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*).*

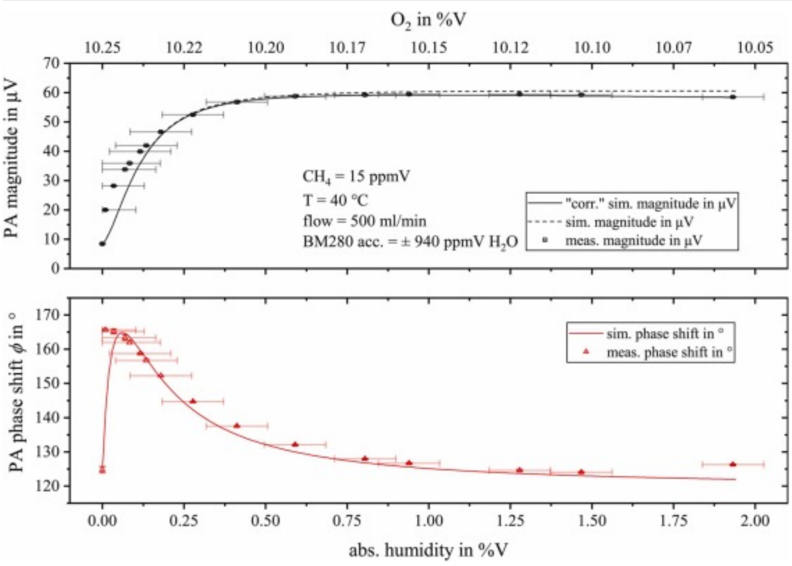

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Fig. 11. Measured photoacoustic magnitude (black squares, upper graph) and phase shift ϕ (red triangles, lower graph) for 15 ppmV methane diluted in a nitrogen, oxygen mixture with rising humidity content. The calculation results obtained from CoNRad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

Response to reviewer #2

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 following issues to their satisfaction.

In the presented manuscript data of ambient trace methane measurements made with a photoacoustic spectrometer over period of several days at the site of a meteorological observatory is described. Applying previously published methods for photoacoustic signal correction, determined concentration levels are quantitatively compared to a high-end cavity ringdown reference instrument, showing agreement within +-100 ppbv over the whole measurement period.

1. **General Comments & Impression**

The overall impression of the manuscript is good to fair. While the comparison of a photoacoustic instrument to a cavity ring down instrument with comparable accuracy at trace levels over an extended period of time is well worth publishing, the manuscript may benefit from including some information about the applied signal corrections as well as some more details about the measurement location.

We added chapter 2 to discuss the effect non-radiative relaxation on the photoacoustic signal, as well as the functionality of the compensation algorithm CoNRad. In *chapter 3.1*. we additionally added information about signal corrections, which are not linked to the relaxational characteristic and provided the equation for signal compensation (*equation 2*).

Regarding the measurement location we added*: "The mountain Hohenpeißenberg (47.48◦ N, 11.01◦ E) is located southwest of Munich at around 985 meters above sea level." in the introduction.*

Also, proper initial introduction of the main correction algorithm (CoNRad) with references, and shortening the general discussion about photoacoustic spectroscopy and the introductory limit of detection discussion, would help conveying the key points in the manuscript.

CoNRad is now introduced in more detail in *chapter 2*.

We shortened the discussion about the reported photoacoustic methane sensors in literature to "*Regarding photoacoustic methane detection recent literature provides several publications reporting ppbV - level limit of detection using infrared laser sources (Elefante et al. (2019); Elefante et al. (2020); Giglio et al. (2020); Gong et al. (2021); Li et al. (2022); Xiao et al. (2022)*"

In the general discussion about photoacoustic spectroscopy we deleted unnecessary sentences.

I. **Specific Comments & Questions**

Reviewer: **Line 16 & 19: Initially, the targeted accuracy of 2 ppbv is mentioned. After that, the 3 sigma precision of the cavity ringdown instrument is quoted, without going into detail about the device accuracy. What is the long-term stability/accuracy of the CRDS device and is the device calibration traceable to some standard?**

We added two columns in *Table 1*, which include the CH_4 readings of the CRDS devices over the measurement period. From this information the long-term stability, as well as the accuracy can be obtained.

The reference gas tank was filled and calibrated by the ICOS Flask and Calibration Laboratory (FCL)(https://www.icos-cal.eu/fcl) and is linked to the WMO X2004A scale. We added a sentence to the manuscript.

- **Line 17: What is the targeted measurement rated or maximum averaging time for the specified 2 ppbv accuracy?**

According to (https://doi.org/10.18160/GK28-2188), which specifies the requirements for the measurement devices, used in the ICOS program, no specification concerning the averaging time is given.

- **Line 69: This is the first mentioning of the algorithm CoNRad and without any reference or detailed explanation, making the reader wonder about the significance of this method to the presented manuscript.**

The reviewer is right, as mentioned in one of the previous points we added *chapter 2* to discuss the effect non-radiative relaxation on the photoacoustic signal, as well as the functionality of the compensation algorithm CoNRad.

