Characterisation of interferences to in-situ observations of δ\textsuperscript{13}CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} when using a Cavity Ring Down Spectrometer at industrial sites.

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Abstract

The increase of atmospheric methane (CH\textsubscript{4}) is the second largest contributor to the increased radiative forcing since the industrial revolution. Natural gas extraction and distribution is associated with CH\textsubscript{4} leaks of uncertain magnitude that has spurred interest for developing new methods to measure them. Using a CRDS instrument we evaluate two methane identification methods commonly used to better constrain emission estimates from natural gas leaks, namely stable isotope analysis and the ethane: methane ratio (C\textsubscript{2}H\textsubscript{6}:CH\textsubscript{4}). Recently it has come to light that CRDS measurements of δ\textsuperscript{13}CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} in the near infrared spectral domain are subject to cross sensitivities due to absorption from multiple gases. These sensitivities translate into biases in the retrieval of δ\textsuperscript{13}CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} concentrations in air samples, and should thus be accounted for during data processing. Here we present extensive laboratory tests using two CRDS instruments to characterize their cross sensitivities and propose corrections to calculate unbiased δ\textsuperscript{13}CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}. Methane isotopic measurements were found to be subject to interference from elevated C\textsubscript{2}H\textsubscript{6} concentrations (a secondary component in many natural gas types) resulting in heavier δ\textsuperscript{13}CH\textsubscript{4} by +23.5‰ per ppm C\textsubscript{2}H\textsubscript{6}/ ppm CH\textsubscript{4}. Measured C\textsubscript{2}H\textsubscript{6} is subject to absorption interference from a number of other trace gases, the predominant being H\textsubscript{2}O (with an average linear sensitivity of 0.9 ppm C\textsubscript{2}H\textsubscript{6} per % H\textsubscript{2}O in ambient conditions, meaning that the presence of H\textsubscript{2}O causes the inference of too high C\textsubscript{2}H\textsubscript{6} mixing ratios if no correction is applied). Yet, this sensitivity was found to be discontinuous with a strong hysteresis effect. Throughout the range of C\textsubscript{2}H\textsubscript{6} concentrations measured in this study (0–5 ppm C\textsubscript{2}H\textsubscript{6}), both CRDS instruments consistently measure concentrations double that reported by a GC, thus we have calculated a calibration factor of 0.5. To demonstrate the significance of the corrections we test the source identification methods on air measured at a natural gas compressor station. The presence of C\textsubscript{2}H\textsubscript{6} in gas emissions at an average level of 0.3 ppm was found to shift the isotopic signature by 2.5‰. We find that after correction and calibration the average C\textsubscript{2}H\textsubscript{6}:CH\textsubscript{4} ratio shifts by +0.06. These results indicate that when using such a CRDS instrument in conditions of elevated C\textsubscript{2}H\textsubscript{6} for CH\textsubscript{4} source determination it is imperative to account for the biases discussed within this study.

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1. Introduction

With increasing efforts to mitigate anthropogenic greenhouse gas emissions, opportunities to reduce leaks from fossil fuel derived methane (\(\text{fCH}_4\)) is of particular importance as they currently account for approximately 30% of all anthropogenic methane emissions [Kirschke et al., 2013]. At present, technically feasible mitigation methods hold the potential to half future global anthropogenic CH\(_4\) emissions by 2030. Of this mitigation potential more than 60% can be realised in the fossil fuel industry [Hoglund-Isaksson, 2012]. However for effective implementation, sources, locations and magnitudes of emissions must be well known.

The global increase in the production and utilisation of natural gas, of which methane is the primary component, has brought to light questions in regards to its associated fugitive emissions, i.e. leaks. Recent estimates of CH\(_4\) leaks vary widely (1-10% of global production) [Allen et al., 2014] and US inventories of natural gas CH\(_4\) emissions have uncertainties of up 30% [EPA, 2016]. To address this issue the ability to distinguish between biogenic and different anthropogenic sources is of vital importance. For this reason methane isotopes (\(\delta^{13}\text{CH}_4\)) are commonly used to better understand global and local emissions as demonstrated in a number of studies [Lamb et al., 1995, Lowry et al., 2001, Hiller et al., 2014]. The discrimination of sources with relatively close isotopic composition such as associated-oil gas and natural gas, whose isotopic signatures can be separated by only ~4 ‰ [Stevens et al., 1988], requires precise and reliable \(\delta^{13}\text{CH}_4\) measurements.

