Supplement to “Measuring acetylene with a cavity ring-down spectroscopy gas analyser and its use as a tracer to quantify methane emissions” by Adil Shah *et al.*

S1 Picarro G2203 raw methane mole fraction calibration

The Picarro G2203 measures $[CH_4]_r$ alongside measurements of $[C_2H_2]_r$. These measurements may be useful when using this gas analyser during an acetylene tracer release downwind of a methane source, rather than relying on a separate methane gas analyser. To evaluate the quality of Picarro G2203 $[CH_4]_r$ measurements, a methane calibration was conducted. This used calibrated $[CH_4]$ measurements from the Picarro G2401 as a reference. Measurements from the test to characterise MFC blending performance (used to derive $[C_2H_2]$ reference standards) were used from **Sect. 2**. Picarro G2203 $[CH_4]_r$ measurements from this test, shown in **Fig. S1**, are compared to corresponding calibrated Picarro G2401 $[CH_4]$ measurements (which are shown in **Fig. 5** (a)). For both datasets, a 5-minute average Picarro G2203 $[CH_4]_r$ and calibrated Picarro G2401 $[CH_4]$ value was taken from towards the end of each 15-minute sampling step. However, for each 60-minute $[CH_4]_0$ sampling period, a 30-minute average was used. These averages are compared in **Fig. S2**. A linear regression was applied, yielding a gain factor of 1.00807 and an offset of −0.00398 ppm, with a RMSE of ±0.000274 ppm. Although a more accurate fit could be obtained by directly sampling reference gas standards, a calibrated Picarro G2203 $[CH_4]_r$ measurement is not the objective of this work. This secondary calibration is sufficient to demonstrate the excellent capability of the Picarro G2203 to measure $[CH_4]$, even when using raw uncalibrated measurements.

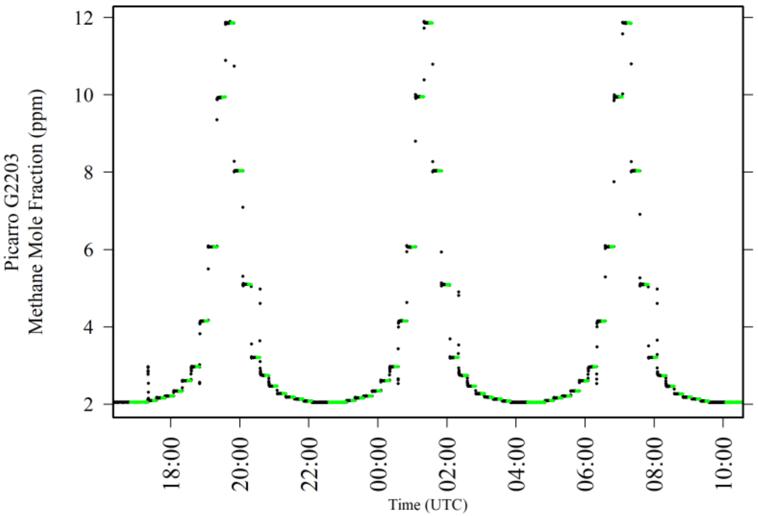

Figure S1: Picarro G2203 $[CH_4]_r$ plotted as black dots, derived from three testing cycles by blending gas from the methane calibration cylinder with natural ambient compressed air. Periods used to derive averages are highlighted as green dots in (a).

