Response to Interactive discussion Anonymous Referee #3

General comments

The paper investigates interferences caused by volatile organic compounds (VOCs) in the photoacoustic measurement of ammonia in air on agricultural farms. The commercially available PAS instrument that was used in this work contains a broadband infrared light source and six optical filters for spectral selection. The filter set is suitable for the specific detection of NH3, CH4, CO2, H2O, N2O and SF6 in atmospheric mixtures at ppmv level, if no other absorbing species interfere. The experiments described in the manuscipt show very clearly that VOCs, such as methanol, ethanol or acetic acid observed in a dairy farm can cause significant interferences and are detected by the PAS instrument with higher sensitivity than ammonia. Similar results are found for greenhouse gases that are measured by the PAS instrument. A comparison to a reference technique (PTR-MS), which measured ammonia and VOCs, demonstrates that the PAS instrument can overestimate ammonia concentrations by up to an order of magnitude due to spectral interferences by VOCs. The authors conclude that the PAS measurements of ammonia can be corrected, if the concentrations of the interfering VOCs are known.

This work is relevant as the described type of PAS instrument has been widely used for emission measurements of ammonia and greenhouse gases in agriculture. Although there have been experimental indications of interferences in the literature, there is little quantitative information available about cross-sensitivities to trace gases such as VOCs that can be co-emitted on animal farms. The paper presents new results, which help to understand the quality of PAS measurements of agricultural emissions. As such emissions play a role for air quality and climate, the topic of the paper is suitable for AMT. However, before it can be accepted for publication, major revisions of the manuscript are needed as outlined in the following.

Response: Thank you very much for the general comments and all valuable comments.

1. The discussion about the general applicability of the PAS instrument for measurement of ammonia and greenhouse gases in agriculture needs to be broadened.

It should be pointed out more clearly that the technique used in the Innova instrument "is capable of measuring almost any gas that absorbs infrared light" (quotation from the Lumasense web page). The document "Detection limits for various gases" on the Lumasense web page lists almost 300 different organic gases that can be detected at the ppmv level. The method is based on nondispersive broadband spectroscopy and selectivity is achieved by using appropriate wavelength filter, with one filter for each targeted trace gas. If the number of absorbing gases is larger than the number of optical filters, possible interferences are no surprise! The key questions are: (a) what is the magnitude of interferences that can be expected in agricultural environments, and (b) is it possible to quantify and correct interferences in a reasonable way? Both questions are adressed by the authors, but a more detailed discussion is needed.

Response: In principle, the technique used in the Innova instrument "is capable of measuring almost any gas that absorbs infrared light". Now this is pointed out clearly in the introduction (Line 68-70). The two key questions “(a) what is the magnitude of interferences that can be expected in agricultural environments, and (b) is it possible to quantify and correct interferences in a reasonable way?” are now included in the introduction in order to help to clarify the purpose of this study. Please see Line 84-86 in the revised manuscript.

(a) The authors show in Figure 5A and 5C that the PAS measurements of ammonia are higher than by PTR-MS, but quantitative statements of the measurement errors and interferences are missing in the text. The figure shows discrepancies between the two techniques of up to a factor of ten. How much of the difference can be explained by calibration errors? What is the measurement precision of the data points in Figure 5? If the PTR-MS measurements are assumed to be interference free (is this a justified assumption?), the discrepancies must be due to interferences in the PAS measurements, which apparently can be up to an order of magnitude greater than the correct ammonia concentration. The overestimation should be explicitly quantified!

Response: In Figure 5A and 5C, the factor is typically between 1 and 5, with few cases close to 10 (see Table S3). Only a small part of this difference can be explained by calibration errors. For the PTR-MS, the calibration error is around 10-15%. For the Innova 1312, the calibration error is around 20%. The measurement precision (ratio of standard deviation/averaged concentration) of the data points in Figure 5 was around 1%-3%. For ammonia measurement by PTR-MS, the measurements are interference free. Thus the discrepancies are surely caused by the PAS measurements, with some overestimation as the reviewer mentioned (the corrected ammonia fit generally ok though, as showed in Fig.5B and 5D). The overestimation possibly due to the interaction effects by various VOCs on the interference correction, but the quantification is difficult since we did not investigate the effects of interference when simultaneous present of multiple VOCs.

(b) The authors argue that the interferences can be corrected if the interfering VOCs are measured by another technique (line 504 - 508). I agree that this would require a considerable additional effort. This effort should be explained in more detail. How accurate should the corrected data be? What accuracy and precision does this mean for measuring VOCs and determining their correction factors? The considerable additional effort appears to offset the advantage of the easy handling of the PAS instrument. It should therefore be discussed if alternative measurement techniques, for example CRDS (available for NH3, CH4, CO, CO2, H2O) would offer a better performance than PAS for agriculture emission measurements.

The authors conclude that the interferences listed in Table 2 can be corrected. I am not completely convinced that this is generally true. In the example in Figure 5, the interference is dominated by a single VOC (ethanol). Would the correction also work if two or more VOCs caused a similarly large interference at the same time? Are the interference corrections of individual substances (Table 2) independent of each other? See also Comment 25 below.

Response: Indeed, if the VOCs could be measured by another technique such as PTR-MS, interferences could possibly be corrected, but considerable additional efforts needed for correcting the data, and obviously it does not make sense to buy a PTR-MS in order to correct a PAS. The accuracy of the corrected data should certainly be as higher as better and at least to be able to reflect the right concentration within lower range of ppbv. Thus the required accuracy and precision for the measured VOCs should also be relatively high as lower range of ppbv. This additional effort certainly offset the advantage of the easy handling of the PAS instrument, and alternative measurement techniques, for example CRDS may indeed offer a better performance than PAS for agriculture emission measurements. The recent publication by Kamp et al., 2019 demonstrated that CRDS (Picarro G2103, only measuring ammonia and water) can measure ammonia with great precision without interferences and therefore have a better performance compared to PAS.

Regarding the correction factors (now changed to empirical relationships as suggested) listed in Table 2, we have to acknowledge that we don’t know if the effects are always additive – although they are likely to be. In the field study, ethanol certainly dominated the VOC matrix in general, but other types of VOC also contribute significantly. For example, the averaged ratio of ethanol concentration to the sum of the 8 VOCs (tested in lab with obtained correction factors) was 0.64 (±0.11) for Location Two in the field study. From this single application it seemed that the obtained empirical relationships to be additive, but a complete investigation is indeed needed in the future. This part is now revised accordingly and please see Line 552-560.

2. The title of the paper is not sufficiently descriptive. Spectral selection in PAS can be achieved in different ways with different specificities, for example, by optical filters in combination with broadband light sources (this work), by narrow bandwith lasers, interferometry, etc.. The title should inform about the technique that was used in this work. E.g. "Photoacoustic measurement using a broadband light source and optical filters may significantly overestimate ...".

Response: We agree with you, that we only tested PAS using a broadband light source and optical filters. We now have revised the title as suggested.

3. The paper needs language editing which will eventually be provided by the publisher during

the production process.

Reference

https://www.lumasenseinc.com/FR/produits/gas-sensing/gas-monitoringinstruments/photoacoustic-spectroscopy-pas/photoacoustic-gas-monitor-innova-1512/photoacoustic-gas-monitor-innova-1512.html.

Specific comments

1. Line 24 and line 40. Specify the greenhouse gases to which you refer.

Response: The greenhouse gases are now specified in the revised manuscript.

2. Line 28 - 37. Be more quantitative and specific! What were the concentration levels of ammonia and VOCs which were studied in this work? Was is meant by "various levels of interference"? Quantitative information of cross-sensitivities (ppmv of false ammonia/ppmv of VOC) should be given here. How large were the corrections (order of magnitude) which were applied to the PAS readings in the field experiments? What is meant by "reasonably correlated" (Line 35)?

Response: Yes, “various levels of interference” was meant for various VOCs levels which were tested for interference test while no ammonia was presented. We now add quantitative correction factors for highest VOC on ammonia interference (see Line 32-33). In the field experiment, data from corrected from PAS were correlated with the data from PTR-MS for ammonia, by applying the correction factors obtained from the single VOC test for interference. In the field experiments, the corrections for the PAS readings for Location One and Location Two were 2.14 (±0.75) and 2.88 (±1.85), respectively. The “reasonable” has been deleted in the sentence. These have been revised in the revised manuscript and please see Line 32-38.

3. Line 51 - 56. The concentration range in emission studies of ammonia and greenhouse gases in agriculture should be quantified and distinguished from concentrations in rural background air. What are the analytical requirements (concentration range, time resolution, limit-of-detection) for measurements in a dairy farm?

Response: The quantification of concentration range for ammonia and greenhouse gases in agriculture were done by a number of relevant studies previously. For example, Rong et al. (2015) quantified a dairy farm indoor and outdoor ammonia and greenhouse gases concentrations for both summer and winter periods, as follows: ammonia (indoor: 0.38-15.5 ppmv; outdoor: 0.2-3.3 ppmv); methane (indoor: 2.1-219 ppmv; outdoor: 1.1-11.1 ppmv); nitrous oxide (indoor: 0.19-0.83 ppmv; outdoor: 0.23-0.43 ppmv); carbon dioxide (indoor: 418-

2727 ppmv; outdoor: 402-646 ppmv). Although a lot of these quantification were performed by using PAS and the interference quantification were missing, these data could give some hints regarding the analytical requirements for the measurements in a dairy farm. For example, for nitrous oxide measurement in a dairy farm, the concentration range is between 200-300 ppbv and around 1 ppmv, time resolution should be as high as per few minutes in order to catch dynamic change, and the limit of detection needs a lower range of ppbv since the concentration level in a dairy farm is generally close to background air. PAS can meet this requirement but likely face interference problem.

4. Line 55 - 56. Which methods were compared? What was the reason for the 30% discrepancies?

Response: In the reference, three measurement techniques were used for measuring ammonia emission rates, e.g., external tracer ratio method (SF6 was used), internal tracer ratio (ITR) method (SF6 was also used), and flux sampler method. As the authors claimed, all three methods were validated, with however statistically significant biases for the measured release rate and no clear explanation for the biases was provided.

5. Line 62 ff. Here and in Section 2.1, more details of the measurement principle of PAS should be given. What kind of light source is used (spectral range, emission bandwith, continuous or pulsed)? What causes the cell pressure changes? How are they detected? What is the range of optical absorbances? Is the signal linearly dependent on the concentration of each analyte? Does the method need regular calibration by the user and how is calibration achieved?

Response: The infra-red light source is used. Innova 1312 used the filter of UA0982 (CO2), UA0985 (N2O), UA0936 (NH3), UA0972 (Freon 134a), and UA0969 (CH4). Infrared radiation can interact with a molecule and transfer energy to it if the frequency of the radiation is exactly the same as the frequency of a vibration within the molecule. When the molecule absorbs this radiation it vibrates with greater amplitude. This increased activity is short-lived, however, and the excited molecule very quickly transfers its extra energy to other molecules in the vicinity by colliding with them and causing them to travel more quickly. The increased molecular speeds means that the temperature in the measurement chamber increases and when the chamber is sealed the pressure also increases. The amount of light absorbed can be measured by measuring either the heat energy released or associated pressure increase. Both parameters are proportional to the concentration of the absorbing species. Because calorimetric detectors have slow response times and are insufficiently sensitive, the pressure increase is the preferred

measurement parameter. A microphone is an excellent detector of fluctuating pressure.
It is stated on the brochure of Innova 1312 'Linear response over a wide dynamic range'. On the manual of Innova 1312, there is a chapter to explain how the users can conduct a self-calibration after moving the instrument around. In our experiments, the instrument was calibrated by the company and the instrument was calibrated on a certified gas cylinder of NH_3 in the lab. Now more details are given in the revised manuscript, section 2.1 (please see Line 171-186).

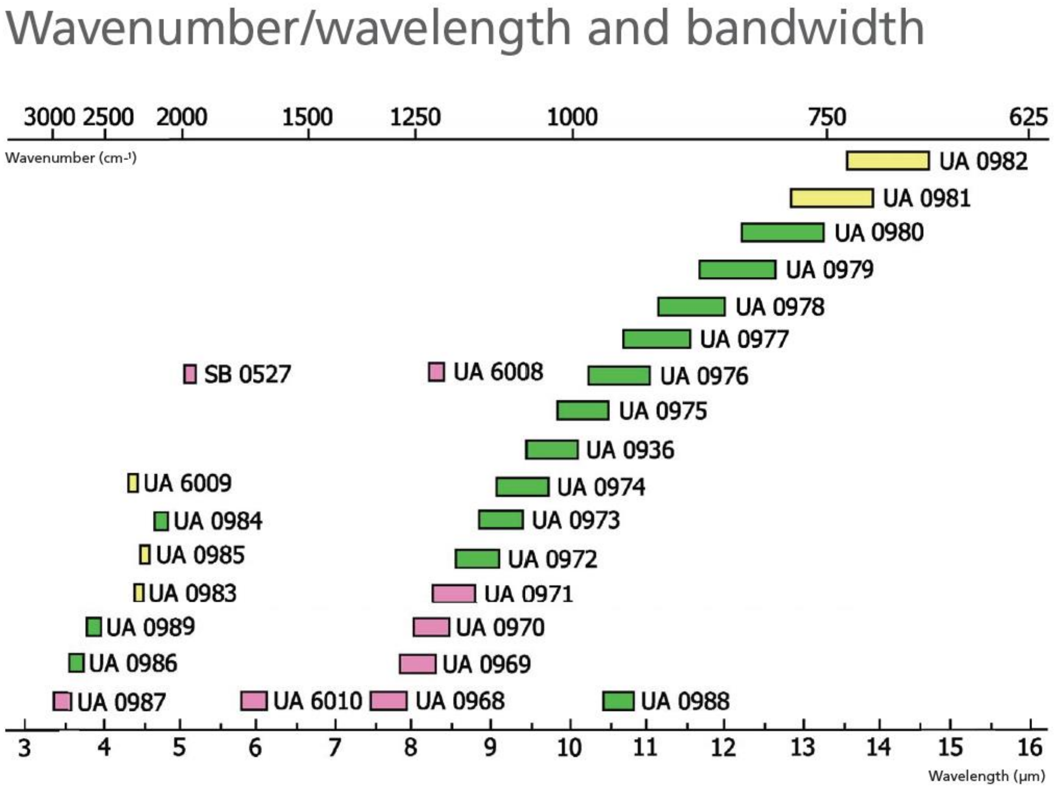

Fig. 1 Centre wavelength and half-power bandwidths of the optical filters

6. Line 74 - 77. How is the cross compensation achieved? Is it performed online in the instrument or by postprocessing of raw data by the user? How large are typical corrections and what is the residual error?

Response: If the gas is targeted, the cross compensation can be achieved by the instrument online. The user can also output the raw data. For example, water vapor absorbs infra-red light at most wavelengths so that it will contribute to the total acoustic signal in the analysis cell no matter which optical filter is used. A special optical filter is permanently installed in the filter carousel of the 1312, which allows water vapor's contribution to the measured separately during each measurement cycle. The 1312 is thus able to compensate for water-vapor's interference. The corrections will be depending on the overlaps of the gas IR spectra but the residual error after the cross compensation is negligible according to Zhao et al. (2012).

7. Line 117 - 172. Please compare the specifications for ammonia measurements by PAS, CRDS, and PTR-MS in a table. It should include the lower limit of detection (LOD), dynamic

range, response time, measurement time, accuracy, possible interferences.

Response: These specifications are related to "experiment 1: laboratory test on ammonia calibration", therefore we now add relevant information to Table 1, as shown in the revised manuscript.

8. Line 130. It is not clear, what was tested. Calibration procedure? PTR-MS instrument? How was the PTR-MS calibrated?

Response: The ammonia calibration test was done by applying PTR-MS instruments, as described in the section "**2.2 Experiment 1: laboratory test on ammonia calibration**". The instrument calibration was performed based on specific reaction rate constants and transmission (accuracy better than 12%), as described in our previous study (Liu et al., 2018). This is now clarified in the revised manuscript at Line 144-146.

9. Line 148. It is not clear, what was tested. See Comment 8.

Response: The calibration test was done by applying the CRDS instrument (Picarro), as described in the section "**2.2 Experiment 1: laboratory test on ammonia calibration**". The accuracy of the CRDS instrument is routinely checked against a certified reference gas as described by Kamp et al (2019). This is now clarified in the revised manuscript at Line 158-160.