Ethane (C\(_2\)H\(_6\)) is a secondary component in natural gas and can be used as a marker to distinguish between different CH\(_4\) sources. Use of the C\(_2\)H\(_6\)/CH\(_4\) ratio provides a robust identifier for the gas of interest. Recent findings in the US found coal bed C\(_2\)H\(_6\)/CH\(_4\) ratios ranging between 0-0.045, while dry and wet gas sources displayed differing ratios of <0.06 and >0.06 respectively [Yacovitch et al., 2014, Roscioli et al., 2015].

Laser spectrometers, especially based on Cavity Ring Down Spectroscopy (CRDS) are now a common deployment for site-scale CH\(_4\) measurement campaigns [Yvon-Lewis et al., 2011, Phillips et al., 2013, Subramanian et al., 2015]. However, with the advent of such novel technologies, there lies the risk of unknown interference of laser absorption which can cause biases to measurements. Some examples of which are discussed in Rella et al., (2015) and many others [e.g. K.Malowany et al., 2015, Vogel et al., 2013, Nara et al., 2012]. Using a CRDS instrument we show that the presence of C\(_2\)H\(_6\) is causing significant interference on the measured \(^{13}\text{CH}_4\) spectral lines thus resulting in shifted reported \(\delta^{13}\text{CH}_4\) values. We propose a method to correct these interferences, and test it on measurements of natural gas samples performed at an industrial natural gas site.

The CRDS instruments used throughout this study are Picarro G2201-i analysers (Picarro INC, Santa Clara, USA) whose measured gasses include CH\(_4\), CO\(_2\), H\(_2\)O and, although not intended for use, C\(_2\)H\(_6\). This model comprises two lasers, the first quantifies mole fractions of \(^{12}\text{CH}_4\), \(^{13}\text{CO}_2\) and \(^{13}\text{CO}_2\), by measuring spectral lines roughly at 6057cm\(^{-1}\) whereas the second laser focuses on \(^{13}\text{CH}_4\), H\(_2\)O and C\(_2\)H\(_6\) mole fractions, measuring at approximately 6029cm\(^{-1}\). The resulting spectrograms are fit with two non-linear models in order to determine concentrations; the primary fit is performed excluding the model function of C\(_2\)H\(_6\) while the second includes this function thus adding
the ability to measure C$_2$H$_6$ [Rella et al., 2015]. Such a method for measuring C$_2$H$_6$ concentrations is crude, thus the uncalibrated C$_2$H$_6$ concentration data is stored in private archived files which until now have been used primarily for the detection of sample contamination. The measurements of δ$^{13}$CH$_4$ and δ$^{13}$CO$_2$ are calculated using the ratios of the concentrations of $^{12}$CH$_4$, $^{13}$CH$_4$, $^{12}$CO$_2$ and $^{13}$CO$_2$ respectively.

Presented here is an experimental procedure to correct the interference caused by C$_2$H$_6$ on the retrieval of δ$^{13}$CH$_4$ using such a CRDS instrument for application to in-situ or continuous measurements of δ$^{13}$CH$_4$ strongly contaminated by C$_2$H$_6$, i.e. in the vicinity of flCH$_4$ sources. Literature suggests ethane mixing ratios ranging from 0.3 ppm to 3 ppm C$_2$H$_6$ for measurements taken within proximity of oil and gas leaks [e.g. Gilman et al., 2013, Jackson et al., 2014], while C$_2$H$_6$ in French and British background air stations is in the order of 1-2 ppb [Derwent et al., 2014, Waked et al., 2016]. Thus, our interference correction is designed for application to samples containing pure natural gas, or in the close proximity of leaks, i.e. suitable for emission factor and source apportionment studies.

The step by step procedure of the experimental methods developed to quantify the cross sensitivities and the proposed calibration for δ$^{13}$CH$_4$ and C$_2$H$_6$ are depicted in Fig. 1, and presented in detail in Sect. 2. Section 3 encompasses a discussion of the results, including analysis of the instrumental responses for two spectrometers with an evaluation of the stability and repeatability of the suggested corrections. Finally, field measurements were performed at a natural gas compressor station of which the aim was to identify emissions between two natural gas pipelines. In Sect. 5 the importance of the corrections for field measurements is demonstrated by applying our methods to data retrieved during this period while also revealing the instruments potential to measure C$_2$H$_6$.