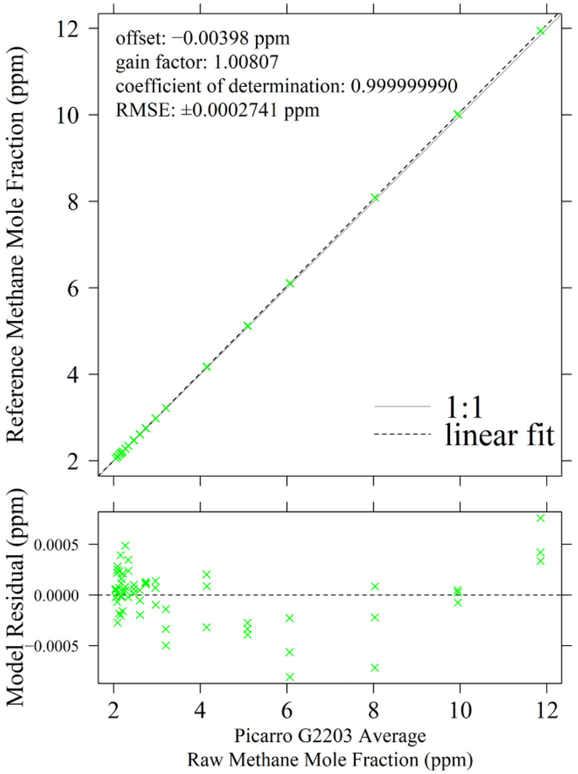

Figure S2: (top) Picarro G2203 5-minute average $[CH_4]_r$ measurements, when combining gas from the methane calibration cylinder with natural ambient compressed air, plotted against reference $[CH_4]$ levels (green crosses), with a linear regression model shown as a dashed black line and an identity line shown as a solid light grey line. (bottom) Corresponding model residuals between Picarro G2203 $[CH_4]_r$ and reference Picarro G2401 $[CH_4]$ (green crosses), with a 0 ppm $[CH_4]$ residual shown as a horizonal dashed black line.

S2 Raw acetylene mole fraction artefact due to humidifying and drying gas

During calibration testing, the dew-point generator was used to humidify the gas stream which was then dried using the Nafion-based gas dryer, followed by the magnesium perchlorate scrubber. Calibration was conducted in this way to capture any potential artefacts due to use of Nafion-based gas dryer in conjunction with the magnesium perchlorate scrubber during field sampling. However, this assumes that the dew-point generator does not itself cause any artefacts, with it being absent in the field. Use of a dew-point generator could be concerning due to the relatively high solubility of acetylene in water (Priestley and Schwarz, 1940); gas bubbles through the dew-point generator water reservoir during humidification making it easy for gas exchange. Therefore, the effect on $[C_2H_2]_r$ measurements of using the dew-point generator, in conjunction with the Nafion-based gas dryer and the magnesium perchlorate scrubber, was tested. It was not possible to test the effect of the Nafion-based gas dryer independently of the dew-point generator as it requires wet sampling gas to operate normally.

During this test, gas from a compressed air cylinder was blended with gas from the acetylene calibration cylinder to four $[C_2H_2]_t$ settings in 15-minute steps, as illustrated in **Fig. S3**. At each $[C_2H_2]_t$ level, both pure gas was sampled from the gas blend (which is naturally dry) as well as sampling the same gas which was humidified and dried. Two three-way ball values were used to manually alternate between the two gas streams. A 5-minute average $[C_2H_2]_r$ measurement was taken at the end of each 15-minute sampling period, which is given in **Fig. S3**, alongside its standard deviation variability. These results show that the two gas stream produced identical $[C_2H_2]_r$ measurements, within the bounds of uncertainty. This confirms that the combined effect of using the dew-point generator, the Nafion-based gas dryer and the magnesium perchlorate scrubber has no significant effect on $[C_2H_2]$, compared to sampling pure dry gas without humidification and drying.