10. Line 162 - 171. See Comments 5 and 6.

Response: This is now revised as suggested. Pease see Line 171-178.

11. Line 166. The filter for H2O is missing in Table S1. Are the filters for the other target species correctly named in Table S1? According to the document "Detection limits for various gases" (Lumasense web page*) filters "936" and "972" provide no sensitivity for ammonia and SF6, respectively. [*https://www.lumasenseinc.com/FR/produits/gas-sensing/gas-monitoringinstruments/photoacoustic-spectroscopy-pas/photoacoustic-gas-monitor-innova-1512/photoacoustic-gas-monitor-innova-1512.html]

Response: The filter for H_2O is always included so this filter typically was not considered as other filters which could be different from instrument to instrument. Thus we didn't include H_2O filter in Table S1, while other target species are correctly named and included, with information provided by the producer. The detailed optical filters can also be seen from the response for comment 5. Since the version of 1512 is different than the version we used for the experiment, it is likely they updated the filters in the newer version of instrument.

12. Line 168 - 171. Have you checked the validity of the cross compensation of interferences from target gases or do you rely on the specificiations given by the supplier of the instrument?

Response: We did not check the validity of the cross compensation of interferences, and we rely on the specifications given by the producer. Usually the cross compensation for targeted gases is a routine work and could be done with the calibration process through a self-calibration or calibrated by the producer. On the manual of Innova 1312, there is a chapter to explain how the users can conduct a self-calibration after moving the instrument around.

13. Line 188 - 190. Is there a reason to assume that the time response of the PAS instrument depends on the magnitude of the ammonia concentration?

Response: Higher concentrations will reach saturation faster and therefore responses are quicker.

14. Line 191 - 207. The purpose of the experimental setup (Figure 1) is not entirely clear. Was is used as a quantitative source of VOC concentrations for calibration of the PTR-MS? If so, which method was applied to determine the VOC concentrations in the gas phase? Details should be given! Or was the setup simply used as a source of VOC/air mixtures and the VOC concentrations were measured by a calibrated PTR-MS. If this is case, how was the PTR-MS calibrated for the selected VOCs?

Response: In fact, Figure 1 was the experimental setup for '2.4 Experiment 3: Laboratory test for correction factors', not for the selection of VOCs in '2.3 Experiment 2: VOCs selection test'. For the selection of VOCs, a clean plastic container which contained half-filled silage was used, with the air dragged by the PTR-MS. For the laboratory test for correction factors, a setup showed in Figure 1 was simply used as a source of single VOC+air mixture and the specific VOC concentration was measured by the PTR-MS which was calibrated as discussed above. The uncertainty is mainly coming from the transmission and reaction rate estimation, which is around 10-15% (Cappellin et al., 2012).

15. Line 206 - 207. The selected components (methanol, ethanol etc.) should be mentioned with reference to Section 3.2.

Response: As we thought that the selection of VOCs were the part of results for section 3.2, therefore we did not include the specific list of selected components in the materials and methods section 2.3. Now we have mentioned the selected components in the revised manuscript, please see Line 223-225.

16. Line 212 - 220. What is the meaning of a "pre-tested water solution" (Line 213) ? What were the concentrations of the liquid solutions and their temperature? How were the VOC concentrations in the gas phase quantified? How stable were the gas-phase concentrations? How large was the water vapor concentration in the diluted gas which was fed into the instruments?

Response: "pre-tested" was now removed in order to clarify the text. The water solution was prepared by using a volume ratio of VOC:Water as 1:5, with purging by clean air controlled by

2 mass flow controllers in order to reach a desired range for test (See Line 240-241). The temperature was not controlled and was assume to be room temperature. The VOC concentration was quantified by the calibrated PTR-MS. The water vapor concentration in the diluted gas which was fed into the instruments (not for PTR-MS) was typically from a few hundred ppbv up to 50 ppmv (as can be seen from Fig.S1). For the PTR-MS, a further dilution was applied, when the VOC concentration was higher than 10 ppmv.

17. Line 221 - 224. What is the meaning and function of "excess flow". The excess flow should be indicated in Figure 1.

Response: The excess flow is the extra flow required by the instrument of Innova and Picarro, in order to keep the right pressure in the instrument. The two arrows near PAS and CRDS in Figure 1 indicate the excess flow, where the exhaust line is added as suggested.

18. Line 236. Which company has manufactured the Multiplexer 1309? How does it work and what are the materials that come into contact with the sampled air?

Response: . The Multiplexer 1309 was also manufactured by the Danish company Lumasense Technology A/S, and now the information has been added as shown in Line 243-244. This product now has a new version as ‘Multipoint Sampler - INNOVA 1409’ (https://www.lumasenseinc.com/EN/products/gas-sensing/innova-gas-monitoring/photoacoustic-spectroscopy-pas/multipoint-sampler-1409/multipoint-sampler-innova-1409.html). The materials that come into contact with the sampled air is PTFE.

19. Line 244. Which "selected VOCs" and "odorants" were measured? The term "odorant" should be defined.

Response: s. The ‘selected VOCs’ are now clarified as ‘all VOCs showed in section 2.3 were included’, while the term of ‘odorant’ is defined and the selection were also given. Please see Line 264-265 in the revised manuscript.

20. Line 245 - 246. What is meant by "background"? Where were the four sampling lines going to?

Response: The four sampling lines going to the four locations with ‘two selected locations inside the farm, one location in the pit ventilation, one location outside the farm.’. The background site was selected as the outside air beside the trailer, where the instruments were standing. This is now clarified in the revised manuscript, please see Line 267-268 in the revised manuscript.

21. Line 251 - 254. For which compounds were calibrations performed? The suppliers of the calibration gas mixtures and permeation device should be mentioned. What is the accuracy of the calibrations?

Response: Permeation tubes (VICI Metronics, Inc., Houston, TX, USA) included acetic acid, propanoic acid, butanoic acid, pentanoic acid and 4-methylphenol. Gas mixtures (all 5 ppmv in nitrogen) included hydrogen sulfide (AGA, Copenhagen, Denmark), methanethiol (AGA, Copenhagen, Denmark), and dimethyl sulfide (Air Liquide, Horsens, Denmark). Details regarding the calibration procedures could be found in our previous study, with accuracy with 12% error and in most cases within 8% (Liu et al., 2018). This is now clarified in the revised manuscript, please see Line 275-281.

22. Line 281 - 282. "Background concentrations of ammonia measured..." can be misunderstood and should be rephrased. Do you mean instrumental baseline (instrumental offset) when ammonia-free zero air is measured? Is there a plausible explanation for the background values of the CRDS and PAS instruments?

Response: Yes, we meant the instrumental baseline when ammonia-free zero air was measured. Now the sentence is revised in order to avoid misunderstanding. For PAS, the baseline is probably due to water vapor interference. For CRDS the baseline is really low (1 ppbv), since low ppbv concentrations are present more or less everywhere, e.g. from human breath.

23. Line 292 - 296, Figure 2B. The result of the instrumental comparison needs more discussion. Are the calibrations of the two instruments (CRDS, PTR-MS) independent? What is the statistical error of the slope of the linear fit? Are the differences between the two instruments statistically significant and can they be explained by instrumental calibration errors? The measurement comparison between PAS and CRDS (or PTR-MS) should also be shown and discussed.

Response: The ammonia concentration was simultaneously measured by the CRDS and the PTR-MS for Figure 2B. The SD of the slope of the linear fit was 0.005 which is really small. Therefore, the error is not much, and probably the slope is not significantly different from 1. The simultaneously measurement (calibration and comparison) between PAS and CRDS (or PTR-MS) for Ammonia was not performed in this study, but should be investigated in the future.

24. Line 300 - 315. What could be the reason for the concentration dependence of the PAS response time? Why are the PAS values elevated at 18:43 (Fig. 2C) and decrease until 19:00, while CRDS and PTR-MS show constant values. After the ammonia concentration has been switched to zero, the decay of the PAS signal seems to have at least two time constants. There is an initial fast decay that is followed by a tail with a slow decay. What could be the reason for the time behaviour? How long does it take until the PAS signal reaches baseline values?

Response: The three instruments were only used at the same time from around 19.00, and data before this time were from another test. Therefore, showing of the PAS values at 18.43 in the figure was not appropriate. Now we have corrected this error in the revised Figure.2C. We don’t have an explanation for the time behavior (two time constants), which may be included in the future study. It took around half an hour for the PAS signal reaches baseline values.

25. Line 378 - 380. Interferences in ammonia PAS measurements have been studied for single VOCs in air. Have you tested whether the interferences are additive in a multicomponent gas mixture? Additivity would at least require that the optical absorbances of the interfering VOCs are small (avoiding line saturation). (Non)linearity of the relationships seen in Figure 4 may give useful information. For a mixture with multiple interfering VOCs, a valid correction using the information from Table 2 can only be expected, if the interferences are independent of each other. This aspect needs to be discussed.

Response: Only single VOC was tested in the lab regarding interreference on PAS and correction factors were obtained for single VOC. We have to acknowledge that we don't know if the effects are always additive – although they are likely to be. In the field study, ethanol certainly dominated the VOC matrix in general, but other types of VOC also contribute significantly. For example, the averaged ratio of ethanol concentration to the sum of the 8 VOCs (tested in lab with obtained correction factors) was 0.64 (±0.11) for Location Two in the field study. From this single application it seemed that the obtained empirical relationships to be additive, but a complete investigation is indeed needed in the future. This part is now revised accordingly and please see Line 553-560.

26. Table 2. For which concentration ranges were the relationships tested? This information should be included in the table. Is there a physical explanation for negative interferences?

Response: . The concentration range indeed should be clarified, and now it is added in the text for Table 2. The negative interferences can usually be explained by the internal cross compensation procedure for one target filter (first target filter, such as NH3 filter) on positive artifacts at another target filter (second target filter, such as CH4 filter) caused by non-target gas (such as VOC) on the second target filter. This physical explanation was included in a few relevant references such as Zhao et al. (2012).

27. Line 412 - 425. Is there a physical explanation for the nonlinear behaviour of the VOC interference in measurements of N2O? Are the nonlinear interferences additive when two or more interfering VOCs are present in measured air?

Response: . We do not have physical explanation for the nonlinear behavior of the VOC interference in measurements of N2O, and we also don't know if these nonlinear interferences are additive or not when multiple VOC presented. In the field measurement, we could not determine the N2O concentration by other instrument than PAS, and therefore could not determine the interference for N2O by VOCs. In the future, this might be worth a sophisticated investigation just for N2O interference.

28. In Figure 2B, 4, 5B, 5D, S2, S3 and Table 2, results from statistical data treatments are shown. More information should be given on how fitted lines (curves) and fitted parameters were obtained. Were measurements corrected for offsets (background)? How were linear fits

obtained (least square fits? with or without error weighting?). Is it justified to force the fit through the origin? Fitted parameters should be given with 1δ errors. The meaning of the plotted error bars in Figure 4 should be explained. The error bars (statistical errors?) are significantly larger than the scatter of the data points around the fitted line. What does that mean?

Response: All measurements were corrected from background and the linear fits were least square fits without error weighting. From the figures, fitting equations were given. The fitting equations given that the fits were forced through the origin(zero). In the revised manuscript, this is now clarified for the mentioned Figures and table. Fitted parameters are given with 1δ errors, as shown in Table 2. The plotted error bars in Figure 4 were representing the standard deviations for the measured VOC by the PTR-MS under a selected VOC level (x-axis) and for the measured NH3/N2O level by the PAS meanwhile (y-axis). This is now in the text for Figure 4. The error bars are statistical errors, which are generally within reasonable range.

Technical comments

1. Materials and methods. More information about used gases (nitrogen, zero air), chemicals (organic compounds listed in Table 2) and the water used for VOC solutions should be given. Suppliers and purity grades need to be specified. How was zero air generated? How were the solutions of VOCs in water prepared?

Response: . The zero air was supplied from a HiQ zero air station (Linde AG, Munich, Germany). Nitrogen and clean air were supplied through a charcoal/silica gel filter. The 8 selected VOCs were purchased from Sigma-Aldrich with at least analytical grade purity. The water solution was prepared by using a volume ratio of VOC:Water as 1:5, with purging by clean air controlled by 2 mass flow controllers in order to reach a desired range for test.The manuscript was revised accordingly (Line 240-241).

2. Line 34. The term "field study" may be confused with a study under natural ambient conditions. Change sentence to "measured by PAS in a dairy farm".

Response: . “from a field study” is now revised to “in a dairy farm” as suggested.

3. Line 41 - 42. Ammonia causes soil acidification?

Response: . With the nitrification process the ammonia transfer to nitrate and hydrogen into the soil and increase the soil acidification.

4. Line 67 - 70. PAS is a general term for a spectroscopic method, but here you refer to a particular instrument (Innova 1312). Therefore, it is better to say: "Besides, the Innova 1312

has the advantages ...".

Response: . We have revised according to the suggestion.

5. Line 69. Change to "Usually, water vapor is also measured in order ...": Changed now.

6. Line 73. Change to "absorption of infrared light": Changed now.

7. Line 80. There is a word missing in "interference of has not been well studied...": “of” is now deleted.

8. Line 81. "Mathot et al., 2007" is missing in the Reference section.: This reference is now added to the Reference section.

9. Line 118-199: Change to "were used to measure trace gas concentrations in air".: Changed now.

10. Line 125 - 127. The sentence is not clear and should be rephrased.: The sentence is now rephrased.

11. Line 141. Either "acceleration of the ring down " or "reduction of ring down time ".: This is now revised.

12. Line 143. "Normal" ring down time needs to be explained.: This is now explained.

13. Line 173. Change to "Instrumental background signals, ammonia calibrations and instrumental time responses were characterized for the PAS, PTR-MS and CRDS instruments".: Changed now.

14. Line 180. Delete "for the calibration test".: Deleted now.

15. Line 181. The desired concentration range should be specified.: Specified now.

16. Line 197. Which kind of plastic material was used for the container? Was it emission free?

Response: Teflon plastic was used and it was emission free. Manuscript was revised accordingly.

17. Line 254. A reference for "Standard conditions as described previously ..." should be provided.: Reference is given now.

18. Line 293. Change to "in which the slope of the fitted line (k = 0.96 ± ?) ..." It’s changed now.

19. Line 304. "90% decay time" needs to be defined. It’s defined now.

20. Line 380. Change to "...VOC concentrations be measured simultaneously by other

instruments". It is revised as “VOC concentrations be measured simultaneously by expensive analyzers as PTR-MS”

21. Line 382. The term "correction factor" should be defined. It is now revised to empirical relationship (ER) as suggested in another comment to Table 2.

22. Figure 1. The exhaust line should be marked.: Exhaust line is now marked.

23. Figure 2. All axis should show tic marks. Concentrations at the x and y axis of Figure 2B and at the y axis of Figure 2C should be given in ppmv.

Figure 2C caption: change to "Instrumental response of PTR-MS, PAS and CRDS instruments to a rectangular ammonia concentration pulse."

Figure 2D caption: change to "Instrumental response of PTR-MS, PAS and CRDS instruments to a stepwise increase in ammonia concentration."

Response: Figure 2 is now revised as suggested. Figure 2D caption changed to “Instrumental response of PAS instrument to a stepwise increase in ammonia concentration.”

24. Figure 4. All axis should show tic marks. Concentrations at the x and y axis of Figure 4A and 4B should be given in ppmv. The Figure caption mentions red, green and purple lines. The colour designation should be made consistent with the plotted lines.

Response: Figure 4 is now revised as suggested.

25. Figure 5. All axis should show tic marks. Concentrations at the x and y axis of Figure 5B and 5D should be given in ppmv. Draw 1:1 lines in A and C as reference.

Response: It’s been revised as suggested.

26. Figure S1. Concentrations should be given in ppmv.: It’s been revised.

27. Figure S2. All axis should show tic marks. "ppm" should be "ppmv".

28. Figure S3. All axis should show tic marks. Concentrations should be given in ppmv. What is the difference between the upper and lower panel in Figure S3? It’s been revised. The difference is Location One and Location Two for the up and down panel, respectively.

29. Table 1. Units should be ppmv (to be consistent with text and figures).

Response: Table 1 is now revised. For the detection limit, we kept ppbv since the values are basically within lower range of ppbv.

30. Table 2 caption must be rephrased. The table does not show correction factors, but empirical relationships describing the functional dependence of the interference in the measurement

of the target compound (e.g., NH3) on VOC concentrations.