2. Methods

Laboratory tests were conducted with the aim to characterize the instruments response to concentration changes in gasses found at fossil fuel sites (e.g. gas extraction or compressor stations). This includes the cross-sensitivities of CO$_2$, CH$_4$, and H$_2$O on C$_2$H$_6$ and the effect of concentration changes of C$_2$H$_6$ on δ$^{13}$CH$_4$. It is likely for there to be additional gases with the potential for interference; in this study we focus on those which have been reported to have significant effect on C$_2$H$_6$ and δ$^{13}$CH$_4$ measurements by Rella et al., (2015). We also define and describe a new procedure to calibrate both C$_2$H$_6$ and δ$^{13}$CH$_4$.

In order to assess intra-instrument variability the majority of tests were undertaken with two instruments of the same model in parallel. To determine the stability over time, tests were repeated throughout the course of one year. In the following chapter the general setup used for the majority of experiments is described after which we enter a more detailed description of the processes involved in each step individually.

2.1 Experimental Setup:

2.1.1 Method:
Each cross sensitivity is measured by creating a gas dilution series designed to control the concentrations of the gas responsible for the interference in steps while keeping concentrations of the other gas components constant (in particular the component subject to interference). Thus, any shift in the measured concentrations of a (component) gas that has been kept constant allows us to characterise a bias due to a cross sensitivity which can be evaluated for a large range of concentrations. The experimental set-up used for such experiments includes two CRDS instruments (Picarro G2201-i) running in parallel in a laboratory at ambient conditions (25°C, 100m above sea level (a.s.l)). The instruments were used in iCO2-iCH4 auto switching mode, in which we consider only the ‘high precision’ mode of δ13CH4 throughout the study. For the dilution series, a working gas is diluted in steps using a setup of two Mass Flow Controllers (MFC) (El-flow, Bronkhorst, Ruurlu, The Netherlands), as shown in Fig. 2. A T-junction splits the intended gas flow to both instruments; the total flow is greater than the flow drawn into the instruments, hence to maintain an inlet pressure close to ambient the setup includes an open split to vent additional gas. In order to assess variability and error, each experiment is repeated a minimum of 3 times consecutively. Each step within a dilution series is measured for an appropriate time to allow for stable measurement conditions (minimum 10 minutes) and optimal instrumental measurement uncertainties. During data processing initial data points are eliminated according to the observed settling time. To detect instrumental drift between experiments, a target gas is measured before commencing each dilution sequence. An overview of each cross interference targeted, with information on the gasses used and ranges spanned in laboratory tests can be found in Table 1.

2.1.2 Gases:

Throughout the experiments 4 categories of gas were used: a zero air gas with measured residual concentrations of <1ppm CO2, <30ppb CH4, ~170ppb CO, <1ppb C2H6 (Deuste-Steininger,Walldorf, Germany), working gases with variable concentrations of CO2 and CH4 in a natural air matrix (Deuste-Steininger,Walldorf, Germany), a C2H6 standard of 52 ppm in Nitrogen (National Physics Laboratory (NPL), Teddington, United Kingdom), and dried ambient air in 40L aluminium cylinders filled using an oil-free RIX compressor (RIX industries, Benicia, USA). Details of the gas mixture used in each dilution series depends on the response targeted within the experiment.

Information can be found in Table 1 and are also discussed in further detail throughout this chapter.

2.2 Determination of C2H6 corrections from H2O, CH4 and CO2 interference

The value of C2H6 based on the standard CRDS data processing package (hereafter, the raw value) is biased by cross-sensitivities with H2O, CO2 and CH4 which must be identified and corrected before other corrections or calibrations can take place. For the three gasses targeted within this sub-section, C2H6 concentrations are consistently <1 ppb so that any shifts in the raw C2H6 is due to the cross sensitivity to other components in the measured samples. With the aim of altering the water vapour content of a sample, the experimental setup described in Fig. 2 was modified by incorporating a humidifier. The humidifier consists of a liquid flow controller (Liqui-flow, Bronkhorst, Ruurlu, The Netherlands) and a mass flow controller (El-flow, Bronkhorst, Ruurlu, The Netherlands) fed into a controlled evaporator mixer (CME) (Bronkhorst, Ruurlu, The Netherlands). The tube...
departure the CME contains a gas flow of 2L/min and is heated to 40°C to prevent any condensation. A short description and diagram of the humidifying bench can found in Laurent et al., (2015).

