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.