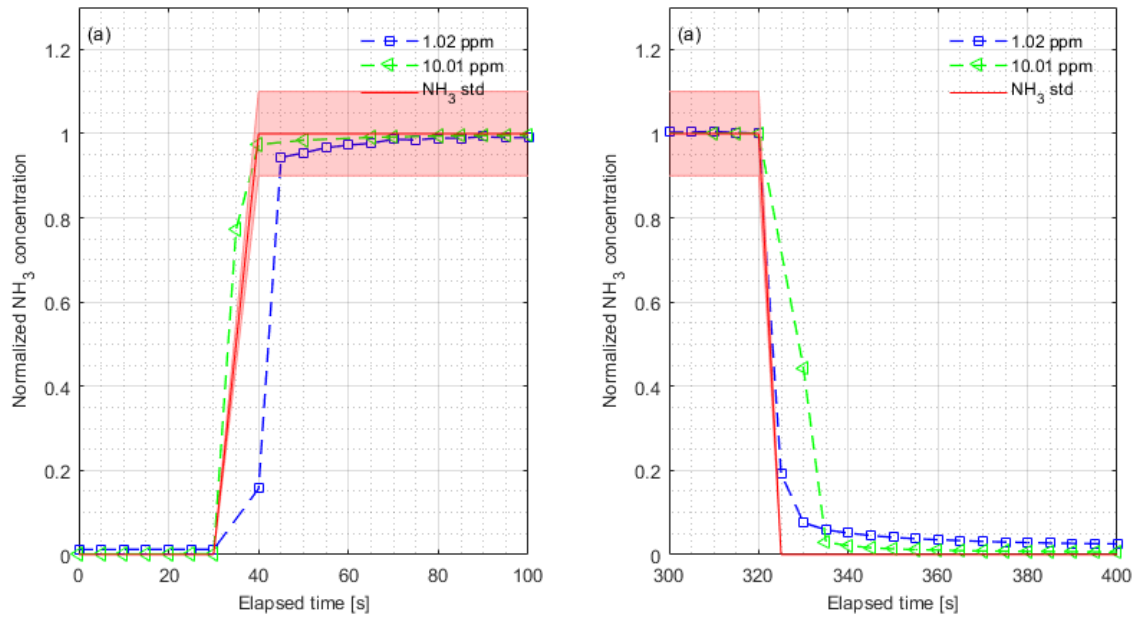



Figure 3. (a) Rise time and (b) fall time for the CRDS measurements normalized to final concentrations during laboratory testing of the response to a step change to 1.02 ppm (blue) and 10.01 ppm (green). The in NH_3 to 1.02 ppm with rise time (1/e) = 8.1 s and fall time (1/e) = 3.2 s; 10.01 ppm with rise time = 3.6 s and fall time = 4.8 s. The red lines and areas represent the NH_3 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.