The H₂O interference on C₂H₆ was measured by using the humidifier to vary the H₂O content of zero air gas in the range of 0.25%-2.5% H₂O, representing the range of real world conditions. The humidifier set up cannot reliably reach humidity’s below 0.2% H₂O, a range frequently reached when measuring cylinders or dried air. Therefore to focus on H₂O content within this low range, a second experiment was conducted in which a H₂O scrubber (Magnesium Perchlorate, Fisher Scientific, Loughborough, UK) was connected to the CRDS instrument inlet while measuring ambient air. As the efficiency of the scrubber decreases over time, a slow increase of H₂O spanning low concentrations in the range of 0%-0.5% can be observed.

The CH₄ interference on C₂H₆ was measured by creating a dilution series of variable CH₄ content using zero air and a working gas of 6ppm CH₄, 360ppm CO₂, 310ppb N₂O and 50ppb CO in natural air. Methane concentrations ranged from 0 – 6ppm. To keep other causes of interference at a minimum the gas mixture passed through two scrubbers; the first a CO₂ scrubber (Ascarite(ii), Acros Organics, USA), and the second a H₂O scrubber (Magnesium Perchlorate, Fisher Scientific, Loughborough, UK). As an independent check on the linearity of the response functions each dilution sequence was repeated at two different humidities, 0% H₂O and 1% H₂O respectively.

The CO₂ interference on C₂H₆ was measured with a dilution series ranging 0-1500ppm CO₂ created by mixing zero air and a working gas of 2000ppm CO₂, 1.7ppm CH₄ and 50ppb CO in natural air. Any interference due to CH₄ was accounted for during data processing. This test was repeated at 5 different humidities ranging between 0-1.5% H₂O.

2.3 C₂H₆ calibration setup

In order to correctly use the C₂H₆ data from CRDS instruments, the data must be calibrated to an internationally recognised scale. To achieve this, the set up described in Sect. 2.1 was modified to include the ability to fill removable samples whose concentrations could be independently verified. Hence 1L glass flasks were incorporated into the setup, as shown in Fig. 2. A gas mixture using the C₂H₆ standard and an ambient air cylinder was created via two MFCs before passing through the flask on its way to the instruments inlets. Each step in the dilution series requires an individual flask, which was flushed for 20 minutes and then analysed for 10 minutes with an average precision of 0.02ppm C₂H₆ on the CRDS instrument. The flask is subsequently sealed and removed for analysis on a Gas Chromatograph (GC) [Chrompack Varian 3400, Varian Inc, USA] which uses National Physics Laboratory (NPL) standards, and has an uncertainty better than 5%. The system is described in more detail in Bonsang and Kanakidou (2001).

In total 17 flasks were filled with gas mixtures spanning from 0ppm to 5ppm C₂H₆, covering the range expected near a leak of ffCH₄. In order to calibrate the linearity of the response at very high concentrations which may be expected from pure natural gas samples we conducted a measurement at 100% of the C₂H₆ standard (52 ppm ± 1 ppm).
2.4 Determining the correction for $\delta^{13}$CH$_4$

Measured $\delta^{13}$CH$_4$ is altered in the presence of C$_2$H$_6$. To understand the magnitude of this effect, experiments were conducted using the method described in Sect. 2.1. The dilution series uses the C$_2$H$_6$ standard and a cylinder filled with ambient air, i.e. with a negligible C$_2$H$_6$ mixing ratio (<1 ppb) to create concentration values spanning from 0-4 ppm C$_2$H$_6$. As there is only one source of CH$_4$ in the experiment, the addition of C$_2$H$_6$ should not affect the value of $\delta^{13}$CH$_4$, hence any change seen is an apparent shift of $\delta^{13}$CH$_4$ due to C$_2$H$_6$ interference. This concentration range was chosen as it encompasses a C$_2$H$_6$:CH$_4$ ratio of 0 to 1, well within the likely range to be measured from fossil fuel sources [Yacovitch et al., 2014].