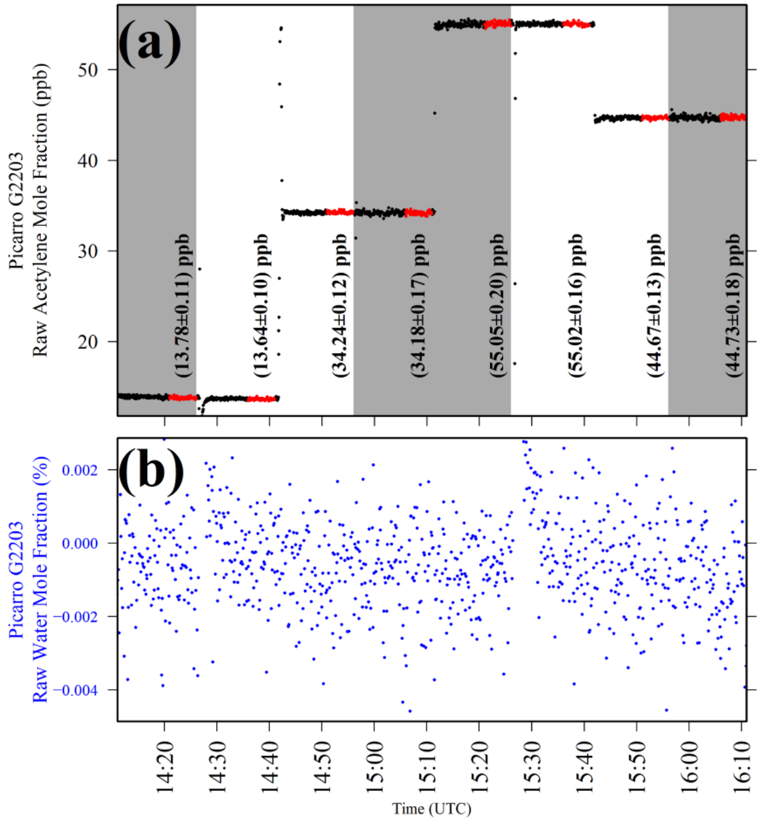

Figure S3: (a) Picarro G2203 $[C_2H_2]_r$ plotted as black dots and (b) Picarro G2203 $[H_2O]_r$ plotted as blue dots, when sampling four different $[C_2H_2]_t$ settings by blending gas from the acetylene calibration cylinder with natural ambient compressed air. At each $[C_2H_2]_t$ setting, pure dry gas was sampled (light grey shaded periods in (a)) as well as sampling gas passing through the dew-point generator, the Nafion-based gas dryer and the magnesium perchlorate scrubber (unshaded periods in (a)). Periods used to derive averages are highlighted as red dots in (a). A 5-minte average and standard deviation $[C_2H_2]_r$ measurement is shown on the plot for each $[C_2H_2]_t$ setting passing through both gas streams in (a). The $[C_2H_2]_r$ and $[H_2O]_r$ plot range in (a) and (b), respectively, correspond to the range measured during 5-minute averaging periods.

S3 Picarro G2401 water mole fraction during water characterisation tests

The effect of $[H_2O]_r$ changes on Picarro G2203 $[C_2H_2]_r$ measurements was tested at nine different $[C_2H_2]_r$ levels in **Sect. 2**. During this test, erratic Picarro G2203 $[H_2O]_r$ measurements were occasionally observed. However, simultaneous measurements made by the Picarro G2401 gas analyser, measuring the same gas stream, did not observe erratic $[H_2O]_r$ measurements, as illustrated in **Fig. S4**. This therefore confirms that erratic Picarro G2203 $[H_2O]_r$ measurements are an artefact of the gas analyser, rather than due to the contents of the gas mixture.

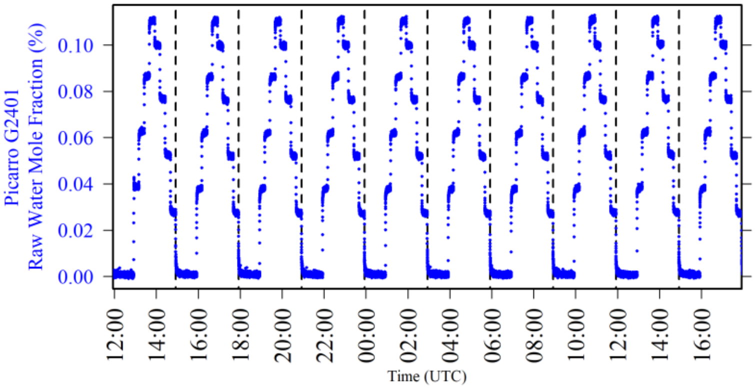

Figure S4: Picarro G2401 $[H_2O]_r$ plotted as blue dots when sampling nine different low $[H_2O]$ levels at five different $[C_2H_2]_t$ settings over two testing cycles, with the change between each different $[C_2H_2]_t$ setting indicated by dashed vertical lines.

S4 Unstable Picarro G2203 raw acetylene mole fraction measurements

When sampling at $[C_2H_2]$ levels of less than 1.16 ppb, the Picarro G2203 reported unstable $[C_2H_2]_r$ measurements that occasionally resolved to the $[C_2H_2]_r$ level observed at 0 ppb $[C_2H_2]$. An example of this is given in **Fig. S5** when gas from the acetylene calibration cylinder was blended with compressed ambient air to sample $[C_2H_2]$ of 0.349 ppb, following a transition from sampling 0.967 ppb $[C_2H_2]$. The data presented in **Fig. S5** is a subset of the data presented in **Fig. 6** (a).