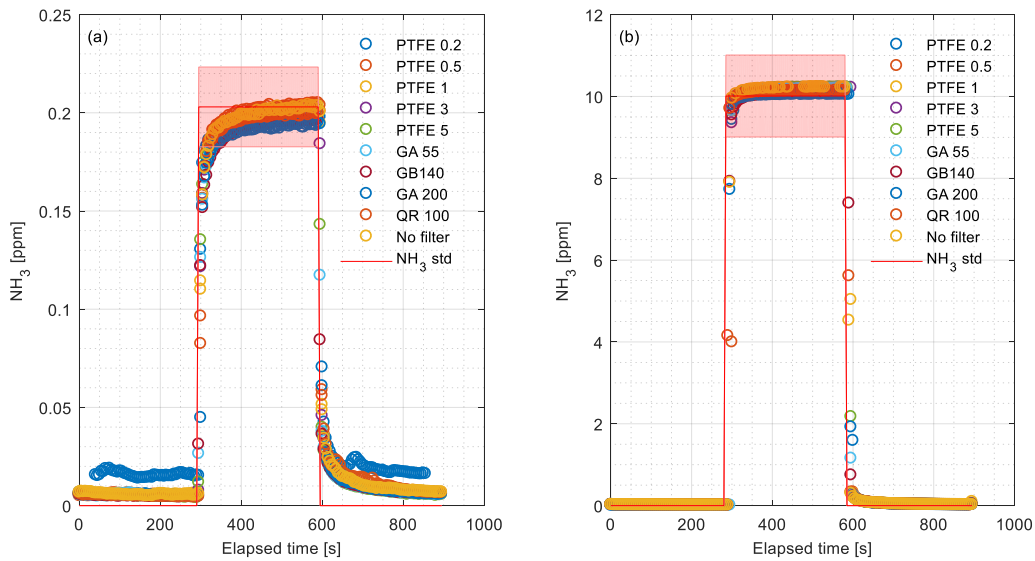



Figure 4. The response to a step change in NH_3 at (a) 0.203 ppm and (b) 10.01 ppm with and without external inlet filters during laboratory testing. The red line and area represent the NH_3 standard gas concentration with 10% accuracy. See the legend abbreviations in Table 1.

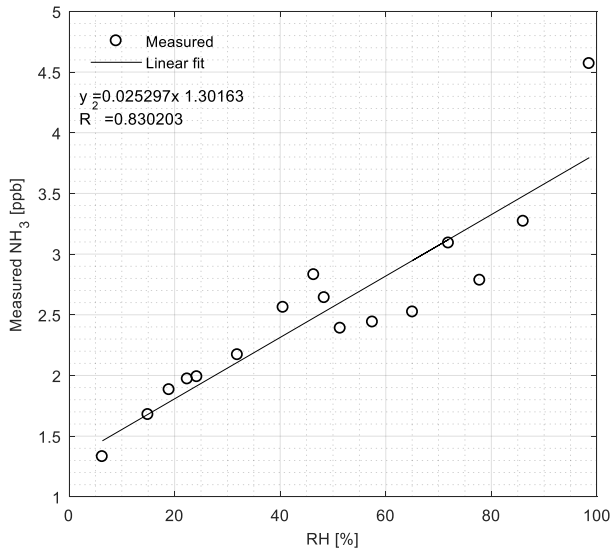



Figure 5. The CRDS signals of NH₃ (ppb) in zero air at different concentrations of water vapor, ranging from 6 to 99 % relative humidity (RH) at 22°C under laboratory conditions. Symbols represent measured values and the line is the fitted linear regression model.

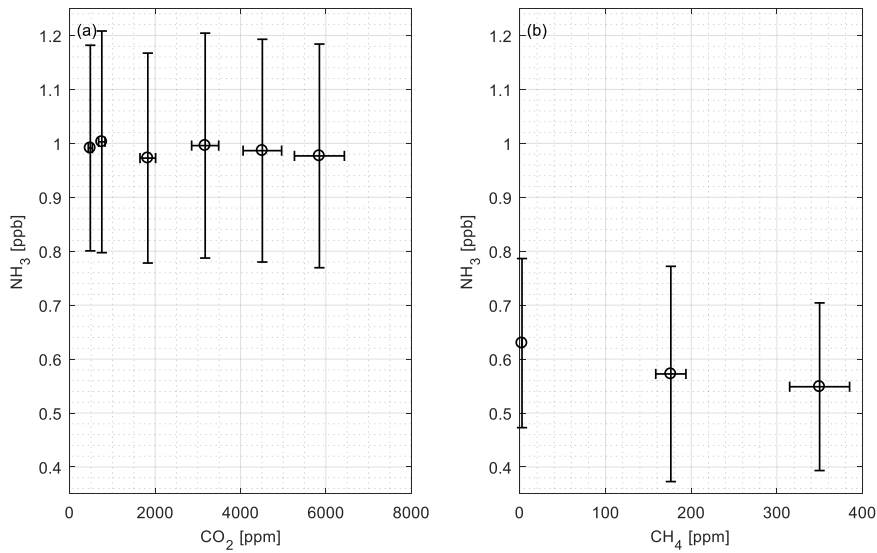



Figure 6. The CRDS signals of NH₃ in zero air response to various concentrations of (a) CO₂ (480-5848 ppm) and (b) CH₄ (2.42-350 ppm) under laboratory conditions. Symbols represent measured values and vertical and horizontal bars the standard deviation of the measurements.

