

Dear Editor,

Following suggestions from the two co-authors, we have now modified the original manuscript, taking on board all suggestions. All changes to the manuscript are highlighted as track changes (see attachment). Please also find attached a point-by-point response to each reviewer comment.

Yours faithfully,

Adil Shah

# Response 1 to Reviewer 1

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

## Summary:

This is a more impactful paper than the current title implies (see specific comments below). The study describes sources of systematic error affecting methane flux estimation using the tracer dispersion method, with acetylene as the tracer. It considers water vapour and other sources of spectroscopic/retrieval error, but the true novelty in the paper is most captured by the potential flux error that arises from non-calibration of acetylene analysers when used as a proxy for CH<sub>4</sub>. While the study is specific to the Picarro C2H<sub>2</sub> analyser, the general need remains the same. The paper arrives at one flux bias number (7.6% - I think there's more to offer than this though), which is not insignificant in CH<sub>4</sub> emissions quantification methods. Calibration such as that described here is rarely used by those using tracer methods for survey work, but clearly should be.

We thank the reviewer for taking the time to review our manuscript and for their valuable comments, which have helped to make significant improvements to the manuscript.

The paper is an excellent fit to AMT and its readers. The paper has value to scientists and industry using Picarro (and other IR) analysers and those following methane emissions quantification methods and datasets. It is a well-presented, rigorous, and detailed study. While it is refreshing to see such a detailed, lengthy, and complete technical study such as this, some of the important conclusions of the paper get lost at present (see specific comments).

We are grateful to the reviewer for their confidence in our research. We appreciate the time the reviewer has taken to understand the fundamental outcomes of this research and its overall importance. We have made every effort to address their concerns. We agree that the emphasis of key outcomes could be improved, which we address through several modifications to the manuscript, as discussed in the responses below.

I wholeheartedly recommend publication, and the comments below are constructive in the hope that the potential of the study can be better realised. I also have some technical questions which may need to be addressed satisfactorily.

We thank the reviewer for their kind recommendation for publication. We hope we have addressed all of the reviewer's questions in the responses below.

## Specific comments

1. Title: When I first saw the title, I thought this paper was about the simple calibration of an analyser. It is a fair bit more than this. It is about how calibration of an instrument significantly affects flux calculations. I would recommend a better title to attract readers to this important fact. It would be good to be explicit in the title that this is about impact on accuracy of fluxes.

We fully agree with the viewpoint of the reviewer. We have renamed the article to "Accuracy of tracer-based methane flux quantification: underlying impact of calibrating acetylene measurements". We hope this now emphasises the implications of failing to calibrate tracer gas measurements on methane fluxes.

2. Introduction: I'm really not sure the historical discussion of the discovery of the greenhouse effect is needed (with very old references in places). It is not explicitly linked to the content of the paper. Also, CH<sub>4</sub> is the second-most important GHG according to the IPCC, after CO<sub>2</sub> (not the third) – please correct, or otherwise clarify. If you are referring to GWP rather than RF (or something else), please be clear. Line 42 cites Dlugokencky et al., 2011 – please use the most recent reference for this regular review from Dlugokencky).

The reviewer is correct to state that methane is the second-most important anthropogenic greenhouse gas, according to the IPCC. We now explicitly clarify that the original statement refers to greenhouse gases in terms of overall radiative forcing.

We have included a more recent reference to Schmidt *et al.* (2010) to reflect this. We thank the reviewer for this advice, to avoid ambiguity.

We recognise that some of the references are old. We have now added some more recent references to this introductory paragraph. For example, another citation to the latest IPCC report is made when discussing the effective radiative forcing of methane. In addition, we have now cited Saunio *et al.* (2024), which was not accepted for publication prior to submission of this manuscript. While we have included some of the latest publications to bring this section up to date, we would also prefer to maintain some older references to emphasise the prolonged nature of the issue of quantifying methane emissions. For example, in the same location as our citation to Dlugokencky *et al.* (2011), we also cited a more recent work from Lan *et al.* (2021), in the original manuscript. In this specific example there is a benefit to include references from different dates as this shows that uncertainties in the global methane budget has been a long and persistent problem. Hence, this fuels the motivation for the remainder of the manuscript.

Regarding the request to include the latest citation from Dlugokencky, it is not clear to us which specific work the reviewer is referring to here. We have already included the review from Lan *et al.* (2021). We have now included two additional review papers from the year 2019 and 2021 by Nisbet *et al.*, with Dlugokencky as a co-author in both articles. Perhaps, our citation to Saunio *et al.* (2024) can also satisfy this requirement, with Dlugokencky as a co-author in this work as well. We hope these are sufficiently recent citations to co-authored works by Dlugokencky, but we are unable to find a more recent paper by Dlugokencky as first author.

3. Line 100 – N<sub>2</sub>O has a lifetime >100 years (greater than CH<sub>4</sub>). The sentence here implies that use of N<sub>2</sub>O may be less problematic than CH<sub>4</sub> (calling N<sub>2</sub>O “finite lifetime”). All gases have a finite lifetime in any case. Please clarify and correct this misleading sentence.

The reviewer makes a very valid point here and we agree that this could be misleading. We have now provided the duration of the nitrous oxide lifetime in the text and removed the word “finite”.

4. Acetylene calibration: Ok.... So C<sub>2</sub>H<sub>2</sub> standards aren't readily available. I understand that. Instead, an empirical calibration of mass flow controllers was used to produce a diluted air matrix. To do this, certified CH<sub>4</sub> standards were used to define the dilution characteristics of specific mass flow controllers. This sounds ok, but I do have some questions. 1/ Was the same MFC tested repeatedly (e.g. on different days, after switching on and off etc), and were the results always consistent? If not, can you be confident that there was no drift in the MFC rates when switching between CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>? 2/ Can you be certain that there are no biases between these 2 gases in terms of the experimental setup, e.g. C<sub>2</sub>H<sub>2</sub> may be more sticky than CH<sub>4</sub> in sample lines – was flushing and equilibrium time used, or can you be sure there are no residual effects? 3/ When you take into account the precision of the CH<sub>4</sub> standard (i.e. how well known the concentration of the CH<sub>4</sub> reference cylinder is), how does that precision manifest as a percentage of the concentration of acetylene after dilution? And is that percentage similar to the gain factor calculated for C<sub>2</sub>H<sub>2</sub>? It would be worth including a discussion of this in the paper for completeness and the avoidance of doubt.

In response to the first concern, the behaviour of mass-flow controllers has indeed been observed to change with time, as stated in the manuscript. For this reason, absolutely no changes were made to any of the flow connections, except for swapping the methane calibration cylinder with the acetylene calibration cylinder. The mass-flow controllers were not powered off for the full duration of each calibration test (during both methane and acetylene enhancements). We now emphasise these points further in Section 2.4. We are confident that the mass-flow controllers did not drift during each calibration test as the same methane gas blend was sampled three times, with each blend sampled 5.75 hours apart. The average standard deviation between each of the three [CH<sub>4</sub>] averages measured by the Picarro G2401 was  $\pm 2$  ppb (see end of Section 2.3), with [CH<sub>4</sub>] reaching up to 12 ppm. Both methane and acetylene enhancements were measured within a 48-hour window as previously stated in Section 2.4, making it unlikely for any significant drift to occur during this period, considering the null drift observed over 11.5 hours.

The reviewer raises an astute point concerning the effect of the laboratory set-up on acetylene. The majority of gas during testing passed through Synflex 1300 tubing. Therefore, we have now conducted an additional  $[C_2H_2]_r$  test by alternating the same gas stream, passing through either pure stainless steel or Synflex 1300. The average measured  $[C_2H_2]_r$  was compared between the two gas streams and found to be identical (within uncertainty). This therefore confirms that Synflex 1300 has no noticeable effect on  $[C_2H_2]_r$ , compared to stainless steel. It is highly unlikely that Synflex 1300 and stainless steel have the exact same impact on acetylene. It can therefore be assumed that Synflex 1300 has no net effect on acetylene, allowing for its use during laboratory testing. The results of this new analysis are presented in Section S2 in the Supplement, with the outcome of the analysis summarised at the start of Section 2.1, when presenting the use of Synflex 1300 for the first time. We thank the reviewer for motivating us to include this very useful analysis.

The final point is an interesting one, regarding the declared  $[CH_4]$  level in the methane calibration cylinder. We thank the reviewer for noticing this, due to their robust review of our methods. As this  $[CH_4]$  level could not be accurately measured for verification (due to the argon content of this cylinder), all  $[C_2H_2]_r$  (and hence all  $C_{MFC}$ ) values rely on the accuracy of the declared  $[CH_4]$  level of the methane calibration cylinder, which has an uncertainty of  $\pm 0.5\%$ . Therefore, a new sensitivity analysis was conducted on the importance of this uncertainty range; a range of  $C_{MFC}$  values was calculated using the range in possible  $[C_2H_2]_r$  values (at each MFC setting), taking into account the uncertainty range in the declared  $[CH_4]$  of the methane calibration cylinder. Rather than simply testing the effect of the variation in  $C_{MFC}$  on deriving  $[C_2H_2]$  standards (used to calibrate Picarro G2203  $[C_2H_2]_r$  measurements), we decided to also include the effect of the  $\pm 3\%$  uncertainty associated with the declared  $[C_2H_2]$  level of the acetylene calibration cylinder. This yielded a range in  $[C_2H_2]_r$  levels (at each MFC setting) which were combined with corresponding  $C_{MFC}$  values to obtain  $[C_2H_2]$  reference standards. This analysis is presented in Section S5 in the Supplement, where Picarro G2203  $[C_2H_2]_r$  calibration fits are presented by both maximising and minimising  $[C_2H_2]$  standards. This results in a possible extreme gain factor range of between 0.911 and 0.977, which is presented in Section 2.4. It is important to note that this means that even in a worst-case scenario, the acetylene calibration gain factor is still significantly less than 1. Therefore, an acetylene calibration remains essential.

5. Flux error: A single number is given from the field trials of 7.6%. But a percentage isn't really that useful to those reading the paper, as a percentage of the flux will depend on all the factors you list that affect the quality of tracer release experiments and fluxes derived from them. A reader taking away the 7.6% number and using it as a guide to the effect of calibration would not be remembering something useful. However, I think you have all that you need here to derive a range of biases for different  $CH_4$  fluxes and acetylene release rates. They're all linearly scalable. So, rather than 7.6%, would it not be better to include a table in the paper that describes  $CH_4$  mass flux (g/s) error (and percent error), for a range of different assumed  $CH_4$  emission fluxes, or even simply  $C_2H_2/CH_4$  concentration ratios? This would be far more meaningful, and a better guide to others assessing how important calibration may be to their surveys. If you don't take up this recommendation, the discussion needs to be very explicit that the 7.6% number is not indicative of mass flux error due to instrument calibration and is unique to the conditions of this study (reducing the paper's impact).

We feel that the reviewer reached a different conclusion regarding the significance of this bias value, compared to the actual message we intended to convey. Perhaps this is because the original version of the manuscript lacked some discussion on the significance and origin of the bias value, which we now seek to rectify. This 7.6% value represents a bias that is largely independent of the sampling circumstances themselves including issues with sensor placement or downwind sampling location. Meanwhile, there is a  $\pm 56\%$  random uncertainty between flux estimates which is unrelated to the acetylene calibration. This random uncertainty is indeed specific to the sampling campaign, which is discussed in depth in Section 4.2. However, this  $\pm 56\%$  value is not the focus of this paper.

The 7.6% bias emphasised in the abstract and conclusion is principally due to the acetylene calibration. An acetylene calibration gain factor of 0.94 should result in a purely theoretical flux bias using uncalibrated measurements of exactly 6%, following eq. (4). However, this number is not exactly 6% for a number of reasons. The calibration was not valid below 1.19 ppb, meaning that all such  $[C_2H_2]$  measurements were fixed to 0 ppb. To account for this, a threshold methane mole fraction was also used, below which all  $[CH_4]$  measurements were set to the background methane mole fraction. Finally, the

calibrated  $[\text{C}_2\text{H}_2]$  data included a small linear offset which is only valid above 1.38 ppb  $[\text{C}_2\text{H}_2]_r$ . These effects collectively cause flux bias to vary from exactly 6%.

The reviewer is therefore technically correct to state that this 7.6% bias is specific to this study. A higher number of  $[\text{C}_2\text{H}_2]_r$  measurements below 1.19 ppb from different transects will result in more  $[\text{C}_2\text{H}_2]$  values being fixed to 0 ppb. Alongside this, the specific location and magnitude of  $[\text{CH}_4]$  and  $[\text{C}_2\text{H}_2]$  measurements from each transect effects the  $[\text{CH}_4]$  threshold, designed to correct for the aforementioned effect. Hence, the magnitude of flux underestimation quantified for each transect using uncalibrated measurements instead of calibrated measurements varies. But by taking an average of fourteen different transects, individual variability in flux underestimation should average out. Therefore, although this 7.6% bias is specific to this study, we still believe it has merit, as it illustrates a typical order of magnitude level of flux bias induced by using uncalibrated measurements from a real-world sampling campaign, using the Picarro G2203 for tracer-based methane fluxes.

To include these points in the manuscript, additional extensive discussion has been included towards the end of Section 4.2. We hope this clarifies any doubt regarding the significance of this 7.6% flux underestimation using uncalibrated  $[\text{C}_2\text{H}_2]_r$  measurements. We thank the reviewer for raising this, thus enabling us to thoroughly clarify this point.

6. There are a lot of important points to take from this paper, but they get lost in the extremely thorough discussion (and the conclusions). I would recommend completely changing the conclusions section to avoid unnecessary repetition of methods and instead focus on the salient conclusions about water vapour, need for acetylene calibration, and potential for flux error. It may also be useful to contextualise the error potential in terms of the magnitude of error from other flux methods (i.e. is it a comparable error if this calibration is ignored?). The important aspects of this useful paper will otherwise get missed.

We thank the reviewer for recognising the useful points in this paper. We agree that the key points of the paper may get lost in the conclusion in its original form. We have therefore rewritten the majority of the conclusion section and shortened it to place greater emphasis on the key outcomes of this work, with less focus on the methods. For example, details of the acetylene flow meter have now been omitted, with only the  $Q_{\text{acetylene}}$  provided.

We have removed any discussion from Section 5 on the cause of the  $\pm 56\%$  random uncertainty as it is a distraction and not the main focus of this work. Issues in the tracer flux method itself are also not the key outcome of this study. We thank the reviewer for their feedback, allowing us to place greater emphasis on the importance of the 8% bias, which is the main result, induced by failure to calibrate the Picarro G2203.

Regarding the suggestion to compare different flux uncertainties, in our opinion, the 8% uncertainty bias presented in this manuscript is not directly comparable to random uncertainties from other flux methods; a bias systematically forces the flux in one direction whereas a random uncertainty averages out over a sufficient number of samples. Furthermore, comparing flux errors from various flux methods is not the objective of this study, which will be the subject of a forthcoming study, as previously stated at the start of Section 4.1.

#### Technical comments:

1/ Line 152 – Full stop after bracket.

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

# Response 1 to Reviewer 2

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 the 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 Allen 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 [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> 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<sub>MFC</sub> factors, which correct [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> to obtain reference [C<sub>2</sub>H<sub>2</sub>] levels. These C<sub>MFC</sub> factors were derived by comparing [CH<sub>4</sub>]<sub>r</sub> to accurate [CH<sub>4</sub>] 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 [CH<sub>4</sub>] 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  $[\text{C}_2\text{H}_2]_r$  and  $[\text{CH}_4]_r$  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,  $[\text{C}_2\text{H}_2]_r$  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: " $[\text{H}_2\text{O}]_r$ ". Should it be " $[\text{C}_2\text{H}_2]_r$ "?

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.

Modified manuscript

# Accuracy of tracer-based methane flux quantification: underlying impact of calibrating acetylene measurements with a cavity ring-down spectroscopy gas analyser and its use as a tracer to quantify methane emissions

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**Abstract.** Facility-scale methane emission fluxes can be derived by comparing tracer and methane mole fraction measurements downwind of a methane emission source, where a co-located tracer gas is released at a known flux rate. Acetylene is a commonly used methane tracer for methane due to its availability, low cost and low atmospheric background. Acetylene mole fraction can be measured using infrared gas analysers such as the cavity ring-down spectroscopy Picarro G2203, using cavity ring-down spectroscopy. However, failure to calibrate tracer gas analysers may influence methane flux estimation, due to inaccurate raw tracer mole fraction measurements diverge from their true levels. We conducted extensive Picarro G2203 laboratory characterisation testing. Picarro G2203 acetylene measurements were calibrated by diluting a high concentration of acetylene with ambient air. In order to determine the precise level of acetylene in each dilution blend, a calibration gas mixture was determined by diluting a high concentration methane source was diluted in an identical way, with reliable methane mole fraction measurements used to quantify the true level of dilution. A linear calibration fit applied to raw acetylene mole fraction measured by the Picarro G2203 showed it was found that these raw Picarro G2203 acetylene mole fraction measurements could be corrected through direct multiplication with a calibration gain factor of 0.94, derived by applying a linear fit between raw measured and reference acetylene mole fraction. However, this specific calibration for the Picarro G2203 tested in this study is only valid from an acetylene mole fraction of 1.16 ppb, below which unstable measurements were observed by the Picarro G2203 tested in this study. The same Picarro G2203 was used during a field study to was then conducted by performing fourteen successful transects downwind of an active landfill site, where a point-source acetylene was release was conducted from a single point location at a fixed flow rate. Methane fluxes were derived by integrating the methane and acetylene mole fraction plumes, as a function of distance along the sampling road. This resulted in a  $\pm 56\%$  flux variability of 56% between methane flux estimates from different transects which was principally due to flux errors associated with the tracer release location and downwind sampling positioning. Methane fluxes were also derived using raw uncalibrated Picarro G2203 acetylene mole fraction measurements instead of calibrated measurements, which resulted an average methane emission flux

underestimation of approximately 87.6% for this specific study, compared to fluxes derived using calibrated measurements. Unlike a random uncertainty, this 7.6% bias represents a consistent flux underestimation that cannot be reduced by with improvements to the field sampling methodology; the only solution is using calibrated acetylene mole fraction measurements. The magnitude of the bias is principally due to the 0.94 multiplicative gain factor. Therefore, a similar level of methane flux bias can be expected in other studies when using uncalibrated acetylene mole fraction measurements from the Picarro G2203 tested in this work. This study therefore emphasises the equal importance of calibrating both-target as well as tracer gas measurements, regardless of the instrument being used to obtain these measurements. Otherwise, biases can be induced within target gas flux estimates. For the example of methane, this can influence our understanding of the role of certain facility-scale emissions within the global methane budget.

## 1. Introduction

The greenhouse effect, which was first proposed over a century ago, is responsible for elevating Earth's near-surface temperature (Arrhenius, 1896). It is caused by various atmospheric species of which methane is the third most important (Mitchell, 1989), in terms of overall radiative forcing (Schmidt *et al.*, 2010). Methane had an effective radiative forcing in 2019 compared to prior to the onset of the industrial era (defined here as the year 1850) of 0.504 W m<sup>-2</sup> in 2019 (Forster *et al.*, 2021), which was one quarter that of carbon dioxide (Dentener *et al.*, 2021). Methane has an annualised average background mole fraction of greater than 1.9 ppm (Dlugokencky *et al.*, 1994, Lan *et al.*, 2024), which is over twice as high as it has ever been up to 800 000 years prior to the onset of the industrial era, defined here as the year 1850 (Chappellaz *et al.*, 1990, Etheridge *et al.*, 1998, Louergue *et al.*, 2008). Recent estimates suggest that direct anthropogenic emissions may be responsible for over 50% of total methane emissions (Saunois *et al.*, 2024). Yet there remain large uncertainties in the global methane budget (Dlugokencky *et al.*, 2011, Kirschke *et al.*, 2013, Nisbet *et al.*, 2019, Saunois *et al.*, 2020, Lan *et al.*, 2021, which is in large part due to uncertainties in emissions from anthropogenic facility-scale sources (Jackson *et al.*, 2020, Nisbet *et al.*, 2021, Bastviken *et al.*, 2022, Saunois *et al.*, 2024) such as oil and gas extraction infrastructure (Foulds *et al.*, 2022, Wang *et al.*, 2022), agricultural facilities (Shah *et al.*, 2020, Hayek and Miller, 2021, Marklein *et al.*, 2021), wastewater treatment facilities (Moore *et al.*, 2023, Song *et al.*, 2023) and landfill sites (Maasakkers *et al.*, 2022, Kumar *et al.*, 2024, Wang *et al.*, 2024). Saunois *et al.* (2024) estimated that landfills and waste collectively contributed towards approximately 109% of total methane emissions in the year 2024.

Emissions from individual facility-scale methane sources can be quantified either using inventory-based bottom-up methods or atmospheric measurement-based top-down methods (Chen and Prinn, 2006, Nisbet and Weiss, 2010, Alvarez *et al.*, 2018, Desjardins *et al.*, 2018, Vaughn *et al.*, 2018). Bottom-up fluxes typically multiply a quantitative activity factor (representative of the amount of an emitting activity taking place) by a qualitative emission factor (Saunois *et al.*, 2016, Allen *et al.*, 2022). These bottom-up emission factors may be more general values assigned for a geographical region (Scarpelli *et al.*, 2020, Bai

*et al.*, 2023), developed from knowledge of source emissions (Wolf *et al.*, 2017, Lin *et al.*, 2021) or informed by process models (Scheutz *et al.*, 2009, Stavert *et al.*, 2021). Meanwhile, most top-down emission estimates rely on atmospheric methane measurements combined with wind data to infer emissions within an inversion model (Denmead *et al.*, 2000, Ars *et al.*, 2017, Cusworth *et al.*, 2021). Top-down facility-scale methane emission flux ( $Q_{\text{methane}}$ ) estimates are essential to complement, improve and verify corresponding bottom-up estimates (Guha *et al.*, 2020, Delre *et al.*, 2017, Hayek and Miller, 2021, Marklein *et al.*, 2021, Johnson *et al.*, 2023).

