

Responses to individual reviewer comments (black text) are given below, in red text.

The manuscript entitled “Measuring acetylene with a cavity ring-down spectroscopy gas analyser and its use as a tracer to quantify methane emissions” by Shah et al. highlights the necessity of careful calibration when apply a commercial instrument measuring acetylene in quantifying methane emission flux. It provides valuable insight on the uncertainty of methane emission flux estimation which could be easily overlooked. The manuscript is well organized and presents instructive information on the experimental setup. I think it well fits the scope of AMT journal and recommend the publication after minor revision. The following comments shall be considered during the revision.

We thank the reviewer for taking the time to thoroughly review this manuscript and for their useful comments. We thank the reviewer for spotting some key details, due to their meticulous review of our work. We address their individual comments below.

Compared to the major message (i.e., systematic bias can originate from uncaredful calibration of the PICARRO instrument) the authors want to deliver, some detailed description on the experiment seems redundant in the main text. For example, discussion on the Allan variance obtained from zero air measurement, description on safety control of C<sub>2</sub>H<sub>2</sub> release, etc.. I suggest the authors move those parts which are not directly relevant on the major message to Supplementary Materials, and revise the manuscript in a more concise way.

This is a useful suggestion. We have now moved details on the Allan variance test conducted at [C<sub>2</sub>H<sub>2</sub>] a 0 ppb to the supplementary material, as it has little direct relevance for the rest of the manuscript. We have also moved information on the safety exclusion zone to the supplement. However, we have maintained some details on the acetylene release equipment as it adds value to the completeness of the manuscript, though we have made efforts to further reduce the size of this section by making the text more concise.

The PICARRO G2303 instrument used in this study showed 6% bias of measured C<sub>2</sub>H<sub>2</sub> concentration. This results in on average 7.6% bias in estimating CH<sub>4</sub> emission. It is well known that the sensitivity of optical instrument could drift with time. Therefore, the 6% bias could be largely instrument dependent. I suggest the authors specify this point. Moreover, the authors applied a complicated dilution system for their calibration. Detailed correction for the bias introduced by dilution is thus needed. The authors have described the reason of using high concentration C<sub>2</sub>H<sub>2</sub>. Does it mean that the calibration of PICARRO G2303 shall all following the same way?

The reviewer is totally correct to highlight that the 0.94 gain factor is specific to the Picarro G2203 instrument tested in this study. Calibration coefficients may vary for a different instrument used in a different study. We now emphasise this point in Section 2, when discussing the acetylene calibration fit. We also include this point more explicitly at the end of Section 4.2, when discussing the implications of using raw mole fraction measurements on calculated flux bias.

Regarding the topic of sensor drift, cavity ring-down spectroscopy is typically one of the most stable mole fraction techniques for measuring greenhouse gases. Previous studies on methane and carbon dioxide mole fraction have shown minimal changes in calibration factors over prolonged time periods. Based on this, we assume that calibration factors for [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements can also remain valid over prolonged periods, in the context of [C<sub>2</sub>H<sub>2</sub>]

enhancements expected during sampling downwind of an acetylene release. Unfortunately, the long-term stability of  $[\text{C}_2\text{H}_2]_r$  measurements has never been evaluated (to our knowledge), which would be an interesting subject of future research. This point has now been included in Section 2.4, where the calibration coefficients are presented. Some further discussion has also been added in Section 4.2.

Our dilution approach eliminates the effects of biases in MFC flow rates due to the use of  $C_{\text{MFC}}$  factors, which correct  $[\text{C}_2\text{H}_2]_t$  to obtain reference  $[\text{C}_2\text{H}_2]$  levels. These  $C_{\text{MFC}}$  factors were derived by comparing  $[\text{CH}_4]_t$  to accurate  $[\text{CH}_4]$  measurements made by the Picarro G2401 reference gas analyser. This dilution method is incredibly stable and does not drift over time as repeating the same dilution procedure three times, with gaps of 5.75 hours, resulted in average  $[\text{CH}_4]$  values with a standard deviation variability of  $(\pm 2 \pm 1)$  ppb, as previously presented in the manuscript. However, it is possible there is an overall uncertainty associated with  $[\text{C}_2\text{H}_2]_r$  calibration, as  $[\text{C}_2\text{H}_2]_t$  and  $[\text{CH}_4]_t$  rely on declared calibration cylinder mole fractions, with uncertainty ranges of  $\pm 3\%$  and  $\pm 0.5\%$ , respectively. The influence of this is now investigated in Section S5 in the Supplement, by deriving calibration coefficients by propagating uncertainties from the extremities of the calibration cylinder mole fraction uncertainty ranges.