2.5 Calibration of $\delta^{13}$CH$_4$

The reported $\delta^{13}$CH$_4$ was calibrated to Royal Holloway University of London (RHUL) scale using 4 calibration gases spanning -25‰ to -65‰ that were created by different dilutions of pure CH$_4$ and CO$_2$ with ambient air of which aliquots were measured multiple times by Isotope Ratio Mass Spectrometry (IRMS) at RHUL. The precision for $\delta^{13}$CH$_4$ obtainable with this IRMS is reported as 0.05‰, detailed information on the measurement system can be found in Fisher et al. (2006). The calibration factor is determined from a linear regression and calibrations were performed before and after the laboratory experiments. To ensure the calibration is reliable, it is repeated 3 times over a period of 3 days. The mean isotopic values of each repetition are all included within one linear regression under the assumption that the system does not vary significantly over this period. A target gas was measured regularly to track any drift in $\delta^{13}$CH$_4$ and to act as an independent check on the quality of the calibration.

3. Results and Discussion:

This study focuses on determining a reliable correction and calibration scheme for a Picarro G2201-i when measuring methane sources with C$_2$H$_6$ interference. Findings from the experiments described in Sect. 2 are discussed in detail here.

In order to calibrate $\delta^{13}$CH$_4$ and C$_2$H$_6$ values, there are a series of corrections that must take place (see Fig. 1). The initial correction to be applied is on C$_2$H$_6$ due to interference from CH$_4$, CO$_2$ and H$_2$O. Particular emphasis is placed on this correction due to the discovery of significant non-linear behaviour in the presence of H$_2$O, CH$_4$ and CO$_2$ in the sample gas. Once the C$_2$H$_6$ has been corrected, the calibration of C$_2$H$_6$ using independent GC measurements, the C$_2$H$_6$ interference correction on $\delta^{13}$CH$_4$ and finally the calibration of $\delta^{13}$CH$_4$ can be effected.

For our results to be applicable to future studies we examine the inter-instrument variability, stability over time, compare our results to current literature and discuss the uncertainties attributed to our results. Throughout this study we refer to raw, uncorrected C$_2$H$_6$ and $\delta^{13}$CH$_4$ concentrations as “reported” to highlight that they may be influenced by interferences and have not yet undergone correction treatment. Within this section often negative C$_2$H$_6$
concentrations are mentioned, we note that this is the “reported” C$_2$H$_6$ concentration by the instrument. Unless otherwise stated, the standard deviation reported is calculated from one minute averages and depicted as error bars within figures.

### 3.1. Correcting reported C$_2$H$_6$

#### 3.1.1 H$_2$O interference on C$_2$H$_6$

The effect of water vapour on reported C$_2$H$_6$ was determined by performing experiments in which the humidity of zero air was varied between 0-2.5% (as described in Sect. 2.2). H$_2$O content was found to be the dominating source of interference to reported C$_2$H$_6$; its presence decreases the reported concentration of C$_2$H$_6$ with increasing H$_2$O concentration. Furthermore, we have found that the response function exhibits a hysteresis effect, which, although small, can be considerable when changing from dry to undried air samples (between dry calibration gas and undried ambient air). Figure 3 shows the differing response functions obtained when measuring dried (dark blue markers) or undried (light blue markers) ambient air during the night preceding the experiment. When the CRDS instrument measures dry air prior to the experiment, a discontinuity is observed at 0.16% H$_2$O. Figure 4a shows this effect in more detail; prior to 0.16% H$_2$O the response function exhibits a stable linear response. The correction within this low range was found to be the same for both instruments, 0.44 ± 0.03 ppm C$_2$H$_6$/% H$_2$O. After passing the 0.16% H$_2$O threshold the response exhibits a discontinuity whose magnitude and subsequent slope are also dependent on the air moisture beforehand. This can also be seen in Fig. 4a whereby two repetitions (A and B depicted by dark and light blue points respectively) experience a difference in the magnitude of the discontinuity of 0.1ppm in reported C$_2$H$_6$. The discontinuity is seen to occur when the instrument passes the 0.16% H$_2$O threshold, whether this be when moving from dry to wet air, or vice versa (see Fig. 4b). If measuring undried air before the experiment, the interference due to H$_2$O can be described well by a linear response (blue markers in Fig. 3), and potentially causes large biases from the true C$_2$H$_6$. For example, if measuring at 1% H$_2$O both instruments display a change in reported C$_2$H$_6$ of approximately -0.9ppm. Individually the response function calculated for instruments CFIDS 2072 and 2067 differed slightly showing -0.72 ± 0.03 ppm C$_2$H$_6$/% H$_2$O and -1.00 ± 0.01 ppm C$_2$H$_6$/% H$_2$O with $R^2$ values of 0.98 and 0.99 respectively. The hysteresis effect is not as evident within this range, however a shift in the slope of 0.1 ppm C$_2$H$_6$/% H$_2$O has been measured between the first and third repetition of the experiment.