Various approaches can be employed to derive top-down  $Q_{\text{methane}}$  (Johnson and Johnson, 1995, Bastviken *et al.*, 2022). Some methods use remote sensing sampling, where mole fraction measurements are integrated over a certain distance (Cusworth *et al.*, 2020, Hrad *et al.*, 2021, Maasakkers *et al.*, 2022, Cossel *et al.*, 2023). However, ~~here~~ we focus ~~here~~ on methods using *in situ* sampling, which provides methane mole fraction ( $[\text{CH}_4]$ ) measurements at the sampling point (Feitz *et al.*, 2018). There are many ways to derive top-down  $Q_{\text{methane}}$  estimates by applying an extensive variety of inversion dispersion methods to downwind *in situ* sampling (Flesch *et al.*, 1995, Sonderfeld *et al.*, 2017, Hrad *et al.*, 2021, Shaw *et al.*, 2021, Liu *et al.*, 2024). Rather than using measurements from a single location, downwind sampling transects can be used in more accurate flux methods. For example, both one-dimensional (Foster-Wittig *et al.*, 2015, Yacovitch *et al.*, 2015, Albertson *et al.*, 2016, Riddick *et al.*, 2020, Kumar *et al.*, 2021, Kumar *et al.*, 2022) and two-dimensional (Lee *et al.*, 2018, Shah *et al.*, 2019) downwind transects can be used within Gaussian plume modelling, while mass-balance box modelling can be applied to two-dimensional downwind sampling (Denmead *et al.*, 1998, Foulds *et al.*, 2022, Pühl *et al.*, 2024).

As well as simply using downwind  $[\text{CH}_4]$  *in situ* sampling, top-down  $Q_{\text{methane}}$  values can be derived using a tracer gas release, where the release of a carefully controlled quantity of a tracer gas is co-located with the methane emission source (Lamb *et al.*, 1995, Czepiel *et al.*, 1996). Tracer-based  $Q_{\text{methane}}$  estimation relies on simultaneous *in situ* downwind measurements of both  $[\text{CH}_4]$  and the tracer gas mole fraction, with no wind measurements required (Johnson and Johnson, 1995, Mønster *et al.*, 2014, Ars *et al.*, 2017). The ratio between the enhancement (above background levels) of the mole fractions of the two gases can be used to yield  $Q_{\text{methane}}$  by direct multiplication with the known tracer release rate (Yacovitch *et al.*, 2017, Feitz *et al.*, 2018, Mønster *et al.*, 2019). A more accurate  $Q_{\text{methane}}$  estimate can be derived by taking the ratio between integrated downwind methane and tracer gas plumes (Scheutz *et al.*, 2011, Mønster *et al.*, 2015, Yver Kwok *et al.*, 2015a), which is especially useful to minimise errors due to suboptimal acetylene release co-location with the methane emission source (Ars *et al.*, 2017). Although this manuscript focuses on methane as the target gas of interest, the same principles and outcomes apply to any other target gas whose emission flux is derived using a tracer gas release.

The well-established tracer-based flux method has widely been considered to be a more accurate top-down flux quantification approach for localised facility-scale sources, against which to test other methods, although good execution of the method (*i.e.* suitable tracer release location and downwind sampling location) is essential for optimal flux  $Q_{\text{methane}}$  estimation (Yver Kwok *et al.*, 2015a, Bell *et al.*, 2017, Mønster *et al.*, 2019, Song *et al.*, 2023). The accuracy of tracer-based fluxes has been confirmed

during various controlled release experiments using co-located [target gas methane](#) and tracer point source releases (Mønster *et al.*, 2014, Feitz *et al.*, 2018, Liu *et al.*, 2024), but also with an offset tracer and [target gas methane](#) source, which can result in greater flux uncertainty (Ars *et al.*, 2017, Fredenslund *et al.*, 2019). Raw tracer-based  $Q_{\text{methane}}$  has been derived in countless previous studies from a multitude of facility-scale methane sources, for example from cattle (Johnson *et al.*, 1994, Daube *et al.*, 2019, Vechi *et al.*, 2022), oil and gas extraction infrastructure (Lamb *et al.*, 1995, Omara *et al.*, 2016, Yacovitch *et al.*, 2017), anaerobic digesters (Scheutz and Fredenslund, 2019), wastewater treatment facilities (Yver Kwok *et al.*, 2015a, Delre *et al.*, 2017, Delre *et al.*, 2018) and landfill sites (Czepiel *et al.*, 1996, Galle *et al.*, 2001, Mønster *et al.*, 2015, Matarachiera *et al.*, 2019, Mønster *et al.*, 2019).

The choice of tracer gas for methane has also evolved (Scheutz *et al.*, 2009, Delre *et al.*, 2018, Mønster *et al.*, 2019). Originally, sulphur hexafluoride was favoured (Johnson and Johnson, 1995, Czepiel *et al.*, 1996) due to its inert properties and almost absent atmospheric background. However, sulphur hexafluoride is an incredibly potent greenhouse gas with an atmospheric lifetime of roughly 1 000 years (Kovács *et al.*, 2017). Carbon dioxide has also been used as a tracer gas (Lamb *et al.*, 1995, Allen *et al.*, 2019), but it has extensive background variability due to a multitude of localised sources and sinks (Grimmond *et al.*, 2002, Schwandner *et al.*, 2017). Nitrous oxide is a more recent alternative tracer gas option to quantify methane emissions (Galle *et al.*, 2001, Mønster *et al.*, 2015, Omara *et al.*, 2016). Though this is a potent greenhouse gas, it has [an finite](#) atmospheric lifetime [of approximately 110 years \(Prather et al., 2015\)](#) due to its reaction with atmospheric oxygen radicals and due to soil consumption (Cicerone, 1989, Kroeze, 1994, Tian *et al.*, 2020). Finally, acetylene has more recently been used as a tracer for methane (Yver Kwok *et al.*, 2015a, Fredenslund *et al.*, 2019, Scheutz and Fredenslund, 2019, Vechi *et al.*, 2022). It readily reacts with the hydroxyl radical, resulting in a relatively short lifetime of up to a month (Kanakidou *et al.*, 1988, Gupta *et al.*, 1998, Hopkins *et al.*, 2002, Crounse *et al.*, 2009). Acetylene is also cheap to produce. However, it has a flammable atmospheric range of between 2.5% and approximately 80% (Williams and Smith, 1969), which is the largest range of any readily available gas. Nevertheless, background levels of no greater than 1 ppb (Kanakidou *et al.*, 1988, Gupta *et al.*, 1998, Hopkins *et al.*, 2002, Xiao *et al.*, 2007), makes it a preferred option compared to nitrous oxide, which can otherwise be emitted from many sources including agricultural activities, resulting in a variable atmospheric nitrous oxide background (Tian *et al.*, 2020).

The ability to obtain *in situ* measurements of both methane and the chosen tracer gas underpins the accuracy of any derived tracer-based flux. Acetylene mole fraction ( $[C_2H_2]$ ) has traditionally been measured using flame-ionisation gas chromatography (Kanakidou *et al.*, 1988, Hopkins *et al.*, 2002, Crounse *et al.*, 2009) and Fourier-transform infrared (IR) spectroscopy (Xiao *et al.*, 2007, Feitz *et al.*, 2018), which are both slow *in situ* techniques. The recent use of acetylene as methane tracer has largely been facilitated by the development of fast-response (less than 1-minute sampling frequency) *in situ* measurement techniques. Yacovitch *et al.* (2017) derived tracer-based fluxes with a sensor using direct IR spectroscopy with a tuneable laser, manufactured by Aerodyne Research, Inc. (Billerica, Massachusetts, USA), with a detection limit of 78 ppt and a  $[C_2H_2]$  linear calibration uncertainty of 3% (assuming a zero intercept). This calibration was performed by diluting

gas from an acetylene cylinder, although the  $[C_2H_2]$  testing range is not provided (Yacovitch *et al.*, 2017). The Ultraportable Methane-Acetylene Analyzer (ABB Ltd, Zürich, Switzerland) has also been used to measure  $[C_2H_2]$ , which uses off-axis integrated cavity output spectroscopy, with a manufacturer-rated precision of less than 1 ppb at 0.2 Hz (Fredenslund *et al.*, 2019). Feitz *et al.* (2018) tested this instrument to verify ~~its~~for linearity using two cylinders ~~with a  $[C_2H_2]$  of~~containing 4.100 ppb  ~~$[C_2H_2]$~~  and 20.600 ppb  ~~$[C_2H_2]$~~ , although without providing correlation results.

The Picarro G2203 (Picarro, Inc., Santa Clara, California, USA) is one of the most widely used acetylene gas analysers, which has been operated in numerous tracer release studies (Mønster *et al.*, 2015, Yver Kwok *et al.*, 2015a, Ars *et al.*, 2017, Delre *et al.*, 2017, Delre *et al.*, 2018, Vechi *et al.*, 2022). It uses cavity ring-down spectroscopy (CRDS) to detect small  $[C_2H_2]$  enhancements of less than 1 ppb (Mønster *et al.*, 2014). The Picarro G2203 has a manufacturer-rated precision of less than  $\pm 0.6$  ppb at 0.5 Hz (Picarro, Inc., 2015). Mønster *et al.* (2014) provided a brief testing overview of the Picarro G1203 (which is spectroscopically similar to the Picarro G2203, but with older electronics) using a testing cylinder ~~containing~~with a  $[C_2H_2]$  of 103 ppb  ~~$[C_2H_2]$~~  in synthetic air, with a 10%  $[C_2H_2]$  ~~accuracy~~uncertainty. However, they provided limited details on their characterisation testing procedure, such as whether the gas was diluted to sample lower  $[C_2H_2]$  levels and the number of sampling steps, if any (Mønster *et al.*, 2014). In a tracer release study by Omara *et al.* (2016), regular Picarro G2203 calibrations were conducted using a single ~~100 ppb  $[C_2H_2]$~~  gas standard ~~with a  $[C_2H_2]$  of 100 ppb~~ to check for drift. They measured a raw acetylene mole fraction ( $[C_2H_2]_r$ ) of  $(112 \pm 3.2)$  ppb (Omara *et al.*, 2016); this +12% error emphasises the risk in using raw measurements from tracer gas analysers.

To summarise, there exists a large body of research having used tracer-based methods to estimate  $Q_{\text{methane}}$ , but a lack of emphasis in calibrating the tracer gas measurement in these previous studies. It is vitally important to conduct independent rigorous testing of gas analysers such as the Picarro G2203, across the full  $[C_2H_2]$  range expected during field sampling. This is essential due to the reliance of tracer-based  $Q_{\text{methane}}$  estimates to inform site operators and policy makers. Any disparity in  $[C_2H_2]$  measurements may be projected as persistent biases in  $Q_{\text{methane}}$  estimates, emphasising the key importance of this work.

We provide here the first detailed characterisation, to our knowledge, of the Picarro G2203 gas analyser for measuring  $[C_2H_2]$  in **Sect. 2**, including the influence of water. We describe the implementation of the gas analyser to conduct an acetylene release from a landfill site in France in **Sect. 3**. We also present a comprehensive description of the equipment used within our acetylene release method in **Sect. 3**. The purpose of this study is not to evaluate emissions from this specific landfill site in the context of methane emissions compared to other sources, but rather to focus on the tracer-based flux quantification method itself. In this study, the chosen landfill site serves only as a complex heterogeneous test site with which to test our methods and the specificities of this particular site are beyond the scope of this work.  ~~$Q_{\text{methane}}$  Flux~~ results from this study site are presented in **Sect. 4**, where we discuss the variability in  $Q_{\text{methane}}$  results and disparity between  $Q_{\text{methane}}$  values derived using raw versus calibrated mole fraction measurements. We summarise the implications on  $Q_{\text{methane}}$  quantification of using raw mole fraction measurements without applying an acetylene calibration in **Sect. 5**.



**2.1 Testing equipment**

The Picarro G2203 gas analyser uses CRDS to measure  $[\text{C}_2\text{H}_2]_r$ , raw water mole fraction ( $[\text{H}_2\text{O}]_r$ ) and raw methane mole fraction ( $[\text{CH}_4]_r$ ). This section is dedicated to characterising Picarro G2203  $[\text{C}_2\text{H}_2]_r$  measurements, with a Picarro G2203  $[\text{CH}_4]_r$  measurement calibration provided in **Sect. S1** in the **Supplement**. A Picarro G2401 (Picarro, Inc.) gas analyser was ~~also~~ used during this Picarro G2203 characterisation work, which also measures  $[\text{H}_2\text{O}]_r$  and  $[\text{CH}_4]_r$ , but not  $[\text{C}_2\text{H}_2]_r$ . The CRDS method used by the Picarro G2230 and Picarro G2401 gas analysers derives mole fraction measurements using a spectrum of the characteristic exponential decay “ring-down” time of IR radiation leaking out of a cavity (Paldus and Kachanov, 2005) held under controlled pressure and temperature (Crosson, 2008). IR radiation from a tuneable distributing feedback laser is injected into the cavity at discrete points across a narrow wavelength range, which is tuned to the absorption peak of interest (Crosson, 2008). IR absorption occurs in the cavity following the Beer-Lambert Law at absorbing wavelengths (Lambert, 1760). Following laser build-up, the laser is switched off and radiation leaks out of the cavity (Paldus and Kachanov, 2005). The ring-down times of leaking radiation are used to produce an absorbance spectrum as a function of wavelength. The ratio between the maximum absorbance signal and the signal at a baseline wavelength (representative of sampling in an empty cavity) is used to derive gas mole fraction using internal instrumental algorithms.

Throughout each laboratory test conducted during this work, the Picarro G2203 and Picarro G2401 were connected in parallel. Both the Picarro G2203 and Picarro G2401 record raw mole fraction measurements for each gas individually, each with a unique timestamp. Therefore, all Picarro G2401 measurements were shifted to the Picarro G2203 timestamp, by applying a lag time correction. ~~At the time of testing, Picarro G2203  $[\text{C}_2\text{H}_2]_r$  measurements had an average observed sampling frequency of  $(0.3 \pm 0.1)$  Hz in dry conditions.~~ The observed time interval between each  $[\text{C}_2\text{H}_2]_r$  measurement for the Picarro G2203 used in this particular study followed a roughly 40 s periodic cycle every ten measurements of roughly 2 s, 4 s, 2 s, 4 s, 2 s, 4 s, 2 s, 4 s, 2 s and 13 s between measurements. This sampling cycle is automatically determined by the gas analyser and may be due to different IR wavelength ranges being scanned at each step (a larger scan takes more time, but is useful for a better IR absorbance baseline fit), alongside  $[\text{CH}_4]_r$  and  $[\text{H}_2\text{O}]_r$  samples also being made, with a different laser used to sample water and methane independently of acetylene. Therefore, at the time of testing, Picarro G2203  $[\text{C}_2\text{H}_2]_r$  measurements had an overall observed sampling frequency of 0.24 Hz in dry conditions (when averaging over the discontinuous sampling rate). All  $[\text{C}_2\text{H}_2]_r$  and  $[\text{CH}_4]_r$  measurements presented in this manuscript are ~~defined as wetraw~~ measurements, with no applied internal instrumental water correction ~~applied to this data~~. This means to say that they represent mole fractions of gases compared to all air molecules, including those of water when present.

During characterisation testing, a specially prepared 20 dm<sup>3</sup> acetylene calibration cylinder was used (Air Products N.V., Diegem, Belgium). This was volumetrically filled with a ~~declared~~  $[\text{C}_2\text{H}_2]$  of 10 180 ppb in argon with a  $\pm 3\%$  uncertainty, according to the cylinder provider. This high  $[\text{C}_2\text{H}_2]$  level was chosen to allow for high levels of dilution, to minimise the

effect of the argon in this cylinder on the natural balance of air; changes in air composition can affect spectral fitting by changing the shape of IR absorption peaks (Lim *et al.*, 2007, Rella *et al.*, 2013). A 20 dm<sup>3</sup> methane calibration cylinder (Air Products N.V.) was also used during testing. This was gravimetrically filled with a declared [CH<sub>4</sub>] of 995.4 ppm in argon with a ±0.5% uncertainty, according to the cylinder provider. Unfortunately, it was not possible to further verify the declared [CH<sub>4</sub>] level in the methane calibration cylinder using a reference instrument, due to its high argon content. Dilution of these two calibration cylinders was performed using gas from three cylinders containing natural ambient compressed outside air, assumed to contain a background acetylene mole fraction ([C<sub>2</sub>H<sub>2</sub>]<sub>0</sub>) level of 0 ppb (due to the absence of nearby acetylene sources).

All tests were conducted using mass-flow controller (MFC) units (EL-FLOW Select, Bronkhorst High-Tech B. V., AK Ruurlo, Netherlands), which were used to generate gas blends and to control gas flow. All laboratory testing was conducted using either stainless-steel (SS) tubing or Synflex 1300 tubing (Eaton Corporation plc, Dublin, Ireland) with an outer diameter (OD) of 0.25 inches, in conjunction with standard SS Swagelok fittings (Swagelok Company, Solon, Ohio, USA) which were used to connect tubing and various components. The influence of Synflex 1300 tubing on [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> is evaluated in Sect. S2 of the Supplement, which shows no a measurable effect on [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub>, allowing for its use during laboratory testing. The gas stream was filtered using 2 µm particle filters (SS-4FW-2, Swagelok Company) to protect downstream instrumentation. One of either two diaphragm pumps was used during testing to pressurise the gas stream: the N86KN.18 (KNF DAC GmbH, Hamburg, Germany) has fittings compatible with Swagelok fittings whereas the 1410VD/12VDC (Gardner Denver Thomas GmbH, Fürstentfeldbruck, Germany) has barbed fittings which were connected to short lengths of Tygon S3 E-3603 tubing (Saint-Gobain Performance Plastics, Inc., Solon, Ohio, USA) to which Swagelok fittings were attached. A needle valve (SS-4MG, Swagelok Company) was used to stabilise and restrict the pressure downstream of the diaphragm pumps. A check valve (SS-4C-1, Swagelok Company) was also used to direct gas flow during testing.

As water vapour is naturally present in air, the [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> response of the Picarro G2203 was tested under various water mole fraction ([H<sub>2</sub>O]) levels which could be controlled using three different methods. Water could be added to the gas stream using a dew-point generator (LI-610, LI-COR, Inc., Lincoln, Nebraska, USA) to saturate passing gas to a fixed dew-point setting. This was incorporated into the gas stream by connecting standard plastic Swagelok fittings to the standard Bev-A-Line IV tubing (Thermoplastic Processes Inc, Georgetown, Delaware, USA) used by the dew-point generator, which has an OD of 0.25 inches and an inner diameter of 0.125 inches. The internal pump of the dew-point generator was by-passed by cutting and adding a standard plastic Swagelok fitting to the Bev-A-Line IV tubing on the instrument labelled as “to condenser”. A three-way ball valve (B-42XS4, Swagelok Company) was placed both upstream and downstream of the dew-point generator; these were used to direct the instrument away from the gas line and towards a direct vent to the atmosphere (*i.e.* with no connection) when adding water to the condenser, to ensure an atmospheric pressure both upstream and downstream of the dew-point generator. Conversely water could be removed from the gas stream using a Nafion-based gas dryer (MD-070-144S-4, Perma Pure LLC, Lakewood, New Jersey, USA), which contains a Nafion membrane (The Chemours Company FC, LLC,

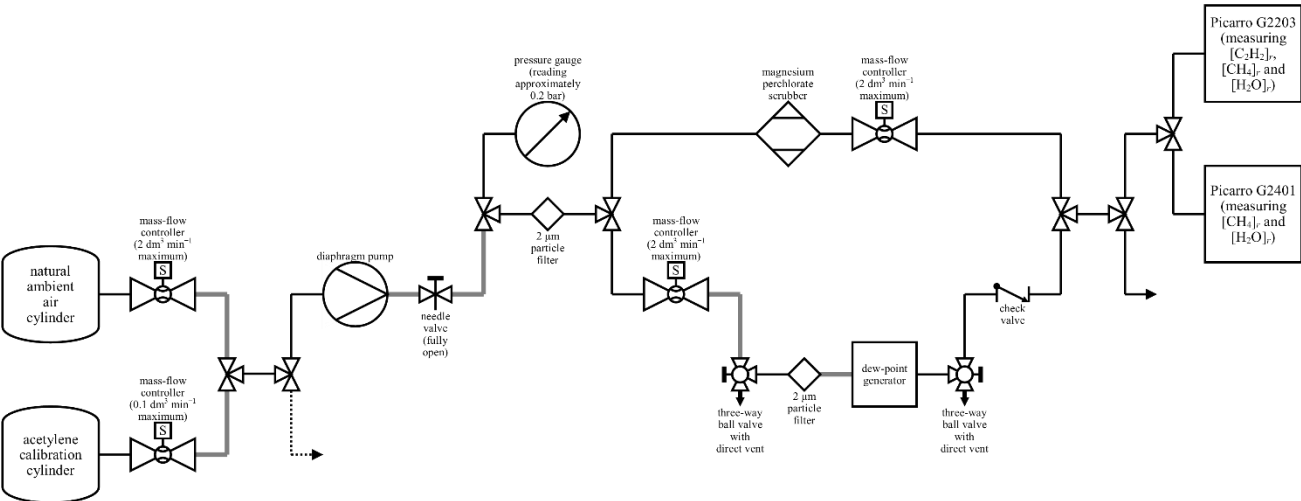
Wilmington, Delaware, USA), which reduced observed Picarro G2203 [H<sub>2</sub>O]<sub>r</sub> measurements to less than 0.1%. The Nafion-based gas dryer was connected in reflux mode during testing, whereby the gas dryer was placed between the Picarro G2203 and its downstream vacuum pump, to create a vacuum outside the Nafion membrane through which the sample gas passed, as described in detail by Welp *et al.* (2013). Water could be dried further through chemical absorption, [by passing the gas stream through using](#) magnesium perchlorate grains (ThermoFisher (Kandel) GmbH, Kandel, Germany) in a water scrubber. The effect of any potential artefacts of the Nafion-based gas dryer, the magnesium perchlorate scrubber and the dew-point generator [is present](#) was tested in **Sect. S32** in the **Supplement**, [which show](#) ~~ing~~ no significant effect on [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> response. It was especially important to verify this for the dew-point generator which bubbles gas through a water reservoir, as acetylene has a solubility in water of 1.1 g dm<sup>-3</sup> at 20° C (Priestley and Schwarz, 1940).