Response: Table 2 is revised as suggested.

31. Table 3. Do standard deviations apply to the mean values, or do they represent the variability of single measurements? The concentration values for ethanol and methanol should be reasonably rounded.

Response: Yes the standard deviation apply to the mean values. It's now clarified in the revised manuscript.

32. Table S1. "Filter center" should be changed to "Center wavelength". What is the meaning of "Band width (%)" ? Is it related to "Filter bandpass"?

Response: "Filter center" is now changed to "Center wavelength" as suggested. Yes the "Band width (%)" is related to "Filter bandpass" which is calculated based on the center wavelength and band width (e.g., 2171=2215-2215*2.0/100 for UA0985).

Reference:

Cappellin, L., Karl, T., Probst, M., Ismailova, O.,Winkler, P.M., Soukoulis, C., Aprea, E., Märk, T.D., Gasperi, F., Biasioli, F., 2012. On quantitative determination of volatile organic compound concentrations using proton transfer reaction time-of-flight mass spectrometry. Environ. Sci. Technol. 46, 2283–2290.

Kamp, J.N., Chowdhury, A., Adamsen, A.P.S., Feilberg, A.: Negligible influence of livestock contaminants and sampling system on ammonia measurements with cavity ring-down spectroscopy. Atmos. Meas. Tech., 12, 2837–2850, https://doi.org/10.5194/amt-12-2837-2019, 2019.

Zhao, Y., Pan, Y., Rutherford, J., and Mitloehner, F. M.: Estimation of the Interference in Multi-Gas Measurements Using Infrared Photoacoustic Analyzers, Atmos., 3, 246–265, https://doi.org/10.3390/atmos3020246, 2012.

Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2018-412-AC1, 2019

Atmospheric Measurement Techniques
Discussions

Interactive comment on “Photoacoustic measurement may significantly overestimate NH_3 emissions from cattle houses due to VOC interferences” *by* Dezhao Liu et al.

Dezhao Liu et al.

dezhao_l@163.com

Received and published: 23 March 2019

Response to Interactive discussion: ’amt-2018-412’, Anonymous Referee #2, 19 Feb 2019:

General comments This manuscript describes experiments investigating VOC interference during NH3 measurements using PAS in cattle barn emissions. The novelty is the analysis of VOC interference. PTR-MS measurmenst were used for this purpose. The experimental design is sound. Some details of M&M should be worked out. Correction factors are proposed which should improve emission factor determination for cattle barns emissions. The necessity to perform both PTR-MS as well as PAS complicates

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Discussion paper

the emission measurements. In the discussion attention could be paid to the pissble transferability to other emission sources e.g. pig farm emissions.

Response: Thank you for the comments. Some details of M&M are now clarified, according to the detailed comments from the referee. We do also agree that the measurements performed both by PTR-MS and the PAS complicates the emission measurements, but also give more detailed information and confirmation regarding measured emissions from cattle barn. Usually the VOCs from cattle barns are significantly lower in pig farm compared to cattle barn, so the interreference should be lower. However, the transferability should certainly be careful since the source the level of the VOCs pollutants are significantly different, as suggested by the referee.

Detrailed comments 190. her CRDS is introduced without any further explanation. In line 96 “two PAS instruments . . .” are mentioned. Ths is confusing. Please explain why CRDS is included. Response: Thanks for the comments. CRDS was first introduced in Line 109, and the technique was explained at Line 141 to Line 161. In line 96, “two PAS instruments . . .” means that the reference of Hassouna et al. (2013) used two PAS instruments for their study. This is now clarified in the manuscript and please see Line 96. The reason why CRDS was included was to further confirm that no ammonia was presented while VOCs was measured by the PTR-MS and caused interference when measured by PAS. Due to the fact that the PTR-MS had high background on measuring ammonia, the measurement by the CRDS meanwhile could therefore make a solid and second confirmation of our measurement.

195-199. The hedaspace in the silage box was analused by PTR-MS tehrefore a floxw of 75 ml/min was withdrawn. Was here any balance gas introduced into the bow compensating the sampled air? Response: Thanks for the comment. Indeed 75 ml/min was withdrawn from the headspace in the silage box, while another 75 ml/min of zero air was supplied and controlled by a mass flow controller, before measured by the PTR-MS (inlet flow was set to 150 ml/min). Since the silage box was not closed, with two oval holding holes on sides, therefore the balance gas from the room air would com-

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pensate the sampled air from the headspace in the silage box. 203. What is meant by “pretested”? Response: Thanks for the comment. The pre-test for water solution preparation used a ratio of VOC:Water as 1:5, and the ratio between VOC and water was adjusted if the purged concentration after dilution (by zero air controlled by 2 mass flow controllers) measured by the PTR-MS was not within the desired range (too low or too high). Please see the explaination at Line 221-224.

218. More information should be given on how the water solution containing VOC was prepared. pH? Concentrations? . . . Response: Thanks for the comment. The pre-test for water solution preparation used a ratio of VOC:Water as 1:5, and the ratio between VOC and water was adjusted if the purged concentration after dilution (by zero air controlled by 2 mass flow controllers) measured by the PTR-MS was not within the desired range (too low or too high). The pH was not measured for the water solution. The concentration level was varied depending on flow rate and an example could be seen in Figure 4.

Table 1. Suggestion: use consequently (throughout the paper) the acronyms for the methods (PTR-MS; CDRS; PAS) not the instrumental brand names. Response: Thanks for the suggestion. The instrumental brand names are now avoided as far as possible throughout the paper, and the acronyms for the methods (PTR-MS; CDRS; PAS) are used instead.

Figure 3. How were the concentrations calculated? Just by the instrumental data base or own calibration. Response: The PTR-MS can measure VOC concentrations directly, and the calculation of VOC concentrations by the PTR-MS was depended on a number of parameters especially the reaction rate between VOC and protonated water. Nevertheless, the ethanol was corrected and calibrated separately according to ethanol fragmentation.

Figure 4 Why ppbv in [A] and [B] and ppmv in [C] and [D]? Are the concentration ranges (acetic acid up to 40 ppmv) realistic for cattle barn emissions? Response: Thanks for

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the comment. All the concentration unit in Figure 4 are now revised to ppbv. Acetic acid of 40 ppmv might not be common for cattle barn emissions, but could happen within a short period at a specific location such as nearby the silage and within feeding.

Table 2. For some compounds the correlations are based on 4 data points only (N). Validity? Response: Thanks for the comment. Indeed, in some cases the data points were only 4, which might need further validation in such cases. Still, the correlation coefficients showed in the table seems to be reasonable, indicating the validity of this method and data.

394-396. What is the meaning for field measurements? Response: The field measurements means the measurements performed in the field for a full-scale cattle barn.

Table 5. Explain in the M&M section how the concentrations of the individual compounds were calculated. Response: Thanks for the comment. I guess the referee means “Table 3” here, where the VOC concentrations were determined directly by the PTR-MS, based on estimated reaction rate constants described by Liu et al. (Liu et al., 2018). The manuscript now is revised accordingly and please see Line 259-260.

Table 5. Acetic acid concentrations here are between 50 and 100 ppbv. In Figure 4 concentrations up to 40 ppmv are tested. Relevance? Response: Thanks for the comment. The averaged acetic acid concentration for Location 2 was 69 ppbv with standard deviation of 62 ppbv. Since the measurement location was not close to the silage feeding in the cattle barn, the concentration of acetic acid near the location of silage feeding might be significantly higher than this concentration range. Another reason for performing high acetic acid concentration up to 40 ppmv was to investigate the linear range of the correction factors found in this study.

539. Which greenhouse gases. Specify. Response: Thanks for the comment. The greenhouse gases are CH4, N2O and CO2, which is now specified in the revised manuscript. Please see Line 518-519 in the revised manuscript.

Please also note the supplement to this comment:
https://www.atmos-meas-tech-discuss.net/amt-2018-412/amt-2018-412-AC1-supplement.pdf

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Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-412, 2019.

Response to Interactive discussion Anonymous Referee #3

General comments

The paper investigates interferences caused by volatile organic compounds (VOCs) in the photoacoustic measurement of ammonia in air on agricultural farms. The commercially available PAS instrument that was used in this work contains a broadband infrared light source and six optical filters for spectral selection. The filter set is suitable for the specific detection of NH3, CH4, CO2, H2O, N2O and SF6 in atmospheric mixtures at ppmv level, if no other absorbing species interfere. The experiments described in the manuscipt show very clearly that VOCs, such as methanol, ethanol or acetic acid observed in a dairy farm can cause significant interferences and are detected by the PAS instrument with higher sensitivity than ammonia. Similar results are found for greenhouse gases that are measured by the PAS instrument. A comparison to a reference technique (PTR-MS), which measured ammonia and VOCs, demonstrates that the PAS instrument can overestimate ammonia concentrations by up to an order of magnitude due to spectral interferences by VOCs. The authors conclude that the PAS measurements of ammonia can be corrected, if the concentrations of the interfering VOCs are known.

This work is relevant as the described type of PAS instrument has been widely used for emission measurements of ammonia and greenhouse gases in agriculture. Although there have been experimental indications of interferences in the literature, there is little quantitative information available about cross-sensitivities to trace gases such as VOCs that can be co-emitted on animal farms. The paper presents new results, which help to understand the quality of PAS measurements of agricultural emissions. As such emissions play a role for air quality and climate, the topic of the paper is suitable for AMT. However, before it can be accepted for publication, major revisions of the manuscript are needed as outlined in the following.

Response: Thank you very much for the general comments and all valuable comments.

1. The discussion about the general applicability of the PAS instrument for measurement of ammonia and greenhouse gases in agriculture needs to be broadened.

It should be pointed out more clearly that the technique used in the Innova instrument "is capable of measuring almost any gas that absorbs infrared light" (quotation from the Lumasense web page). The document "Detection limits for various gases" on the Lumasense web page lists almost 300 different organic gases that can be detected at the ppmv level. The method is based on nondispersive broadband spectroscopy and selectivity is achieved by using appropriate wavelength filter, with one filter for each targeted trace gas. If the number of absorbing gases is larger than the number of optical filters, possible interferences are no surprise! The key questions are: (a) what is the magnitude of interferences that can be expected in agricultural environments, and (b) is it possible to quantify and correct interferences in a reasonable way? Both questions are adressed by the authors, but a more detailed discussion is needed.

Response: In principle, the technique used in the Innova instrument "is capable of measuring almost any gas that absorbs infrared light". Now this is pointed out clearly in the introduction (Line 68-70). The two key questions “(a) what is the magnitude of interferences that can be expected in agricultural environments, and (b) is it possible to quantify and correct interferences in a reasonable way?” are now included in the introduction in order to help to clarify the purpose of this study. Please see Line 84-86 in the revised manuscript.

(a) The authors show in Figure 5A and 5C that the PAS measurements of ammonia are higher than by PTR-MS, but quantitative statements of the measurement errors and interferences are missing in the text. The figure shows discrepancies between the two techniques of up to a factor of ten. How much of the difference can be explained by calibration errors? What is the measurement precision of the data points in Figure 5? If the PTR-MS measurements are assumed to be interference free (is this a justified assumption?), the discrepancies must be due to interferences in the PAS measurements, which apparently can be up to an order of magnitude greater than the correct ammonia concentration. The overestimation should be explicitly quantified!

Response: In Figure 5A and 5C, the factor is typically between 1 and 5, with few cases close to 10 (see Table S3). Only a small part of this difference can be explained by calibration errors. For the PTR-MS, the calibration error is around 10-15%. For the Innova 1312, the calibration error is around 20%. The measurement precision (ratio of standard deviation/averaged concentration) of the data points in Figure 5 was around 1%-3%. For ammonia measurement by PTR-MS, the measurements are interference free. Thus the discrepancies are surely caused by the PAS measurements, with some overestimation as the reviewer mentioned (the corrected ammonia fit generally ok though, as showed in Fig.5B and 5D). The overestimation possibly due to the interaction effects by various VOCs on the interference correction, but the quantification is difficult since we did not investigate the effects of interference when simultaneous present of multiple VOCs.

(b) The authors argue that the interferences can be corrected if the interfering VOCs are measured by another technique (line 504 - 508). I agree that this would require a considerable additional effort. This effort should be explained in more detail. How accurate should the corrected data be? What accuracy and precision does this mean for measuring VOCs and determining their correction factors? The considerable additional effort appears to offset the advantage of the easy handling of the PAS instrument. It should therefore be discussed if alternative measurement techniques, for example CRDS (available for NH3, CH4, CO, CO2, H2O) would offer a better performance than PAS for agriculture emission measurements.

The authors conclude that the interferences listed in Table 2 can be corrected. I am not completely convinced that this is generally true. In the example in Figure 5, the interference is dominated by a single VOC (ethanol). Would the correction also work if two or more VOCs caused a similarly large interference at the same time? Are the interference corrections of individual substances (Table 2) independent of each other? See also Comment 25 below.

Response: Indeed, if the VOCs could be measured by another technique such as PTR-MS, interferences could possibly be corrected, but considerable additional efforts needed for correcting the data, and obviously it does not make sense to buy a PTR-MS in order to correct a PAS. The accuracy of the corrected data should certainly be as higher as better and at least to be able to reflect the right concentration within lower range of ppbv. Thus the required accuracy and precision for the measured VOCs should also be relatively high as lower range of ppbv. This additional effort certainly offset the advantage of the easy handling of the PAS instrument, and alternative measurement techniques, for example CRDS may indeed offer a better performance than PAS for agriculture emission measurements. The recent publication by Kamp et al., 2019 demonstrated that CRDS (Picarro G2103, only measuring ammonia and water) can measure ammonia with great precision without interferences and therefore have a better performance compared to PAS.

Regarding the correction factors (now changed to empirical relationships as suggested) listed in Table 2, we have to acknowledge that we don't know if the effects are always additive – although they are likely to be. In the field study, ethanol certainly dominated the VOC matrix in general, but other types of VOC also contribute significantly. For example, the averaged ratio of ethanol concentration to the sum of the 8 VOCs (tested in lab with obtained correction factors) was 0.64 (±0.11) for Location Two in the field study. From this single application it seemed that the obtained empirical relationships to be additive, but a complete investigation is indeed needed in the future. This part is now revised accordingly and please see Line 552-560.

2. The title of the paper is not sufficiently descriptive. Spectral selection in PAS can be achieved in different ways with different specificities, for example, by optical filters in combination with broadband light sources (this work), by narrow bandwith lasers, interferometry, etc.. The title should inform about the technique that was used in this work. E.g. "Photoacoustic measurement using a broadband light source and optical filters may significantly overestimate ...".

Response: We agree with you, that we only tested PAS using a broadband light source and optical filters. We now have revised the title as suggested.

3. The paper needs language editing which will eventually be provided by the publisher during

the production process.

Reference

https://www.lumasenseinc.com/FR/produits/gas-sensing/gas-monitoringinstruments/photoacoustic-spectroscopy-pas/photoacoustic-gas-monitor-innova-1512/photoacoustic-gas-monitor-innova-1512.html.

Specific comments

1. Line 24 and line 40. Specify the greenhouse gases to which you refer.

Response: The greenhouse gases are now specified in the revised manuscript.

2. Line 28 - 37. Be more quantitative and specific! What were the concentration levels of ammonia and VOCs which were studied in this work? Was is meant by "various levels of interference"? Quantitative information of cross-sensitivities (ppmv of false ammonia/ppmv of VOC) should be given here. How large were the corrections (order of magnitude) which were applied to the PAS readings in the field experiments? What is meant by "reasonably correlated" (Line 35)?

Response: Yes, “various levels of interference” was meant for various VOCs levels which were tested for interference test while no ammonia was presented. We now add quantitative correction factors for highest VOC on ammonia interference (see Line 32-33). In the field experiment, data from corrected from PAS were correlated with the data from PTR-MS for ammonia, by applying the correction factors obtained from the single VOC test for interference. In the field experiments, the corrections for the PAS readings for Location One and Location Two were 2.14 (±0.75) and 2.88 (±1.85), respectively. The “reasonable” has been deleted in the sentence. These have been revised in the revised manuscript and please see Line 32-38.

3. Line 51 - 56. The concentration range in emission studies of ammonia and greenhouse gases in agriculture should be quantified and distinguished from concentrations in rural background air. What are the analytical requirements (concentration range, time resolution, limit-of-detection) for measurements in a dairy farm?