Line 169: Why applying such a measurement cycle?

This measurement cycle was not applied, but was beyond our control. The Picarro G2203 automatically provided measurements following this cycle. The possible reason for this is that the Picarro G2203 acquires a full acetylene absorbance spectrum to characterise baseline absorbance and then obtains a shorter reduced spectrum around the acetylene peak maximum. We have now clarified this point in the manuscript.

Line 170: "... are defined as wet measurement". This is confusing since the field measurements were conducted in dry conditions.

This is an interesting point and we understand the potential confusion. The point being made here is that all such measurements are raw, with no water-correction applied. These measurements include the effect of water when water is present. We have now clarified this in the manuscript and replaced the word "wet" with "raw".

Line 245: There are biased between the red dots and the gray lines under dry conditions in panel (a). Is this caused by the error introduced during dilution? Better provide a short statement in the following paragraph.

The reviewer makes an interesting observation that when sampling dry gas blends,  $[\text{C}_2\text{H}_2]_t$  is consistently lower than  $[\text{C}_2\text{H}_2]_r$ . This is likely due to MFC offsets during dilution. However, this may also be related to the lack of calibration. As a calibration has not been conducted at this stage in the manuscript, we now present both options as possible causes of this disparity. Following the reviewer's recommendation, we now add a short discussion in the paragraph following this Figure 3. This is a very useful suggestion, as it now makes it clear that this analysis can only be used to compare empirical measurements.

Line 273: "6%". Should it be "6 ppb"?

We thank the reviewer for spotting this oversight, which we have now corrected.

Line 276: "[H2O]". Should it be "[C2H2]r"?

In fact, this refers to erroneous  $[\text{H}_2\text{O}]_r$  spikes and not  $[\text{C}_2\text{H}_2]_r$  spikes, measured by the Picarro G2203 gas analyser. To make this clearer, we have reorganised this sentence and now explicitly direct the reader to Figure 3 (b), where this phenomenon can be observed.

Line 291: What dose  $[\text{C}_2\text{H}_2]_t$  stand for?

This stands for “targeted acetylene mole fraction”, which is already defined at the start of Section 2.1. We hope that this previous definition is sufficient. In addition, we have now included the text “according to the MFC” in brackets in this location, to avoid confusion.

Line 432: “ppm” should be “ppb”.

Yes, this is correct. We thank the reviewer for spotting this.

Line 439: “shorter” should be “longer”.

We thank the reviewer from spotting this error.

Line 508: What is the placement height of the anemometer?

We were not able to make an accurate measurement of the anemometer height, as it dropped over time due to issues with the mast. However, we approximate a height above ground level of approximately 6 m. But in any case, this is irrelevant for flux computations using the tracer-based flux method.

Line 524: What is the sampling height? Would the height influence the large fluctuation showing in Figure 13?

Although we did not record the precise height above ground level of the air inlet during the campaign, we approximate this to be 2 m, based on the height of the vehicle.

The influence of sampling height on tracer-based methane flux variability is expected to be minimal, with the boundaries of the landfill site being approximately 300 m away from the sampling road. Sampling took place in a sufficiently flat area with no large hills or obstacles to cause topographical variation between the emission source and the point of measurement, allowing for a smooth view of the plume. However, it is true that the methane and acetylene plumes were offset as the acetylene release was not perfectly co-located with the landfill methane source, with methane emissions taking place unevenly over a large diffuse area. As a result, each gas may experience a slightly different transport path under different turbulent patterns between the point of emission and the point of measurement, leading to spatial or temporal separation in the plumes as they move downwind. Although near-surface turbulence could explain part of the variability shown in Figure 13, the turbulent conditions were approximately the same for the methane and acetylene plumes. Therefore, this variability is not exacerbated by sampling at 2 m above ground level, as opposed to sampling from some different sampling height.