## 2.2. Water tests

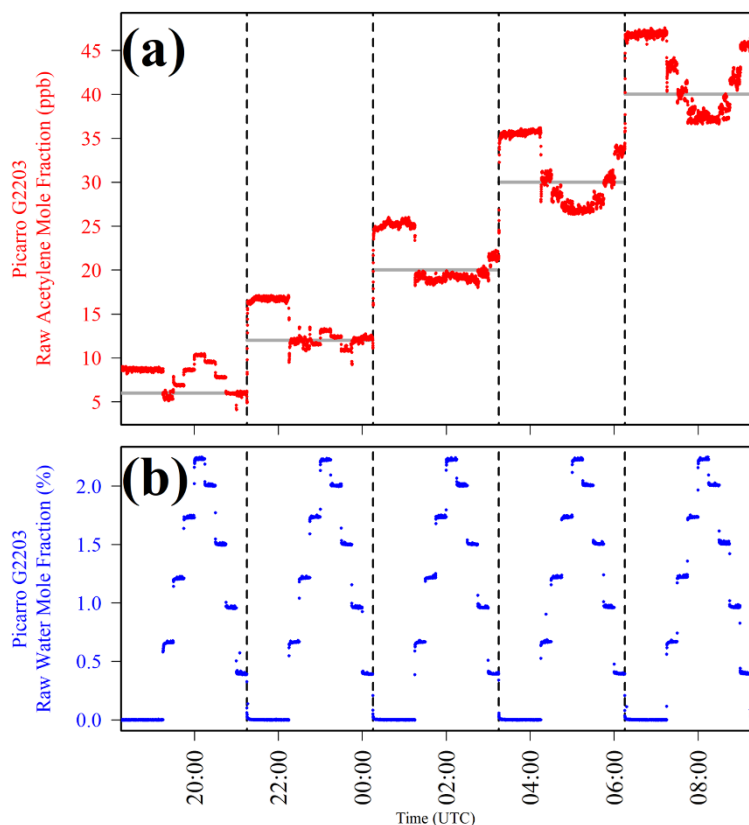
Water can potentially affect IR mole fraction measurements of any gas due to three key reasons, as described by Rella *et al.* (2013). Two of these reasons are specifically due to IR spectroscopy, although the [magnitude and](#) importance of each of these effects depends on the specific measured gas in question. Firstly, spectral interference can occur where a water IR absorption line overlaps with a target gas absorption line ([this can affect baseline fitting in the CRDS method](#)). Secondly, an independent peak broadening effect occurs whereby the shape of the absorption peak for the target gas of interest can change due to interactions with water in the gas mixture, which effect the dipole of the target gas in question, therefore causing a change in the peak shape. Although any gas can affect the peak shape and cause spectral overlap, the natural balance of air is usually a constant blend of nitrogen, oxygen and argon resulting in a constant effect on the methane spectrum, with water the main variable in ambient air. It is therefore conventional to characterise IR peak shape in the absence of water. Finally, a natural dilution effect occurs (which is not exclusive to IR spectroscopy) where the fraction of target gas molecules that would otherwise be present in dry gas is reduced due to the additional presence of water in the overall gas mixture. It is therefore a standard procedure to convert all gas mole fraction measurements into dry mole fractions as a first step, to which water can then be subsequently reintroduced at a later stage, if required in flux analysis.

An evaluation of the influence of specific spectral effects of water on [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements is beyond the scope of this study. In this work, the net influence of [H<sub>2</sub>O] on [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements is instead characterised empirically. Preliminary testing was conducted by sampling five different targeted acetylene mole fraction ([C<sub>2</sub>H<sub>2</sub>]<sub>t</sub>) levels (6 ppb, 12 ppb, 20 ppb, 30 ppb and 40 ppb) by directly blending gas from the acetylene calibration cylinder with gas from a natural ambient compressed air cylinder. This is illustrated schematically in **Fig. 1** for this test, where the check valve was used to avoid back-flow into the dew-point generator when sampling pure dry gas, therefore minimising the mixing of residual wet air with the dry gas stream. Nine different [H<sub>2</sub>O] levels were sampled at each [C<sub>2</sub>H<sub>2</sub>]<sub>t</sub> setting. This was achieved by humidifying a portion of gas using the dew-point generator with a 20° C setting and then blending this with dry air from the same original gas stream, passing through

the magnesium perchlorate scrubber, to ensure dryness. First, dry air was sampled for 60 minutes before sampling each wet setting for 15 minutes. The results of this test are presented in **Fig. 2**.



**Figure 1: A schematic of the set-up during water testing.** An arrow represents a vent to the atmosphere. Solid black lines represent either SS tubing or Synflex 1300 tubing with an OD of 0.25 inches. Solid grey lines represent SS connections between two components of approximately 0.04 m. The black dashed line represents SS tubing with an OD of 0.125 inches. All connections used standard SS Swagelok fittings. Maximum MFC flow rates are representative of corresponding volumetric flow rates for dry air at 101 325 Pa and 273.15 K. The three-way ball valves were directed towards the gas stream during testing and away from the direct vent to [the](#) atmosphere.



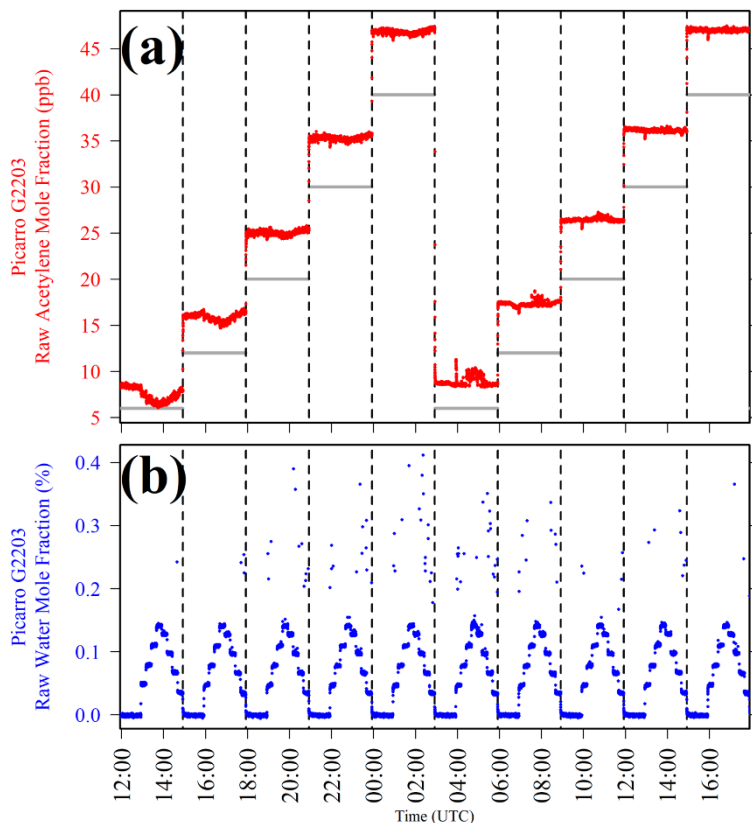
**Figure 2:** (a) Picarro G2203  $[C_2H_2]_r$  plotted as red dots and (b) Picarro G2203  $[H_2O]_r$  plotted as blue dots, when sampling nine different  $[H_2O]_r$  levels at five different  $[C_2H_2]_r$  settings, with the change between each different  $[C_2H_2]_r$  setting indicated by dashed vertical lines.  $[C_2H_2]_r$  calculated from MFC settings is plotted in (a) as light grey lines.

**Figure 2** shows that at each fixed  $[C_2H_2]_r$  level (the periods between vertical dashed lines),  $[C_2H_2]_r$  as measured by the Picarro G2203 (red dots in **Fig. 2 (a)**) changed in response to  $[H_2O]_r$ . However,  $[C_2H_2]_r$  (light grey lines in **Fig. 2 (a)**) is consistently lower than  $[C_2H_2]_r$  (red dots in **Fig. 2 (a)**) when sampling in dry conditions (see blue dots in **Fig. 2 (b)**). This is either because  $[C_2H_2]_r$  is not calibrated, because of MFC offsets during gas blending or a combination of both effects. In any case, this means that this analysis must be treated as an empirical test to evaluate the effect of Picarro G2203  $[H_2O]_r$  measurements on  $[C_2H_2]_r$  measurements. The relationship between  $[C_2H_2]_r$  and  $[C_2H_2]$  is discussed in the subsequent subsections.

**Figure 2** shows that the nature of the  $[C_2H_2]_r$  response as a function of increasing  $[H_2O]_r$  (blue dots in **Fig. 2 (b)**) was not consistent at the different tested  $[C_2H_2]_r$  levels. (light grey lines in **Fig. 2 (a)**) At a  $[C_2H_2]_r$  of 6 ppb,  $[C_2H_2]_r$  appeared to increase with increasing  $[H_2O]_r$ . Yet at a  $[C_2H_2]_r$  of 12 ppb  $[C_2H_2]_r$  and 20 ppb  $[C_2H_2]_r$ , there was no clear  $[H_2O]_r$  relationship with  $[C_2H_2]_r$ . At a  $[C_2H_2]_r$  of 30 ppb and 40 ppb  $[C_2H_2]_r$ ,  $[C_2H_2]_r$  appeared to decrease with  $[H_2O]_r$ . While use of a dew-point generator may potentially explain this behaviour (due to solubility of acetylene in the water reservoir (Priestley and Schwarz, 1940)), testing presented in **Sect. S32** in the **Supplement** shows no such effect, suggesting making it clear that these effects presented in **Fig. 2** are due to the gas analyser itself. In addition,  $[C_2H_2]_r$  measurements were excessively noisy in the presence

of water compared to dry sampling conditions, particularly at higher  $[C_2H_2]_r$  levels. The specific cause of these water effects on  $[C_2H_2]_r$  (in the context of spectral effects) is beyond the scope of this empirical study. Nevertheless, ~~this result allows us to conclude that~~ noisy  $[C_2H_2]_r$  measurements at high  $[H_2O]_r$ , combined with the inconsistent directions of  $[C_2H_2]_r$  changes in response to  $[H_2O]_r$  changes, suggests that it is not straightforward to derive a reliable simple empirical water correction model across a  $[H_2O]$  range typically observed in ambient atmospheric conditions.

**Figure 2** shows that  $[C_2H_2]_r$  response was most stable (least noisy) at lower  $[H_2O]$  levels. Therefore  $[C_2H_2]_r$  response to  $[H_2O]_r$  was instead tested in dryer conditions. This simulates a  $[H_2O]$  range experienced with sole use of the Nafion-based gas dryer, which reduces  $[H_2O]_r$  measurements to less than 0.1%. Such a correction could be useful if using the Nafion-based drier to obtain semi-dry gas sampling during eventual field deployment. In this test, the dew-point generator was fixed to a 0° C setting to enable a lower range of  $[H_2O]$  levels to be sampled. The same procedure as for the previous test was carried out, but in this test, the entire procedure was performed twice to test for repeatability. The results of this test are presented in **Fig. 3**.



**Figure 3:** (a) Picarro G2203  $[C_2H_2]_r$  plotted as red dots and (b) Picarro G2203  $[H_2O]_r$  plotted as blue dots, when sampling nine different low  $[H_2O]$  levels at five different  $[C_2H_2]_r$  settings over two testing cycles, with the change between each different  $[C_2H_2]_r$  setting indicated by dashed vertical lines.  $[C_2H_2]_r$  calculated from MFC settings is plotted in (a) as light grey lines.

**Figure 3** shows that despite limiting  $[\text{H}_2\text{O}]_r$  measurements to mostly below 0.2% (blue dots in **Fig. 3** (b)),  $[\text{C}_2\text{H}_2]_r$  remained unpredictable at each fixed  $[\text{C}_2\text{H}_2]_t$  setting, (although  $[\text{C}_2\text{H}_2]_r$  appeared relatively stable at the highest  $[\text{C}_2\text{H}_2]_t$  levels in this water test). It is particularly concerning that  $[\text{C}_2\text{H}_2]_r$  first decreased with increasing  $[\text{H}_2\text{O}]_r$  at 6 ppb%  $[\text{C}_2\text{H}_2]_t$ , while the opposite behaviour was observed during the second period at the same  $[\text{C}_2\text{H}_2]_t$  level. At the other  $[\text{C}_2\text{H}_2]_t$  settings, the relationship between  $[\text{C}_2\text{H}_2]_r$  and  $[\text{H}_2\text{O}]_r$  was less obvious. Nevertheless, it is clear that there is some impact on  $[\text{C}_2\text{H}_2]_r$  due to the presence of water. This test also shows that  $[\text{H}_2\text{O}]_r$  occasionally spiked, which can be seen in Fig. 3 (b); yet Picarro G2401  $[\text{H}_2\text{O}]_r$  measurements were used to confirm that when there were no corresponding  $[\text{H}_2\text{O}]$  spike, which was confirmed by Picarro G2401  $[\text{H}_2\text{O}]_r$  measurements (see **Sect. S43** in the **Supplement**). This means that in reality, these  $[\text{H}_2\text{O}]_r$  outliers were an artefact of the instrumental Picarro G2203 response. This is probably due to issues in spectral water fitting at low (but non-zero)  $[\text{H}_2\text{O}]_r$  levels. It can therefore be concluded that a reliable and repeatable  $[\text{H}_2\text{O}]_r$  correction is difficult to apply to  $[\text{C}_2\text{H}_2]_r$  as the relationship is too unpredictable, even if limiting  $[\text{H}_2\text{O}]_r$  to below 0.1% with a Nafion-based gas dryer during field deployment. Therefore, optimum Picarro G2203 field sampling requires fully dry conditions. This avoids the complications associated with having to devise a reliable  $[\text{H}_2\text{O}]_r$  correction and also, with having to identify and remove spurious  $[\text{H}_2\text{O}]_r$  spikes. It follows that  $[\text{C}_2\text{H}_2]_r$  response should be calibrated in fully dry conditions.

### 2.3 Calibration gas blending characterisation

In order to calibrate dry Picarro G2203  $[\text{C}_2\text{H}_2]_r$  measurement response, precise reference  $[\text{C}_2\text{H}_2]$  testing gas mixtures are required. As we had no access to acetylene gas standards for with which to calibrate  $[\text{C}_2\text{H}_2]_r$  response, gas from the acetylene calibration cylinder could instead be carefully diluted using precise MFC blends. However, preliminary testing revealed MFC flow rates to be unreliable and offset from their predicted settings, which may be due to MFC contamination (due to particles, debris or oils, for example, getting trapped inside the instrument) or general ageing over time. This was especially concerning at low flow rate settings, compared to the maximum range of each MFC.

To characterise any disparity between the actual  $[\text{C}_2\text{H}_2]$  level in the gas mixture and  $[\text{C}_2\text{H}_2]_r$  (according to MFC settings), an empirical mass-flow controller correction factor ( $C_{\text{MFC}}$ ) was derived, with each  $C_{\text{MFC}}$  value corresponding to a specific set of MFC settings. This factor can be directly applied to the enhancement in  $[\text{C}_2\text{H}_2]_t$  above the  $[\text{C}_2\text{H}_2]_0$  level in the dilution gas where

$$[\text{C}_2\text{H}_2] = \left( C_{\text{MFC}} \cdot ([\text{C}_2\text{H}_2]_t - [\text{C}_2\text{H}_2]_0) \right) + [\text{C}_2\text{H}_2]_0, \quad (1)$$

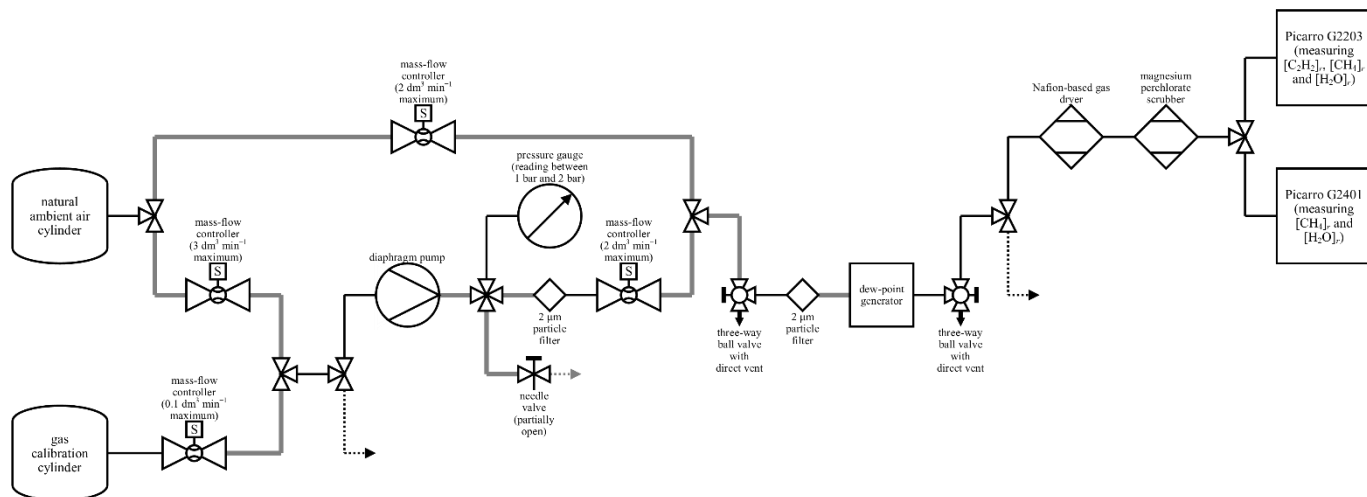
to yield reference  $[\text{C}_2\text{H}_2]$  levels.  $C_{\text{MFC}}$  values can be derived as a function of each set of MFC settings by comparing targeted and measured mole fraction levels of a different proxy gas, when blended with a dilution gas using the same MFC settings. Methane was used as a proxy gas for this purpose following

$$C_{\text{MFC}} = \frac{[\text{CH}_4] - [\text{CH}_4]_0}{[\text{CH}_4]_t - [\text{CH}_4]_0}, \quad (2)$$

which uses the enhancement in targeted methane mole fraction ( $[\text{CH}_4]_t$ ) above the background methane mole fraction ( $[\text{CH}_4]_0$ ) level in the dilution gas. Accurate  $[\text{CH}_4]$  measurements could be obtained ~~here~~ by calibrating Picarro G2401  $[\text{CH}_4]_t$  measurements using six certified gas standards traceable to the World Meteorological Organisation (WMO) greenhouse gas scale for methane (WMO X2004A) of between 1.6 ppm and 3.3 ppm  $[\text{CH}_4]$ . This yielded a gain factor of 1.0073 and an offset of  $-0.002647$  ppm with a calibration root-mean squared error (RMSE) of  $\pm 0.000079$  ppm, for the Picarro G2401 used in this work. This method makes the effect of any specific MFC errors in  $[\text{C}_2\text{H}_2]_t$  and  $[\text{CH}_4]_t$  estimation redundant, as they cancel out when correcting  $[\text{C}_2\text{H}_2]_t$  using Eq. (1) in conjunction with Eq. (2).

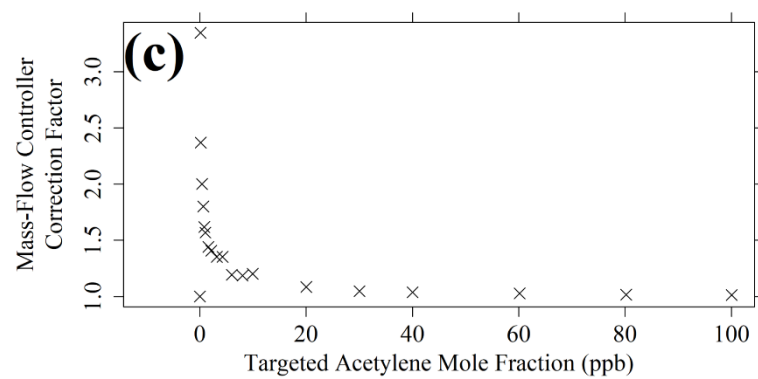
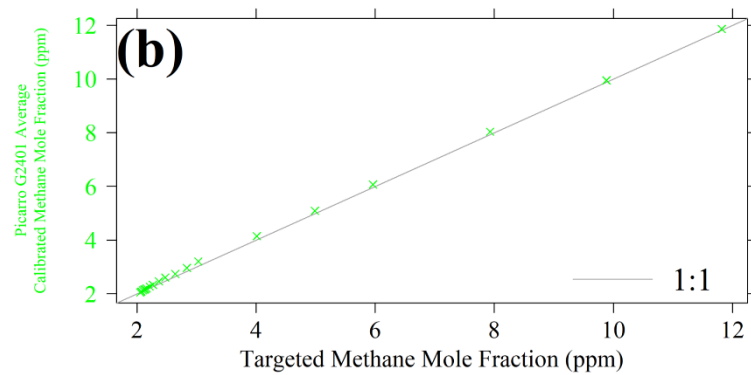
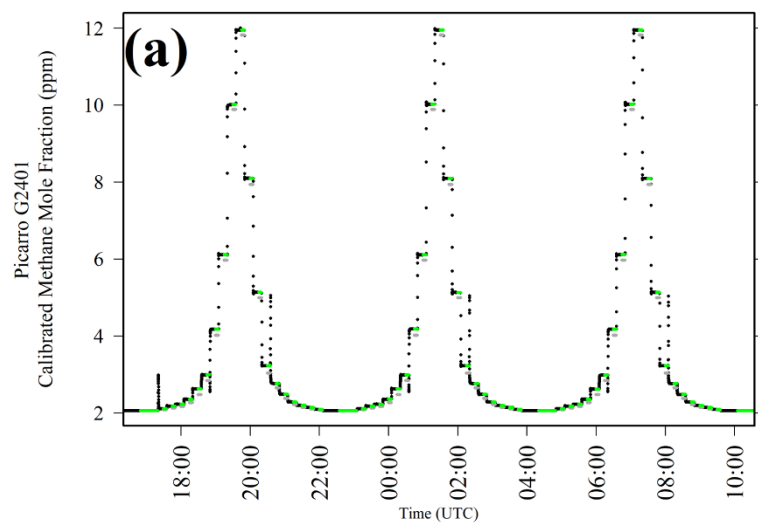
To derive  $C_{\text{MFC}}$ , the methane calibration cylinder was used as it is gravimetrically filled with a fixed  $[\text{CH}_4]$  level declared by the cylinder provider, although a  $\pm 0.5\%$   $[\text{CH}_4]$  uncertainty induces uncertainty in  $[\text{CH}_4]_t$  calculation and hence,  $C_{\text{MFC}}$  calculation, the effects of which are evaluated in in Sect. S5 of the Supplement. Gas from the methane calibration cylinder was blended with gas from a natural ambient compressed air cylinder, with a  $[\text{CH}_4]_0$  of 2.057 ppm. Twenty different  $[\text{CH}_4]_t$  levels were targeted between  $[\text{CH}_4]_0$  and 11.82 ppm. First,  $[\text{CH}_4]_0$  (*i.e.* pure natural ambient compressed air) was sampled for 60 minutes before sampling each other  $[\text{CH}_4]_t$  setting for 15 minutes. This cycle was repeated three times before finally sampling  $[\text{CH}_4]_0$  for 60 minutes. As the methane calibration cylinder has a high (995.4 ppm)  $[\text{CH}_4]$  content, the total quantity of gas from this cylinder reaching the gas analysers was less than 1% (*i.e.* representing a small argon enhancement and thus, causing minimal influence on spectral shape). Low  $[\text{CH}_4]_t$  levels were obtained through a system of double dilution, as illustrated schematically in **Fig. 4**. First, gas from the methane calibration cylinder was diluted with natural ambient compressed air. This was then subsampled and blended with compressed air a second time.