Response: The quantification of concentration range for ammonia and greenhouse gases in agriculture were done by a number of relevant studies previously. For example, Rong et al. (2015) quantified a dairy farm indoor and outdoor ammonia and greenhouse gases concentrations for both summer and winter periods, as follows: ammonia (indoor: 0.38-15.5 ppmv; outdoor: 0.2-3.3 ppmv); methane (indoor: 2.1-219 ppmv; outdoor: 1.1-11.1 ppmv); nitrous oxide (indoor: 0.19-0.83 ppmv; outdoor: 0.23-0.43 ppmv); carbon dioxide (indoor: 418-

2727 ppmv; outdoor: 402-646 ppmv). Although a lot of these quantification were performed by using PAS and the interference quantification were missing, these data could give some hints regarding the analytical requirements for the measurements in a dairy farm. For example, for nitrous oxide measurement in a dairy farm, the concentration range is between 200-300 ppbv and around 1 ppmv, time resolution should be as high as per few minutes in order to catch dynamic change, and the limit of detection needs a lower range of ppbv since the concentration level in a dairy farm is generally close to background air. PAS can meet this requirement but likely face interference problem.

4. Line 55 - 56. Which methods were compared? What was the reason for the 30% discrepancies?

Response: In the reference, three measurement techniques were used for measuring ammonia emission rates, e.g., external tracer ratio method (SF6 was used), internal tracer ratio (ITR) method (SF6 was also used), and flux sampler method. As the authors claimed, all three methods were validated, with however statistically significant biases for the measured release rate and no clear explanation for the biases was provided.

5. Line 62 ff. Here and in Section 2.1, more details of the measurement principle of PAS should be given. What kind of light source is used (spectral range, emission bandwith, continuous or pulsed)? What causes the cell pressure changes? How are they detected? What is the range of optical absorbances? Is the signal linearly dependent on the concentration of each analyte? Does the method need regular calibration by the user and how is calibration achieved?

Response: The infra-red light source is used. Innova 1312 used the filter of UA0982 (CO2), UA0985 (N2O), UA0936 (NH3), UA0972 (Freon 134a), and UA0969 (CH4). Infrared radiation can interact with a molecule and transfer energy to it if the frequency of the radiation is exactly the same as the frequency of a vibration within the molecule. When the molecule absorbs this radiation it vibrates with greater amplitude. This increased activity is short-lived, however, and the excited molecule very quickly transfers its extra energy to other molecules in the vicinity by colliding with them and causing them to travel more quickly. The increased molecular speeds means that the temperature in the measurement chamber increases and when the chamber is sealed the pressure also increases. The amount of light absorbed can be measured by measuring either the heat energy released or associated pressure increase. Both parameters are proportional to the concentration of the absorbing species. Because calorimetric detectors have slow response times and are insufficiently sensitive, the pressure increase is the preferred

measurement parameter. A microphone is an excellent detector of fluctuating pressure.
It is stated on the brochure of Innova 1312 'Linear response over a wide dynamic range'. On the manual of Innova 1312, there is a chapter to explain how the users can conduct a self-calibration after moving the instrument around. In our experiments, the instrument was calibrated by the company and the instrument was calibrated on a certified gas cylinder of NH_3 in the lab. Now more details are given in the revised manuscript, section 2.1 (please see Line 171-186).

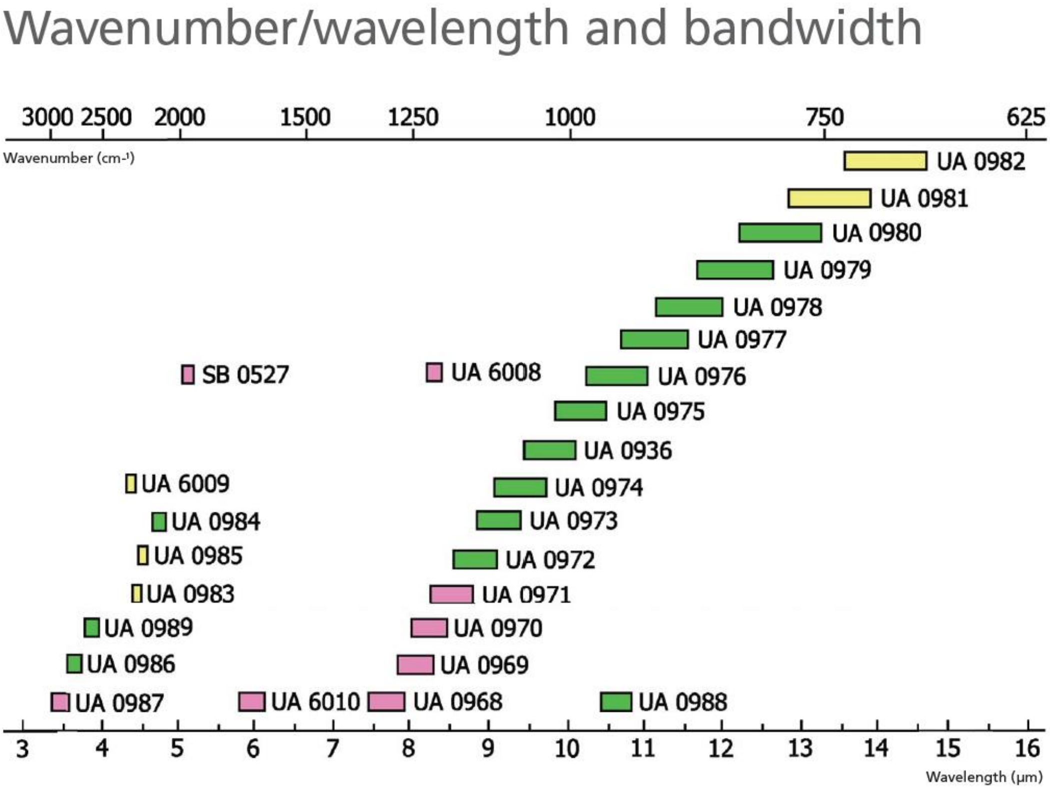

Fig. 1 Centre wavelength and half-power bandwidths of the optical filters

6. Line 74 - 77. How is the cross compensation achieved? Is it performed online in the instrument or by postprocessing of raw data by the user? How large are typical corrections and what is the residual error?

Response: If the gas is targeted, the cross compensation can be achieved by the instrument online. The user can also output the raw data. For example, water vapor absorbs infra-red light at most wavelengths so that it will contribute to the total acoustic signal in the analysis cell no matter which optical filter is used. A special optical filter is permanently installed in the filter carousel of the 1312, which allows water vapor's contribution to the measured separately during each measurement cycle. The 1312 is thus able to compensate for water-vapor's interference. The corrections will be depending on the overlaps of the gas IR spectra but the residual error after the cross compensation is negligible according to Zhao et al. (2012).

7. Line 117 - 172. Please compare the specifications for ammonia measurements by PAS, CRDS, and PTR-MS in a table. It should include the lower limit of detection (LOD), dynamic

range, response time, measurement time, accuracy, possible interferences.

Response: These specifications are related to "experiment 1: laboratory test on ammonia calibration", therefore we now add relevant information to Table 1, as shown in the revised manuscript.

8. Line 130. It is not clear, what was tested. Calibration procedure? PTR-MS instrument? How was the PTR-MS calibrated?

Response: The ammonia calibration test was done by applying PTR-MS instruments, as described in the section "**2.2 Experiment 1: laboratory test on ammonia calibration**". The instrument calibration was performed based on specific reaction rate constants and transmission (accuracy better than 12%), as described in our previous study (Liu et al., 2018). This is now clarified in the revised manuscript at Line 144-146.

9. Line 148. It is not clear, what was tested. See Comment 8.

Response: The calibration test was done by applying the CRDS instrument (Picarro), as described in the section "**2.2 Experiment 1: laboratory test on ammonia calibration**". The accuracy of the CRDS instrument is routinely checked against a certified reference gas as described by Kamp et al (2019). This is now clarified in the revised manuscript at Line 158-160.

10. Line 162 - 171. See Comments 5 and 6.

Response: This is now revised as suggested. Pease see Line 171-178.

11. Line 166. The filter for H2O is missing in Table S1. Are the filters for the other target species correctly named in Table S1? According to the document "Detection limits for various gases" (Lumasense web page*) filters "936" and "972" provide no sensitivity for ammonia and SF6, respectively. [*https://www.lumasenseinc.com/FR/produits/gas-sensing/gas-monitoringinstruments/photoacoustic-spectroscopy-pas/photoacoustic-gas-monitor-innova-1512/photoacoustic-gas-monitor-innova-1512.html]

Response: The filter for H_2O is always included so this filter typically was not considered as other filters which could be different from instrument to instrument. Thus we didn't include H_2O filter in Table S1, while other target species are correctly named and included, with information provided by the producer. The detailed optical filters can also be seen from the response for comment 5. Since the version of 1512 is different than the version we used for the experiment, it is likely they updated the filters in the newer version of instrument.

12. Line 168 - 171. Have you checked the validity of the cross compensation of interferences from target gases or do you rely on the specificiations given by the supplier of the instrument?

Response: We did not check the validity of the cross compensation of interferences, and we rely on the specifications given by the producer. Usually the cross compensation for targeted gases is a routine work and could be done with the calibration process through a self-calibration or calibrated by the producer. On the manual of Innova 1312, there is a chapter to explain how the users can conduct a self-calibration after moving the instrument around.

13. Line 188 - 190. Is there a reason to assume that the time response of the PAS instrument depends on the magnitude of the ammonia concentration?

Response: Higher concentrations will reach saturation faster and therefore responses are quicker.

14. Line 191 - 207. The purpose of the experimental setup (Figure 1) is not entirely clear. Was is used as a quantitative source of VOC concentrations for calibration of the PTR-MS? If so, which method was applied to determine the VOC concentrations in the gas phase? Details should be given! Or was the setup simply used as a source of VOC/air mixtures and the VOC concentrations were measured by a calibrated PTR-MS. If this is case, how was the PTR-MS calibrated for the selected VOCs?

Response: In fact, Figure 1 was the experimental setup for '2.4 Experiment 3: Laboratory test for correction factors', not for the selection of VOCs in '2.3 Experiment 2: VOCs selection test'. For the selection of VOCs, a clean plastic container which contained half-filled silage was used, with the air dragged by the PTR-MS. For the laboratory test for correction factors, a setup showed in Figure 1 was simply used as a source of single VOC+air mixture and the specific VOC concentration was measured by the PTR-MS which was calibrated as discussed above. The uncertainty is mainly coming from the transmission and reaction rate estimation, which is around 10-15% (Cappellin et al., 2012).

15. Line 206 - 207. The selected components (methanol, ethanol etc.) should be mentioned with reference to Section 3.2.

Response: As we thought that the selection of VOCs were the part of results for section 3.2, therefore we did not include the specific list of selected components in the materials and methods section 2.3. Now we have mentioned the selected components in the revised manuscript, please see Line 223-225.

16. Line 212 - 220. What is the meaning of a "pre-tested water solution" (Line 213) ? What were the concentrations of the liquid solutions and their temperature? How were the VOC concentrations in the gas phase quantified? How stable were the gas-phase concentrations? How large was the water vapor concentration in the diluted gas which was fed into the instruments?

Response: "pre-tested" was now removed in order to clarify the text. The water solution was prepared by using a volume ratio of VOC:Water as 1:5, with purging by clean air controlled by

2 mass flow controllers in order to reach a desired range for test (See Line 240-241). The temperature was not controlled and was assume to be room temperature. The VOC concentration was quantified by the calibrated PTR-MS. The water vapor concentration in the diluted gas which was fed into the instruments (not for PTR-MS) was typically from a few hundred ppbv up to 50 ppmv (as can be seen from Fig.S1). For the PTR-MS, a further dilution was applied, when the VOC concentration was higher than 10 ppmv.

17. Line 221 - 224. What is the meaning and function of "excess flow". The excess flow should be indicated in Figure 1.

Response: The excess flow is the extra flow required by the instrument of Innova and Picarro, in order to keep the right pressure in the instrument. The two arrows near PAS and CRDS in Figure 1 indicate the excess flow, where the exhaust line is added as suggested.

18. Line 236. Which company has manufactured the Multiplexer 1309? How does it work and what are the materials that come into contact with the sampled air?

Response: . The Multiplexer 1309 was also manufactured by the Danish company Lumasense Technology A/S, and now the information has been added as shown in Line 243-244. This product now has a new version as ‘Multipoint Sampler - INNOVA 1409’ (https://www.lumasenseinc.com/EN/products/gas-sensing/innova-gas-monitoring/photoacoustic-spectroscopy-pas/multipoint-sampler-1409/multipoint-sampler-innova-1409.html). The materials that come into contact with the sampled air is PTFE.

19. Line 244. Which "selected VOCs" and "odorants" were measured? The term "odorant" should be defined.

Response: s. The ‘selected VOCs’ are now clarified as ‘all VOCs showed in section 2.3 were included’, while the term of ‘odorant’ is defined and the selection were also given. Please see Line 264-265 in the revised manuscript.

20. Line 245 - 246. What is meant by "background"? Where were the four sampling lines going to?

Response: The four sampling lines going to the four locations with ‘two selected locations inside the farm, one location in the pit ventilation, one location outside the farm.’. The background site was selected as the outside air beside the trailer, where the instruments were standing. This is now clarified in the revised manuscript, please see Line 267-268 in the revised manuscript.

21. Line 251 - 254. For which compounds were calibrations performed? The suppliers of the calibration gas mixtures and permeation device should be mentioned. What is the accuracy of the calibrations?

Response: Permeation tubes (VICI Metronics, Inc., Houston, TX, USA) included acetic acid, propanoic acid, butanoic acid, pentanoic acid and 4-methylphenol. Gas mixtures (all 5 ppmv in nitrogen) included hydrogen sulfide (AGA, Copenhagen, Denmark), methanethiol (AGA, Copenhagen, Denmark), and dimethyl sulfide (Air Liquide, Horsens, Denmark). Details regarding the calibration procedures could be found in our previous study, with accuracy with 12% error and in most cases within 8% (Liu et al., 2018). This is now clarified in the revised manuscript, please see Line 275-281.

22. Line 281 - 282. "Background concentrations of ammonia measured..." can be misunderstood and should be rephrased. Do you mean instrumental baseline (instrumental offset) when ammonia-free zero air is measured? Is there a plausible explanation for the background values of the CRDS and PAS instruments?

Response: Yes, we meant the instrumental baseline when ammonia-free zero air was measured. Now the sentence is revised in order to avoid misunderstanding. For PAS, the baseline is probably due to water vapor interference. For CRDS the baseline is really low (1 ppbv), since low ppbv concentrations are present more or less everywhere, e.g. from human breath.

23. Line 292 - 296, Figure 2B. The result of the instrumental comparison needs more discussion. Are the calibrations of the two instruments (CRDS, PTR-MS) independent? What is the statistical error of the slope of the linear fit? Are the differences between the two instruments statistically significant and can they be explained by instrumental calibration errors? The measurement comparison between PAS and CRDS (or PTR-MS) should also be shown and discussed.

Response: The ammonia concentration was simultaneously measured by the CRDS and the PTR-MS for Figure 2B. The SD of the slope of the linear fit was 0.005 which is really small. Therefore, the error is not much, and probably the slope is not significantly different from 1. The simultaneously measurement (calibration and comparison) between PAS and CRDS (or PTR-MS) for Ammonia was not performed in this study, but should be investigated in the future.

24. Line 300 - 315. What could be the reason for the concentration dependence of the PAS response time? Why are the PAS values elevated at 18:43 (Fig. 2C) and decrease until 19:00, while CRDS and PTR-MS show constant values. After the ammonia concentration has been switched to zero, the decay of the PAS signal seems to have at least two time constants. There is an initial fast decay that is followed by a tail with a slow decay. What could be the reason for the time behaviour? How long does it take until the PAS signal reaches baseline values?

Response: The three instruments were only used at the same time from around 19.00, and data before this time were from another test. Therefore, showing of the PAS values at 18.43 in the figure was not appropriate. Now we have corrected this error in the revised Figure.2C. We don’t have an explanation for the time behavior (two time constants), which may be included in the future study. It took around half an hour for the PAS signal reaches baseline values.

