Response to reviewer #1

Comments from the reviewer are marked as **bold**, author responses are marked as red, the changes in the manuscript are marked as *red italic.*

The authors thank the reviewer for taking their time to review this manuscript and the provided valuable feedback. We hope that we have addressed the mentioned issues to their satisfaction.

Overall, the paper is an interesting report on a short measurement campaign at a measurement station with the aim of demonstrating that photoacoustics with clever evaluation algorithms can indeed be a sensitive and cost-effective alternative to expensive established analysers.

The paper, however, gives the impression that it seems somewhat pieced together. This is noticeable, for example, in acronyms that were not introduced in time or the justification why the sample gas for the PA sensor has to be humidified.

The task for the authors are, from my perspective:

- Make the text more consistent overall, explain acronyms and special terms briefly, even when referring to corresponding papers, so that the reader gets all the important information without having to jump to other papers first.

Please see the revised manuscript.

- Please take into account the comments that I have included in the attached supplement (pdf).

Please see the following points (1) – (16)

- Please use the typical format defined by copernicus.org for literature references.

We are not sure what the reviewer referring to. In our opinion the citation style is consistent with the journal format.

Response to the comments in the submitted manuscript:

1. Original manuscript (title): “Ambient methane monitoring at Hohenpeißenberg utilizing photoacoustic spectroscopy and cavity ring down spectroscopy”

-Reviewer:**Think about adding 'in comparison' or similar, the methods used are not complementary but alternative**

We changed the title of the manuscript to *“Comparison of photoacoustic spectroscopy and cavity ring down spectroscopy for ambient methane monitoring at Hohenpeißenberg”*

2. Original manuscript (line 7-8): “... PA devices are often susceptible to cross-sensitivities related to environmental influences.”

-Reviewer**: environmental influences like vibration? Are the measured gas probes preconditioned? What you want to say, depending on probe technique?**

No, the gas probes are not preconditioned in any way.

We changed “However, PA devices are often susceptible to cross-sensitivities related to environmental influences. The obtained results show that relaxation effects due to fluctuating environmental conditions, e.g. ambient humidity, are a non-negligible factor in PA sensor systems” to

"However, PA devices are often susceptible to cross-sensitivities related to fluctuating environmental conditions, e.g. ambient humidity. The obtained results show that for PA sensor systems non-radiative relaxation effects induced by varying humidity are a non-negligible factor."

3. Original manuscript (line 31): **"**As an alternative to elaborate measurements in cities, low-cost devices with suitable CH4 resolution (< 200 ppbV) could be installed at multiple locations and combined to a sensor network…**"**

– Reviewer: could be more explained and motivated.

In order to elaborate this point we added: *"*As an alternative to elaborate measurements in cities, low-cost devices with suitable CH_4 resolution (< 200 ppbV) could be installed at multiple locations and combined to a sensor network, which allows *continuous* remote leakage detection *or emission monitoring*."

4. Original manuscript (line 50): **"**The emitted optical power of the light source is designated as P_0 .**"**

– Reviewer: this is the netto incoming power of light source into the designated gas matrix.

The reviewer is right, we changed this in the revised version.

5. Original manuscript (line 51): **"**This quantity depends on the efficiency of the individual energy transitions involved in the relaxation process …**"**

– Reviewer: of all involved energy transitions of the mixture of individual gas components

The reviewer is right, we changed this in the revised version.

– Reviewer: maybe an abstract scheme could make the explanation more transparent ...

We added the applied non-radiative relaxational cascade in the *appendix (Figure A1).* Furthermore we added a short theoretical chapter dealing with the issue of non-radiative relaxation and CoNRad in the revised manuscript *(see chapter 2).*

6. Original manuscript (line 64): "The LoD of the sensor used in this work was determined…"

-Reviewer: **please introduce shortly or refer to chapter 2.1 at least**

We added *"The photoacoustic sensor used in this work provides a limit of detection of 6.8 ppbV and will be briefly introduced in chapter 3.1 (for a detailed description see Pangerl et al. (2022)).*"

7. Original manuscript (line 66): "This decrease in optical power can be attributed to deterioration processes of the light source."

-Reviewer: **is not relevant here for the rough overview given here, especially since the statement is not specific enough**

We deleted this sentence.

8. Original manuscript (line 69): "Without including the algorithm CoNRad for data evaluation …"

-Reviewer: **please introduce shortly in order to make the paper fully consistent**

We added an additional theory *chapter 2,* which briefly introduces the relaxational issue as well as the functionality of CoNRad.

9. Reviewer (Figure 1): **introduce DWD, where?**

The reviewer is right, we now introduced the abbreviation of the German Weather Service (DWD) .

10. Original manuscript (line 105): “During the measurement campaign, the target gas was used a total of seven times for 30 minutes per interval to avoid and detect potential sensor drifts.”