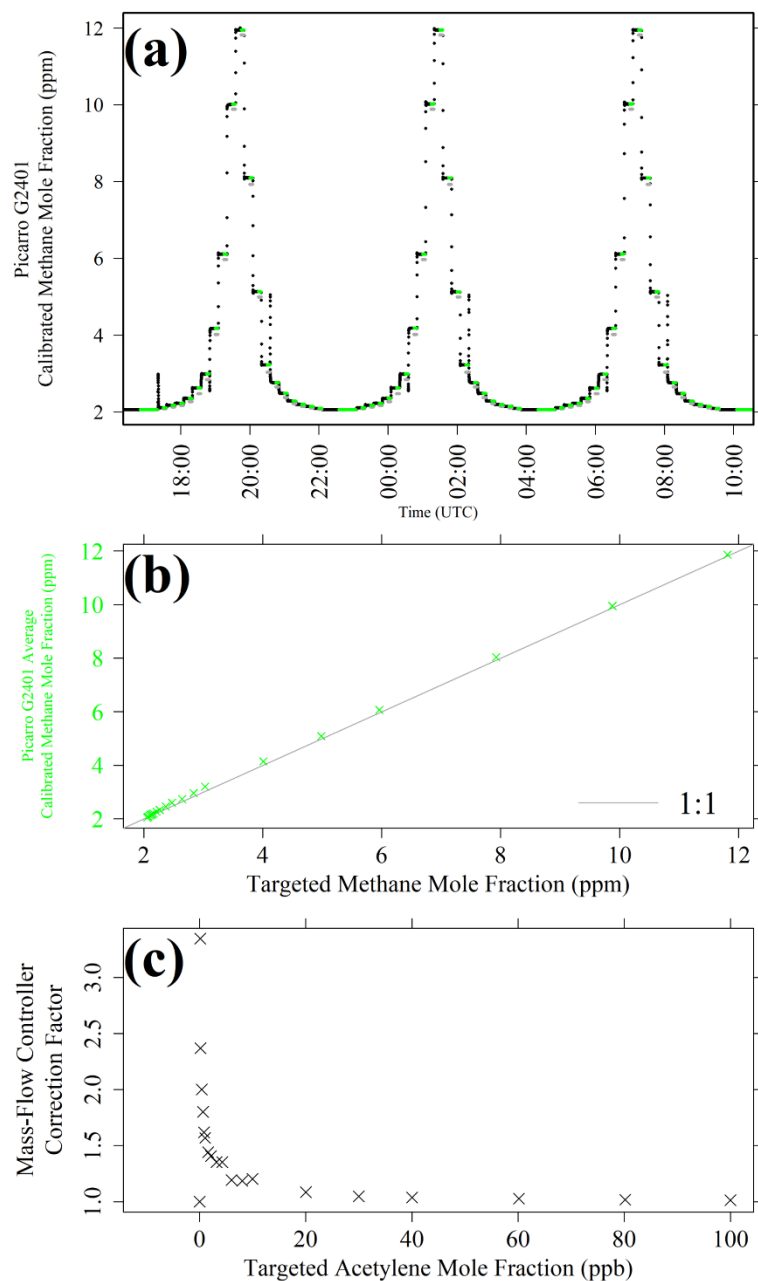




**Figure 4:** A schematic of the set-up during acetylene calibration and MFC blending characterisation. An arrow represents a vent to the atmosphere. Solid black lines represent either SS tubing or Synflex 1300 tubing with an OD of 0.25 inches. Solid grey lines represent SS connections between two components of approximately 0.04 m. The black dashed line represents SS tubing with an OD<sub>outer diameter</sub> of 0.125 inches. The grey dashed line represents SS tubing with an OD of 0.0625 inches. All connections used standard SS Swagelok fittings. Maximum MFC flow rates are representative of corresponding volumetric flow rates for dry air at 101 325 Pa and 273.15 K. The gas calibration cylinder represents was the methane calibration cylinder during MFC blending characterisation and the acetylene calibration cylinder during acetylene calibration. The three-way ball valves were directed towards the gas stream during testing and away from the direct vent to the atmosphere.

**Figure 5** shows Picarro G2401 results for the-methane MFC blending characterisation-test for the Picarro G2401, where all  $[\text{CH}_4]_t$  measurements have been converted into  $[\text{CH}_4]_i$  using the WMO standard calibration coefficients given above. To derive  $C_{\text{MFC}}$  values from this data, a 5-minute average Picarro G2401  $[\text{CH}_4]$  value was taken from towards the end of each 15-minute sampling step (except when sampling  $[\text{CH}_4]_0$ ). This averaging period was used to enable the Picarro G2401 to stabilise and to flush all gas tubing. As the cycle was repeated thrice, each  $[\text{CH}_4]_t$  level has three corresponding 15-minute  $[\text{CH}_4]$  averages, of which the average was used within Eq. (2) to derive  $C_{\text{MFC}}$  values, which are plotted in **Fig. 5** (c) as a function of corresponding  $[\text{C}_2\text{H}_2]_t$  values corresponding to derived using the same MFC settings (see next subsection for details). The standard deviation of each average (*i.e.* the standard deviation between each of three 5-minute  $[\text{CH}_4]$  averages at each  $[\text{C}_2\text{H}_2]_t$  level greater than  $[\text{CH}_4]_0$ ) was on average ( $\pm 0.002 \pm 0.001$ ) ppm. This small variability demonstrates the reliability in MFCs to consistently provide the same gas blends on multiple occasions over time, with a relatively large gap of 5.75 hours between each of the three sampling cycles. In summary **Fig. 5** (c)  $C_{\text{MFC}}$  values show that the influence of a  $[\text{C}_2\text{H}_2]$  enhancement above  $[\text{C}_2\text{H}_2]_0$  can be over 200% larger than a corresponding  $[\text{C}_2\text{H}_2]_t$  enhancement (above  $[\text{C}_2\text{H}_2]_0$ ), emphasising the importance of this MFC blending characterisation approach, as opposed to erroneously assuming  $[\text{C}_2\text{H}_2]$  to simply equal  $[\text{C}_2\text{H}_2]_t$  in the subsequent acetylene calibration analysis.





**Figure 5:** (a) Picarro G2401  $[\text{CH}_4]$  plotted as black dots, (b) corresponding  $[\text{CH}_4]$  5-minute averages plotted as green crosses against [calculated](#)  $[\text{CH}_4]$ , [calculated from MFC settings](#) and (c)  $C_{\text{MFC}}$  as a function of corresponding [calculated](#)  $[\text{C}_2\text{H}_2]$  levels, derived from three testing cycles by blending gas from the methane calibration cylinder with natural ambient compressed air. Periods used to derive averages are highlighted as green dots and corresponding [calculated](#)  $[\text{C}_2\text{H}_2]$  levels are shown in the background as light grey dots in (a). An identity line is shown as a solid light grey line in (b).

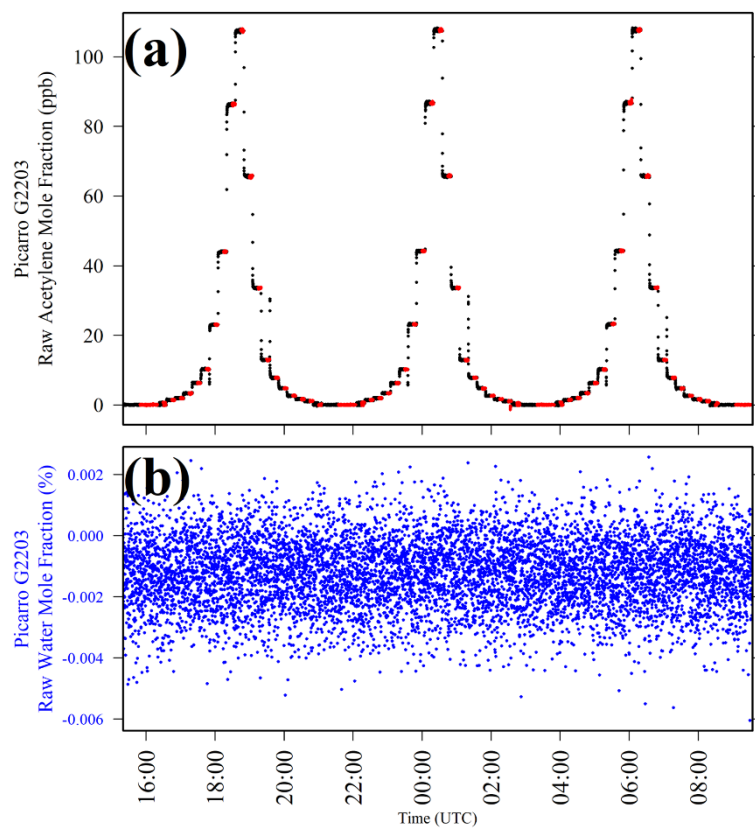
## 2.4. Acetylene calibration

Following the characterisation of MFC gas blending capability at specific MFC flow rate settings, ~~calculated~~  $[\text{C}_2\text{H}_2]_r$  values can be converted into corresponding  $[\text{C}_2\text{H}_2]_l$  levels using Eq. (1). This provides corrected  $[\text{C}_2\text{H}_2]$  gas blend standards with which to calibrate Picarro G2203  $[\text{C}_2\text{H}_2]_r$  measurements. The acetylene calibration cylinder was used here for dilution, however, as for the methane calibration cylinder, the  $\pm 3\%$  volumetric uncertainty in the declared  $[\text{C}_2\text{H}_2]$  level induces uncertainty in  $[\text{C}_2\text{H}_2]_l$  calculation, the influence of which is evaluated in Sect. S5 of the Supplement. Gas from the acetylene calibration cylinder was blended with gas from the same natural ambient compressed air cylinder used during MFC blending characterisation, containing 0 ppb  $[\text{C}_2\text{H}_2]_0$ . The same process of double dilution was used, as illustrated schematically in Fig. 4, with absolutely no changes made to any of the flow connections (except for swapping the methane calibration cylinder with the acetylene calibration cylinder) and with no MFC power loss. Both the MFC blending characterisation test and acetylene calibration test were conducted within a 48-hour window, to minimise drift in MFC performance. Identical flow rate settings to those used during MFC blending characterisation resulted in ~~the sampling of~~ twenty different  $[\text{C}_2\text{H}_2]$  levels ~~being sampled~~ between 0 ppb and 101.3 ppb (*i.e.* where each  $[\text{C}_2\text{H}_2]_l$  level is corrected here by its corresponding  $C_{\text{MFC}}$  value given in Fig. 5 (c)). First, ~~an  $[\text{C}_2\text{H}_2]$  of~~ 0 ppb  ~~$[\text{C}_2\text{H}_2]$~~  was sampled for 60 minutes before sampling each other  $[\text{C}_2\text{H}_2]$  ~~level~~ ~~setting~~ for 15 minutes. ~~Both the MFC blending characterisation test and acetylene calibration test were conducted within a 48-hour window, to minimise drift in MFC performance, and with no MFC power loss.~~ This  $[\text{C}_2\text{H}_2]$  range is deemed to be sufficient to capture most  $[\text{C}_2\text{H}_2]$  measurements typically expected ~~to be measured~~ downwind of a controlled acetylene release, although a larger calibration range may be required if sampling nearer to the source, where higher  $[\text{C}_2\text{H}_2]$  sampling may be expected.

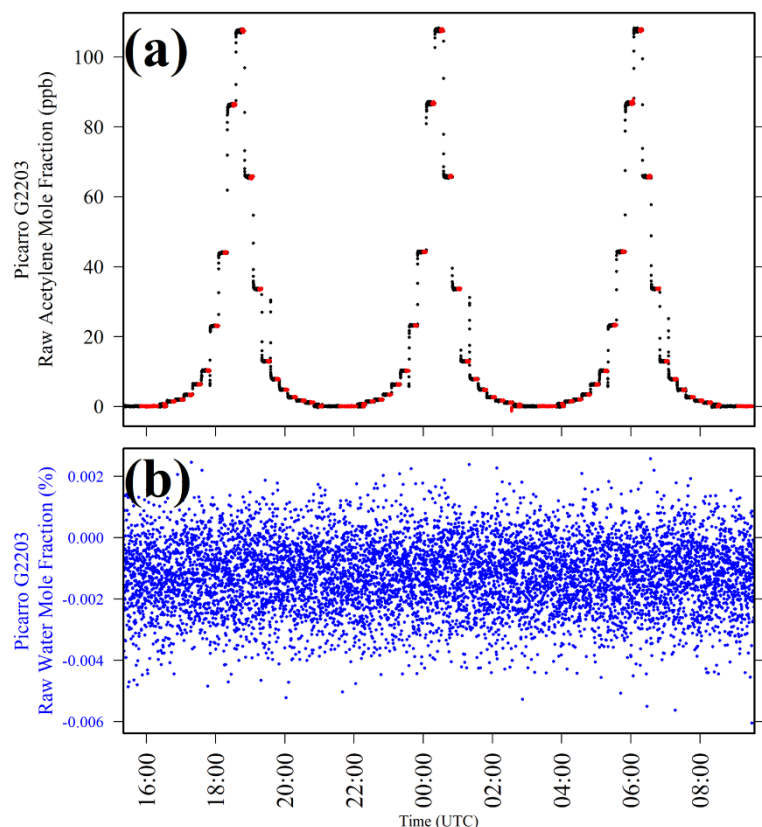
Ordinarily, gas from compressed cylinders is already dry, ~~so no drying is required~~. However, during this test (as well as during ~~the~~ blending characterisation ~~described~~ test above), all gas passed through the dew-point generator with a 8° C setting, to humidify the gas stream. The gas then passed through the Nafion-based gas dryer to significantly reduce  $[\text{H}_2\text{O}]$  before finally passing through the magnesium perchlorate scrubber, to ensure dryness. This counterintuitive procedure of humidification followed by drying was used to best replicate sampling in the field when using both the Nafion-based gas dryer as well as the magnesium perchlorate scrubber, to account for potential artefacts on  $[\text{C}_2\text{H}_2]$  ~~at the point of measurement~~. Although a dew-point generator is not present during field sampling, Sect. S32 in the Supplement shows that this has no noticeable effect on  $[\text{C}_2\text{H}_2]_r$  measurements, alongside the Nafion-based gas dryer and the magnesium perchlorate scrubber. Nevertheless, it was still preferred to carry out this humidification and drying procedure as an added precaution.

Sampling results are presented in Fig. 6 for the Picarro G2203 acetylene calibration ~~test for the Picarro G2203~~. Figure 6 (b) shows a stable Picarro G2203  $[\text{H}_2\text{O}]_r$  level throughout testing, as expected. A calibration could be derived from this data by taking a 5-minute average Picarro G2203  $[\text{C}_2\text{H}_2]_r$  value from towards the end of each 15-minute sampling step. However, for each 60-minute  $[\text{C}_2\text{H}_2]_0$  sampling period, a 30-minute average was used, as  $[\text{C}_2\text{H}_2]_r$  measurements are slightly more noisy at 0 ppb  $[\text{C}_2\text{H}_2]$ . For the lowest three non-zero reference  $[\text{C}_2\text{H}_2]$  ~~level~~ ~~settings~~ (0.349 ppb, 0.464 ppb and 0.867 ppb), unstable

$[\text{C}_2\text{H}_2]_r$  measurements were observed, with  $[\text{C}_2\text{H}_2]_r$  occasionally resolving to the  $[\text{C}_2\text{H}_2]_r$  level observed at 0 ppb  $[\text{C}_2\text{H}_2]$  (see **Sect. S64** in the **Supplement** for an example), despite the fact that the same constant gas stream was being sampled. This probably corresponds to the Picarro G2203 temporarily losing the acetylene IR absorption peak, due to its small size at low  $[\text{C}_2\text{H}_2]$  levels. Therefore, the  $[\text{C}_2\text{H}_2]_r$  calibration ~~was derived~~ excluding these data points.

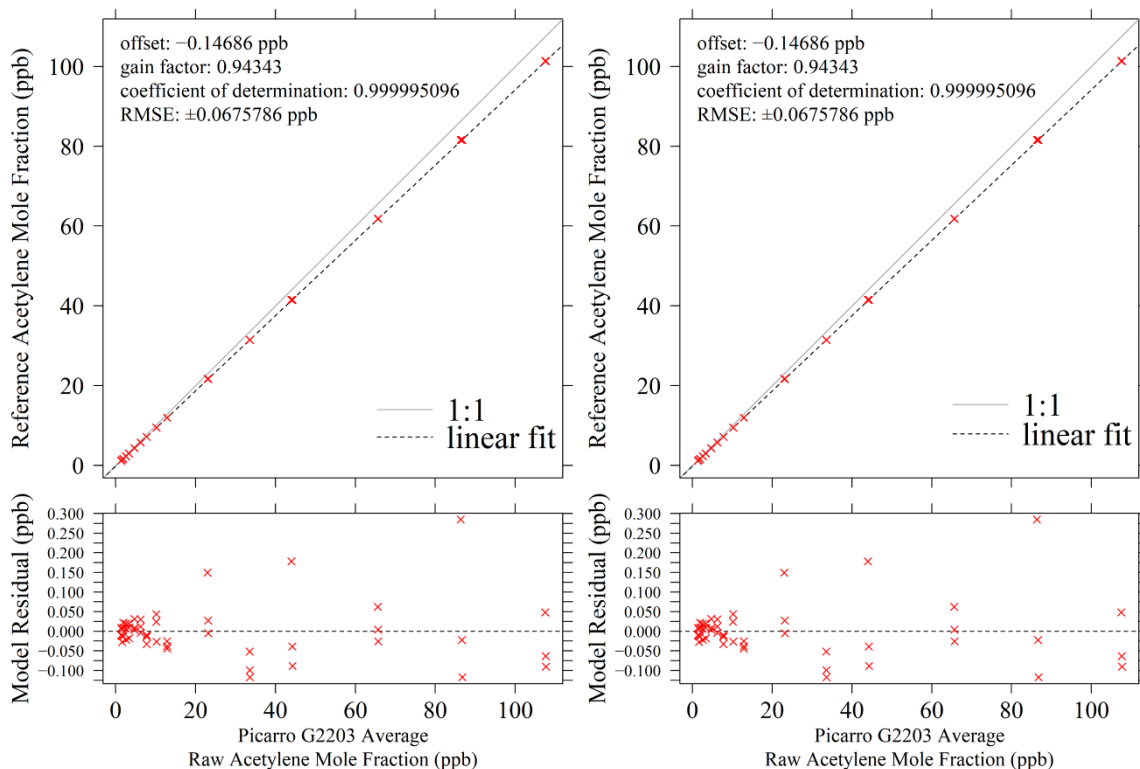


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**Figure 6:** (a) Picarro G2203  $[C_2H_2]_r$  plotted as black dots and (b) Picarro G2203  $[H_2O]_r$  plotted as blue dots, when sampling twenty different standard  $[C_2H_2]$  level settings over three testing cycles by blending gas from the acetylene calibration cylinder with natural ambient compressed air. Periods used to derive averages are highlighted as red dots in (a).

A linear regression was applied by comparing  $[C_2H_2]$  to  $[C_2H_2]_r$  (presented in **Fig. 7**) for all  $[C_2H_2]$  level settings except the lowest four, yielding a gain factor of 0.943 and an offset of  $-0.147$  ppb, with a RMSE of  $\pm 0.0676$  ppb. Due to the high general stability of the CRDS method over periods of years for other gases (Crosson, 2008, Yver Kwok *et al.*, 2015b, Gomez-Pelaez *et al.*, 2019, Yver-Kwok *et al.*, 2021), it can be assumed that these acetylene calibration coefficients remain sufficiently stable over prolonged time periods. Yet, this calibration is only valid when sampling above the lowest stable  $[C_2H_2]$  level of 1.16 ppb (corresponding to  $[C_2H_2]_r$  measurements of greater than 1.38 ppb). It may be possible to sample at a slightly lower  $[C_2H_2]$  level, but further exhaustive testing through trial and error would be required to precisely identify this threshold. The linear calibration fit has a low RMSE of  $\pm 0.0676$  ppb, indicating low fitting uncertainty. However, there may be an additional uncertainty in calibration coefficients as  $[CH_4]_r$  (and hence,  $C_{MFC}$ ) relies on the declared methane calibration cylinder  $[CH_4]$  level and  $[CH_4]_r$  relies on the declared acetylene calibration cylinder  $[C_2H_2]$  level, both of which have an associated uncertainty, as discussed above. The combined effect of these cylinder uncertainties is evaluated in in **Sect. S5** of the **Supplement**, which reveals that in a worst-case scenario, the calibration gain factor could take a range of between 0.911 and 0.977.