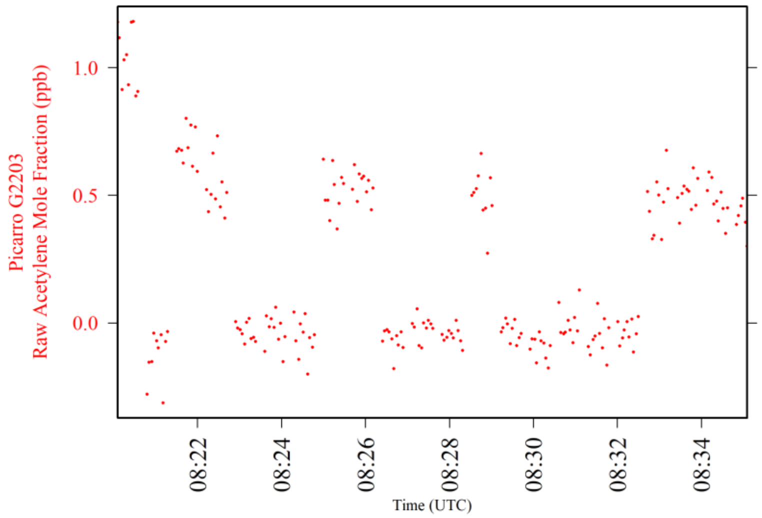

Figure S5: Picarro G2203 $[C_2H_2]_r$ plotted as red dots, starting with the transition from sampling 0.867 $[C_2H_2]$ to sampling 0.349 $[C_2H_2]$ by blending gas from the acetylene calibration cylinder with natural ambient compressed air.

S5 Acetylene calibration using zero-air generator gas for dilution

An acetylene calibration was conducted using the same $[C_2H_2]_t$ range from **Sect. 2**, but using gas from the zero-air generator for dilution instead of gas from a natural ambient compressed air cylinder. The zero-air generator catalytically and thermally oxidises hydrocarbons and carbon monoxide, resulting in a $[CH_4]_0$ of 0 ppm and $[C_2H_2]_0$ of 0 ppb. A similar set-up was used as illustrated schematically in **Fig. 4**, but the natural ambient air cylinder was replaced with the zero-air generator source. An additional diaphragm pump was placed downstream of the zero-air generator to pressurise gas flow, with an upstream vent to maintain the upstream pressure of the pump at atmospheric pressure. For this test, new C_{MFC} values were derived to account for any differences due to MFC performance over time and in the different conditions. Twenty different $[CH_4]_t$ levels between $[CH_4]_0$ and 9.78 ppm were targeted in the same way as when diluting gas from the methane calibration cylinder with natural ambient compressed air, as described in **Sect. 2**. Calibrated $[CH_4]$ measurements from the Picarro G2401 were averaged in the same way as described in **Sect. 2**, to derive C_{MFC} values using Eq. **(2)**, which are presented in **Fig. S6**. This could be used to derive $[C_2H_2]$ standards from $[C_2H_2]_t$. using Eq. **(1)**. The same blending procedure was then performed, but instead using the acetylene calibration cylinder in place of the methane calibration cylinder, to sample twenty different $[C_2H_2]$ levels between $[C_2H_2]_0$ and 100.1 ppm, as shown in **Fig. S7**. The same averaging was performed on this dataset as discussed in **Sect. 2**. Averages made at the four lowest $[C_2H_2]$ levels were excluded from the calibration, following **Sect. 2**, due to unstable Picarro G2203 $[C_2H_2]_r$ measurements. A linear regression was applied to the remaining data, as illustrated in **Fig. S8**, yielding a gain factor of 0.9413 and an offset of +0.0139 ppb, with a RMSE of ±0.0356 ppb.