25. Line 378 - 380. Interferences in ammonia PAS measurements have been studied for single VOCs in air. Have you tested whether the interferences are additive in a multicomponent gas mixture? Additivity would at least require that the optical absorbances of the interfering VOCs are small (avoiding line saturation). (Non)linearity of the relationships seen in Figure 4 may give useful information. For a mixture with multiple interfering VOCs, a valid correction using the information from Table 2 can only be expected, if the interferences are independent of each other. This aspect needs to be discussed.

Response: Only single VOC was tested in the lab regarding interreference on PAS and correction factors were obtained for single VOC. We have to acknowledge that we don't know if the effects are always additive – although they are likely to be. In the field study, ethanol certainly dominated the VOC matrix in general, but other types of VOC also contribute significantly. For example, the averaged ratio of ethanol concentration to the sum of the 8 VOCs (tested in lab with obtained correction factors) was 0.64 (±0.11) for Location Two in the field study. From this single application it seemed that the obtained empirical relationships to be additive, but a complete investigation is indeed needed in the future. This part is now revised accordingly and please see Line 553-560.

26. Table 2. For which concentration ranges were the relationships tested? This information should be included in the table. Is there a physical explanation for negative interferences?

Response: . The concentration range indeed should be clarified, and now it is added in the text for Table 2. The negative interferences can usually be explained by the internal cross compensation procedure for one target filter (first target filter, such as NH3 filter) on positive artifacts at another target filter (second target filter, such as CH4 filter) caused by non-target gas (such as VOC) on the second target filter. This physical explanation was included in a few relevant references such as Zhao et al. (2012).

27. Line 412 - 425. Is there a physical explanation for the nonlinear behaviour of the VOC interference in measurements of N2O? Are the nonlinear interferences additive when two or more interfering VOCs are present in measured air?

Response: . We do not have physical explanation for the nonlinear behavior of the VOC interference in measurements of N2O, and we also don't know if these nonlinear interferences are additive or not when multiple VOC presented. In the field measurement, we could not determine the N2O concentration by other instrument than PAS, and therefore could not determine the interference for N2O by VOCs. In the future, this might be worth a sophisticated investigation just for N2O interference.

28. In Figure 2B, 4, 5B, 5D, S2, S3 and Table 2, results from statistical data treatments are shown. More information should be given on how fitted lines (curves) and fitted parameters were obtained. Were measurements corrected for offsets (background)? How were linear fits

obtained (least square fits? with or without error weighting?). Is it justified to force the fit through the origin? Fitted parameters should be given with 1δ errors. The meaning of the plotted error bars in Figure 4 should be explained. The error bars (statistical errors?) are significantly larger than the scatter of the data points around the fitted line. What does that mean?

Response: All measurements were corrected from background and the linear fits were least square fits without error weighting. From the figures, fitting equations were given. The fitting equations given that the fits were forced through the origin(zero). In the revised manuscript, this is now clarified for the mentioned Figures and table. Fitted parameters are given with 1δ errors, as shown in Table 2. The plotted error bars in Figure 4 were representing the standard deviations for the measured VOC by the PTR-MS under a selected VOC level (x-axis) and for the measured NH_3/N_2O level by the PAS meanwhile (y-axis). This is now in the text for Figure 4. The error bars are statistical errors, which are generally within reasonable range.

Technical comments

1. Materials and methods. More information about used gases (nitrogen, zero air), chemicals (organic compounds listed in Table 2) and the water used for VOC solutions should be given. Suppliers and purity grades need to be specified. How was zero air generated? How were the solutions of VOCs in water prepared?

Response: . The zero air was supplied from a HiQ zero air station (Linde AG, Munich, Germany). Nitrogen and clean air were supplied through a charcoal/silica gel filter. The 8 selected VOCs were purchased from Sigma-Aldrich with at least analytical grade purity. The water solution was prepared by using a volume ratio of VOC:Water as 1:5, with purging by clean air controlled by 2 mass flow controllers in order to reach a desired range for test.The manuscript was revised accordingly (Line 240-241).

2. Line 34. The term "field study" may be confused with a study under natural ambient conditions. Change sentence to "measured by PAS in a dairy farm".

Response: . “from a field study” is now revised to “in a dairy farm” as suggested.

3. Line 41 - 42. Ammonia causes soil acidification?

Response: . With the nitrification process the ammonia transfer to nitrate and hydrogen into the soil and increase the soil acidification.

4. Line 67 - 70. PAS is a general term for a spectroscopic method, but here you refer to a particular instrument (Innova 1312). Therefore, it is better to say: "Besides, the Innova 1312

has the advantages ...".

Response: . We have revised according to the suggestion.

5. Line 69. Change to "Usually, water vapor is also measured in order ...": Changed now.

6. Line 73. Change to "absorption of infrared light": Changed now.

7. Line 80. There is a word missing in "interference of has not been well studied...": “of” is now deleted.

8. Line 81. "Mathot et al., 2007" is missing in the Reference section.: This reference is now added to the Reference section.

9. Line 118-199: Change to "were used to measure trace gas concentrations in air".: Changed now.

10. Line 125 - 127. The sentence is not clear and should be rephrased.: The sentence is now rephrased.

11. Line 141. Either "acceleration of the ring down " or "reduction of ring down time ".: This is now revised.

12. Line 143. "Normal" ring down time needs to be explained.: This is now explained.

13. Line 173. Change to "Instrumental background signals, ammonia calibrations and instrumental time responses were characterized for the PAS, PTR-MS and CRDS instruments".: Changed now.

14. Line 180. Delete "for the calibration test".: Deleted now.

15. Line 181. The desired concentration range should be specified.: Specified now.

16. Line 197. Which kind of plastic material was used for the container? Was it emission free?

Response: Teflon plastic was used and it was emission free. Manuscript was revised accordingly.

17. Line 254. A reference for "Standard conditions as described previously ..." should be provided.: Reference is given now.

18. Line 293. Change to "in which the slope of the fitted line (k = 0.96 ± ?) ..." It’s changed now.

19. Line 304. "90% decay time" needs to be defined. It’s defined now.

20. Line 380. Change to "...VOC concentrations be measured simultaneously by other

instruments". It is revised as “VOC concentrations be measured simultaneously by expensive analyzers as PTR-MS”

21. Line 382. The term "correction factor" should be defined. It is now revised to empirical relationship (ER) as suggested in another comment to Table 2.

22. Figure 1. The exhaust line should be marked.: Exhaust line is now marked.

23. Figure 2. All axis should show tic marks. Concentrations at the x and y axis of Figure 2B and at the y axis of Figure 2C should be given in ppmv.

Figure 2C caption: change to "Instrumental response of PTR-MS, PAS and CRDS instruments to a rectangular ammonia concentration pulse."

Figure 2D caption: change to "Instrumental response of PTR-MS, PAS and CRDS instruments to a stepwise increase in ammonia concentration."

Response: Figure 2 is now revised as suggested. Figure 2D caption changed to “Instrumental response of PAS instrument to a stepwise increase in ammonia concentration.”

24. Figure 4. All axis should show tic marks. Concentrations at the x and y axis of Figure 4A and 4B should be given in ppmv. The Figure caption mentions red, green and purple lines. The colour designation should be made consistent with the plotted lines.

Response: Figure 4 is now revised as suggested.

25. Figure 5. All axis should show tic marks. Concentrations at the x and y axis of Figure 5B and 5D should be given in ppmv. Draw 1:1 lines in A and C as reference.

Response: It’s been revised as suggested.

26. Figure S1. Concentrations should be given in ppmv.: It’s been revised.

27. Figure S2. All axis should show tic marks. "ppm" should be "ppmv".

28. Figure S3. All axis should show tic marks. Concentrations should be given in ppmv. What is the difference between the upper and lower panel in Figure S3? It’s been revised. The difference is Location One and Location Two for the up and down panel, respectively.

29. Table 1. Units should be ppmv (to be consistent with text and figures).

Response: Table 1 is now revised. For the detection limit, we kept ppbv since the values are basically within lower range of ppbv.

30. Table 2 caption must be rephrased. The table does not show correction factors, but empirical relationships describing the functional dependence of the interference in the measurement

of the target compound (e.g., NH3) on VOC concentrations.

Response: Table 2 is revised as suggested.

31. Table 3. Do standard deviations apply to the mean values, or do they represent the variability of single measurements? The concentration values for ethanol and methanol should be reasonably rounded.

Response: Yes the standard deviation apply to the mean values. It's now clarified in the revised manuscript.

32. Table S1. "Filter center" should be changed to "Center wavelength". What is the meaning of "Band width (%)" ? Is it related to "Filter bandpass"?

Response: "Filter center" is now changed to "Center wavelength" as suggested. Yes the "Band width (%)" is related to "Filter bandpass" which is calculated based on the center wavelength and band width (e.g., 2171=2215-2215*2.0/100 for UA0985).

Reference:

Cappellin, L., Karl, T., Probst, M., Ismailova, O.,Winkler, P.M., Soukoulis, C., Aprea, E., Märk, T.D., Gasperi, F., Biasioli, F., 2012. On quantitative determination of volatile organic compound concentrations using proton transfer reaction time-of-flight mass spectrometry. Environ. Sci. Technol. 46, 2283–2290.

Kamp, J.N., Chowdhury, A., Adamsen, A.P.S., Feilberg, A.: Negligible influence of livestock contaminants and sampling system on ammonia measurements with cavity ring-down spectroscopy. Atmos. Meas. Tech., 12, 2837–2850, https://doi.org/10.5194/amt-12-2837-2019, 2019.

Zhao, Y., Pan, Y., Rutherford, J., and Mitloehner, F. M.: Estimation of the Interference in Multi-Gas Measurements Using Infrared Photoacoustic Analyzers, Atmos., 3, 246–265, https://doi.org/10.3390/atmos3020246, 2012.

Response to amt-2018-412-SC1:

Comment:

It has been reported that the measurements of ammonia around livestock facilities by PAS could be interfered by the VOCs, a systematic calibration is still in great need. This research conducted precisely test and calibration on the interference of VOCs on the measurement of NH3, NO2, CH4 by PAS method. The results confirmed the significant influence of the VOCs on the measurement of these compounds. Moreover, the authors dedicate to building correction factors for the interference and verifying the factors in the field tests successfully. Overall, this is high-quality research and the results deserve to be carefully read by researches on field measurement of NH3, NO2, CH4 by PAS method.

Response: Thanks for the comment. The interference was investigated previously indeed and we here performed a more systematic calibration and possible correction. Although the usage of correction factors require additional measurements on VOC concentrations, it still make a possibility to correct the PAS data, since PAS is widely applied for measuring ammonia and greenhouse gas concentrations.

Response to SC2:

We were always surprised how confident researchers have been in trace gas instruments using broadband light sources for the determination of gaseous emissions from agriculture. The present paper focuses on interferences occurring in ammonia concentration determination by INNOVA instruments. It convincingly shows the severe limitations of this measurement technology and documents the strong influence of other gases on the readout of these devices. Reliable concentration measurements need in addition the determination of a large variety of compounds in order to perform the suggested correction algorithms. This is a paradoxical situation, as such measurements need complex and costly instrumentation that will make the use of broadband filter based instruments redundant. In some cases cheaper NH3 passive samplers or liquid impingers can be used as a robust and reliable alternative, if high time resolution is not required. Innova-based NH3 concentration measurements are likely influenced by compensating errors. The positive interferences discussed in this paper focus on the detection side, but in parallel there are potential losses of NH3 in the inlet tubing/lines and switching valves, especially in multiport systems. Within livestock production systems rather high dew points are present that facilitate absorption onto most types of surfaces. Often low flow rates are used, tubing is not heated, and some inlet filters are put in place to protect the analyzer from dust ingress, which all exacerbate the adsorption/desorption problem.

It is also striking that in many peer-reviewed articles reporting emission data based on Innova or similar instruments, detailed information on the sampling and analytical system are missing, which prevents a critical re-evaluation of such data. Consequently, emission factors based on these instruments should be taken with great caution.

Fifteen years ago, we investigated in detail the dependence of the concentration output, for a large range of CO2-CH4-N2O-H2O mixtures, of three different Innova's (1312, 1314) as a function of the cell temperature and the water vapor (dew point). An overview of the measurements is given in the supplement. These analyses are the base of the evaluation algorithm developed by Flechard et al. (2005) for the determination of N2O concentrations, which showed the large influence of CO2, water vapour and temperature. Another striking result was the large influence of the water content and the cell temperature on the CH4 concentration. The contribution of H2O to the CH4 raw signal depends on the ratio of the two gases. It will e.g. be less important in cow stable, compared to our INNOVA experiment where CH4 was only a couple of ppm.

Only in case Innova devices are operated in a temperature-controlled environment, with the dew point being kept constant, can reliable CH4 measurements be made.

Reference Flechard, C. R., Neftel, A., Jocher, M., Ammann, C., and Fuhrer, J.: Bidirectional soil-atmosphere N2O exchange over two mown grassland systems with contrasting management practices, Glob. Change Biol., 11, 2114–2127, 2005.

Albrecht Neftel Neftel Research Expertise Christoph Flechard INRA, Rennes

Please also note the supplement to this comment:
https://www.atmos-meas-tech-discuss.net/amt-2018-412/amt-2018-412-SC2-supplement.pdf

Response: Thanks for the comment. We agree that reliable concentration measurements need in addition the determination of a large variety of compounds in order to perform the suggested correction algorithms. Nevertheless, depending on the application case, the dominating compounds might be limited to a few major ones, where the measurements and correction likely be possible. Still, we agree that such measurements generally need complex and costly instrumentation which make the use of broadband filter-based instruments less attractive.

In this study, we focused on interference for the detection side, there are indeed some potential losses of NH3 in the inlet tubing/lines and switching valves, which we did not investigate in this study. Typically, the PTFE tubing is used, therefore the adsorption/desorption problem was not focused but need systematic investigation in the future.

We agree very well that we have to take great care when using emission data from many peer-reviewed articles based on Innova or similar instruments, especially when detailed information on the sampling and analytical system are missing, and the corresponding emission factors should not be used otherwise.

We admit that we did not look into the effect of temperature which seem to influence significantly the greenhouse gas concentration measurement especially memthane. In the future this should be investigated together with combined interference effects from various compounds on ammonia and greenhouse gas measurement by the broadband light PAS.

Photoacoustic measurement with infrared band-pass filters significantly overestimate NH_3 emissions from cattle houses due to VOCs interferences

Dezhao Liu[1,2*], Li Rong[2], Jesper Kamp[2], Xianwang Kong[1], Anders Peter S. Adamsen[3], Albarune Chowdhury[2], Anders Feilberg[2*]

1- Zhejiang University, College of Biosystems Engineering and Food Science, Yuhangtang Road 866, 310058 Hangzhou, China
2- Aarhus University, Department of Engineering, Finlandsgade 22, 8200 Aarhus N, Denmark
3- APSA, c/o Agro Business Park, Niels Pedersens Allé 2, DK-8830 Tjele, Denmark

Corresponding author: Dezhao Liu: dezhaoliu@zju.edu.cn;

Anders Feilberg: af@eng.au.dk

Abstract: Infrared photoacoustic spectroscopy using band-pass filters (PAS) is a widely used method for measurement of NH_3 and greenhouse gas emissions (CH_4, N_2O and CO_2) especially in agriculture, but non-targeted gases such as volatile organic compounds (VOCs) from cattle barns may interfere with target gases causing inaccurate results. This study made an estimation of NH_3 interference in PAS caused by selected non-targeted VOCs which were simultaneously measured by a PAS and a PTR-MS (proton transfer reaction mass spectrometry). Laboratory calibrations were performed for NH_3 measurement and VOCs were selected based on a headspace test of the feeding material (maize silage). Strong interferences of VOCs were observed on NH_3 and greenhouse emissions measured by PAS. Particularly, ethanol, methanol, 1-butanol, 1-propanol and acetic acid were found to have the highest interferences on NH_3, giving empirical relationships in the range of 0.7 to 3.3 ppmv NH_3 per ppmv VOC. A linear response was typically obtained, except for a non-linear relation for VOCs on N_2O concentration. The corrected online NH_3 concentrations measured by PAS in a dairy farm (with empirical relationships 2.1±0.8 and 2.9±1.9 for Location One and Location Two, respectively) were confirmed to be correlated ($R^2 = 0.73$ and 0.79) to the NH_3 concentration measured simultaneously by the PTR-MS, when the empirical corrections obtained from single VOC tests were applied.