#### 3.1.2 CO$_2$ interference on C$_2$H$_6$

First tests revealed that the CO$_2$ interference on C$_2$H$_6$ is not fully independent of the H$_2$O levels of the sample. Therefore, the correction of the CO$_2$ interference on C$_2$H$_6$ was examined extensively at varying H$_2$O water vapour levels. The set-up of these experiments has been discussed within the Sect. 2, for which an example of the time series can be seen in Fig. 5. The H$_2$O content was set at four different water vapour levels (0%, 0.5%, 1% and 1.5%) and dried air was measured between each level to minimise the hysteresis effect observed within the H$_2$O correction tests. For each H$_2$O level, a CO$_2$ dilution series (of minimum 3 concentrations) was created in order to detect any covariance on the CO$_2$ interference arising due to water vapour content. For both instruments an increase in the CO$_2$...
concentration results in lower reported values of C$_2$H$_6$ and it is furthermore apparent, that the magnitude of this interference is dependent on air humidity. For a dry sample gas (H$_2$O <0.16% - demonstrated in the left hand column of Fig. 6), the interference for both instruments is found to be highly stable and well characterised by a linear slope of $1 \times 10^{-4} \pm 1 \times 10^{-5}$ ppmC$_2$H$_6$/ppmCO$_2$ with a $R^2$ value of 0.9. In contrast, for water vapour levels ≥ 0.5% H$_2$O (see right hand column of Fig. 6) measurements exhibit a higher scatter between repetitions. This is mainly attributed to a drifting intercept however the experiments also show a smaller $R^2$ of 0.8. The slope obtained for each repetition is largely within observed uncertainties, thus we combined the results to obtain a characteristic linear slope of $3.8 \times 10^{-4} \pm 1 \times 10^{-5}$ ppmC$_2$H$_6$/ppmCO$_2$ and $3.9 \times 10^{-4} \pm 1 \times 10^{-5}$ for ≥0.5% water vapour for instruments CFIDS 2072 and 2069 respectively. Therefore, measuring undried ambient air the presence of CO$_2$ at a level in the range of 400 ppm will typically induce a shift in the reported C$_2$H$_6$ of approximately -0.15 ppm C$_2$H$_6$, whereas if the air is dried the reported shift is much smaller, being approximately -0.04 ppm C$_2$H$_6$.

### 3.1.3 CH$_4$ interference on C$_2$H$_6$

The CH$_4$ effect on C$_2$H$_6$, as shown in Fig. 7, is less prominent by at least an order of magnitude than both the H$_2$O and CO$_2$ interferences. At dried ambient CH$_4$ concentrations a typical change in reported C$_2$H$_6$ of approximately -0.008 ppm is observed within both instruments. Dried air experiments show a high scatter of points between repetitions, when combining all data points an $R^2$ value of 0.4 and 0.6 for instruments CFIDS 2072 and 2067 respectively is calculated. Despite its large uncertainty the data suggests both instruments display a similar response with a statistically significant slope. In light of this we use a weighted mean to calculate a linear response of $5 \times 10^{-3} \pm 4 \times 10^{-3}$ ppmC$_2$H$_6$/ppmCH$_4$ for dry air measurements for CFIDS 2067, and $7 \times 10^{-3} \pm 5 \times 10^{-3}$ ppmC$_2$H$_6$/ppmCH$_4$ for CFIDS 2072. The results obtained at 1% H$_2$O show little correlation (as shown in the right hand column of Fig. 7), with both instruments displaying a $R^2$ value of 0.2. An ANOVA test suggests the slopes are not significantly different from zero, thus we omit a CH$_4$ correction for this case.