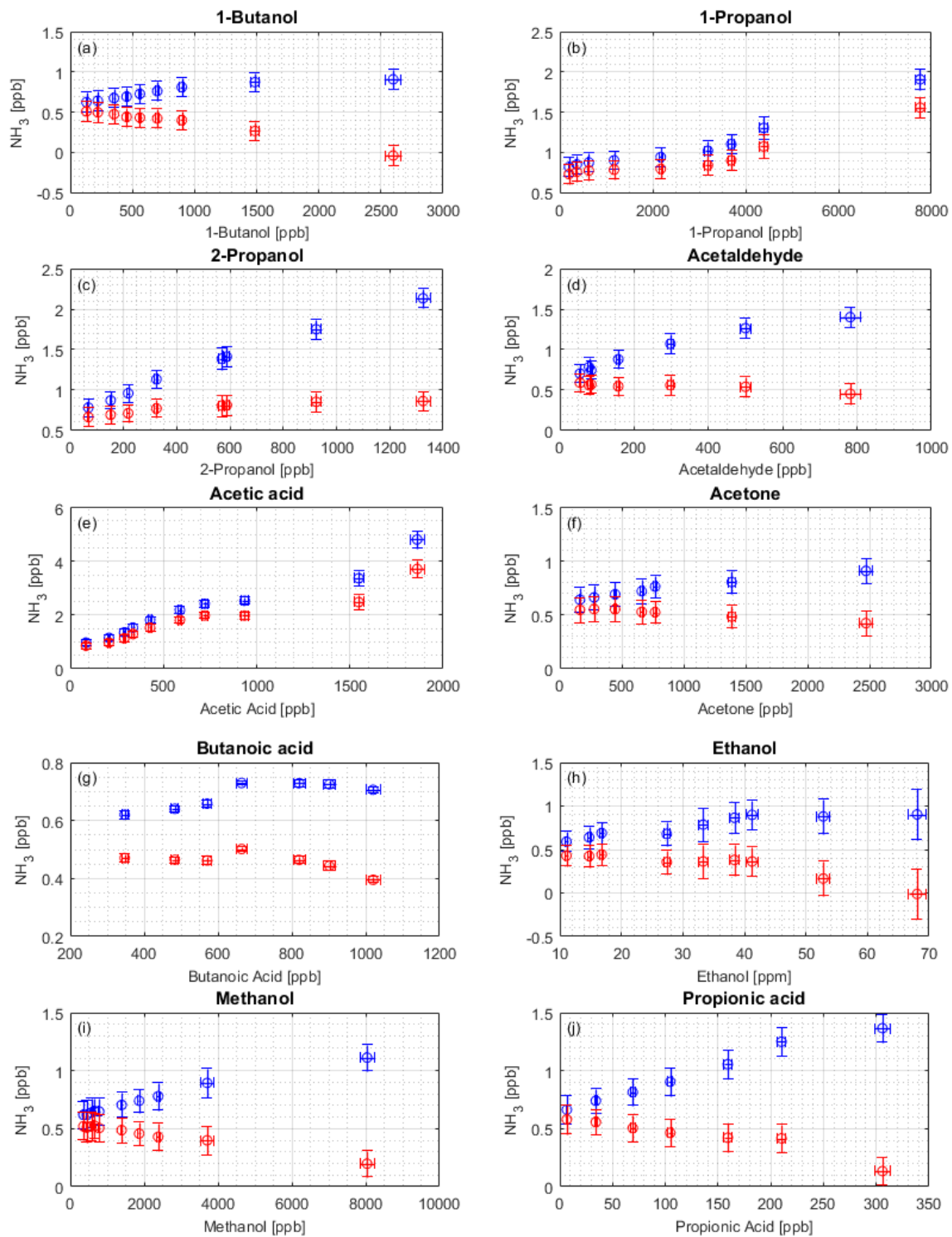



Figure 7. Interference of different organic compounds on the CRDS NH₃ measurement. Blue markers indicate the original data and red markers indicate water corrected data from the regression showed in Figure 5. The compounds are (a) 1-butanol; (b) 1-propanol; (c) 2-propanol; (d) acetaldehyde; (e) acetic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