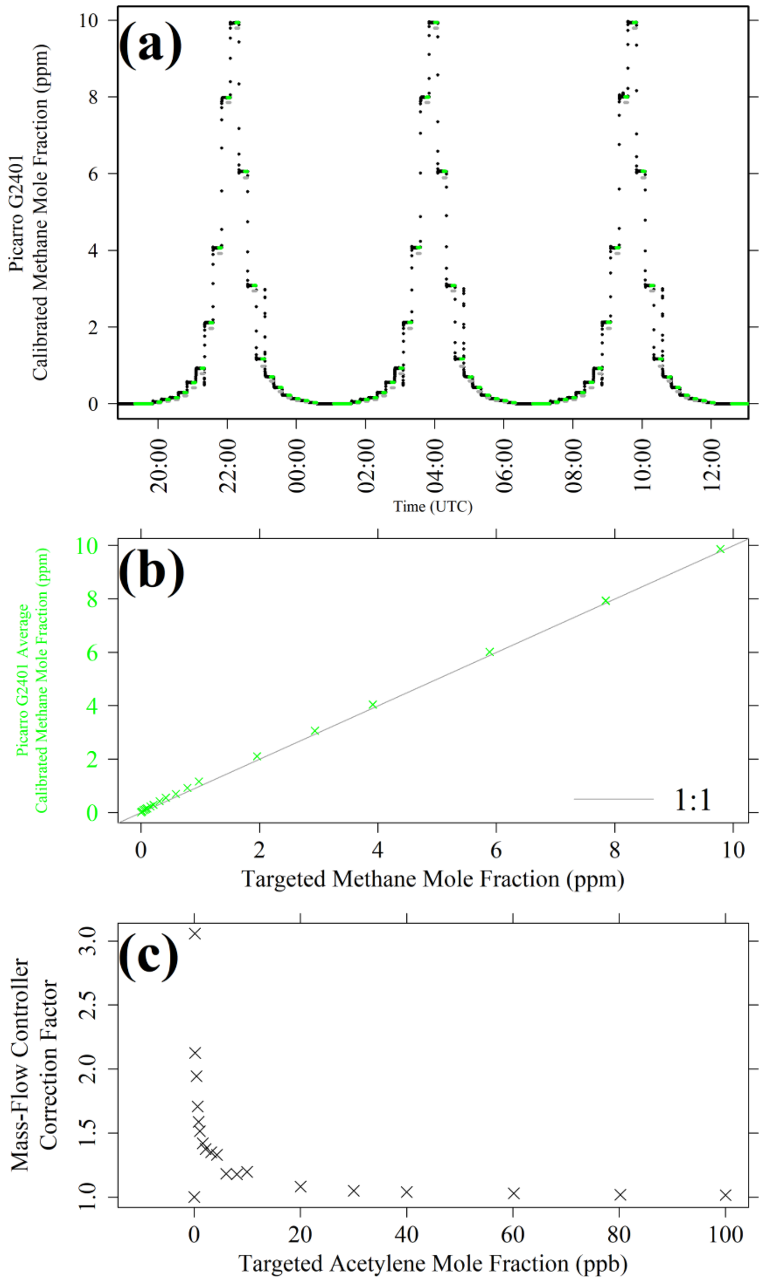

Figure S6: (a) Picarro G2401 [CH_4] plotted as black dots, (b) corresponding [CH_4] 5-minute averages plotted as green crosses against [CH_4]$_t$ calculated from MFC settings and (c) C_{MFC} as a function of corresponding [C_2H_2]$_t$ levels, derived from three testing cycles by blending gas from the methane calibration cylinder with gas from a zero-air generator. Periods used to derive averages are highlighted as green dots and corresponding [C_2H_2]$_t$ 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).