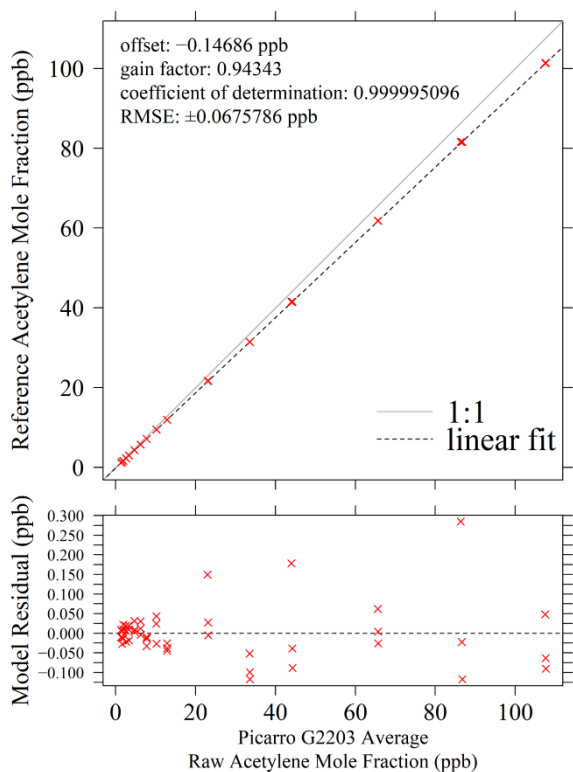


**Figure 7: (top) Picarro G2203 5-minute average  $[C_2H_2]_r$  measurements, when combining gas from the acetylene calibration cylinder with natural ambient compressed air, plotted against reference  $[C_2H_2]$  levels (red crosses), with a linear regression model shown as a dashed black line and an identity line shown as a solid light grey line. (bottom) Corresponding model residuals between  $[C_2H_2]_r$  and  $[C_2H_2]$  (red crosses), with a 0 ppb  $[C_2H_2]$  residual shown as a horizontal dashed black line.**

It is important to note that the calibration results presented in this work are specific to the Picarro G2203 gas analyser tested here. Other instruments may result in other calibration coefficients, which would need to be tested for each individual gas analyser. The Fig. 7 fit shows that when sampling at a fixed  $[C_2H_2]$  of 10 ppb, the Picarro G2203 tested here reports 10.76 ppb  $[C_2H_2]_r$ . This +8% error is the same order of magnitude to the +12% error reported by Omara *et al.* (2016) for Picarro G2203  $[C_2H_2]_r$  measurements when sampling a 100 ppm  $[C_2H_2]$  standard. The error presented here could be significant when deriving tracer-based fluxes of a target gas. This therefore emphasises the importance calibrating all  $[C_2H_2]_r$  measurements obtained during field sampling. Although a calibration could not be derived between 0 ppb and 1.16 ppb  $[C_2H_2]$  using this testing data, it can be concluded that sampling gas containing 0 ppb  $[C_2H_2]$  corresponds to a  $[C_2H_2]_r$  measurement of 0.0125 ppb. This value corresponds to the average of the four measured 30-minute  $[C_2H_2]_r$  averages obtained when sampling 0 ppb  $[C_2H_2]$  during the calibration test. It is also interesting that this value is different to the calibration linear model zero intercept (or offset), which suggests that the Picarro G2203 behaves slightly differently in the absence of acetylene. Although this can be used to correct  $[C_2H_2]_r$  measurements when sampling air containing 0 ppb  $[C_2H_2]$ , it is not always possible to know if a  $[C_2H_2]_r$  measurement made at this 0.0125 ppb level actually corresponds to sampling 0 ppb  $[C_2H_2]$  or whether this erroneously



445 corresponds to a slightly higher [undetectable](#) [C<sub>2</sub>H<sub>2</sub>] level, which remains a limitation of using the Picarro G2203 tested in this work.



450 **Figure 7: (top) Picarro G2203 5-minute average [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements, when combining gas from the acetylene calibration cylinder with natural ambient compressed air, plotted against reference [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> levels (red crosses), with a linear regression model shown as a dashed black line and an identity line shown as a solid light grey line. (bottom) Corresponding model residuals between [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> and [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> (red crosses), with a 0 ppb [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> residual shown as a horizontal dashed black line.**

As an additional test, the calibration procedure was repeated but instead, using gas from the zero-air generator (UHP-300ZA-S, Parker Hannifin Manufacturing Limited, Gateshead, Tyne and Wear, UK) for dilution. Details of this test and presented in **Sect. S75** in the **Supplement**. This test serves to check the validity of the acetylene calibration coefficients given above in a different gas mixture with no background levels of methane present. This additional test yielded a gain factor of 0.941 and an offset of +0.0014 ppb, with a RMSE of ±0.0356 ppb, when comparing standard [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> levels to [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements. This gain factor is almost the same as when using natural ambient compressed air for dilution, with a similar offset close to zero. Nevertheless, small changes in [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> response in different background gases may have an influence on applications in field sampling, which should be considered, although it does not appear to be so important for the Picarro G2203 tested here.

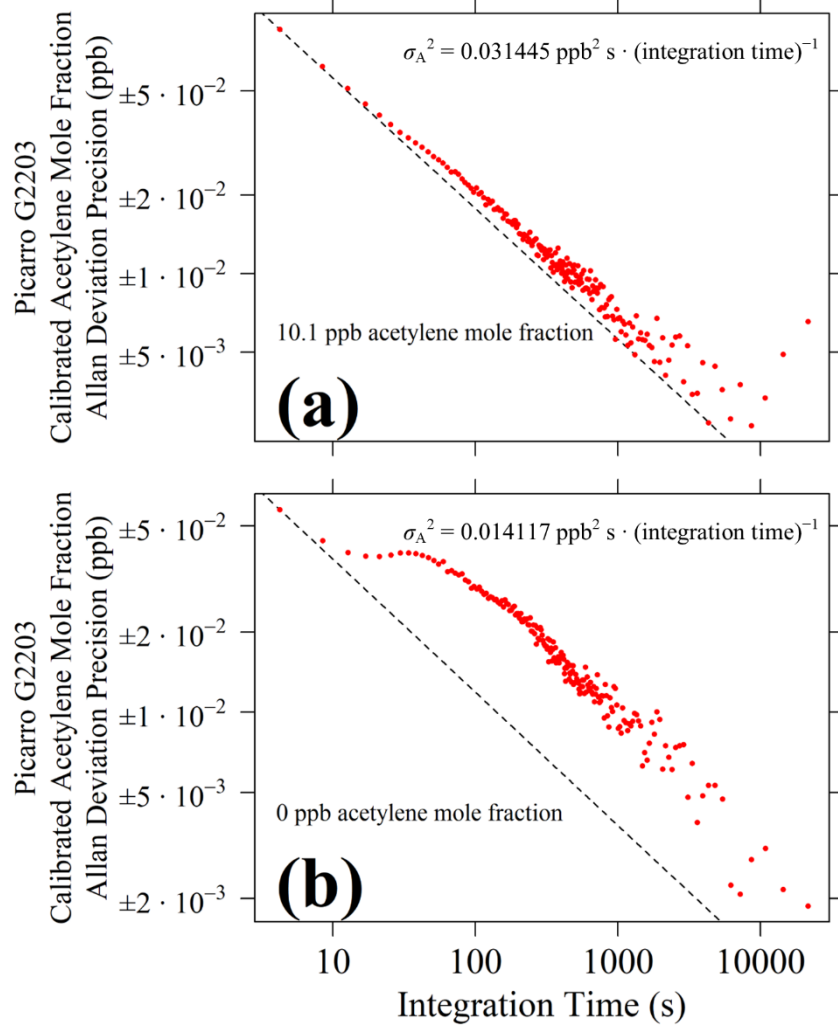
## 2.5 Measurement stability

As a final test, the stability of Picarro G2203 acetylene measurements was assessed by conducting an Allan variance ( $\sigma_A^2$ ) test, which characterises the variability between sets of measurements over different timescales, ranging from the interval between consecutive measurements up until half of the duration of the test (although timescales of greater than a few hours hold little statistical value). ~~Gas from a First, natural ambient compressed air from a cylinder containing 2.076 ppm [CH<sub>4</sub>]~~ was blended with gas from the acetylene calibration cylinder to sample ~~10.9 ppb<sub>a</sub> [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> of 10.9 ppb~~ (corresponding to ~~an [C<sub>2</sub>H<sub>2</sub>] of 10.1 ppb [C<sub>2</sub>H<sub>2</sub>]~~), ~~which was sampled~~ for 12 hours. This blending assumes the MFCs to provide a constant flow rate, as any potential variability in MFC flow rate may be convolved with measurement noise, which is a limitation of this approach. ~~An additional  $\sigma_A^2$  test was performed at an [C<sub>2</sub>H<sub>2</sub>] of Next, pure natural ambient compressed air from the same gas cylinder was sampled for 12 hours, corresponding to 0 ppb, with details and results provided in Sect. S8 of the Supplement[C<sub>2</sub>H<sub>2</sub>]. To~~ conduct this test, a similar set-up was used as for the acetylene calibration, as illustrated schematically in Fig. 4, when sampling 10.1 ppb [C<sub>2</sub>H<sub>2</sub>]. A modified version was used for the 0 ppb [C<sub>2</sub>H<sub>2</sub>] test to save gas, as no dilution is required; the compressed air cylinder was connected directly to a MFC, before subsequent humidification and drying.

To evaluate measurement stability, ~~all~~ [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements were first calibrated using calibration coefficients from the previous subsection, ~~when sampling 10.1 ppb [C<sub>2</sub>H<sub>2</sub>]. [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements made at 0 ppb [C<sub>2</sub>H<sub>2</sub>] were corrected by subtracting 0.0125 ppb, as the linear model fit is not valid below 1.16 ppb [C<sub>2</sub>H<sub>2</sub>] (although, in theory, this offset correction has no effect in this analysis on variance). Then an before performing an  $\sigma_A^2$  test using was conducted on~~ subsets of ~~this each~~ prolonged dataset, as described by Werle *et al.* (1993). As the measurement frequency is inconsistent, the integration time was derived by finding the average of differences between the time corresponding to the first measurement in each subset and the first measurement in the next subset. In addition, the  $\sigma_A^2$  test was repeated ten times by moving the starting and ending datapoint for each of the ten analyses, as the duration between each measurement follows a cycle of ten [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements (as discussed ~~previously above~~). These repeated tests were therefore used to obtain an average of the  $\sigma_A^2$  values and corresponding integration times from the ten analyses.

~~A logarithmic plots~~ showing Allan deviation precision ( $\sigma_A$ ) as a function of integration time ~~is are~~ given in Fig. 8, with a white noise line~~s~~ also shown. The  $\sigma_A$  at the smallest integration time is  $\pm 0.0863$  ppb (4.22 s integration time), ~~which suggests that variability between individual consecutive measurements is small~~ when sampling ~~10.1 ppb [C<sub>2</sub>H<sub>2</sub>] and  $\pm 0.0577$  ppb (4.24 s integration time) when sampling 0 ppb [C<sub>2</sub>H<sub>2</sub>]~~ a single gas. ~~The Values of  $\sigma_A$  at the smallest integration time did not use averaging of multiple measurements and simply took the variance between individual consecutive measurements, as each averaging bin contained one single element. Figure 8 plots shows consistently decreasing  $\sigma_A$  with integration time, as expected, with a trend close to the white noise line. However, the [C<sub>2</sub>H<sub>2</sub>] plot at 0 ppm [C<sub>2</sub>H<sub>2</sub>] has an interesting feature in the first 100 s where  $\sigma_A$  increases slightly before continuing its decline as a function of integration time, following a trend close to the white noise line (although offset from  $\sigma_A$  at the lowest integration time). This could be associated with the roughly 40 s [C<sub>2</sub>H<sub>2</sub>]~~

measurement cycle, with the Picarro G2203 consistently struggling to fit for an absence of acetylene over each of the ten samples. The difference between the two Fig. 8 fits supports the suggestion from the previous subsection, that the Picarro G2203  $[\text{C}_2\text{H}_2]$  response is different at very low  $[\text{C}_2\text{H}_2]$  levels, close to 0 ppb. Nevertheless, neither  $\sigma_A^2$  test shows a clear sustained inflection in  $\sigma_A$  decrease with integration time. This suggests that there is minimal drift over a 12-hour period compared to variability between individual measurements. This 12-hour duration is far longer than a typical field sampling campaign (a few hours), demonstrating that Picarro G2203 measurements are unlikely to drift during field sampling. Furthermore, both tests reveal an  $\sigma_A$  of less than  $\pm 0.1$  ppb at the lowest integration time which suggests that variability between individual consecutive measurements is small, when sampling a single gas.



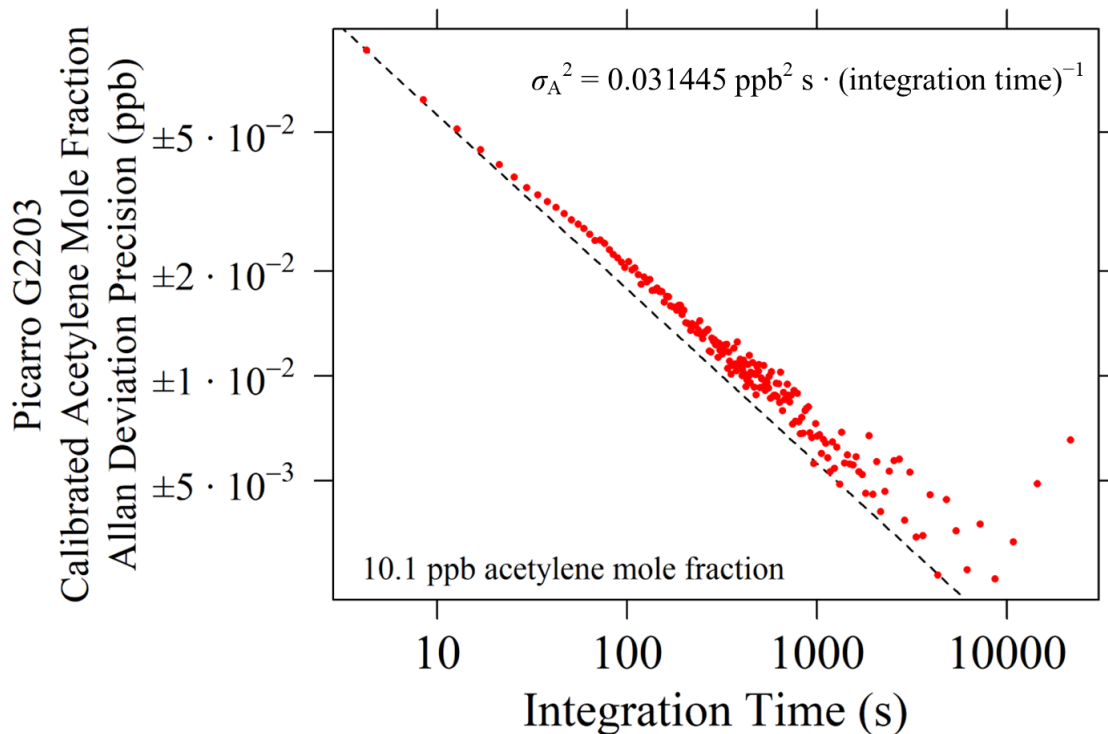


Figure 8:  $\sigma_A$  for Picarro G2203 calibrated  $[\text{C}_2\text{H}_2]$  measurements as a function of integration time derived from an average of ten different tests, plotted as red dots, when (a) sampling an  $[\text{C}_2\text{H}_2]$  of 10.1 ppb  $[\text{C}_2\text{H}_2]$  and (b) sampling 0 ppb  $[\text{C}_2\text{H}_2]$ . Logarithmic axes are used in each plot. The black dashed line depicts white noise, with this fit forced to intersect with  $\sigma_A$  at the lowest integration time (the fitting coefficient is provided inside the each plot).

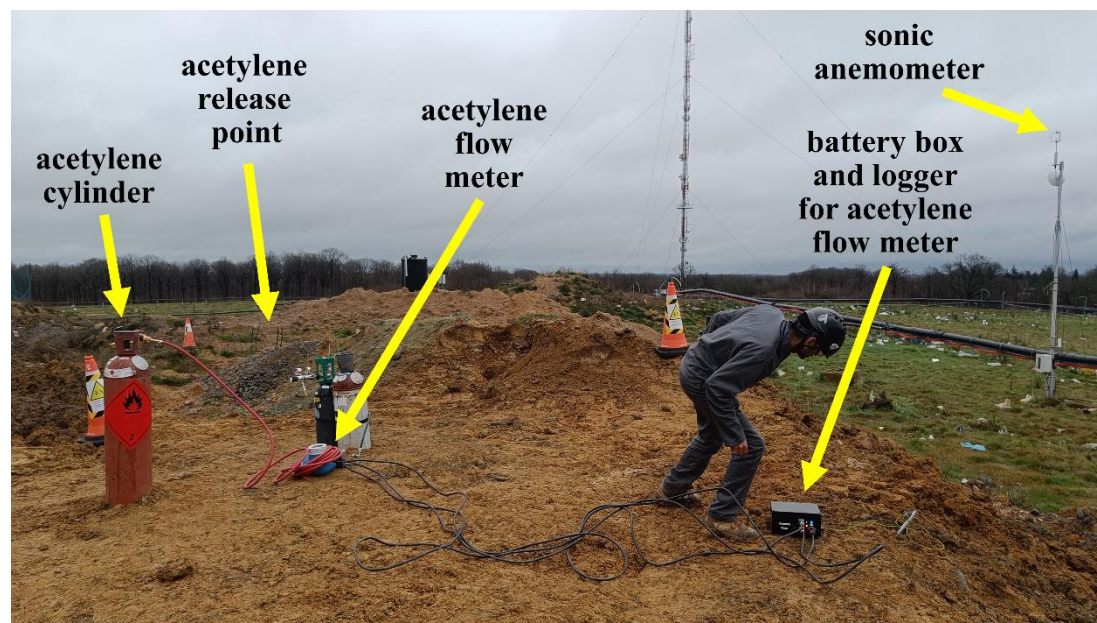
### 3 Field testing methane flux inversion method using an acetylene tracer release

#### 3.1 Acetylene release method

Standard details on the acetylene release method itself are provided here. Dry acetylene with a 99.5% purity is released from an 8.7 kg acetylene gas cylinder (Acétylène Industriel X50S, Air Products S.A.S., Saint Quentin Fallavier, France), with a 99.5% purity; as gas from such cylinders is naturally dry, it is released pure without any treatment. The cylinder is connected to an acetylene regulator (0783640, GCE Ltd, Warrington, UK), with a maximum output pressure of 1.5 bar. The acetylene Gas flow rate ( $Q_{\text{acetylene}}$ ) is manually adjusted using a downstream metering valve (SS-4L, Swagelok Company). As the gauge pressure of gaseous acetylene gauge pressure must not exceed be kept below 1.5 bar for safety reasons, the pressure range of the acetylene regulator pressure range is targeted to between 0.5 bar and 1.0 bar whilst simultaneously adjusting the metering valve for the desired flow rate. As only 10% of the cylinder contents of the cylinder can safely be released emitted per hour, the maximum sustained acetylene flow rate ( $Q_{\text{acetylene}}$ ) level from this acetylene cylinder is 0.23942 g s<sup>-1</sup>.  $Q_{\text{acetylene}}$  is measured using an acetylene flow meter (8C3B04-20X1/0, Cubemass C 300, Endress+Hauser Group Services AG, Reinach,

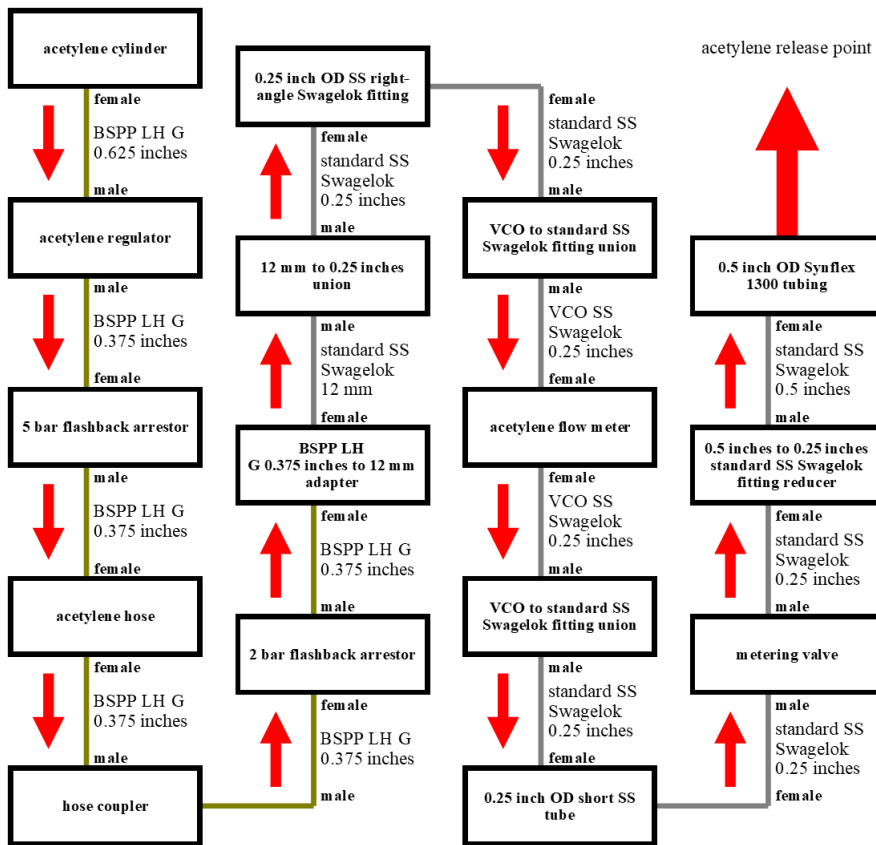
Switzerland), which ~~measures  $Q_{\text{acetylene}}$  using~~ the Coriolis technique (Baker, 2016), with an accuracy of no greater than  $0.00389 \text{ g s}^{-1}$  ~~when sampling below an  $Q_{\text{acetylene}}$  of  $0.778 \text{ g s}^{-1}$  and no greater than 0.005 multiplied by  $Q_{\text{acetylene}}$  itself when measuring above an  $Q_{\text{acetylene}}$  of  $0.778 \text{ g s}^{-1}$ .~~ Further ~~details on the~~ acetylene flow meter ~~details~~ are provided in **Sect. S96** of the **Supplement**. Following each acetylene release, all equipment downstream of the regulator is flushed with nitrogen gas.

