

## ***Interactive comment on “Photoacoustic measurement may significantly overestimate NH<sub>3</sub> emissions from cattle houses due to VOC interferences” by Dezhao Liu et al.***

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

General comments This manuscript describes experiments investigating VOC interference during NH<sub>3</sub> measurements using PAS in cattle barn emissions. The novelty is the analysis of VOC interference. PTR-MS measurements 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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the emission measurements. In the discussion attention could be paid to the possible 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 interference 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.

Detailed comments 190. her CRDS is introduced without any further explanation. In line 96 “two PAS instruments . . .” are mentioned. This 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 headspace in the silage box was analysed by PTR-MS therefore a flow of 75 ml/min was withdrawn. Was here any balance gas introduced into the box 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 explanation 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 CH<sub>4</sub>, N<sub>2</sub>O and CO<sub>2</sub>, which is now specified in the revised manuscript. Please see Line 518-519 in the revised manuscript.

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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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