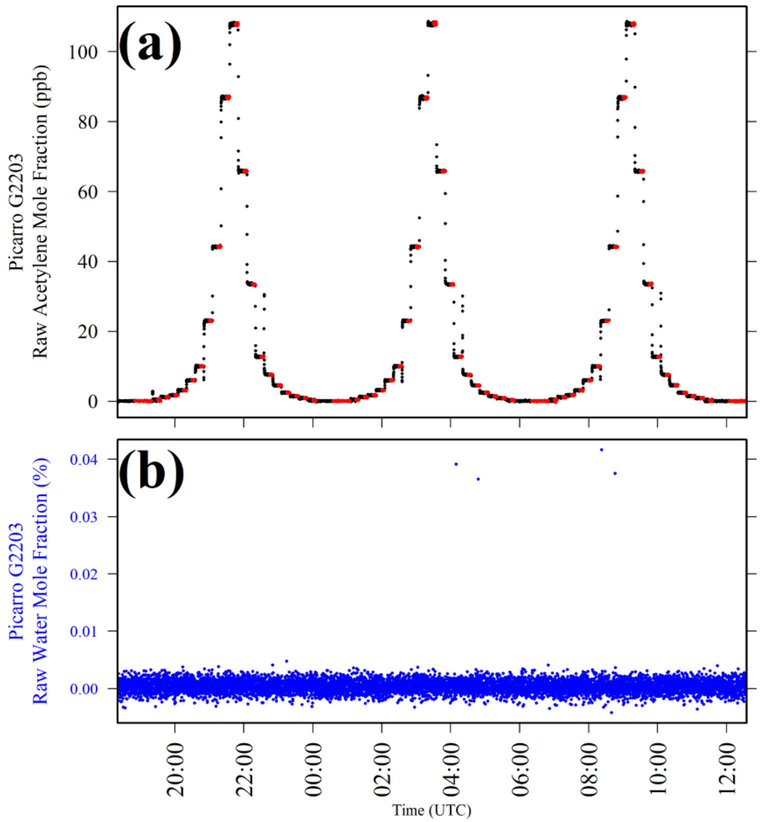

Figure S7: (a) Picarro G2203 $[C_2H_2]_r$ plotted as black dots and (b) Picarro G2203 $[H_2O]_r$ plotted as blue dots, when sampling twenty different standard $[C_2H_2]$ settings over three testing cycles by blending gas from the acetylene calibration cylinder with gas from a zero-air generator. Periods used to derive averages are highlighted as red dots in (a).

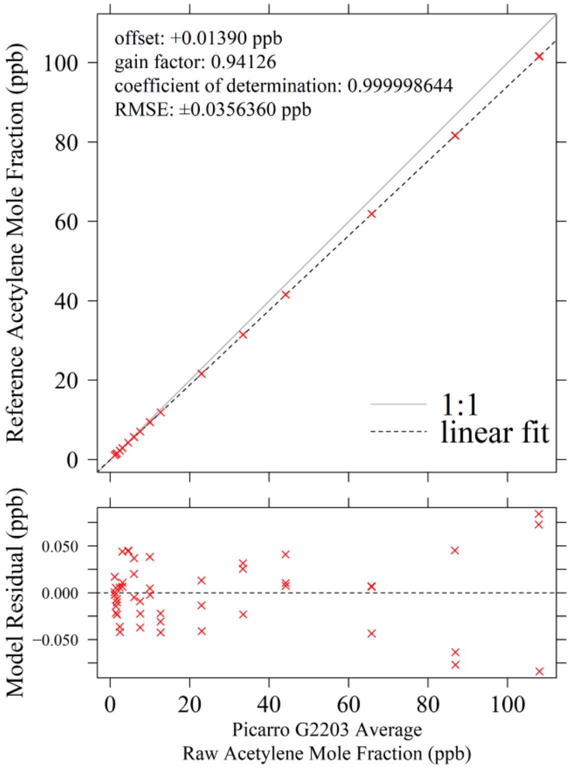

Figure S8: (top) Picarro G2203 5-minute average $[C_2H_2]_r$ measurements, when combining gas from the acetylene calibration cylinder with gas from the zero-air generator, plotted against reference $[C_2H_2]$ levels (red crosses), with a linear regression model shown as a dashed black line and an identity 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 horizonal dashed black line.

S6 Acetylene flow meter

The acetylene flow meter uses the Coriolis technique, described in detail by Baker (2016), to measure $Q_{\mathrm{acetylene}}$ up to a maximum of 8.67 g s^{-1} under a gauge pressure of 1 bar (maximum flow rate increases with absolute pressure). The flow meter has been factory calibrated using rigs traceable to ISO 17025, with error limits based on ISO 11631. It requires a direct current power supply of between 19.2 V and 28.8 V, which is provided by converting the output from a 12 V lithium ion phosphate battery up to 24 V.

During operation, $Q_{\mathrm{acetylene}}$ can be viewed on a display interface. A current loop also outputs analogue $Q_{\mathrm{acetylene}}$ data within a range of between 4 mA and 20 mA; this is connected to an analogue current to voltage converter (SEN0262, Zhiwei Robotics Corp, Shanghai, China). The voltage output from the analogue current to voltage converter is connected to an analogue to digital converter chip (MCP3424, Microchip Technology Inc., Chandler, Arizona, USA) which is ready-mounted on a board (ADC Pi board, Apexweb Ltd, Swanage, Dorset, UK); this is connected to a logging computer (Raspberry Pi Zero W, Raspberry Pi Foundation, Cambridge, UK), which records 16 bit voltage measurements (corresponding to a 0.154 mV voltage resolution) at 1 Hz. A baseline voltage correction is applied to all voltage measurements during acetylene gas release, by applying a linear fit as a function of time to voltage measurements before and after gas release, corresponding to zero gas flow. An Internet time synchronisation proceeds any data logging on the logging computer.