The acetylene release point is connected to the rest of the acetylene release equipment using Synflex 1300 tubing with an OD of 0.5 inches ~~(the null effect of Synflex 1300 on acetylene is discussed in Sect. S2 of the Supplement)~~. A 0.5 inches to 0.25 inches standard SS Swagelok fitting reducer (SS-810-R-4, Swagelok Company) ~~is used to connect~~s to this wider tube, ~~which is~~ chosen to minimise the pressure drop up to the release point. At the point of release, the tubing is split into four upwards-facing co-located Synflex 1300 tubes all with an OD of 0.5 inches, as illustrated in **Fig. 9**, to promote more even ~~plume dissipation of the plume above ground level~~. A ~~6 m~~ safety exclusion zone is designated ~~around as being 6 m away from~~ the release point ~~as described in Sect. S10 of the Supplement, based on with all acetylene release equipment placed outside this zone. This distance was calculated such that  $[\text{C}_2\text{H}_2]$  cannot exceed its lower atmospheric flammable limit of 2.5% (Williams and Smith, 1969) considering a  $Q_{\text{acetylene}}$  of  $0.5 \text{ g s}^{-1}$  and using Gaussian plume modelling in the worst case Pasquill stability class (Turner, 1994), with a mean wind speed of  $0.1 \text{ m s}^{-1}$  to accentuate  $[\text{C}_2\text{H}_2]$ . The boundaries of the safety exclusion zone are designated by cones, with the zone being constantly manned by the release operator who stands outside the zone and continuously surveys the acetylene release equipment.~~



**Figure 9:** A photograph of the acetylene release equipment when deployed during the campaign at the landfill site. The cones indicate the boundaries of the safety exclusion zone (not all cones are visible).

A schematic illustration of the entire acetylene release set-up is shown in **Fig. 10**. All components are selected for compatibility with acetylene. Equipment for acetylene conventionally has British Standard Pipe parallel (BSPP) left-hand (LH) G threads. BSPP LH G threads are converted into threads for standard SS Swagelok fittings using a SS 12 mm to 0.25 inches union (SS-12M0-6-4, Swagelok Company) and a brass BSPP LH G 0.375 inches to 12 mm adapter. In addition, the acetylene flow meter has threads for VCO SS Swagelok fittings, which are converted into threads for standard SS Swagelok fittings using a VCO to standard SS Swagelok fitting union (SS-4-VCO-6-400, Swagelok Company). Acetylene release equipment is protected from ~~exposure to~~ flammable-gas mixtures using non-return valves. Flashback arrestors prevent an accidental flame from reaching upstream components and eventually, potentially entering the acetylene cylinder. A 5 bar flashback arrestor with a built-in non-return valve (50951, GCE Ltd) is connected directly downstream of the acetylene regulator. A 10 m reinforced high tensile synthetic textile acetylene hose (GCE Ltd) with an in-built non-return valve ~~is used to connect~~ the cylinder to the acetylene flow meter. An additional 2.0 bar flashback arrestor with a built-in non-return valve (Flashback Arrestor Super 66, WITT-Gasetechnik GmbH & Co KG, Witten, Germany) is connected upstream of the acetylene flow meter. ~~The entire acetylene release set up is illustrated schematically in Fig. 10. All fittings and connectors were selected for compatibility with acetylene, with any copper alloys (including brass) containing no more than 65% copper.~~



**Figure 10: A schematic of each individual component (in black boxes) used when conducting an acetylene release. Dark yellow lines indicate brass connections and grey lines indicate SS connections. The thread type between each component is given next to each line and the gender of the threads is given in bold text outside of each box. The direction of acetylene gas flow is indicated by red arrows.**

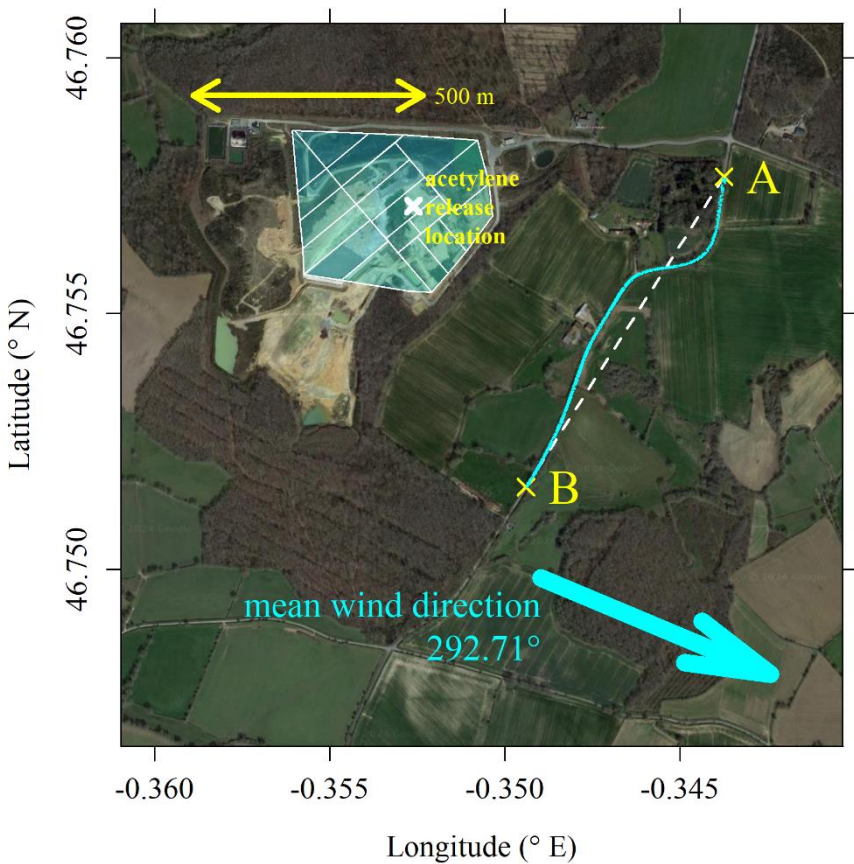
Equipment for use with acetylene conventionally uses threads for British Standard Pipe parallel (BSPP) left hand (LH) G fittings, as opposed to right hand fittings which are conventionally used in most other applications. These BSPP LH G fittings are converted into threads for standard SS Swagelok fittings using a SS 12 mm to 0.25 inches union (SS 12M0 6 4, Swagelok Company) and a brass BSPP LH G 0.375 inches to 12 mm adapter. In addition, the inlet and outlet for the acetylene flow meter has threads for VCO SS Swagelok fittings. A VCO to standard SS Swagelok fitting union (SS 4 VCO 6 400, Swagelok Company) is therefore used to obtain threads for standard SS Swagelok fittings, for integration with the rest of the set up.

### 3.2 Landfill site release campaign

To test our acetylene release and corresponding  $Q_{\text{methane}}$  calculation methods, an acetylene release was conducted from within a landfill site. This particular landfill site was chosen as it a known facility-scale methane source, for which we were able to acquire site access. The specificities of this specific study site (for example waste content, waste quantity, site age and site management) are irrelevant in this study; this study is dedicated to the acetylene release method itself in the context of  $Q_{\text{methane}}$



quantification methods in general. Therefore, the magnitude of any derived  $Q_{\text{methane}}$  rate is beyond the scope of this study and will be discussed in a future publication. An aerial photograph of the site is shown in **Fig. 11**. The acetylene release location from within the site was selected due to accessibility with regards to transportation and installation of a heavy acetylene cylinder. We were not authorised to conduct a release from a more central location due to site activities and the presence of active open landfill cells. In general, the acetylene release location should be as close to the source as possible, to trace emission of the methane source as it disperses through the atmosphere, although this can be difficult from a complex heterogeneous [area](#) source such as a landfill site (Fredenslund *et al.*, 2019). The complications associated with tracer release positioning is discussed in further detail in **Sect. 4**. A three-dimensional sonic anemometer (WindMaster Pro, Gill Instruments Limited, Lymington, Hampshire, UK) measured winds at 20 Hz, near to the acetylene release point, as illustrated in **Fig. 10**, which was visually aligned with an uncertainty of [approximately  \$\pm 4^\circ\$](#)  [and erected to a height of approximately 6 m above ground level](#).



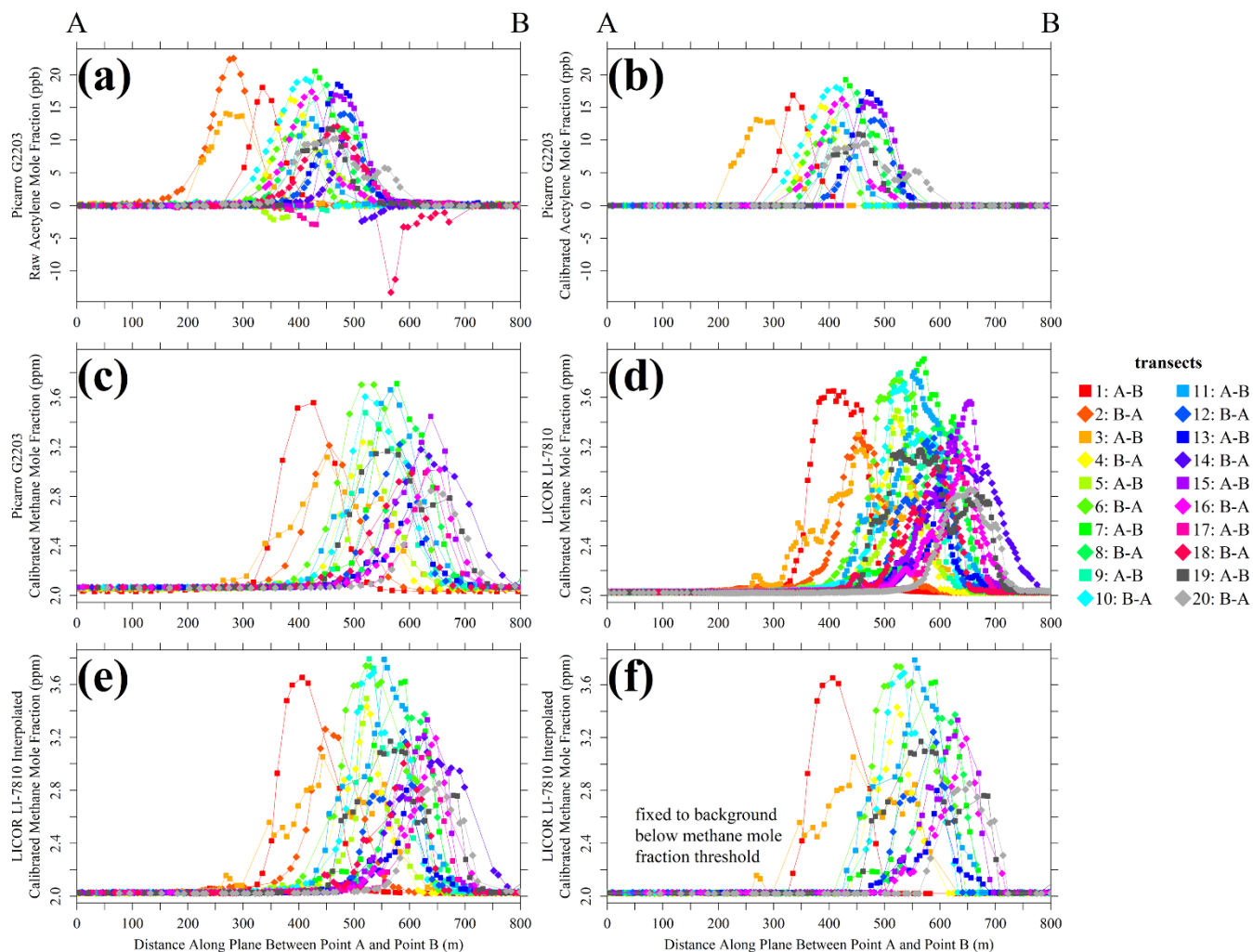
**Figure 11:** The location of the acetylene release (white cross) which was conducted at ground level, plotted on top of a background map. Transparent shaded cyan polygons indicate both active and inactive cells, as identified by the landfill site operator. The location of Picarro G2203 [ $\text{C}_2\text{H}_2$ ] measurements are shown as cyan dots on a sampling road between Point A and Point B, indicated by the yellow crosses. The plane between Point A and Point B is shown as a dashed white line. The average direction in which the wind vector was blowing is shown as a cyan arrow, as recorded by the sonic anemometer, from 20 minutes before the first transect until the end of the final transect. The background image is taken from Google Maps (imagery (2024): Maxar Technologies).

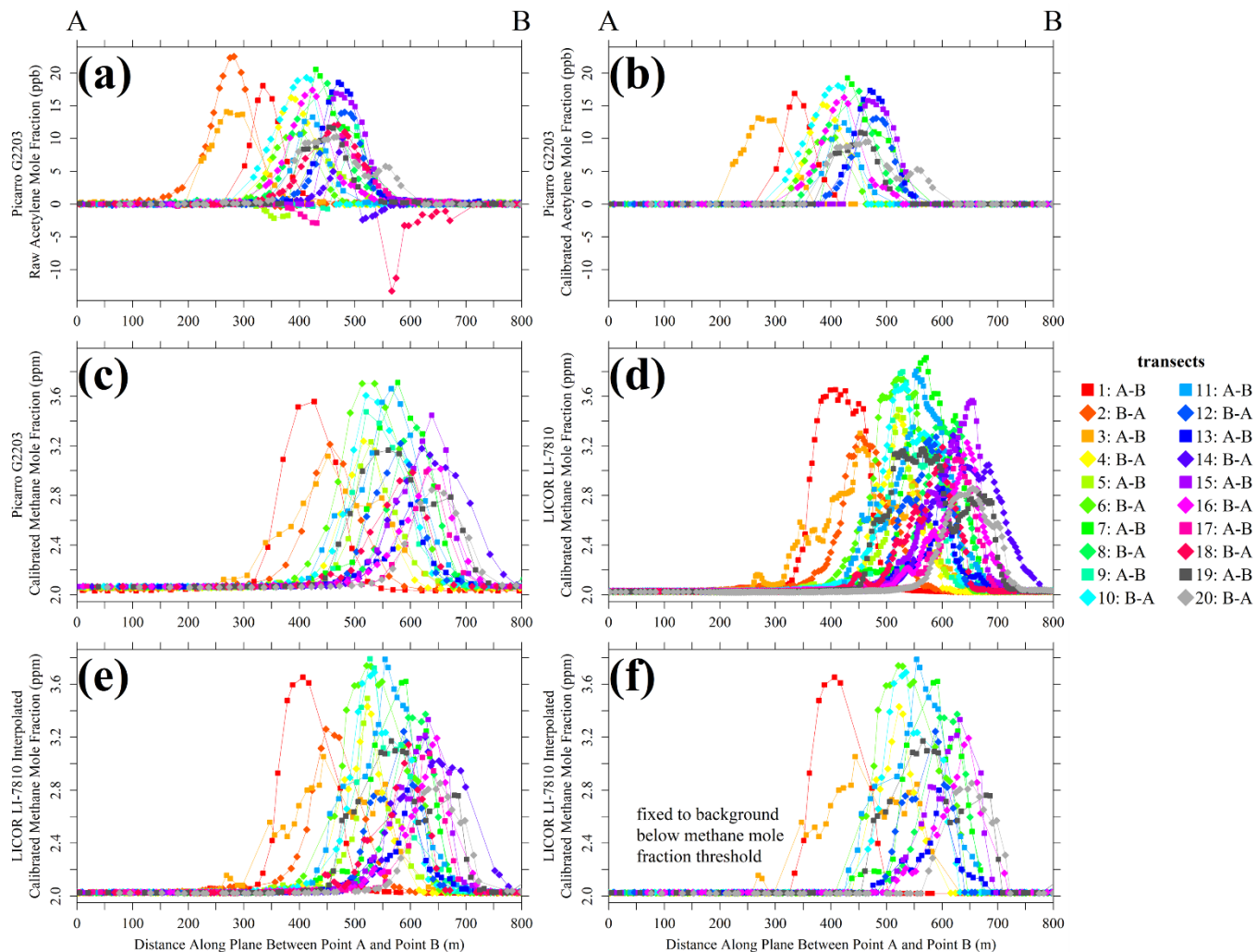
Rather than relying on stationary (zero-dimensional) downwind sampling, the methane and acetylene plumes were instead sampled through multiple plume transects for subsequent integration, as  $Q_{\text{methane}}$  derived from one-dimensional transects results in improved flux accuracy (as discussed in **Sect. 1**). Twenty vehicular transects were conducted on a nearby downwind sampling road during the acetylene release. The position and nature of downwind transects can have an impact on  $Q_{\text{methane}}$  estimates if the acetylene release location is not perfectly co-located with the methane source, which is discussed in further detail in **Sect. 4**. The vehicle was equipped with the Picarro G2203 gas analyser, for which all sampled air passed through the Nafion-based gas dryer followed by a magnesium perchlorate scrubber. The air inlet was fixed to the roof of the vehicle (approximately 2 m above ground level). The Picarro G2203 was powered using a portable mains power supply bank. A LI-COR LI-7810 (LI-COR, Inc.) gas analyser was also installed in the vehicle which shared the same air inlet as the Picarro G2203 (but was connected upstream of the dryer), measuring  $[\text{CH}_4]_r$  and  $[\text{H}_2\text{O}]_r$  at a frequency of approximately 1 Hz. The LI-COR LI-7810 was powered by its internal battery. A global navigation satellite system (GNSS) positional logger made measurements of vehicular position at 1 Hz. The timestamp of Picarro G2203 and LI-COR LI-7810 measurements were individually adjusted to GNSS time by breathing into the air inlets at a fixed GNSS time and recording the time of the  $[\text{CH}_4]_r$  responses. This could be achieved as a member of our team exhales methane; most humans do not exhale detectable methane enhancements (Dawson *et al.*, 2023).

The sampling campaign duration is defined as 20 minutes before the start of first transect up to the time of the point of the final transect.  $Q_{\text{acetylene}}$  was largely stable for the full duration of the sampling campaign, with an average  $Q_{\text{acetylene}}$  level of  $0.239 \text{ g s}^{-1}$  and a standard deviation variability of  $\pm 0.001 \text{ g s}^{-1}$ , as presented in **Sect. S117** in the **Supplement**. The 20-minute period of continuous acetylene flow in advance of vehicular sampling allowed the acetylene plume to become well-establish itself and to stabilise in the atmosphere (Fredenslund *et al.*, 2019). The average wind direction was  $292.7^\circ$  with respect to True North and the average wind speed was  $3.84 \text{ m s}^{-1}$ , for the duration of the sampling campaign (see **Sect. S117** in the **Supplement**).

The limits of the sampling road for  $Q_{\text{methane}}$  calculation purposes were defined as being between Point A and Point B (indicated in **Fig. 11** as yellow crosses); although vehicular sampling protruded these points to sample on a longer stretch of road, the landfill emission plumes remained within this spatial range, serving as sensible limits for subsequent analysis. All Picarro G2203  $[\text{C}_2\text{H}_2]_r$  measurements from each transect are projected onto the vertical plane between Point A and Point B in **Fig. 12** (a). During six transects (transect 2, 5, 9, 14, 17 and 18), a feature containing  $[\text{C}_2\text{H}_2]_r$  measurements of less than  $-0.5 \text{ ppb}$  was observed. These negative  $[\text{C}_2\text{H}_2]_r$  measurements were observed just before observing the acetylene peak, making these periods clearly distinguishable from instrumental noise. Furthermore, consistent negative  $[\text{C}_2\text{H}_2]_r$  measurements were made during each feature, as opposed to random noise which generally varied between randomly positive and negative measurements. These erroneous measurements were probably due to complications associated with the Picarro G2203 internal spectral fitting algorithms, in response to a sudden sharp  $[\text{C}_2\text{H}_2]$  change. This may have been due to mis-fitting issues as the Picarro G2203

takes some time to complete a scan against all wavelengths across the acetylene IR absorption peak. These six transects have therefore been removed from the subsequent flux analysis, resulting in fourteen remaining successful transects.





**Figure 12:** (a) Raw Picarro G2203  $[\text{C}_2\text{H}_2]_r$  measurements, (b) calibrated Picarro G2203  $[\text{C}_2\text{H}_2]_r$  measurements, (c) calibrated Picarro G2203  $[\text{CH}_4]$  measurements, (d) calibrated LI-COR LI-7810  $[\text{CH}_4]$  measurements, (e) calibrated LI-COR LI-7810  $[\text{CH}_4]$  measurements interpolated to the Picarro G2203  $[\text{C}_2\text{H}_2]_r$  timestamp and (f) calibrated LI-COR LI-7810  $[\text{CH}_4]$  measurements interpolated to the Picarro G2203  $[\text{C}_2\text{H}_2]_r$  timestamp with  $[\text{CH}_4]$  below  $[\text{CH}_4]_{\text{threshold}}$  set to  $[\text{CH}_4]_0$  for each transect, all plotted as coloured dots (see legend for transect colours) on the plane between Point A and Point B downwind of a landfill site. Only successful transects are shown in (b) and (f).