### 3.1.4 Combining the CO$_2$, CH$_4$ and H$_2$O correction on C$_2$H$_6$

To fully take into account all (known) C$_2$H$_6$ cross-sensitivities the corrections to reported C$_2$H$_6$ need to be combined. As we have found the instrument behaviour to be not strictly linear (independent) for different component concentrations and as the discontinuity in reported C$_2$H$_6$ for 0.16% H$_2$O and its subsequent slope is hard to predict, we do not calculate a correction for the effect. We rather choose to report correction coefficients for the two found linear regimes, i.e. for continuous measurements with sample humidities below 0.16% and sample humidities above 0.16%. Within each range the proposed correction formula is given as:

$$[C_2H_6]_{\text{corrected}} = \frac{[C_2H_6]_{\text{raw}} + A^* [H_2O] + B^* [CH_4] + C^* [CO_2]}{[H_2O]}$$  \hspace{1cm} \text{(Eq. 1)}$$

If the humidity is limited to less than 0.16% before and during measurements, $A = 0.44 \pm 0.03$ ppmC$_2$H$_6$/%H$_2$O, $B = 5 \times 10^{-3} \pm 4 \times 10^{-3}$ ppmC$_2$H$_6$/ppmCH$_4$, $C = 1 \times 10^{-4} \pm 1 \times 10^{-5}$ ppmC$_2$H$_6$/ppmCO$_2$. Both instruments demonstrated good agreement for all the correction factors calculated at <0.16% H$_2$O.
Corrections for measurements undertaken at concentrations higher than or equal to 0.16% H\textsubscript{2}O are: $A=0.7 \pm 0.03$ ppmC\textsubscript{2}H\textsubscript{6}/ppm CH\textsubscript{4}$, $B=0$ ppmC\textsubscript{2}H\textsubscript{6}/ppmCH\textsubscript{4}$, $C=3.8 \times 10^{-4} \pm 2 \times 10^{-5}$ ppmC\textsubscript{2}H\textsubscript{6}/ppmCO\textsubscript{2}$ for CFIDS 2072 and $A=1 \pm 0.01$ ppmC\textsubscript{2}H\textsubscript{6}/ppm CH\textsubscript{4}$, $B=0$ ppmC\textsubscript{2}H\textsubscript{6}/ppmCH\textsubscript{4}$, $C=3.9 \times 10^{-4} \pm 2 \times 10^{-5}$ ppmC\textsubscript{2}H\textsubscript{6}/ppmCO\textsubscript{2}$ for CFIDS 2067.

### 3.2 C\textsubscript{2}H\textsubscript{6} calibration

To make use of the corrected CRDS based C\textsubscript{2}H\textsubscript{6} it should be calibrated to match an internationally recognised scale. To calibrate the C\textsubscript{2}H\textsubscript{6} to such a scale, whole-air samples were measured by CRDS and independently on a calibrated Gas Chromatograph, as discussed within Sect. 2. The calibration factor is determined by comparing the corrected C\textsubscript{2}H\textsubscript{6} resulting from CRDS and C\textsubscript{2}H\textsubscript{6} as confirmed by the GC, plotted in Fig. 8a. The relationship was found to be linear throughout the range of 0-5 ppm C\textsubscript{2}H\textsubscript{6} with a slope of 0.505 $\pm$ 0.007 and 0.52 $\pm$ 0.01 for instruments CFIDS 2072 and 2067 respectively. The results are reported in Table 2 from which we can see the intercept of the calibration for instrument CFIDS 2072 shifts between the experiment in February and that in October, while the slope remains constant over long periods of time. The change in the intercept is attributed to a C\textsubscript{2}H\textsubscript{6} baseline drift which we have monitored over time using regular target gas measurements, example given in Fig. 8b. To account for this drift, and any elevated baselines (such as that of CFIDS 2067 – see Table 2) a regular measurement of a working gas is necessary. By tracking the baseline drifts using this working gas (which can also serve as a target gas for other gases) we can calculate the instrument offset. For the full calibration we thus suggest using Eq. (2), where $D$ is the calibration factor (slope) for the instrument, i.e. for CFIDS 2072 $D=0.505\pm 0.007$ and $\Delta$ [WGS] the baseline drift determined using the working gas.

\[
[C_{2}H_{6}]_{\text{calibrated}} = D \times ([C_{2}H_{6}]_{\text{corrected}} - \Delta [\text{WGS}]) \quad \text{Eq. (2)}
\]