- **Line 75: The authors mention "ppbV-level-precise GHG monitoring", while accuracy may be more relevant.**

We added*: "In the time period investigated, the PA sensor does not show any trends in sensitivity (see Table 1), however, it is evident that it is advisable to calibrate the PA sensor frequently in order to maintain the accuracy of the sensor. The G2301, on the other hand, does not show any significant fluctuations in its methane calibration values."*

- **Line 84 to 94: The general discussion about excitational relaxation losses for methane in ambient air is misplaced in the section about the photoacoustic sensor and should be moved to the introduction or included in a theoretical section.**

We moved the non-radiative relaxational discussion to the added *chapter 2*.

- **Line 103: What are the uncertainties of the concentrations in the reference gas cylinder? What is the specific reason for including 312 ppmv CO2 in the reference gas? Please specify the volume fractions for the components of "dry natural air".**

The reference gas tank was calibrated by the Flask and Calibration Laboratory and provides an uncertainty for methane of 0.5 ppbV. Regarding other components of the reference gas, this mixture is not synthetic air, but natural air. Meaning, that the reference gas mimics natural/ambient air the best way possible, containing mainly N_2 and O_2, but also of noble gases and several trace gases.

We added in chapter 3.2. *"Dry natural air was chosen as the reference gas, which consists mostly of N_2 and O_2 but also includes noble gases as well as trace gases (CH_4, CO_2, N_2O, CO). The reference gas tank was filled and calibrated by the ICOS Flask and Calibration Laboratory (FCL) and is linked to the WMO X2004A scale, which provides 2020 ppbV CH_4 with an uncertainty below 0.5 ppbV (Jordan and Schumacher, 2022)"*

Line 105: How were the seven reference gas measurements used to "avoid" sensor drifts? What were the differences in measured and true reference gas concentrations? (quantitatively) How high was the deviation of the measured concentration of the reference CRDS instrument to the concentration of the reference gas? This information would be beneficial also in Table 1.

The PA sensor was recalibrated each time. We added the CRDS calibration values in *Table 1*.

- **Line 135: What processing and corrections have been applied to the "raw PA data"?**

The "raw PA data" was compensated for relaxational effects (using CoNRad) and for changes in the Q-factor and f_{res} (using the ARMS). The adiabatic exponent γ, as well as the optical power after the PA measurement cell were also considered. Compared to the relaxational effects the other parameter had no significant impact as they remained nearly constant.

We added more information about the signal correction in *chapter 2* and *3.1.,* as well as *equation (2).*

- **Line 138: Does CoNRad only compensate for the efficiency of non-radiative excitational relaxation? What other effects have been compensated for?**

Please see comments above.

1. **Technical Comments & Suggestions**

- **Line 8: As relaxational effects and relaxation time constants in photoacoustic spectroscopy and spectroscopy in general are manifold (hydrodynamic, excited state, etc.), I would suggest specifying the type of relaxation more precisely whenever possible.**

The reviewer is right. We rephrased *to "non-radiative relaxation".*

- **Line 16: Is there a reference publication for the specific CH4 instrument requirements agreed upon by ICOS?**

Yes, it was now included (https://doi.org/10.18160/GK28-2188).

- **Line 23 & 25: The statements about methane concentrations "by up to 2.7 ppmv" and "by about 40 ppmv" are incompatible**.

The reviewer is right, we rephrased "*In 2021 Defratyka et al. installed a cavity ring down system (G2201-i, Picarro, Inc., USA) on a car and identified several methane sources in Paris which increased the CH_4 concentration up to 2.7 parts per million (ppmV, 10^{-6}) (Defratyka et al., 2021)."* And deleted ~~"The highest emission as assigned to a ventilation grid, which increased the CH_4 concentration by about 40 ppmV."~~

- **Line 43: The cited equation (1) should describe the *sound pressure amplitude* for harmonic excitation.**

We changed this in the revised manuscript.

- **Line 48: Is N_i really the volume ratio or is it the volume fraction?**

The reviewer is right. This was a mistake by us. We meant the volume fraction. This was now changed in the manuscript.

- **Line 49: Is P_0 really the optical power or is it the optical power amplitude of the modulated light source?**

For the applied WM modulation of the laser P_0 is the optical power inside the measurement cell. We rewrote: "*The optical power of the light source inside the photoacoustic measurement cell is designated as P_0*"

- **Caption of Figure 1: Abbreviation "DWD" is not defined**.

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

- **Line 103: Perhaps the term "reference gas" is less confusing than the term "target gas".**

We changed *"target gas"* to *"reference gas"*

- **Line 108: Only white noise is mentioned. Is the argument deliberately limited to white noise?**

As the PA sensor measured every 10 minutes for only 1 minute (3 single point measurements each 20s long), the dominant noise on the signal is white noise. This could be confirmed by an Allan deviation analysis since other types of noise become relevant only at longer measurement intervals. Therefore only white noise was mentioned.