For the fourteen remaining transects, all  $[\text{C}_2\text{H}_2]_r$  measurements above 1.38 ppb from the Picarro G2203 were converted into dry calibrated measurements using laboratory-derived coefficients from **Sect. 2**. These calibrated  $[\text{C}_2\text{H}_2]$  measurements are presented in **Fig. 12** (b), as a function of distance along the plane between Point A and Point B. All Picarro G2203  $[\text{C}_2\text{H}_2]_r$  measurements of less than 1.38 ppb were fixed to 0 ppb  $[\text{C}_2\text{H}_2]$ , as this sampling may be unstable and some non-zero  $[\text{C}_2\text{H}_2]$  sampling in this range can erroneously resolve to the  $[\text{C}_2\text{H}_2]_r$  observed at 0 ppb  $[\text{C}_2\text{H}_2]$  (as discussed in **Sect. 2**). The influence of this step when applied to low (but non-zero)  $[\text{C}_2\text{H}_2]$  sampling, on  $Q_{\text{methane}}$ , is dealt with in the next subsection. Picarro G2203  $[\text{CH}_4]_r$  measurements from all twenty transects were converted in dry calibrated  $[\text{CH}_4]$  using the coefficients provided in **Sect.**

**S1** in the **Supplement**. All  $[\text{CH}_4]_r$  measurements from the LI-COR LI-7810 were converted into dry calibrated  $[\text{CH}_4]$ , by first applying an empirical water correction followed by a calibration which could be cross-referenced to standards on the WMO greenhouse gas scale for methane (WMO X2004A). Calibrated Picarro G2203 and LI-COR LI-7810  $[\text{CH}_4]$  measurements from each transect are also shown in **Fig. 12** (c and d, respectively), as a function of distance along the plane between Point A and Point B.

### 3.3 Landfill site methane emission flux calculation

In this study, two sets of  $Q_{\text{methane}}$  values were calculated using both  $[\text{C}_2\text{H}_2]$  as well as  $[\text{C}_2\text{H}_2]_r$  as model input, to compare any influence of Picarro G2203 acetylene calibration on  $Q_{\text{methane}}$  results. The principle of using acetylene as a tracer gas for methane, requires mole fraction measurements from both the acetylene and the methane plume to calculate  $Q_{\text{methane}}$ .  $Q_{\text{methane}}$  was derived in this work by integrating the observed methane and acetylene emission plume as a function of distance along the sampling road. This form of spatial integration is used to apply equal weighting to each mole fraction measurement as a function of distanced covered, especially with irregular spatial measurements due to irregular driving speed and sampling frequency. Although, in theory,  $Q_{\text{methane}}$  can be derived from a single downwind measurement point (as discussed in **Sect. 1**), spatial integration results in better accuracy, especially if the methane and acetylene plumes do not perfectly overlap, as illustrated in **Fig. 12**.

Before conducting this integration, LI-COR LI-7810  $[\text{CH}_4]$  measurements were first interpolated to the lower frequency (and less regular) Picarro G2203  $[\text{C}_2\text{H}_2]$  timestamp so that each  $[\text{C}_2\text{H}_2]$  had a corresponding spatial  $[\text{CH}_4]$  measurement, as shown in **Fig. 12** (e). In general, the likelihood of sampling close to the maximum of each emission plume decreases with larger sampling gaps. Yet, due to the far superior LI-COR LI-7810  $[\text{CH}_4]$  sampling frequency, this data was assumed to capture the full methane plume shape, allowing the loss of sampling points from this [methane](#) plume to replicate the data loss from the acetylene plume. Due to the intermediate Picarro G2203  $[\text{CH}_4]$  sampling frequency, these measurements were not used in this analysis. By contrast, interpolating Picarro G2203  $[\text{C}_2\text{H}_2]$  to the LI-COR LI-7810  $[\text{CH}_4]$  would be less appropriate as acetylene plume measurements would be artificially generated from a lack of information on acetylene plume shape (*i.e.* artificial gap filling). As a general caveat, perfect replication of methane plume information loss requires the methane and acetylene plumes to perfectly overlap in space. As the plumes were slightly offset (see **Fig. 12**), this interpolation method did not result in identical information loss from both the acetylene plume and the methane plume (see **Sect. 4** for discussion). Nevertheless, interpolation to the lower Picarro G2203  $[\text{C}_2\text{H}_2]$  timestamp ensured that the likelihood of loss of information on the methane emission plume using interpolated LI-COR LI-7810  $[\text{CH}_4]$  measurements remained the same, thereby avoiding any bias in multiple  $Q_{\text{methane}}$  estimates derived from individual transects.

$Q_{\text{methane}}$  also requires background [mole fraction values](#) ( $[\text{C}_2\text{H}_2]_0$  and  $[\text{CH}_4]_0$ ) ~~values~~ to characterise the enhancement of the tracer and methane emission plume above the background.  $[\text{CH}_4]_0$  was derived by taking the average of the lowest five non-



interpolated [LI-COR LI-7810](#) [CH<sub>4</sub>] measurements from each transect. This accounts for [CH<sub>4</sub>]<sub>0</sub> natural regional variability over time. This also corrects for any [CH<sub>4</sub>] measurement offset that may occur due to instrumental drift. For acetylene, [C<sub>2</sub>H<sub>2</sub>]<sub>0</sub> was fixed to 0 ppb for all transects, as negligible levels of acetylene are [otherwise](#) expected in the natural ambient background. Thus, this approach does not account for potential changes in [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurement offset. While taking the lowest five [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements from each transect was considered for an uncalibrated [C<sub>2</sub>H<sub>2</sub>]<sub>0</sub>, due to the noisy baseline, this would inevitably result in capturing the noise's weakest values, making this method unsuitable. For the calibrated [C<sub>2</sub>H<sub>2</sub>] data (derived following the procedure outline above), ~~instrumental sensor~~ baseline drift cannot be deduced from the lowest measurements, as all [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> of less than 1.38 ppb are fixed to 0 ppb [C<sub>2</sub>H<sub>2</sub>]. But with the stability of CRDS (Crosson, 2008, [Yver Kwok et al., 2015b](#), [Gomez-Pelaez et al., 2019](#), [Yver-Kwok et al., 2021](#)), drift [in the acetylene calibration](#) is unlikely to be a major issue, which is supported by the  $\sigma_A^2$  test results given in **Sect. 2** which showed no [C<sub>2</sub>H<sub>2</sub>] drift over a period of 12 hours.

As an additional step it is important to take into account the potential loss of low (but non-zero) [C<sub>2</sub>H<sub>2</sub>] sampling due to setting a maximum [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> threshold of 1.38 ppb (corresponding to 1.16 ppb [C<sub>2</sub>H<sub>2</sub>]), below which all [C<sub>2</sub>H<sub>2</sub>] is fixed at 0 ppb. In theory, this is not likely to be an issue away from of the acetylene plume, as there are no major acetylene sources and [C<sub>2</sub>H<sub>2</sub>]<sub>0</sub> is expected to consistently equal 0 ppb. However, a small number of non-zero [C<sub>2</sub>H<sub>2</sub>] enhancements may be lost from the edges of each plume, [leading to a slightly lower acetylene plume integral](#). To replicate this effect on [CH<sub>4</sub>] measurements, any interpolated [CH<sub>4</sub>] measurements below a methane mole fraction threshold ([CH<sub>4</sub>]<sub>threshold</sub>) from each of the fourteen successful transects were fixed to [CH<sub>4</sub>]<sub>0</sub>, as illustrated in **Fig. 12** (f). [CH<sub>4</sub>]<sub>threshold</sub> is calculated for each successful transect using

$$[\text{CH}_4]_{\text{threshold}} = \left( \left( \frac{\text{maximum } [\text{CH}_4] - [\text{CH}_4]_0}{\text{maximum } [\text{C}_2\text{H}_2] - [\text{C}_2\text{H}_2]_0} \right) \cdot 1.16 \text{ ppb} \right) + [\text{CH}_4]_0, \quad (3)$$

which takes the ratio between maximum mole fraction enhancements from each transect [\(using interpolated \[CH<sub>4</sub>\] measurements\)](#). Although this is not a perfect approach as the maximum height of both the methane and acetylene plume were unlikely to be captured (due to large sampling gaps and an offset acetylene plume), the distance of the maximum [C<sub>2</sub>H<sub>2</sub>] and [CH<sub>4</sub>] measurements from the acetylene and methane plume centres, respectively, should average out over a sufficient number of transects, resulting [in](#) a null overall effect on  $Q_{\text{methane}}$ . These modified [CH<sub>4</sub>] values must be used alongside calibrated [C<sub>2</sub>H<sub>2</sub>] measurements, during  $Q_{\text{methane}}$  calculation. However,  $Q_{\text{methane}}$  derived using uncalibrated [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> does not require modified [CH<sub>4</sub>], as this tests flux estimation assuming all uncalibrated [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> measurements to be correct. **Fig. 12** (e and f) shows that interpolated [CH<sub>4</sub>] measurements without this threshold are similar to modified [CH<sub>4</sub>] measurements with the imposed threshold. Nevertheless, this step is important to minimise the effect of inflated methane plumes due to erroneously low [C<sub>2</sub>H<sub>2</sub>] measurements (without corresponding erroneously low [CH<sub>4</sub>] measurements) from biasing  $Q_{\text{methane}}$ .

$Q_{\text{methane}}$  was [finally](#) calculated following

$$Q_{\text{methane}} = Q_{\text{acetylene}} \cdot \left( \frac{\sum_{i=1}^n \frac{1}{2} ([\text{CH}_4]_i - [\text{CH}_4]_0) \cdot \Delta x_i}{\sum_{i=1}^n \frac{1}{2} ([\text{C}_2\text{H}_2]_i - [\text{C}_2\text{H}_2]_0) \cdot \Delta x_i} \right) \cdot \left( \frac{M_{\text{methane}}}{M_{\text{acetylene}}} \right), \quad (4)$$

where  $i$  represents each individual measurement within each transect and  $n$  represents the total number of measurements within each transect.  $\Delta x$  is the average spatial distance between adjacent measurements given by

$$\Delta x_i = \frac{\Delta x_{i-1 \rightarrow i} + \Delta x_{i \rightarrow i+1}}{2}, \quad (5)$$

where  $\Delta x_{a \rightarrow b}$  is the spatial distance between any measurement point  $a$  and any other measurement point  $b$ .  $\Delta x_{a \rightarrow b}$  is derived using the difference in latitude and longitude between point  $a$  and point  $b$ . Equation (4) requires  $[\text{CH}_4]$  and  $[\text{C}_2\text{H}_2]$  to be in the same mole fraction units (*e.g.* ppm) and for both mole fractions to be either dry or wet (dry mole fractions are used here).

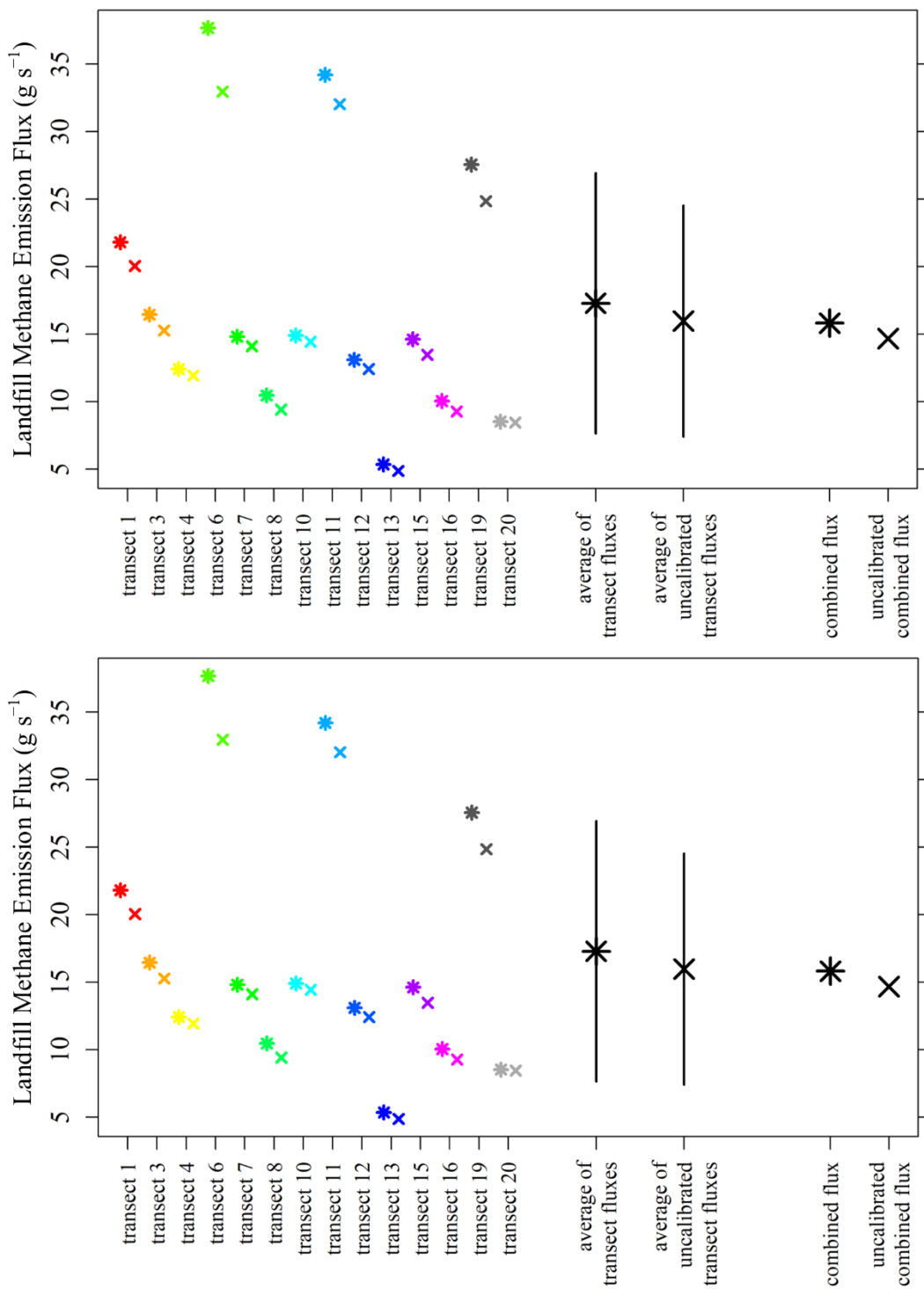
$M_{\text{methane}}$  is the molar mass of methane (16.0425 g mol<sup>-1</sup>) and  $M_{\text{acetylene}}$  is the molar mass of acetylene (26.0373 g mol<sup>-1</sup>).

## 4 Results and discussion

### 4.1 Landfill flux results

Landfill  $Q_{\text{methane}}$  results derived using Eq. (4) are presented in Fig. 13. The average  $Q_{\text{methane}}$  from the fourteen individual vehicular transects is 17.3 g s<sup>-1</sup>, with a standard deviation variability between the different transect  $Q_{\text{methane}}$  estimates of  $\pm 9.6$  g s<sup>-1</sup>, when using calibrated  $[\text{C}_2\text{H}_2]$  (and  $[\text{CH}_4]$  fixed to  $[\text{CH}_4]_0$  below  $[\text{CH}_4]_{\text{threshold}}$ ). The significance of  $Q_{\text{methane}}$  in the context of overall landfill emissions from this specific study site and in comparison to  $Q_{\text{methane}}$  derived using other methods will be discussed in a forthcoming study. A combined  $Q_{\text{methane}}$  was also derived by combining data from all successful transects simultaneously within Eq. (4) (where separate  $[\text{C}_2\text{H}_2]_0$  and  $[\text{CH}_4]_0$  values were subtracted from data corresponding to each transect) to yield a single combined emission  $Q_{\text{methane}}$  estimate of 15.8 g s<sup>-1</sup>. This is consistent with the average of the fourteen individual  $Q_{\text{methane}}$  values, within the standard deviation uncertainty range. Using the uncalibrated  $[\text{C}_2\text{H}_2]_r$  data as Eq. (4) input (and unaltered interpolated  $[\text{CH}_4]$ ) yielded smaller  $Q_{\text{methane}}$  values, with an average of the fourteen individual vehicular transects of 16.0 g s<sup>-1</sup> and a standard deviation variability between the different transects of  $\pm 8.6$  g s<sup>-1</sup>. This represents a  $Q_{\text{methane}}$  underestimation of -7.6% compared to  $Q_{\text{methane}}$  derived using calibrated  $[\text{C}_2\text{H}_2]$  as Eq. (4) input.





**Figure 13: Individual landfill  $Q_{\text{methane}}$  methane flux estimates for each individual transect, corresponding averages and the overall combined landfill  $Q_{\text{methane}}$  methane emission flux estimate, plotted as stars using calibrated  $[\text{C}_2\text{H}_2]$  (with  $[\text{CH}_4]$  below  $[\text{CH}_4]_{\text{threshold}}$  fixed to  $[\text{CH}_4]_0$ ) and crosses using uncalibrated  $[\text{C}_2\text{H}_2]_r$  as Eq. (4) input. The black lines indicate the standard deviation variability between individual methane-transect  $Q_{\text{methane}}$  estimates.**

## 4.2 Discussion

**Figure 13** shows that there is a large disparity between  $Q_{\text{methane}}$  estimates for individual transects, with a  $\pm 56\%$  standard deviation variability. This variability is primarily due to differing turbulent patterns between methane and acetylene plume dispersion, partially caused by a suboptimal acetylene release location (discussed below). This emphasises the importance of conducting a sufficient number of transects to average over this variability, representative of the true emission flux. Although an aspect of calculated  $Q_{\text{methane}}$  variability may be due to variability in true landfill methane emissions (which is a limitation of this work), this is expected to be relatively small over the limited sampling window (less than 3 hours). Landfill emissions are relatively consistent in the absence of abrupt environmental or operational changes. Thus, a constant true landfill  $Q_{\text{methane}}$  methane emission flux value is assumed for all transects, with observed  $Q_{\text{methane}}$  variability between transects driven by limitations in sampling and the nature of the tracer release (discussed below).  $Q_{\text{methane}}$  for transect 13 was particularly low; **Fig. 12** (f) shows that this was due to a disproportionately narrow methane plume compared to a large acetylene plume. If the methane and acetylene plume were to share better spatial overlap, this issue would likely diminish, as both methane and acetylene plumes would be equally small at the time and location of measurement. Transect 20 is similarly resulted in a low  $Q_{\text{methane}}$ , where a small methane plume was detected. Conversely, transect 13 resulted in a small  $Q_{\text{methane}}$  due to a large acetylene plume. Transect 6 resulted in the largest  $Q_{\text{methane}}$  due to a large methane plume. However, transect 7, which included the largest  $[\text{CH}_4]$  measurement (of the fourteen successful transects) did not result in such a high  $Q_{\text{methane}}$  due to the accompanied detection of a substantially sized acetylene plume.

Previous studies have shown that tracer poor localisation with the methane emission source can cause  $Q_{\text{methane}}$  variability (Mønster *et al.*, 2014, Yver Kwok *et al.*, 2015a, Ars *et al.*, 2017), as observed across the fourteen transects  $Q_{\text{methane}}$  values presented here (see **Fig. 13**), resulting in a poor methane and acetylene plume overlap (see **Fig. 12**). Good tracer and methane source co-location is essential for accurate tracer-based fluxes (Delre *et al.*, 2018, Fredenslund *et al.*, 2019, Lui *et al.*, 2024). This ensures good mixing of the entire tracer plume with the methane plume (Matacchiera *et al.*, 2019) with identical dispersion (Johnson *et al.*, 1994, Lamb *et al.*, 1995, Daube *et al.*, 2019, Mønster *et al.*, 2019), such that even a mole fraction ratio at any single point is capable of yielding an accurate emission flux (Omara *et al.*, 2016, Ars *et al.*, 2017). A large disperse methane emission facility such as a landfill site may require multiple acetylene release points for improved plume overlap, such that the individual acetylene plumes overlap into a larger overall acetylene plume more representative of the shape of the complex methane emission plume emanating from the complex heterogeneous surface emission source (Scheutz and Fredenslund, 2019, Matacchiera *et al.*, 2019, Mønster *et al.*, 2019, Vecchi *et al.*, 2022). Yet, organising an acetylene release from other central locations at our landfill study site was challenging, especially from over active waste. Authorisation was secured many months in advance, making short term on-site changes difficult to implement. Furthermore, the ideal tracer release location can be

750 unique to each site (Matacchiera *et al.*, 2019), making it difficult to anticipate. Tracer localisation issues can be addressed by using a hybrid approach such as that of Ars *et al.* (2017), which combined tracer-based fluxes with a statistical inversion and an atmospheric transport model, for significantly improved overall flux estimates despite poor tracer localisation.

In conjunction with acetylene release location, good downwind positioning is essential for good plume mixing and overlap (Scheutz *et al.*, 2011, Daube *et al.*, 2019), to allow sufficient distance between the sources and the sampling location (Galle *et al.*, 2001, Feitz *et al.*, 2018), so the full extent of the emission plume is captured (Mønster *et al.*, 2015, Delre *et al.*, 2018). Tracer-based fluxes are fundamentally limited to locations with downwind site access (Bell *et al.*, 2017). Yet our study had limited sampling options, with only one near-site downwind sampling road. For plumes that do not perfectly overlap (as in this study), integrating along the sampling road requires the road to be straight and perpendicular to wind direction (Yacovitch *et al.*, 2017), to avoid the methane and acetylene plumes being detected at different distances (Ars *et al.*, 2017). Measurements closer to the site have a higher mole fraction with respect to the plane perpendicular to wind direction. But if the sampling road is nearly straight and perpendicular to wind direction (assumed here), the importance of these errors declines. In addition, sampling a sufficient distance from the source can reduce [potential complication issues](#) due to poor tracer co-location with the source, as the two plumes have more time to mix (Fredenslund *et al.*, 2019).

Although a perfectly co-located acetylene release yields ideal  $Q_{\text{methane}}$  estimates, it is also possible to derive  $Q_{\text{methane}}$  if the acetylene source is slightly offset from the methane source (Mønster *et al.*, 2014), as in this study. In such a scenario, the two plumes will be detected at different downwind locations (Ars *et al.*, 2017), but similar [plume dispersion turbulent conditions](#) allow [for similar plume dispersions the ratio between these two integrated plumes to yield a flux](#). Yet this requires the two sources to be an equal distance from the sampling road, perpendicular to wind direction (Mønster *et al.*, 2014, Ars *et al.*, 2017, Daube *et al.*, 2019). It also requires identical wind conditions for the duration of each transect. Otherwise, the methane and acetylene plumes may have dispersed under different conditions upon detection, resulting in lower mole fraction measurements during higher winds and *vice versa*. A similar amount of information is also required from each plume (Delre *et al.*, 2018), which was achieved in this work by interpolating [\[CH<sub>4</sub>\] measurements](#) to the lower (Picarro G2203 [C<sub>2</sub>H<sub>2</sub>]) timestamp, thereby avoiding the contentious practice of gap filling. Although it is difficult to perfectly satisfy all above conditions, getting close enough can yield acceptable  $Q_{\text{methane}}$  estimates.