1 Introduction

Measurements of ammonia and greenhouse gas (CH_4, N_2O and CO_2) emissions are gaining increasing attention due to stronger interests on global change and air pollution. Ammonia not only causes serious environmental problems such as soil acidification and pollution of underground water and surface water (van Breemen et al., 1983; Pearson and Stewart, 1993;

Erisman et al., 2007), but is also important for fine particle formation (Bouwman et al., 1997; Seinfeld and Pandis, 1997; Pinder et al., 2007). Greenhouse gas emissions, on the other hand, are causing climate change (Thomas et al., 2004; Chadwick et al., 2011). Livestock husbandry was estimated to be responsible for more than 80 % of the ammonia emission in Western Europe (Hutchings et al., 2001; EMEP, 2013) and more than 60% in China (Paulot et al., 2014). In the U.S.A, agriculture accounts for ~90 % of the total ammonia emissions (Aneja et al., 2009). Meanwhile, agriculture accounts for 52 and 84 % of global anthropogenic methane and nitrous oxide emissions (Smith et al., 2008). Accurate measurements of ammonia and greenhouse emissions are therefore vital for reliable emission estimation and thereby the possible reduction of these emissions through various efforts, such as air cleaning with biotrickling filters and air scrubbers (Melse and Van der werf, 2005; De Vries and Melse, 2017). For ammonia measurements, more than 30% difference between different methods has been reported (Scholtens et al., 2004).

Infrared photoacoustic spectroscopy (PAS) is a widely-used technique for studies of air emissions especially within agriculture (Osada et al., 1998; Osada and Fukumoto, 2001; Emmenegger et al., 2004; Schilt et al., 2004; Heber et al., 2006; Elia et al., 2006; Blanes-Vidal et al., 2007; Hassouna et al., 2008; Rong et al., 2009; Ngwabie et al., 2011; Cortus et al., 2012; Joo et al., 2013; Wang-Li et al., 2013; Iqbal et al., 2013; Zhao et al., 2016; Ni et al., 2017; Lin et al., 2017). The PAS technique determines the gas concentrations through measuring acoustic signals caused by cell pressure changes when gas absorbs energy from infrared light at a specific wavelength range using an optical filter and a chopper (Iqbal et al., 2013). For example, the Innova 1312 and later versions (Lumasense Technologies, Ballerup, Denmark) uses the PAS principle and was previously verified by the US EPA and recommended by the Air Resources Board in California (CARB, 2000). In principle, this instrument "is capable of measuring almost any gas that absorbs infrared light" (Innova, Lumasense Technology A/S, Denmark). The method is based on nondispersive broadband spectroscopy and selectivity is achieved by using appropriate wavelength filter, with one filter for each targeted trace gas. Innova 1312 and 1412 instruments have been used in a large number of tests to measure NH_3, CH_4, CO_2 and N_2O for agricultural applications. Water vapor is also measured to account for the strong absorption of water throughout the infrared spectrum (Christensen, 1990a). Nevertheless, since the infrared spectroscopic method is applied for measuring gas concentrations in PAS, the overlapping of IR spectra with non-targeted gases can introduce significant interferences due to the absorption of infrared light at similar wavelengths. The specificity is limited by the bandwidth of the optical filters. The interferences can be corrected by the instrument software through cross-compensation for all target gases when the instrument is calibrated (Christensen, 1990a; Lumasense, 2012), but understanding and estimation of interferences from non-targeted gases needs to be considered in each specific measurement situation. This is especially important for agricultural applications where the manure and the animal feed may emit various types of gases depending on the management and operations in the animal houses (Hassouna et al., 2013; Moset et al., 2012). Therefore, two key questions exist: (a) what is the magnitude of interferences that can be expected in agricultural environments, and (b) is it possible to quantify and correct interferences in a reasonable way? Until now, the PAS interference has not been well estimated and corrected for, although interferences were previously suspected in livestock facilities (Phillips et al., 2001; Mathot et al., 2007; Ni & Heber, 2008). Flechard et al. (2005)

suspected that the N_2O concentration from soil measured by PAS (Innova 1312) was heavily influenced by CO_2 and temperature even when cross-interference compensation was applied; they developed an alternative correction algorithm based on controlled $N_2O/CO_2/H_2O$ ratios under selected temperature. Zhao et al (2012) claimed that the internal cross compensation could eliminate the interferences between target gases, and quantified interferences of non-targeted gas of NH_3 on targeted gases of ethanol, methanol, N_2O, CO_2, and CH_4, however, without giving specific relationships. Iqbal et al. (2013) also demonstrated that a careful calibration could eliminate the internal cross interferences of high water vapor and CO_2 concentrations on low concentrations of N_2O at the soil surface by comparison to GC measurements. Nevertheless, tests of interferences by non-targeted VOCs were not included in their study, likely due to the typical low concentrations of VOC in soil (Insam and Seewald, 2010). Hassouna et al. (2013) presented a field study on dairy cow buildings, where interferences on NH_3, CH_4 and N_2O were observed. The interferences were suspected to be caused by VOCs (acetic acid, ethanol and 1-propanol) that they measured simultaneously. In their study, two PAS instruments were applied with one of them allocated with optical filters of these VOCs (NH_3 optical filter was included for both PAS). Still, no empirical relationships were given in terms of tested volatile organic compounds, which were typically emitted from feeding materials such as maize silage (Howard et al., 2010; Malkina et al., 2011). The correction of interferences of non-targeted VOCs on NH_3 emission is also essential for the evaluation of emission abatement technologies such as air scrubbers, especially when the inlet VOC concentrations are relatively high. An overestimation of ammonia removal efficiency could easily be obtained since less interference would be expected for the outlet VOCs especially for water-soluble compounds such as the VOCs investigated in this study.

In this work, an evaluation of interferences by non-targeted VOCs on targeted NH_3 and greenhouse gas measurements by PAS is presented. The interference on NH_3 was tested by simultaneous application of Proton-transfer-reaction mass spectrometry (PTR-MS), Cavity Ring-Down Spectroscopy (CRDS) and PAS. The experiments were as follows: (1) ammonia laboratory calibration by PAS, PTR-MS and CRDS; (2) VOC selection for testing of interference on ammonia measured by PAS; (3) Effect of VOCs on ammonia and greenhouse emissions measured by the PAS; (4) Field confirmation of interferences of non-targeted VOCs on ammonia measurement and test of potential for data correction.

2 Materials and methods

2.1 Instrumentation for gas concentrations measurement

In this study, a PTR-MS, a CRDS NH_3 analyzer and a PAS gas analyzer were used to measure trace gas concentrations in air. PTR-MS is a state-of-the-art and widely used technique for highly sensitive online measurements of VOCs (De Gouw and Warneke, 2007; Blake et al., 2009; Yuan et al., 2017). PTR-MS can also measure a few inorganic compounds such as ammonia (at m/z 18) since the proton affinity (204.0 kcal/mol) of ammonia is higher than that of water (165.0 kcal/mol). Since the intrinsic ion at m/z 18 is always formed in the plasma ion source (Norman et al., 2007), ammonia measurements by PTR-MS are routinely corrected for instrumental background contribution. The typical m/z 18 background signal corresponds to a few hundred ppbv of NH_3. The background signal is relatively stable and still allows for NH_3 detection limits of 20-50 ppb. For agricultural measurement conditions, concentrations are typically from a few hundred ppb to >10 ppm (e.g., Rong et al., 2009). When total gas concentration measured by PTR-MS is higher than approximately 10 ppmv, dilution is needed to keep the primary ion signals stable. A high-sensitivity PTR-MS (Ionicon Analytik GmbH, Innsbruck, Austria) was applied for the test of ammonia calibration in the laboratory, effects of non-targeted VOCs on ammonia measurement and field confirmation of interferences of non-targeted VOCs on ammonia measurement. Standard conditions with a total voltage of 600 V in the drift tube were utilized for the PTR-MS. Pressure and temperature in the drift tube were maintained in the range of 2.1-2.2 mbar and at 60 °C, respectively, which gives an E/N ratio of ca. 135 Townsend. The inlet of the PTR-MS is PEEK tubing of 1.2 m length with 0.64 mm inner diameter (ID) and 1.6 mm outer diameter (OD). The inlet flow to the PTR-MS during calibration test and measurements was kept ~150 mL/min. The inlet temperature was maintained at 60 °C. The instrument calibration was performed based on specific reaction rate constants and mass discrimination factors (accuracy better than 12%), as described in our previous study (Liu et al., 2018). Mass calibration was performed before each test, while mass discrimination calibration was performed for every two weeks.

CRDS determines the gas concentration (e.g., NH_3) by measuring the ring-down time of light in the cavity due to absorption by a targeted gas species, which is compared to the ring-down time without any additional absorption due to a targeted gas species. The light source is a laser with tunable wavelength (von Bobrutzki et al., 2010; Picarro, 2017). The very long effective path length of the light in the cavity (e.g., over 20 km for 25 cm cavity) (Picarro, 2017), enables a significantly higher sensitivity compared to conventional absorption spectroscopy (Berden et al., 2000; von Bobrutzki et al., 2010). There is negligible interference from VOCs on CRDS measurements, which makes CRDS ideal to measure NH_3 concentrations in this setting (Kamp et al., 2019). A G2103 Analyzer (Picarro Inc., Sunnyvale, CA, USA) using CRDS technique was applied in this study for the test of ammonia laboratory calibration and the effect of non-targeted VOCs on ammonia measurement. The accuracy of the CRDS instrument is routinely checked against a certified reference gas as described by Kamp et al (2019). The CRDS analyzer was equipped with two in-line, sub-micron polytetrafluoroethylene (PTFE) particulate matter filters; one at the gas inlet at the back of the analyzer and one at the inlet of the cavity to protect the highly reflective mirrors. The inlet of the CRDS is a PTFE (PTFE) tubing of 1.5 m length with 6.4 mm outer diameter. The optical cavities incorporate precise temperature (±0.005 °C) and pressure (±0.0002 atm) control systems. In this study, both the temperature and pressure of the air sample continuously flowing through the optical cavity are tightly controlled at all times to constant values of 45 °C and 140 Torr, respectively. The measurement interval is around 2 seconds. The CRDS analyzer measured the water vapor simultaneously.

A photoacoustic multi-gas monitor 1312 (Innova, Lumasense Technology A/S, Denmark) was compared with the PTR-MS and the CRDS for ammonia calibration and non-targeted VOCs on ammonia measurement. An infra-red-light source was used for the PAS instrument and the principle for the measurement is as follows. The infrared radiation can interact with a molecule and transfer energy to it if the frequency of the radiation is the same as the frequency of vibration within the molecule. When the molecule absorbs IR light, it vibrates with greater amplitude. This increased activity is short-lived, however, and the excited molecule very quickly transfers its extra energy to other molecules in the vicinity by collision. The increased kinetic energy leads to an increase in the measurement chamber temperature and pressure. A microphone is used to detect the consequently fluctuating pressure. The sample integration time to measure ammonia by PAS was 20 s. The instrument used 6 optical filters for NH_3, CH_4, CO_2, H_2O, N_2O and SF_6. The specifications of the optical filters are shown in Table S1. Water vapor must be included for PAS measurement since the absorbance spectrum of water overlap with other gases such as N_2O and CO_2 thus causing interferences. According to the manufacturer, the Innova 1312 has linear response over a wide dynamic range, with the possibility to make self-calibration (Lumasense, 2012). Before the measurements presented in this study, the supplier calibrated the instrument. During the study the instrument was calibrated based on a certified gas cylinder containing 99.7 (± 10 %) ppmv ammonia (AGA A/S, Copenhagen, Denmark). The interferences between the target gases were therefore supposed to be eliminated through internal cross compensation (Christensen, 1990b; Zhao et al., 2012).

2.2 Experiment 1：laboratory test on ammonia calibration

Instrumental background signals, ammonia calibrations and instrumental response times were characterized for the PAS, PTR-MS and CRDS instruments. For the background measurement, zero air controlled by a mass flow controller (Bronkhorst, Ruurlo, The Netherlands) was supplied, and measurement was performed individually for each instrument. The zero air was supplied from a HiQ zero air station (Linde AG, Munich, Germany). The selected ion measurement mode was used for the PTR-MS with m/z 18 being used for ammonia detection. For the calibration test, a factory-calibrated gas cylinder (AGA A/S, Copenhagen, Denmark) containing 99.7 (± 10 %) ppmv ammonia was used. Mass flow controllers (Bronkhorst, Ruurlo, The Netherlands) were used to dilute the gas from the cylinder with zero air to achieve the desired NH_3 concentration levels (0-11 ppmv). For the test of response decay time, zero air flow was supplied to the instruments at first, then switched to a diluted flow (via 2-levels of mass flow controllers) with ammonia concentration around 5.2 ppmv supplied to all three instruments simultaneously. Subsequently, the ammonia supply was set to zero to test the decay time. Four individual decay time tests were performed for the PAS, to confirm the long decay time of the instrument with low ammonia concentrations (5.2-8.8 ppmv) or high ammonia concentration (99.7 ppmv). For the test of response time for the PAS, two different levels of ammonia concentration were introduced individually to the instrument, to test the dependence of the response time on ammonia concentration.

2.3 Experiment 2: VOCs selection test

A headspace test was performed and VOCs were selected through a PTR-MS measurement as preparation to the interference tests of VOCs on ammonia measured by the PAS. Maize silage is typical feeding material to the cows and silage is generally considered an important source of gaseous VOC in cattle barns. A sample of maize silage was collected from the farm where the field experiment was performed (Skjern, Jutland, Denmark, altitude: 55°59′36.6″, longitude: 8°29′53.52″). The silage was then transferred to the laboratory immediately for the headspace test. A clean PTFE container (58×38×43 cm) with two oval holding holes (6×8 cm) on the sides was used for the headspace test. The container was partly open and the silage filled half of the container. A 1-meter 1/4-inch OD PTFE tube was used for the test, with one end placed around 5 cm above the silage, and the other side connected to a T-piece. One side of the T-piece was connected to a 1/8-inch OD PTFE tube (around a half meter) which was connected to the inlet of the PTR-MS. The flow rate of the PTR-MS was kept at 150 mL/min. A zero-air dilution flow (75 mL/min) was supplied to the T-piece to make 1:1 dilution to keep the total concentration below 10 ppmv. The headspace measurement was performed by the PTR-MS in scan mode, and masses were measured from m/z 21 to m/z 250 with 200 ms for each mass. The selection of VOCs was based on the scan results and relevant literature data on silage VOC, with the following VOCs being selected: ethanol, methanol, acetaldehyde, acetic acid, 2-butanone, acetone, 1-propanol and 1-butanol (Howard et al., 2010; Malkina et al., 2011; Hafner et al., 2013). These 8 selected VOCs were tested for empirical relationships (C_{NH3obs}/C_{VOC}) with respect to contribution to measured NH_3 concentration (C_{NH3obs}). All chemicals were purchased from Sigma-Aldrich with at least analytical grade purity.

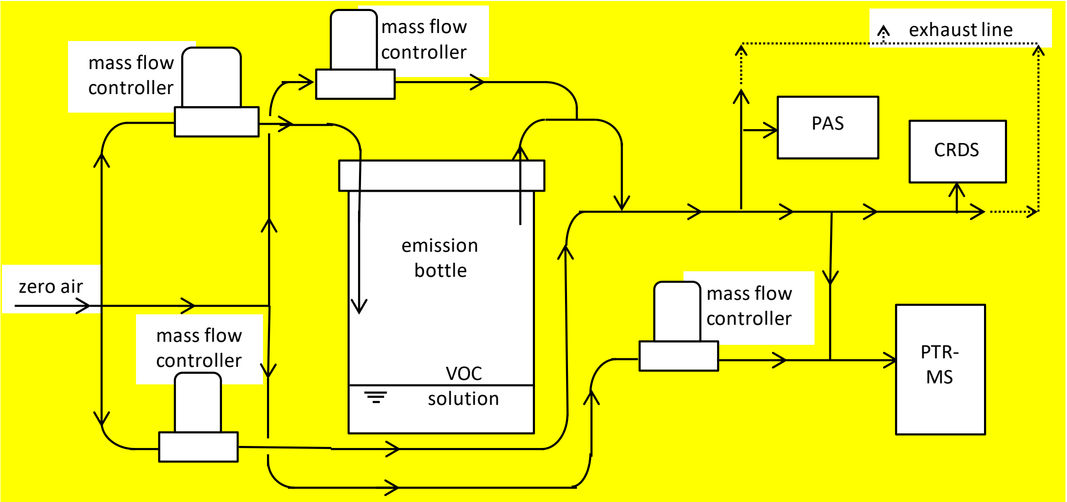

Figure 1. A diagram of the experimental set-up for test of ammonia interference due to VOC.

