

Review of the manuscript "Photoacoustic measurement may significantly overestimate NH₃ emissions from cattle houses due to VOC interferences" by Liu et al. (amt-2018-412)

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 manuscript 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.

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 non-dispersive 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 addressed by the authors, but a more detailed discussion is needed.

(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!

(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.

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 bandwidth 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 ...".

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-monitoring-instruments/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.
2. Line 28 - 37. Be more quantitative and specific! What were the concentration levels of ammonia and VOCs which were studied in this work? What 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)?
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?
4. Line 55 - 56. Which methods were compared? What was the reason for the 30% discrepancies?

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 bandwidth, 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?
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?
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.
8. Line 130. It is not clear, what was tested. Calibration procedure? PTR-MS instrument? How was the PTR-MS calibrated?
9. Line 148. It is not clear, what was tested. See Comment 8.
10. Line 162 - 171. See Comments 5 and 6.
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-monitoring-instruments/photoacoustic-spectroscopy-pas/photoacoustic-gas-monitor-innova-1512/photoacoustic-gas-monitor-innova-1512.html>]
12. Line 168 - 171. Have you checked the validity of the cross compensation of interferences from target gases or do you rely on the specifications given by the supplier of the instrument?
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?
14. Line 191 - 207. The purpose of the experimental setup (Figure 1) is not entirely clear. Was it 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 the case, how was the PTR-MS calibrated for the selected VOCs?
15. Line 206 - 207. The selected components (methanol, ethanol etc.) should be mentioned with reference to Section 3.2.
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?
17. Line 221 - 224. What is the meaning and function of "excess flow". The excess flow should be indicated in Figure 1.
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?
19. Line 244. Which "selected VOCs" and "odorants" were measured? The term "odorant" should be defined.

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

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?

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"
3. Line 41 - 42. Ammonia causes 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 ...".
5. Line 69. Change to "Usually, water vapor is also measured in order ..."
6. Line 73. Change to "absorption of infrared light"
7. Line 80. There is a word missing in "interference of has not been well studied..."
8. Line 81. "Mathot et al., 2007" is missing in the Reference section.
9. Line 118-199: Change to "were used to measure trace gas concentrations in air".
10. Line 125 - 127. The sentence is not clear and should be rephrased.
11. Line 141. Either "acceleration of the ring down " or "reduction of ring down time ".
12. Line 143. "Normal" ring down time needs to be 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".
14. Line 180. Delete "for the calibration test".
15. Line 181. The desired concentration range should be specified.
16. Line 197. Which kind of plastic material was used for the container? Was it emission free?
17. Line 254. A reference for "Standard conditions as described previously ..." should be provided.
18. Line 293. Change to "in which the slope of the fitted line ($k = 0.96 \pm ?$) ..."
19. Line 304. "90% decay time" needs to be defined.
20. Line 380. Change to "...VOC concentrations be measured simultaneously by other instruments".
21. Line 382. The term "correction factor" should be defined.
22. Figure 1. The exhaust line should be 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."
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.
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.
26. Figure S1. Concentrations should be given in ppmv.
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?
29. Table 1. Units should be ppmv (to be consistent with text and figures).

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., NH_3) on VOC concentrations.
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.
32. Table S1. "Filter center" should be changed to "Center wavelength". What is the meaning of "Band width (%)" ? Is it related to "Filter bandpass"?