775 Our [CH<sub>4</sub>] interpolation approach ensured that each [C<sub>2</sub>H<sub>2</sub>] measurement had a corresponding spatiotemporal [CH<sub>4</sub>] measurement. This allowed all measurements to be integrated as a function of distance along the sampling road, using the summation [approach](#) given by Eq. (4). An alternative integration approach is to continuously model the emission plumes as a function of distance, for analytical integration rather than summation (Fredenslund *et al.*, 2019), although this requires a sufficient sampling density to characterise plume shape (Delre *et al.*, 2018). This latter method would be challenging with [the](#) Picarro G2203 instrument used in this work due to its irregular [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> sampling frequency, resulting in large gaps on plume dispersion information from downwind transects, with a maximum measurement time gap of 13 s. Interpolating the higher

frequency LI-COR LI-7810 [CH<sub>4</sub>] [measurements](#) to the lower frequency Picarro G2203 [C<sub>2</sub>H<sub>2</sub>] timestamp mirrored this data loss in our summation integration (Eq. (4)). The average ~~measured~~<sup>observed</sup> [0.24\(0.3±0.1\) Hz](#) [C<sub>2</sub>H<sub>2</sub>] sampling frequency of the Picarro G2203 is lower than 0.5 Hz proposed by the manufacturer (Picarro, Inc., 2015). This may be due to the age and irregular operation of this specific Picarro G2203 gas analyser, which was manufactured in September 2015. It is important to state that the Picarro G2203 used in this study experienced some spectral fitting issues in the past, ~~which~~<sup>These</sup> were resolved following manufacturer support. However, this may have inadvertently resulted in the irregular [low](#) sampling frequency as a residual unresolved issue. During a previous testing campaign, we experienced instrument failure during excessive acetylene exposure, which may explain this effect, although we cannot be certain. The slow sampling rate may also be associated with the unusual behaviour observed when sampling wet air, with [H<sub>2</sub>O]<sub>r</sub> peaks and unpredictable [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> response, as described in **Sect. 2**.

[At the minimum 0.24 Hz sampling frequency of the Picarro G2203 tested in this work, a 0.24 Hz  \$\sigma\_A\$  of ±0.0863 ppb was derived at an \[C<sub>2</sub>H<sub>2</sub>\] of 10.1 ppb. When deriving tracer-based fluxes, it is important to evaluate the magnitude of peak mole fraction enhancements above instrumental noise \(which can be characterised by  \$\sigma\_A\$ \) of any gas analyser, to ensure that the plume is detectable and can be characterised when subtracted from the background mole fraction level \(Yver Kwok \*et al.\*, 2015a, Ars \*et al.\*, 2017, Yacovitch \*et al.\*, 2017, Delre \*et al.\*, 2018, Fredenslund \*et al.\*, 2019\). The average \[C<sub>2</sub>H<sub>2</sub>\] peak height was \(15±3\) ppb for the fourteen useable transects in this study. This is far larger than the 0.24 Hz  \$\sigma\_A\$  at an \[C<sub>2</sub>H<sub>2</sub>\] of 10.1 ppb, allowing it to be concluded that the  \$Q\_{\text{acetylene}}\$  level was sufficiently high and downwind sampling distance was sufficiently close to the source to detect acetylene emission plumes with a sufficiently high \[C<sub>2</sub>H<sub>2</sub>\] resolution.](#)

[Drift in calibration coefficients is also an important consideration for \[C<sub>2</sub>H<sub>2</sub>\] measurements used to derive  \$Q\_{\text{methane}}\$ . In this study, the sampling campaign was conducted in February 2024 and \[C<sub>2</sub>H<sub>2</sub>\]<sub>r</sub> calibration coefficients were derived in October 2024. This assumes that Picarro G2203 \[C<sub>2</sub>H<sub>2</sub>\]<sub>r</sub> measurement performance did not significantly drift during this time window and in different sampling conditions \(\*i.e.\* pressure and temperature\), which is based on the stability of other Picarro instruments used to measure methane and carbon dioxide \(Crosson, 2008, Yver Kwok \*et al.\*, 2015b, Gomez-Pelaez \*et al.\*, 2019, Yver-Kwok \*et al.\*, 2021\). A future investigation on the stability Picarro G2203 \[C<sub>2</sub>H<sub>2</sub>\]<sub>r</sub> calibration coefficients would be useful to confirm this.](#)

The [C<sub>2</sub>H<sub>2</sub>]<sub>r</sub> [measurement](#) response of the Picarro G2203 tested in this work was calibrated by diluting gas from an acetylene calibration cylinder. Methane served as a proxy gas to indicate the level of dilution achieved at each MFC blending step, by diluting gas from a methane calibration cylinder in the exact same way. Thus, any potential MFC blending errors should cancel out in this approach. Yet, there is a ±3% ~~[C<sub>2</sub>H<sub>2</sub>]~~<sup>uncertainty</sup> in the [declared \[C<sub>2</sub>H<sub>2</sub>\] for the](#) acetylene calibration cylinder [and a ±0.5% uncertainty in the declared \[CH<sub>4</sub>\] for the methane calibration cylinder](#), which ~~are~~<sup>is a</sup> limiting factors in this method, [as acetylene calibration depends on these cylinder mole fractions to be known. We show that the Picarro G2203 acetylene calibration gain factor could take a range of between 0.911 and 0.977, assuming these cylinder uncertainties to have a worst-case impact in our \[C<sub>2</sub>H<sub>2</sub>\]<sub>r</sub> calibration procedure, as described in Sect. S5 of the Supplement. This translates to a 10 ppb](#)

$[C_2H_2]_r$  measurement resulting in an extreme  $[C_2H_2]$  range of between 8.96 ppb and 9.61 ppb. Thus  $[C_2H_2]$  is consistently lower than  $[C_2H_2]_r$ , despite the calibration uncertainty induced due to calibration cylinder uncertainties. Fredenslund *et al.* (2019) propose that uncertainty in ~~calibration~~ mole fraction calibration can be treated as a random uncertainty in overall  $Q_{\text{methane}}$  ~~flux~~ estimates, which may be a useful approach (given as 8% in their study). ~~Perhaps such an overall~~ uncertainty ~~budgetingshould instead be treated as a bias, as a poorly calibrated instrument will consistently bias flux estimates in one direction. Nevertheless, the cylinder mole fraction uncertainty is small in this work, compared to the correction induced from the derived calibration which reduces a 10 ppb  $[C_2H_2]_r$  measurement down to 9.29 ppb  $[C_2H_2]$ .~~

Yet it is concerning that the Picarro G2203 reports unstable  $[C_2H_2]_r$  measurements when sampling at low (but non-zero)  $[C_2H_2]$  levels, with a maximum stable  $[C_2H_2]$  level of 1.16 ppb observed during testing. In this low  $[C_2H_2]$  range, Picarro G2203  $[C_2H_2]_r$  measurements occasionally resolved to the  $[C_2H_2]_r$  level observed at 0 ppb  $[C_2H_2]$ . This means that any  $[C_2H_2]_r$  measurement made at below 1.38 ppb bears some uncertainty, as it could correspond to any  $[C_2H_2]$  level between 0 ppb and 1.16 ppb  $[C_2H_2]$ , although this upper uncertainty limit may be reduced slightly with further calibration testing. In this work, it was assumed that  $[C_2H_2]_0$  in ambient air is 0 ppb. Therefore, measurements made away from an observed acetylene plume peak were assumed to equal 0 ppb  $[C_2H_2]$ , with the key uncertainty occurring at the edges of the observed plume, which were also fixed to 0 ppb  $[C_2H_2]$  in this work. This was dealt with by additionally fixing some  $[CH_4]$  measurements (below  $[CH_4]_{\text{threshold}}$ ) from each transect to  $[CH_4]_0$ , to avoid biasing  $Q_{\text{methane}}$  results. Thus, a subset of both  $[C_2H_2]$  and  $[CH_4]$  measurements from each transect were forced to their corresponding background levels.

~~When deriving tracer based fluxes, it is also important to evaluate the magnitude of peak mole fraction enhancements above instrumental noise, to ensure that the plume is detectable and can be characterised when subtracted from the background mole fraction level (Yver Kwok *et al.*, 2015, Ars *et al.*, 2017, Yacovitch *et al.*, 2017, Delre *et al.*, 2018, Fredenslund *et al.*, 2019). The average  $[C_2H_2]$  peak height of  $(15 \pm 3)$  ppb for the fourteen useable transects is far superior than the  $0.24 \text{ Hz } \sigma_A$  of  $\pm 0.0863$  ppb at 10.1 ppb  $[C_2H_2]$ . Thus, we can conclude that the acetylene release emission flux was sufficiently high and downwind sampling distance was sufficiently close to the source to detect acetylene emission plumes with a sufficiently high  $[C_2H_2]$  resolution.~~

~~As a consequenceThe  $Q_{\text{methane}}$  results presented in this work emphasise the importance of calibrating all gas mole fraction measurements, even the use of a tracer gas. To our knowledge, a small number of previous studies using the Picarro G2203 have tested its  $[C_2H_2]_r$  measurement response (Mønster *et al.*, 2014, Omara *et al.*, 2016), with no previous studies demonstrating a calibration procedures for thewith which to correct Picarro G2203  $[C_2H_2]_r$  measurements. used i~~In this study, ~~use ofing~~ raw uncalibrated  $[C_2H_2]_r$  measurements as Eq. (4) input resulted in  $Q_{\text{methane}}$  estimates that were consistently lower than corresponding estimates using calibrated  $[C_2H_2]$  measurements, with an average underestimation of 7.6%. This is a key outcome of this study. This approximately 8% underestimation principally occurs due to the use of calibrated  $[C_2H_2]$  measurements. Yet, in theory, a 0.94 calibration gain factor for acetylene would result in exactly 6%  $Q_{\text{methane}}$  underestimation

using  $[C_2H_2]_r$  instead of  $[C_2H_2]$  as Eq. (4) input. Any gain factor applied to the denominator of Eq. (4) is inversely proportional to  $Q_{\text{methane}}$ . However, an average underestimation of approximately 8% was instead observed in this study for a number of reasons. Setting all  $[C_2H_2]$  measurements below 1.16 ppb  $[CH_4]$  to 0 ppb and thus, applying a  $[CH_4]_{\text{threshold}}$  to  $[CH_4]$  measurements to account for this (as described above) both effect  $Q_{\text{methane}}$  estimation. These two effects are influenced by the location and magnitude of mole fraction measurements made during each specific transect. Additionally, the  $[C_2H_2]_r$  calibration includes a small offset correction ( $-0.147$  ppb) which also influences  $Q_{\text{methane}}$  estimation. These combined effects result in an average  $Q_{\text{methane}}$  underestimation of approximately 8% from the fourteen transects in this study, rather than 6%, although a different level of  $Q_{\text{methane}}$  underestimation was observed for each unique transect due to the different influence of the aforementioned effects. Therefore, while we derived an average  $Q_{\text{methane}}$  bias of approximately  $-8\%$  from a limited number of transects, in theory, an infinite number of transects may further refine this average bias value, causing this value to change slightly. Nevertheless, a similar bias is expected for other studies conducted in similar sampling conditions, using the Picarro G2203 gas analyser tested in this work.

The disparity between  $Q_{\text{methane}}$  results derived from calibrated measurements versus uncalibrated tracer mole fraction measurements presented in this work emphasises the importance of calibrating all gas mole fraction measurements, even those of a tracer gas. To our knowledge, a small number of previous studies using the Picarro G2203 have tested its  $[C_2H_2]_r$  measurement response (Mønster *et al.*, 2014, Omara *et al.*, 2016), with no previous studies demonstrating a calibration with which to correct Picarro G2203  $[C_2H_2]_r$  measurements. Each acetylene gas analyser requires independent characterisation and calibration. In addition, different Picarro G2203 instruments may perform differently when calibrated, resulting in a different influence on  $Q_{\text{methane}}$  bias, which would need to be evaluated in future work.

Various previous studies have derived tracer-based fluxes downwind of controlled tracer releases, reporting various uncertainty ranges (Mønster *et al.*, 2014, Feitz *et al.*, 2018). For example, Ars *et al.* (2017) reported a tracer-based methane flux uncertainty of  $+14\%$  for a controlled tracer release that was perfectly co-located with the methane emission source, although each tracer release study is unique and cannot be compared directly (for example, higher tracer release rates can result in a lower uncertainty). Liu *et al.* (2024) reported an average tracer-based error of 19% compared to known emission fluxes from thirteen integrated transects. Fredenslund *et al.* (2019) conducted an uncertainty budget for their tracer-based flux approach, with an overall error of 15%. Yet the overall uncertainty from these previous studies is generally given as a random uncertainty and does not distinguish between systemic emission bias due to lack of tracer gas calibration and other random methodological errors. This bias may be an important contributory factor within the overall uncertainty of tracer-based flux estimates. For example, consistently using  $[C_2H_2]_r$  measurements from our Picarro G2203 would consistently underestimate Eq. (4)  $Q_{\text{methane}}$ ; this is more concerning than random methodical uncertainties which, should cancel each other out over a sufficiently large sampling average. Such biases may be propagated which may influence our understanding of the importance of certain facility-scale emission sources contributing towards the global methane budget.

## 5. Conclusions

The first detailed characterisation and calibration of  $[C_2H_2]_r$  acetylene measurements made by the Picarro G2203 gas analyser is presented. Initially, water response was tested. This showed that characterising  $[C_2H_2]_r$  characterisation was attempted at different response as a function of  $[H_2O]$  is unfeasible levels, but due to an inconsistent  $[C_2H_2]_r$  measurements were found to be noisy and unpredictable in the presence of water response. Furthermore,  $[H_2O]_r$  measurements were observed appear to episodically erroneously spike at low (but non-zero)  $[H_2O]$  levels, making any such water characterisation of  $[C_2H_2]_r$  response prohibitive. For this reason Instead,  $[C_2H_2]_r$  calibration was conducted characterised in dry conditions. As there are no readily available acetylene gas standards, This calibration was performed by diluting gas from an acetylene calibration cylinder (containing an  $[C_2H_2]$  of 10 180 ppb  $[C_2H_2]$ ) with compressed ambient air was diluted. The quantify the level of acetylene in each dilution, methane was used as a proxy gas blend was inferred from  $[CH_4]$  measurements made when, by first diluting gas from a methane calibration cylinder (with a  $[CH_4]$  of 995.4 ppm) in the exact same way containing methane. The observed Accurate  $[CH_4]$  measurements level were as compared to the predicted  $[CH_4]$  levels to characterise ascertain the MFC blending efficacy, thereby yielding and quantify the correction required to obtain the true mole fraction in the gas blend. This allowed accurate  $[C_2H_2]$  calibration reference standards to be derived, despite systematic uncertainties in the blending method, by conducting the same dilution steps but with the acetylene calibration cylinder in place of the methane calibration cylinder. During calibration testing, it was observed that  $[C_2H_2]_r$  measurements were unstable and erratic at  $[C_2H_2]$  levels of below 1.16 ppb. Therefore is yielded a linear calibration fit with a lower  $[C_2H_2]$  limit of 1.16 ppb was derived, yielding a multiplicative  $[C_2H_2]_r$  correction gain factor with which to correct  $[C_2H_2]_r$  of 0.94, although this is only valid above 1.16 ppb  $[C_2H_2]$ , below which unstable  $[C_2H_2]_r$  measurements were observed. As an additionally,  $\sigma_A^2$  testing yielded, a 0.24 Hz  $\sigma_A$  of  $\pm 0.0863$  ppb was derived at an  $[C_2H_2]$  of approximately 10 ppb  $[C_2H_2]$ , which represents the amount by which  $[C_2H_2]$  is expected to vary between each consecutive measurements. These highlight emphasises the stability of the Picarro G2203  $[C_2H_2]_r$  measurement stability. It is important to emphasise that these results are specific to the Picarro G2203 gas analyser tested in this work; a different instrument may exhibit different behaviour The protocols used here can be applied to other gas analysers, especially in the absence of reference gas standards.

The importance of calibrating  $[C_2H_2]_r$  measurements made by our same Picarro G2203 gas analyser was evaluated in the context used to sample downwind of using a controlled acetylene release alongside a LI-COR LI7810 gas analyser measuring  $[CH_4]$ . The acetylene release was conducted from within an active landfill site which was emitting gas as a tracer gas for methane. Acetylene was released with a fixed  $Q_{acetylene}$  of  $(0.23942 \text{ g s}^{-1})$  from a landfill site, was measured by an acetylene flow meter, using a logging computer to automatically record  $Q_{acetylene}$ . The Picarro G2203 and a separate methane gas analyser sampled during A vehicle conducted twenty ground-level downwind transects, where all gas entering the Picarro G2203 was dried, of which fourteen could be used; six transects were discarded as recorded features containing  $[C_2H_2]_r$  measurements of less than  $-0.5$  ppb were observed, probably due to spectral fitting issues in response to a sharp  $[C_2H_2]$  increase, which the Picarro G2203 probably failed to spectrally fit on first instance.  $[CH_4]$  Calibrated Picarro G2203  $[C_2H_2]$  measurements were used in



combination with corresponding LI-COR LI-7810  $[\text{CH}_4]$  measurements (interpolated to the lower Picarro G2203  $[\text{C}_2\text{H}_2]_r$  timestamp) to derive a landfill methane emission flux. As all Yet, there was no certainty on the magnitude of  $[\text{C}_2\text{H}_2]_r$  measurements of below 1.38 ppb (corresponding to a  $[\text{C}_2\text{H}_2]$  of 1.16 ppb); thus, all such measurements were fixed to 0 ppb the  $[\text{C}_2\text{H}_2]_0$  of 0 ppb. To account for this calibrated dataset, a proportion of  $[\text{C}_2\text{H}_2]_r$  threshold, all  $[\text{CH}_4]$  measurements below a  $[\text{CH}_4]_{\text{threshold}}$  value were also fixed to  $[\text{CH}_4]_0$  for each transect; this step is essential to avoid forcing data points from the acetylene plume to  $[\text{C}_2\text{H}_2]_0$  without applying a similar effect to the methane plume, overall flux bias during  $Q_{\text{methane}}$  calculations.

$Q_{\text{methane}}$  estimates were derived for each transect using the ratio between the integrated methane plume and integrated acetylene plume, with both plumes integrated as a function of distance along the sampling road. This resulted in an average measured landfill  $Q_{\text{methane}}$  for the fourteen successful transects of  $(17.3 \pm 9.6) \text{ g s}^{-1}$ , when derived using calibrated Picarro G2203- $[\text{C}_2\text{H}_2]$  measurements was  $17.3 \text{ g s}^{-1}$ , (with  $[\text{C}_2\text{H}_2]$  less than 1.16 ppb fixed to 0 ppb) and when applying a  $[\text{CH}_4]_{\text{threshold}}$  with a standard deviation variability between the fourteen successful flux estimates of  $\pm 9.6 \text{ g s}^{-1}$ . This large variability can be attributed to the positioning of the source and downwind sampling positioning. The acetylene release point was not perfectly co-located with the centre of the methane source; successfully achieving this is challenging in a complex environment such a landfill site. This manifested itself through methane and acetylene plumes which that did not perfectly overlap on a downwind sampling plane. Another factor was the slow  $[\text{C}_2\text{H}_2]_r$  sampling frequency, with gaps of up to 13 s leading to information of the downwind sampling plumes being lost. A key outcome from this study was the derivation of However, conducting the same fluxes method but using uncalibrated raw Picarro G2203- $[\text{C}_2\text{H}_2]_r$  with no applied  $[\text{CH}_4]_{\text{threshold}}$  resulted in measurements in place of calibrated  $[\text{C}_2\text{H}_2]_r$ , which yielded a lower  $Q_{\text{methane}}$  of  $(16.0 \pm 8.6) \text{ g s}^{-1}$ , which corresponds to approximately 8% underestimation. This negative bias is a direct effect of failure to calibrate the Picarro G2203, although applying a 1.16 ppm  $[\text{C}_2\text{H}_2]$  threshold and  $[\text{CH}_4]_{\text{threshold}}$  influences  $Q_{\text{methane}}$  underestimation magnitude for each individual transect (these effects average out over a sufficient number of transects). Although this approximately 87.6% underestimation (compared to  $Q_{\text{methane}}$  derived using calibrated  $[\text{C}_2\text{H}_2]_r$ ) is smaller than  $Q_{\text{methane}}$  the variability between individual transect flux estimates, it is possible to reduce the  $\pm 56\%$  random flux variability can be reduced by with improvements in the acetylene release methodology, for example by optimising the release location, with improved downwind sampling, sampling during better winds, conducting multiple acetylene releases or releasing acetylene at a higher rate  $Q_{\text{acetylene}}$ . By contrast, the bias induced due to a lack of calibration is persistent and cannot be reduced by changing field sampling conditions. This therefore emphasises the importance of calibrating acetylene gas analysers used to derive tracer-based  $Q_{\text{methane}}$  methane estimates. Failure to do so could result in persistent biases in tracer-based  $Q_{\text{methane}}$  flux estimates and hence, a biased understanding of the contribution of facility-scale methane sources towards the overall global methane budget.



940     **Data availability**

All data during laboratory testing and the field campaign will be published on a public repository upon final publication of this manuscript.

**Author contributions**

945     AS conducted laboratory characterisation testing of the Picarro G2203, with support from OL, LL and CP. CY and OL arranged the supply of gas cylinders. AS and OL devised the acetylene calibration methodology. AS, TD and ML conducted the field sampling campaign. EE, CR and MT arranged for field site access. AS designed all field logging systems. AS and PK devised the emission flux quantification methodology, with support from GB. AS conducted all data analysis. AS wrote an initial draft of the manuscript which was revised by GB, OL, PK, PC, CY, TD and EE. PC, OL, GB, EE and CR organised funding for this work.

950     **Competing interests**

The authors declare that they have no conflict of interest.

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960     **References**

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