2.4 Experiment 3: Laboratory test for empirical relationships

The diagram of the setup for the laboratory calibration test is shown in Figure 1. In the setup, a water solution containing the single VOC was purged from the headspace by dry and clean air (or nitrogen for one test on methanol), with flow controlled by a mass flow controller. The air or nitrogen was supplied through a charcoal/silica gel filter. One-liter airtight glass bottles were used for the water solution containing the VOC, and 1/4-inch OD PTFE tube was used in the setup. The purged air flow was diluted with air through a two-step dilution. The flows were adjusted according to the purged VOC concentration and the desired final VOC concentration. The water solution was prepared by using a volume ratio of VOC:Water of 1:5, with purging by clean air controlled by 2 mass flow controllers in order to reach a desired concentration range. For the laboratory test, the diluted air containing VOC was connected to the PAS, the CRDS and the PTR-MS for simultaneous measurements. The overall flow was maintained at a level above the total maximum sampling flow of all three instruments and excess flow was vented through a T-piece. For the PTR-MS measurement, a further dilution by zero air was typically used to keep the total VOC concentrations below 10 ppmv to avoid depletion of the primary ion, H_3O^+. Selected ion measurement mode was applied for the PTR-MS, with an integration time of 2 seconds for the tested VOC mass. During the experiments, the humidity was kept relatively low and stable, with dry clean air used for dilution for all cases, except for one test on methanol, which was also tested under nitrogen condition.

2.5 Experiment 4: Field test for validation of empirical relationships

The field demonstration test for non-targeted VOCs on ammonia measurement by the PAS was performed in the dairy farm mentioned above (Skjern, Jutland, Denmark), where both the PTR-MS and the PAS were measuring continuously over 20 days. The dairy farm housed 360 cows with an average weight of 650 kg. The ventilation system consisted of natural and mechanical partial pit ventilation system (Rong et al., 2015).

For the field test, the PAS was combined with a Multiplexer 1309 (Lumasense Technology A/S, Denmark) to measure from several sampling points. The PAS and the PTR-MS were placed in a trailer next to the dairy farm. The PAS sample integration time was 5 s and the flushing time was 20 s. The air concentrations were measured by the PAS sequentially between two selected locations inside the farm, one location in the pit ventilation, one location outside the farm. PTFE tubes of 20 meters and 8 mm OD were used for the sampling of air. The sampling lines were connected with the channels of the PAS multi-point sampler via continuously running PTFE membrane pumps to ensure constant flushing. VOCs (all VOCs showed in section 2.3 were included together with VOCs reported in previous studies (Malkina et al., 2011; Hafner et al., 2013)) and NH_3 were measured simultaneously by PTR-MS. Measurements were switched between the four measurement sampling lines (connecting to the four locations mentioned above) and the background (outside air beside the trailer) at 8 min intervals via a custom-built switching box. PTFE tubes were used for the PTR-MS sampling lines, which were connected to PTFE sampling lines before the PTFE membranes pumps. The switching box was equipped with a five-port channel selector (Bio-Chem Valve Inc, USA) controlled automatically by 24V outputs from the PTR-MS. A PTFE tube (ID 1 mm) was used to connect the switching box to the inlet sampling line (1-meter PEEK tube with ID 0.64 mm) of the PTR-MS. For selected compounds, calibration was performed for the PTR-MS before the field measurements using permeation tubes and reference gas mixtures. Permeation tubes (VICI Metronics, Inc., Houston, TX, USA) included acetic acid, propanoic acid, butanoic acid, pentanoic acid and 4-methylphenol. Gas mixtures (all 5 ppmv in nitrogen) included hydrogen sulfide (AGA, Copenhagen, Denmark), methanethiol (AGA, Copenhagen, Denmark), and dimethyl sulfide (Air Liquide, Horsens, Denmark). Details regarding the calibration procedures could be found in our previous study, with accuracies within 12% error and in most cases within 8% (Liu et al., 2018). VOC concentrations were determined directly by the PTR-MS, based on estimated reaction rate constants as described by Liu et al. (2018). Standard conditions as described previously was applied and maintained for the PTR-MS (Feilberg et al., 2010). The mass discrimination was calibrated and adjusted weekly by using a mixture of 14 aromatic compounds between m/z (mass to charge ratio) 79 and 181 (P/N 34423-PI, Restek, Bellefonte, PA). Selected ions were monitored with dwell time between 200 and 2000 ms during each measurement cycle. Masses and dwell time selection was based on ion abundance in full scan mode, relevant literature and experience regarding odorant compounds from dairy buildings as well as from pig houses and pig slurry applications (Shaw et al., 2007; Chung et al., 2009; Liu et al., 2014; Liu et al., 2018).

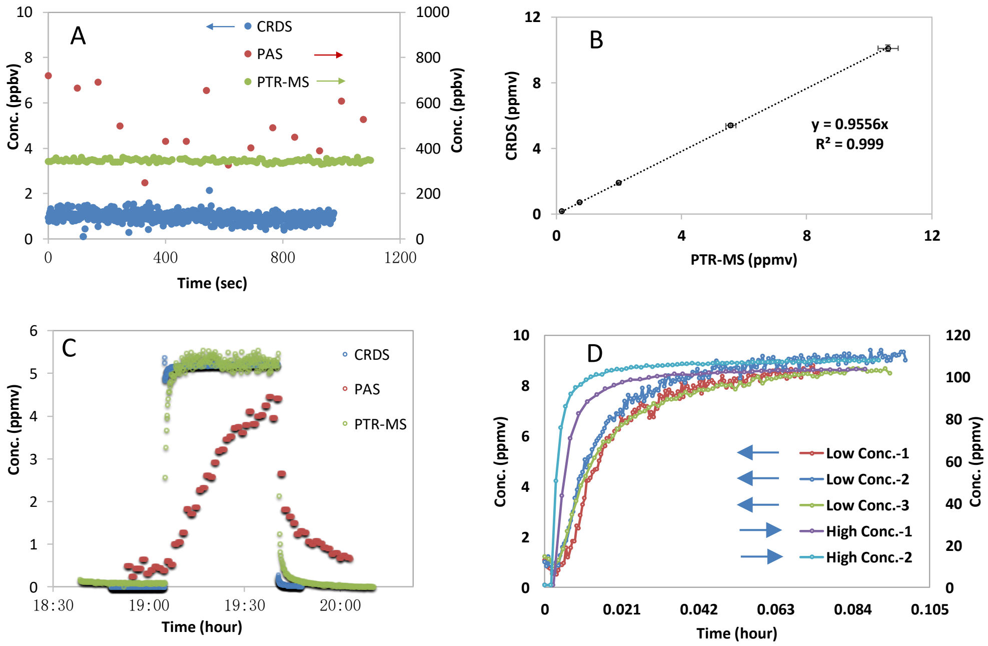

Figure 2. The calibration test of ammonia by the PAS, the PTR-MS and the CRDS. A: Background comparison for the CRDS, the PAS and the PTR-MS for ammonia measurement; B: The calibration of ammonia measured by the PTR-MS and by the CRDS; C: Instrumental response of PTR-MS, PAS and CRDS instruments to a rectangular ammonia concentration pulse.; D: Instrumental response of PAS instrument to a stepwise increase in ammonia concentration (low concentration (3 tests; ~8.9 ppmv) and high concentration (2 tests; 99.7 ppmv); Low Conc.-1, Low Conc.-2 and Low Conc.-3 point to the vertical axis on the left, and to the upper horizontal axis; High Conc.-1 and High Conc.-2 point to the vertical axis on the right, and to the lower horizontal axis; High Conc.-2 was tested without the multiplexer). Data in B has been background-subtracted and the linear fits were least square fits without error weighting.

3 Results and discussion

3.1 Experiment 1：laboratory test on ammonia calibration

The instrumental baseline concentrations of ammonia-free zero air measured by PAS, CRDS and PTR-MS, respectively, are shown in Figure 2A, in which a very low background signal was observed for the CRDS instrument (around 1 ppbv) with a detection limit of 0.7 ppbv (3 times the standard deviation of the background). The higher background for ammonia measured from the PTR-MS is caused by the intrinsic formation of NH_4^+ (m/z 18) in the ion source (Norman et al., 2007). Nevertheless, the measured background signals for ammonia by the PTR-MS was very stable and could be subtracted to give a detection limit of 21 ppbv (3 times the standard deviation of the background). Among the three instruments, the PAS gave the highest background signal for ammonia (corresponding to 502 ± 140 ppb), with a detection limit of 421 ppbv (3 times the standard deviation of the background).

For the calibration test of ammonia, the ammonia concentrations simultaneously measured by the CRDS and the PTR-MS is shown in Figure 2B, in which the linearity ($k = 0.96 \pm 0.005$) and high correlation (R^2=0.999) are generally very satisfactory for both instruments. The measured ammonia concentrations also agreed with expected ammonia concentrations from the ammonia reference gas within the uncertainty of 10% provided by the gas supplier.

Table 1. Instruments comparison regarding the specifications for ammonia measurements.

	LOD(3×SD; ppbv)	Up limit (ppmv)	90% decay time (s)	Measurement time	Accuracy	Possible Interferences
Innova	421(200[*])	(-)[A]	1700-4000 (5.2-8.8 ppmv); 450-550 (100 ppmv)	Less than 2 min	Zero Drift: ± 0.25% [*]	Non-targeted gases with IR spectra Overlapping
PTR-MS	21.5	10[#]	70-80 (5.2 ppmv)	Less than 5 s	(-)	intrinsic ion at m/z 18
Picarro	0.67	>20[&]	4.5-4.7 (5.2 ppmv)	Less than 2 s	(-)	Negligible[&]

* - According to the wall chart given by the producer. https://www.lumasenseinc.com/uploads/Products/Technology_Overview/Technical_Literature_pdf/EN-Lumasense-gas-detection-limits_Wall-Chart.pdf.

A - The producer claimed a "Linear response over a wide dynamic range".

- According to the concentration calculation assumption and producer suggestion, total gas concentration should be lower than 10 ppmv, otherwise dilution is needed.

&- According to Kamp et al., 2019.

For the signal decay test, the instrument decay times for ammonia measurements by PAS, CRDS and PTR-MS were measured simultaneously under a static ammonia concentration of 5.2 ppmv. As shown in Figure 2C, ammonia measured by the CRDS showed the shortest decay time while the PAS gave by far the longest decay time. The estimated decay time is shown in Table 1, in which the 90% decay time (time for the concentration to decrease by 90%) for ammonia measured by the CRDS is around 4.5 - 4.7 second, with the 90% decay time from the PTR-MS estimated to be 70 to 80 seconds. The decay time for ammonia measured by the PAS was remarkably longer, with an estimated 90% decay time of around 30 minutes to more than an hour (for four individual tests with ammonia concentration ranged from 5.2 to 8.8 ppmv). When much higher ammonia concentration was used (99.7 ppmv), the 90% decay time measured by the PAS was shorter (450 to 550 seconds). This result is consistent with the response time tests under two levels of input ammonia concentrations (~ 8.9 ppmv and 99.7 ppmv, respectively), with the response time much shorter when the ammonia concentration is higher, as shown in Figure 2D. Besides, the multiplexer attached to the PAS seemed to increase the response time, as also shown in Figure 2D. However, a very high concentration of about 100 ppmv is not expected in agricultural applications.

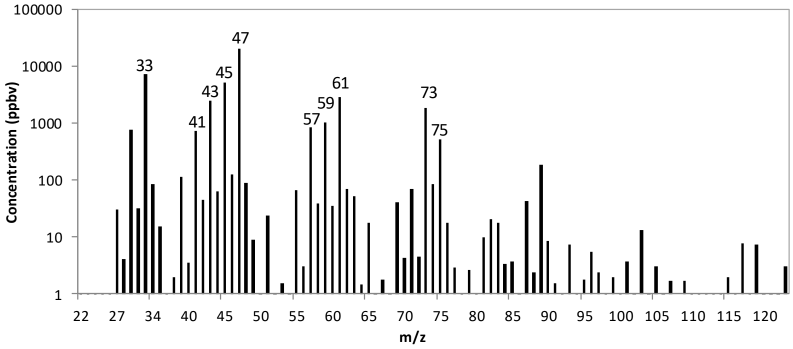

Figure 3. A scan example of the feeding material of silage by using headspace technique measured by the PTR-MS. The m/z 47 is corrected for ethanol fragmentations formed in the PTR-MS through calibration. Selected VOCs for the test in this study were ethanol, methanol, acetaldehyde, acetic acid, 2-butanone, acetone, propanol and butanol.

3.2 Experiment 2: VOCs selection test

The tested VOCs were selected according to a scan test of the headspace from the feeding material of maize silage performed by the PTR-MS, as shown in Figure 3. Due to the fragmentation of ethanol in the PTR-MS measurement (around 10%) (Inomata and Tanimoto, 2009), the concentration corresponding to mass 47 was corrected based on direct calibration under the assumption that mass 47 is solely due to ethanol. The highest peaks of the scan were at masses (m/z): 47, 33, 45, 61, 43, 73, 59, 75, 57 and 41. From the VOCs typically found in the highest concentrations in barns and feeding material (Shaw et al., 2007; Chung et al., 2009; Howard et al., 2010; Malkina et al., 2011; Hafner et al., 2013) and the scan results, a list of VOCs were selected. The following VOCs were selected for the interference tests of non-targeted VOC on ammonia measurement by the PAS: ethanol, methanol, acetaldehyde, acetic acid, 2-butanone, acetone, 1-propanol and 1-butanol. Compounds such as ethanol, methanol, acetic acid and 1-propanol are typically measured in cattle barns and feeding materials in high concentrations (Shaw et al., 2007; Ngwabie et al., 2008; Howard et al., 2010; Hafner et al., 2013).

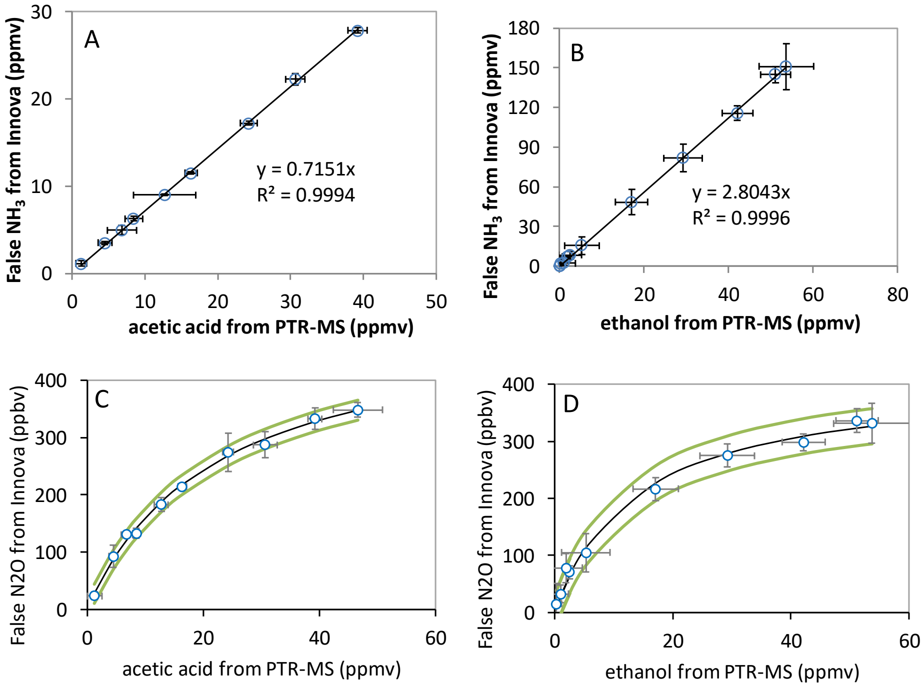

Figure 4. Examples for the interference calibration from non-targeted VOC on NH_3 (A & B) and N_2O (C & D) measured by the PAS. The VOC concentration on the horizontal axis was measured by the PTR-MS, while the NH_3 and N_2O concentrations on vertical axis were from false signals measured meanwhile by the PAS. A: The interference calibration for acetic acid on NH_3; B: The interference calibration for ethanol (corrected for fragments through calibration) on NH_3; C: The interference calibration for ethanol (corrected for fragments through calibration) on N_2O; D: The interference calibration for acetic acid on N_2O. In C & D, the red line indicated the fit curve by equation $y=kx/(x+m)$, and the green and purple curves indicated 95% confidence range. The plotted error bars represent the standard deviations for the measured VOC by the PTR-MS under a selected VOC level (x-axis) and for the measured NH_3/N_2O level by the PAS meanwhile (y-axis). Data were all background-subtracted and the linear fits were least square fits without error weighting.