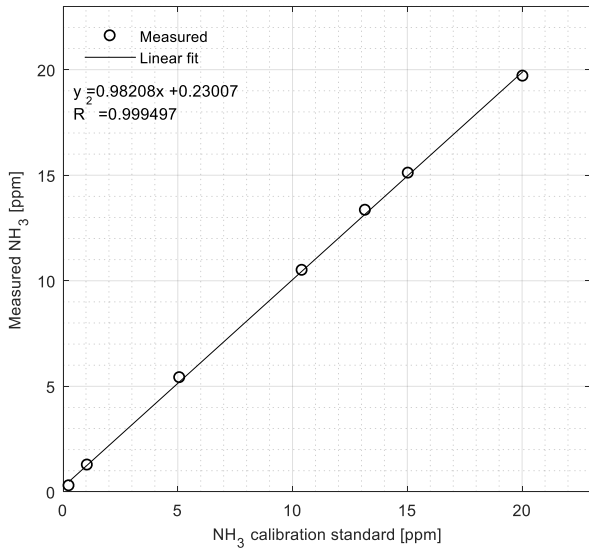



Figure 8. Calibration curve of the CRDS from 0.27 to 20.04 ppm NH₃ conducted under field conditions. Symbols represent measured values and the line is the fitted linear regression model.

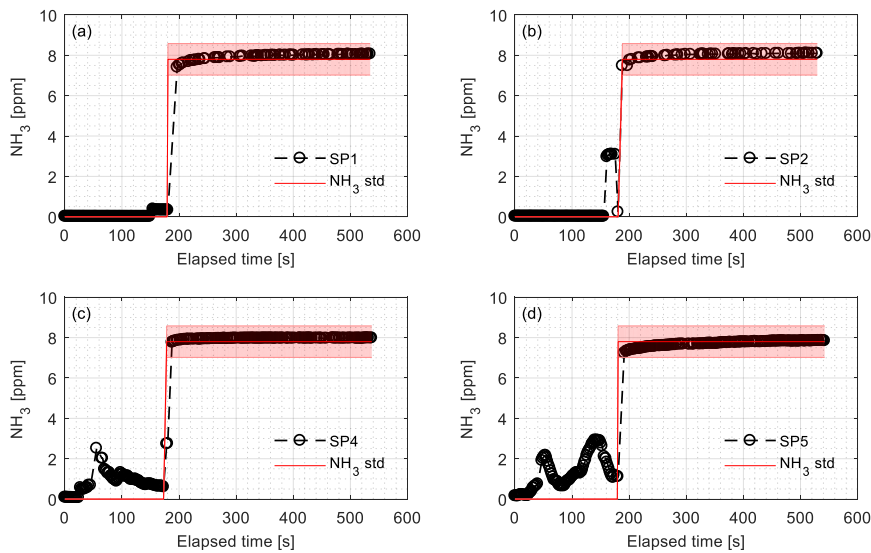



Figure 9. Calibration of the NH₃ sampling and measurement system and associated response times of the CRDS during field-testing. Introduction of 7.8 ppm NH₃ gas was at (a) SP1; (b) SP2; (c) SP4 and (d) SP5 while monitoring the NH₃ concentration at the outlet port connected to the analyzer. SP denotes sampling point. The rise times were 7.3 s, 3.0 s, 8.4 s, and 5.9 s, for SP1, SP2, SP4 and SP5, respectively. The reed line and area represent the NH₃ standard concentration with uncertainty.

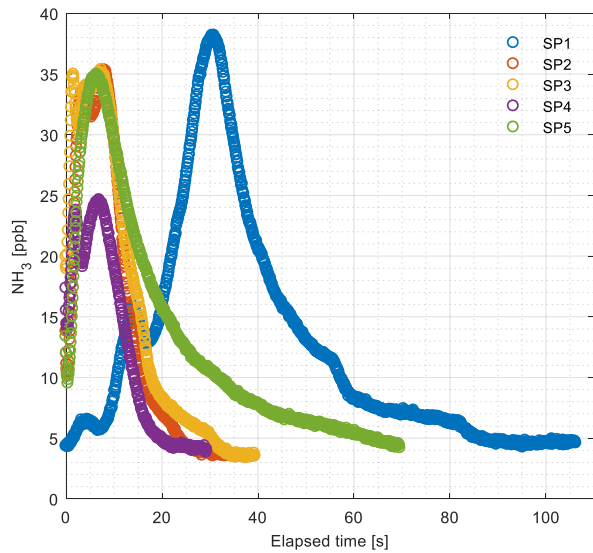



Figure 10. Levels of NH₃ concentration in the 2-week old external particulate filters (PTFE, 0.20 μm pore size) measured by the CRDS in the laboratory. Filters collected from the field were installed before each sampling port. SP denotes sampling point.