The performance of the acetylene flow meter was tested by comparison with flow rate measurements made by a MFC. Compressed outdoor air supplied to our laboratory building was simultaneously sampled by both the acetylene flow meter and the MFC. The MFC used in this test has a maximum flow rate of 15 dm^3 min^{-1} at 273.15 K and 101 325 Pa when sampling dry air, which was logged at approximately 10 Hz. The MFC was fully opened, allowing unimpeded gas flow and flow measurement. The flow rate was varied in rough stages up to 0.3 g s^{-1}. The flow rate and pressure were adjusted during each stage to ensure that the gauge pressure always fell between a range of between 0.5 bar and 1.0 bar, to replicate field operation conditions. Other unstable transition periods led to poor correspondence between the MFC and the acetylene flow meter as the pressure was not stable and adjustments were being made; these periods were identified and excluded from the comparison. All MFC data was interpolated to the lower timestamp of the acetylene flow meter. A comparison is presented in **Fig. S9**, which shows good agreement across the tested range, with a Pearson correlation coefficient of 0.9999627. This test therefore excellent confirms correlation between the two flow rate measurements. It also confirms our ability to derive the acetylene flow meter $Q_{\mathrm{acetylene}}$ measurements from the data output current loop.

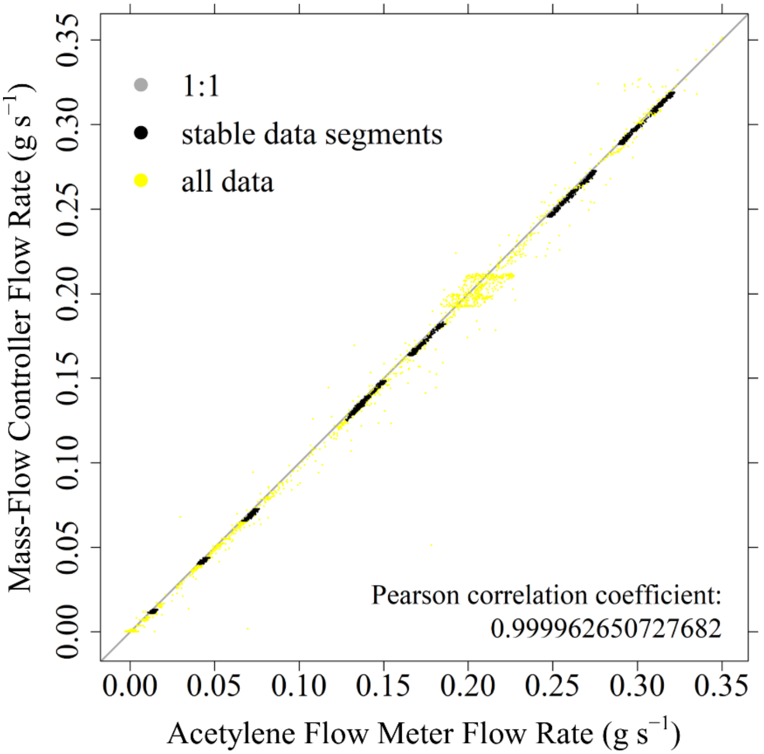

Figure S9: A comparison between Qacetylene measured by the acetylene flow meter (horizontal axis) and a MFC flow rate measurement (vertical axis), plotted as yellow dots. Periods of stable sampling are plotted as black dots. An identity line is shown (light grey) in the background.

S7 Wind conditions and flow rate during sampling

The duration of the sampling campaign is defined a running from 08:34:06.4 (UTC) to 11:00:40.2 (UTC) on 16 February 2024, representing a total duration of 146 minutes and 33.7 s. This corresponds to the period running from 20 minutes before the start of the first transect up until the time of the end of the final transect, on the road between Point A and Point B. Sonic anemometer wind speed and wind direction measurements for the full duration of the acetylene release are presented in **Fig. S10** (b and c, respectively). Acetylene flow meter $Q_{\mathrm{acetylene}}$ measurements are also presented in **Fig. S10** (a). Measurements in **Fig. S10** are highlighted for the full duration of the sampling campaign, as defined here.