3.3 Experiment 3: Laboratory test for empirical relationships

The interference of non-targeted VOC on ammonia measurement by the PAS was investigated using single VOC-containing air as inlet measured simultaneously by PAS, PTR-MS and CRDS, as shown in the setup in Figure 1. An example of the interference test can be seen in Figure S1, where acetic acid was measured simultaneously by the three instruments under various concentration levels. Concentration dependent interference was clear for acetic acid on PAS ammonia measurements.

Table 2. Obtained empirical relationships (slope) describing the functional dependence of the interference in the measurement of the target compound (e.g., NH3) by PAS on non-targeted VOC concentrations. The value in the brackets indicated the uncertainty (SD of the slope) of the linear fit, except for N_2O where correlation coefficient is shown. N is the number of VOC concentration levels tested for determination of empirical relationships. Nonlinear fit was given for N2O, where 'x' is measured VOC concentration and 'y' is the false concentration measured by PAS. The concentration range covered for the tested VOC is as follows: ethanol (7 ppbv-58 ppmv); methanol (5 ppbv-45 ppmv); acetic acid (3 ppbv - 48 ppmv); acetaldehyde (8 ppbv-38 ppmv); 2-butanone (3 ppbv - 60 ppmv); acetone (4 ppbv - 48 ppmv); 1-propanol (5 ppbv - 55 ppmv); 1-butanol (6 ppbv - 52 ppmv).

Compound	N	NH_3	CH_4	N_2O (y: ppbv; x: ppmv)	CO_2	SF_6
ethanol	10	2.81(0.02)	1.88(0.01)	y=411x/(x+14) (0.93)	0.40(0.02)	-0.014(0.002)
methanol	9	3.29(0.72)	3.81(0.67)	y=99x/(x+9) (0.78)	0.45(0.17)	-0.15(0.02)
acetic acid	10	0.72x(0.01)	-3.14x(0.08)	y=514x/(x+22) (0.95)	0.39(0.03)	0.31(0.01)
acetaldehyde	4	(-)	-0.85(0.45)	y=317x/(x+31) (0.98)	(-)	0.044(0.021)
2-butanone	4	-0.13x(0.003)	-4.02(0.04)	y=311x/(x+26) (1.00)	-0.61(0.18)	0.23(0.005)
acetone	6	0.02(0.001)	2.10(0.13)	y=104x/(x+4) (0.99)	(-)	0.015(0.001)
1-propanol	5	2.41(0.21)	2.95(0.38)	y=3569x/(x+602) (1.00)	0.25(0.21)	-0.064(0.012)
1-butanol	7	2.66(0.05)	3.07(0.09)	y=807x/(x+73) (0.99)	(-)	-0.061(0.004)
methanol(N_2)	4	1.03(0.31)	1.46(0.22)	(-)	0.35(0.24)	-0.056(0.010)

In principle, establishing empirical correction factors for each specific compound could be used to minimize the interferences of VOCs on the target gas measurements on a specific instrument with the same filter specifications. This requires, however, that VOC concentrations be measured simultaneously by expensive analyzers such as PTR-MS and will in any case result in higher uncertainties due to accumulated uncertainties from multiple interference relationships. Figure 4A & B show two examples of the calibration lines for acetic acid and ethanol, from which an empirical relationship (ER) between the false ammonia concentration and the tested compound could be obtained (ER=0.72 for acetic acid and ER=2.8 for ethanol).

A linear response of the ammonia interference was observed for all the tested compounds and they had generally low SD for the slope the linear fits. The ER for ammonia interference by other tested VOCs can be found in Table 2, where ethanol, methanol, 1-propanol and 1-butanol give the highest false signals on ammonia measured by the PAS, with ER of 2.8, 3.3, 2.4 and 2.7, respectively. Due to the fact that these compounds are often found in cattle barns and feed silage even in the level of ppmv, especially for ethanol, methanol and 1-propanol (Rabaud et al., 2003; Ngwabie et al., 2008; Howard et al., 2010; Hafner et al., 2013), severe interference on ammonia measured by PAS therefore will occur. While acetic acid gave significant false signals on ammonia (ER=0.72), acetone only showed little interference on ammonia (ER=0.02). Meanwhile, negative false signals were observed for ammonia by 2-butanone (ER=-0.13). Interestingly, the empirical relationship for false ammonia by methanol in nitrogen matrix is significantly different from that by methanol presented in air matrix (ER=1.03 vs 3.29). This observation is possibly related to the relatively rapid vibrational energy transfer between the VOC and oxygen (Harren et al., 2000). While nitrogen has a vibrational frequency around 2360 cm^{-1}, oxygen has a vibrational frequency of 1554 cm^{-1} with only 170 collisions needed to transfer energy to the vibrational mode of O_2 (Lambert, 1977).

Besides the interferences on ammonia by the non-targeted VOCs, other target gases also showed various levels of interferences, as also indicated by previous studies (e.g., Zhao et al., 2012; Hassouna et al., 2013). Because target gases may have more overlap for the infrared spectrum, the primary interference on one target gas caused by the overlap with non-targeted VOCs could therefore influence and cause secondary interference on other target gases (Zhao et al., 2012; Adamsen, 2018). Still, in theory, empirical relationships could be obtained for the interfered gases by the tested VOCs. Specifically, for the interference on methane by non-targeted methanol, 1-butanol, 1-propanol, acetone and ethanol showed positive false signals (ER=3.8, 3.1, 3.0, 2.1, 1.9, respectively). 2-butanone, acetic acid and acetaldehyde showed negative false signals to methane, with ER equal to -4.02, -3.14 and -0.85, respectively. An explanation for the negative false signals could be that absorption takes place in the band for H_2O correction (Adamsen, 2018). All interferences on methane are shown in Table 2. For methanol in nitrogen, the calibration showed a significant difference compared to air (ER=1.46 vs. 3.81).

Meanwhile, the non-targeted VOC also caused false signals on nitrous oxide signals, with a much lower level of interference. Furthermore, the calibrations of the nitrous oxide interference by the non-targeted VOCs seemed not to be following linear relationships. For examples, Figure 4C & D showed the false signals of nitrous oxide caused by ethanol and acetic acid. A non-linear relationship exists between nitrous oxide interference and VOC concentration. The curves could be well fitted to the non-linear equation of $y = kx/(x+m)$, where k represents the maximum interference on nitrous oxide by the single VOC, m represents the half-saturation constant indicating the level higher at which the VOC concentration could cause half of the maximum interference on nitrous oxide. As shown in Table 2, all tested VOCs showed positive non-linear interference to the nitrous oxide signals, and 1-butanol showed the highest maximum interference on nitrous oxide. Interestingly, no interference was observed for nitrous oxide when methanol was presented in a nitrogen matrix, while a relatively lower level of interference by methanol was observed for nitrous oxide when presented in atmospheric air.

Furthermore, some of the tested VOCs also caused interference on carbon dioxide measured by the PAS. The background of carbon dioxide was considered as unchanged during the interference tests. While methanol, ethanol, acetic acid and 1-propanol caused positive false signals for carbon dioxide measured by the PAS (ER = 0.45, 0.40, 0.39, 0.25, respectively), 2-butanone caused negative false signals with ER = -0.61 (Table 2). Other tested VOCs, including acetone, acetaldehyde and 1-butanol, did not show interferences on carbon dioxide measured by the PAS. This is likely because no overlap of the gas infrared adsorption spectra exists between these VOCs and carbon dioxide. As expected, methanol in nitrogen also caused interference on carbon dioxide (ER =0.35) slightly lower than methanol in air.

Besides, SF_6 measurements were interfered by the tested non-targeted VOC, with lower empirical relationship obtained compared to NH_3, CH_4, N_2O and CO_2. Acetic acid and 2-butanone caused the highest interferences on SF_6, with ER of 0.31 and 0.23, respectively. Other tested VOCs caused significantly less interference on SF_6, among which methanol gave the highest negative ER of -0.15. Again, the methanol in nitrogen gave a significantly lower level of interference on SF_6 compared to methanol in air (ER = -0.056 vs -0.15).

Overall, the tested non-target VOCs in this study caused significant interference on target gases, of which ammonia and methane were influenced to the largest degree. Even though less interference was observed for nitrous oxide, this could still cause problems due to the typically low concentration level of this compound in e.g. livestock facilities or soil (Iqbal et al., 2013; Rong et al., 2014).

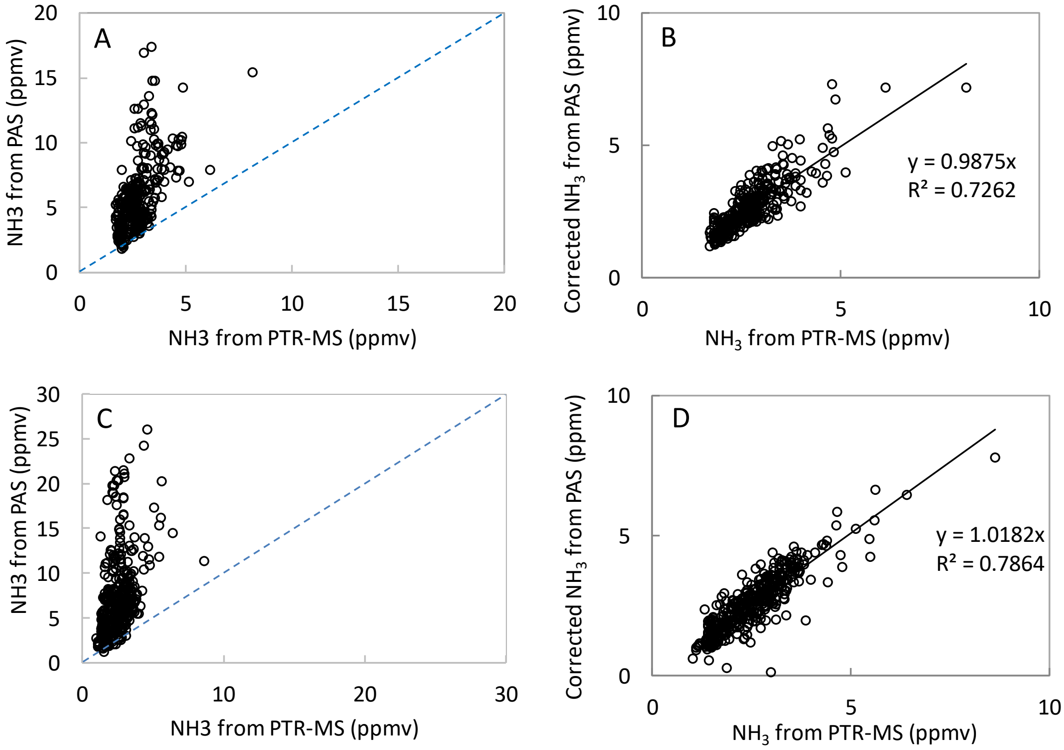

Figure 5. NH_3 concentrations measured by the PAS (vertical axis) and by the PTR-MS (horizontal axis) in the field measurement from Location One before the correction by the tested non-targeted VOCs (A) and after the correction by the tested non-targeted VOCs (B), and from Location Two before the correction by the tested non-targeted VOCs (C) and after the correction by the tested non-targeted VOCs (D). Data from B and D were background corrected and the linear fits were least square fits without error weighting.

3.4 Experiment 4: Field test for validation of empirical relationships

During the field test in the dairy barn, the ammonia measurements by PAS and PTR-MS were compared to each other for one location in the pit and two locations (Location One and Location Two) in the barn. Figure S2 shows ammonia concentration measured by PAS and PTR-MS at the pit ventilation. In the pit ventilation, low concentrations of VOCs were generally obtained and relatively high concentrations of ammonia were observed for both instruments. Thus, no significant interferences were observed for ammonia measured by the PAS, and ammonia measurements by PAS and PTR-MS showed a good agreement as shown in Figure S2. However, for the two measurement points inside the barn, significantly higher ammonia concentrations were obtained from PAS compared to the concentrations measured by PTR-MS (Figure 5 A & C). Table S2 showed the percentage for each range of ratio of PAS/PTR-MS concentrations for the data shown in Figure 5 A & C, where ratio of PAS/PTR-MS concentrations mostly within 1-4. The higher ammonia concentration observed for the PAS measurement is ascribed to interferences from VOCs, some of which had high concentrations, especially for ethanol as shown in Table 3. The relation between the ammonia concentrations measured by PAS and the ethanol concentrations measured by PTR-MS were highly correlated for both measurement locations, with slopes close to 3 (3.0 and 3.1; see Figure S3). These two numbers are generally close to the empirical relationship obtained for ethanol (ER = 2.8). The empirical relationships obtained in 'Experiment 3' were used for data correction of ammonia measurement by PAS since the instrument configurations were kept the same. Thus, the interference of the VOCs on ammonia measurement by PAS could be estimated from the empirical relationships obtained in 'Experiment 3' and used to correct the ammonia data. Figure 5B & D show the corrected ammonia concentrations measured by PAS by using the empirical relationships, together with the measured ammonia concentration by the PTR-MS for both measurement locations. The corrected ammonia concentrations from the PAS are generally in good agreement with the ammonia concentration measured by the PTR-MS, with slopes close to 1 (0.99 and 1.02). It should be noted that although the empirical relationships were obtained for single VOC interferences on ammonia measurement by PAS, they were treated as being additive under field conditions where multiple VOCs presented. Ethanol dominated the VOC composition in general, but other types of VOC also contribute significantly. The average ratio of ethanol concentration to the sum of the 8 VOCs (tested in the lab with obtained empirical relationships) was 0.64 (±0.11) for Location Two in the field study. This single application suggests that the interference is close to additive, but further investigation is needed to confirm this finding. The cattle barn experiment validated that correction from major VOCs is necessary for reliable PAS measurements. In principle, it is possible to estimate the interference on NH3 measured by PAS measurements in field applications. However, it should be noted that a lot of redundant work is needed to make this correction if only NH_3 concentration is measured since the concentrations of several VOCs need to be known to achieve a proper correction.

Table 3. Average concentrations (±standard deviation) of selected VOCs during the field test in the dairy cattle barn for the two sampling locations 1 & 2, both of which are located inside the barn. The standard deviation apply to the mean values.

Compound	Concentrations (ppbv)	
	Location 1	Location 2
ethanol	1421±946	1622±1355
methanol	237±150	241±192
acetic acid	57±41	69±62
acetaldehyde	99±81	92±84
2-butanone	19±11	17±13
acetone	78±30	52±25
1-propanol	71±45	72±68
1-butanol	22±10	16±12
hydrogen sulfide	12±10	11±8
trimethylamine	8.6±3.5	5.7±3.1
dimethyl sulfide	15±9	14±10
4-methylphenol	5.2±2.1	3.8±2.2

4 Conclusions

When measuring NH_3 and greenhouse gas emissions (CH_4, N_2O and CO_2) by PAS, non-target VOCs may interfere significantly with the target gases causing inaccurate results. To confirm and determine the magnitude of interferences, experiments have been conducted by simultaneously using a PAS and a PTR-MS. Results from these experiments provide useful guidelines concerning interferences caused by non-targeted VOCs. The results demonstrate that ethanol, methanol, 1-butanol, 1-propanol and acetic acid are causing the most significant interferences on NH_3 measured by PAS. A field test in a cattle barn validated the interference caused by VOCs on NH_3 measurement by PAS by simultaneously measuring VOCs with PTR-MS.

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

Supplement. The supplementary information is available free of charge at DOI: .

Author contributions. DL, LR and AF designed the setup for the experiments performed; LR, JK and AC contributed to setting up and conducting experiments and acquiring data; DL, AF, JK, XK and APA contributed to writing the manuscript, data interpretation and data analysis; LR, AF and JK assisted in data analysis and manuscript editing.

Competing interests. The authors declare that they have no conflicts of interest.

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