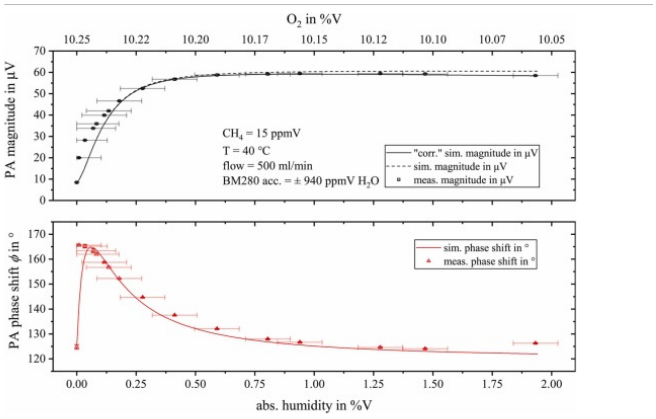
-Reviewer: **seven times for 30 minutes - how long was the interval?**

Over the whole measurement period the two systems were calibrated a total of seven times, each time for 30 minutes.

11. Original manuscript (line 106): “In order to enhance the humidity during target gas operation and thus increase the generated PA signal”

-Reviewer: **was the humidifier always in operation, also for the stream of ambient air? If not, how it was switched on and of, complete the picture please or place a comment**

The humidifier was always in operation. The simulation output of CoNRad for slightly humidified “air-like” gas samples (H2O < 0.25 %V) shows lower confidence in simulation output compared to the measured data, refer to Figure 11 – *(*https://doi.org/10.1016/j.pacs.2022.100371*).*



Download : Download high-res image (230KB)

Download : Download full-size image

Fig. 11. Measured photoacoustic magnitude (black squares, upper graph) and phase shift ϕ (red triangles, lower graph) for 15 ppmV methane diluted in a nitrogen, oxygen mixture with rising humidity content. The calculation results obtained from CoNRad are represent by solid lines.

To avoid this problem we additionally humidified the gas sample by about 0.3%V.

To make this point clearer we rephrased*: “*In order to enhance the humidity during target gas operation and thus increase the generated PA signal by minimizing the influence of relaxation effects a self-developed humidity generator was installed upstream of the PA sensor (Müller et al., 2022).” *to “As the difference between the theoretical calculations of CoNRad and the measured data is highest for only slightly humidified measuring environments (H2O < 0.25 %V), see Figure 11 from Müller et al. (2022), an additional humidification of the sample gases of about 0.3 %V was chosen to avoid this issue. This was realized by a humidity generator installed up-stream of the PA sensor.”*

12. (line 120) Reviewer: **could you say something about measuring mode of the G2301 analyzer? How are the data collected?**

The sample rate of the G2301 was 0.2 Hz, the averaging time was 5 s.

We added this in chapter 3.2.: *"*As shown in Figure 2 the G2301*, operated with a data acquisition rate of 0.2 Hz and an averaging time of 5 s,* was installed in the gas setup parallel to the PA sensor, *…"*

13. Original manuscript (line 122): "It is obvious, that the CH_4 concentration characteristics monitored with both devices agree quite well with each other"

-Reviewer: **is the correction via CoNRad active already?**

Yes, CoNRad, as well as further smaller signal corrections were applied for the mentioned data. For clarity we added in chapter 3.2. *"According to equation (2) the raw photoacoustic signal was corrected for variations in* ε_{relax}*,* γ*, Q,* f_{res} *and* P_0*."*

And in chapter 4*: "*Figure 3 illustrates the CH4 readings in ppbV (a) *obtained* by the PA sensor, *including the previously mentioned signal corrections* (black) and the G2301 data (red), respectively.*"*

14. (line 129) Reviewer: **0.5 %V the question is, do you need this artificial offset of humidity really, especially when your correction algorithm is activated? The algorithm works fine between 0.3 an 0.8 %V isn't it?**

    See point 11.

    Yes, CoNRad works fine in the humidity range between 0.3 and 0.8 %V. Additional humidification is not mandatory, but as for lower humidities, i.e. less than 0.25 %V the prediction of CoNRad shows greater deviations from the measurement, which would be too large for environmental monitoring of methane.

15. Original manuscript (line 142): "The raw values, however, are not normally distributed and show a substantially higher variance."

-Reviewer: **any idea where the neg. peaks or blibs are coming from?**

The red line in figure 4 shows the raw PA data without compensation. The negative peaks correspond to the calibration measurements for which the deviation between G2301 and the PA sensor output is minimal.

16. Original manuscript (line 156): "For complex in highly fluctuating environments, i.e. ambient air,…"

-Reviewer: **this expression is not really accurate, does it refer to the ambient conditions of the sensor, the number of gas components (should remain constant in ambient air) or the strong fluctuation of concentrations in the gas mixture ? ...**

We wanted to refer to the natural humidity variations. We rephrased: *"For measurement applications with varying gas composition, e.g. fluctuating ambient humidity, PA devices essentially require the implementation of algorithmic models, such as CoNRad, in order to compensate for signal losses due to delayed relaxation that otherwise might cause significant errors in PA sensor data. The combination of CoNRad to simulate the non-radiative relaxational cascade and ARMS for real-time monitoring of Q and* f_{res}*, allows for reliable analyte concentration readings with photoacoustic sensors."*