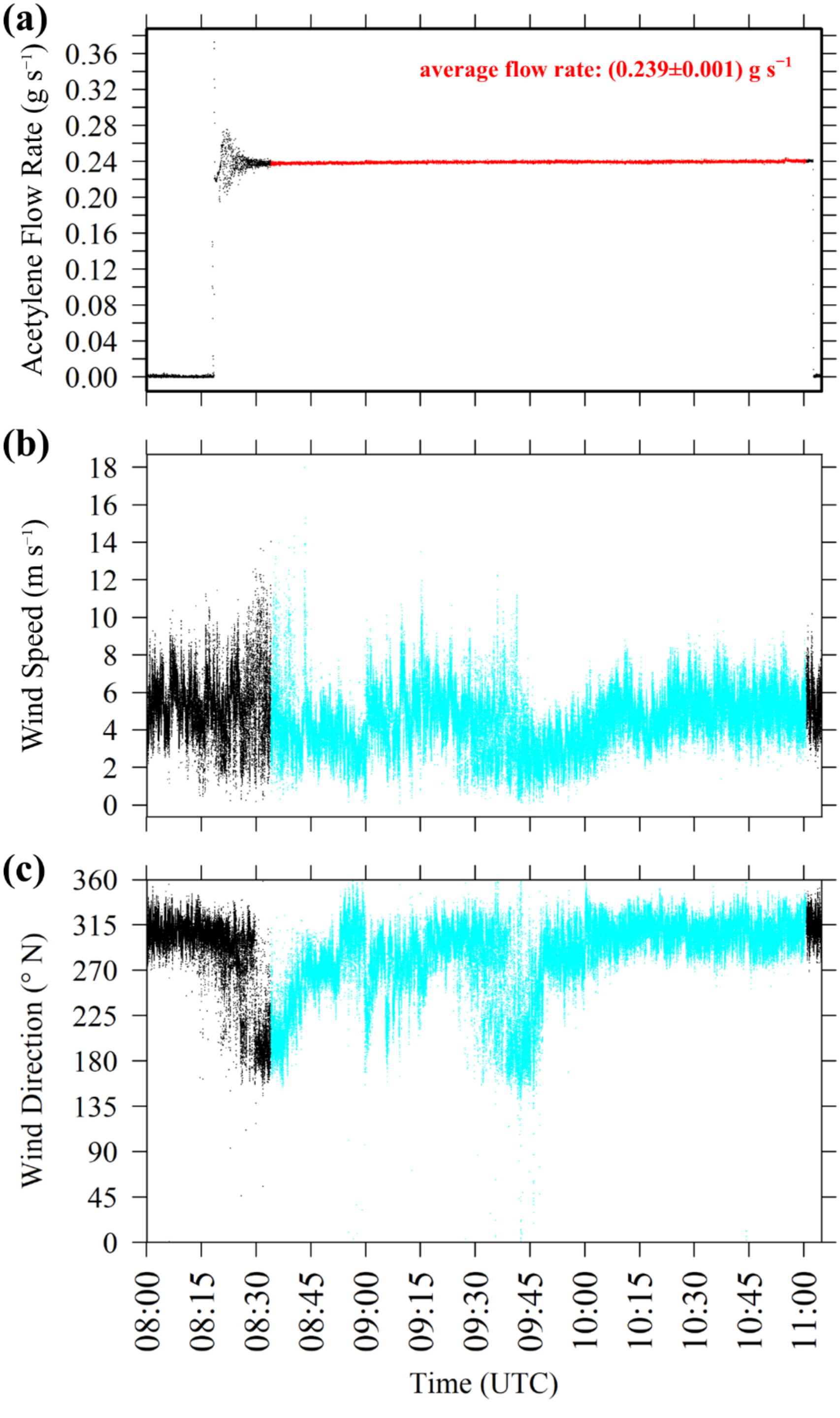

Figure S10: (a) Acetylene flow meter $Q_{\text{acetylene}}$, (b) sonic anemometer 2D scalar wind speed and (c) sonic anemometer 2D wind direction with respect to True North, all plotted as black dots. Periods of sampling from 20 minutes before the first transect up to the end of the final transect and shown as red dots in (a), cyan dots in (b) and cyan dots in (c).