### 3.3 $\delta^{13}$CH\textsubscript{4} correction

By measuring the shift of the reported $\delta^{13}$CH\textsubscript{4} in C\textsubscript{2}H\textsubscript{6}-contaminated samples, we have observed that the instrument reports heavier values of $\delta^{13}$CH\textsubscript{4} in the presence of C\textsubscript{2}H\textsubscript{6}. The shift is a result of increased reported $^{13}$CH\textsubscript{4} in samples containing C\textsubscript{2}H\textsubscript{6} (see Fig. 9). This is most likely caused by the overlapping of spectral lines within the 6029 wavenumber region [Rella et al., 2015]. We calculate the $\delta^{13}$CH\textsubscript{4} correction by taking the slope of $\Delta \delta^{13}$CH\textsubscript{4} (the difference between the reported $\delta^{13}$CH\textsubscript{4} and the initially reported one of the C\textsubscript{2}H\textsubscript{6}-free gas) and the corrected C\textsubscript{2}H\textsubscript{6} to CH\textsubscript{4} ratio. The ratio is used to permit the calculation of the $\delta^{13}$CH\textsubscript{4} response function per ppm CH\textsubscript{4} as the magnitude of interference is dependent on CH\textsubscript{4} concentration [Rella et al., 2015]. The significance of the interference on $\delta^{13}$CH\textsubscript{4} concentrations is illustrated in Fig. 10; as the C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4} ratio increases, the change in the reported $\delta^{13}$CH\textsubscript{4} increases linearly. Results obtained from tests carried out throughout the year, for both instruments are noted in Table 3, and plotted in Fig. 10. The correction equation can be expressed as:

\[
[\delta^{13}\text{CH}_4]_{\text{CORRECTED}} = [\delta^{13}\text{CH}_4]_{\text{RAW}} - E \times C_{2}\text{H}_6_{\text{CORRECTED}} / \text{CH}_4 + F \quad \text{Eq. (3)}
\]

where $E$ is the slope of the response function and $F$ is the intercept. $E$ and $F$ are $+23.6 \pm 0.4$‰ ppm CH\textsubscript{4}/ppm C\textsubscript{2}H\textsubscript{6} and approximately $+0.4\pm0.2$‰ for instrument CFIDS 2072 and $+23.3 \pm 0.7$‰ ppm CH\textsubscript{4}/ppm C\textsubscript{2}H\textsubscript{6} and
approximately -2.4 ±0.4‰ for instrument CFIDS 2067 respectively. These corrections contain the inherent δ\(^{13}\)CH\(_4\) offset of the instrument. When calibrating the δ\(^{13}\)CH\(_4\) to a known scale (as described in Sect. 2.5) any instrumental offset will be incorporated within the calibration, therefore the correction equations can be simplified to:

\[
[\delta^{13}\text{CH}_4]_{\text{CORRECTED}} = [\delta^{13}\text{CH}_4]_{\text{RAW}} - E \cdot C_{2H_6,\text{CORRECTED}} / \text{CH}_4. \tag{4}
\]

Also highlighted in Fig. 10 is the typical measurement range for the majority of ffCH\(_4\) sources related to dry and wet natural gas relative to calibrated C\(_2\)H\(_6\)/CH\(_4\) ratios given on the upper abscissa; whereby dry gas refers to natural gas that occurs in the absence of condensate/liquid hydrocarbons (C\(_2\)H\(_6\)/CH\(_4\) = 1-6%) while wet gas typically contains higher concentrations of complex hydrocarbons (C\(_2\)H\(_6\)/CH\(_4\) >6%) [Yacovitch et al., 2014]. It is clear that within this range the bias on methane isotopic signatures is significant; dry gas will alter the reported δ\(^{13}\)CH\(_4\) by 0.8-4‰, while wet gas can cause a shift of up to 13‰ depending on its C\(_2\)H\(_6\)/CH\(_4\) ratio.

3.4 δ\(^{13}\)CH\(_4\) calibration

Full instrument calibrations as described in Sect. 2.4 were performed once in 2014 and 2015. The δ\(^{13}\)CH\(_4\) values obtained for the calibration gases by RHUL are measured by IRMS and are therefore not subject to interferences. The calibration gas aliquots were measured with an average standard deviation of 0.03‰. To calibrate δ\(^{13}\)CH\(_4\) corrected, the δ\(^{13}\)CH\(_4\) corrected was calculated for each calibration gas and used within the linear regression. The calibrations were linear with R\(^2\)=0.99 on both occasions and no change (within our uncertainties) was observed between the two tests. By measuring an ambient air target regularly we later detected a shift in the δ\(^{13}\)CH\(_4\) baseline. Two further calibrations were performed in 2016 to assess this incident which confirmed that the offsets of the linear regressions were significantly shifted, while the slopes agreed well with previous calibrations. Therefore to account for a baseline drift it is important to measure a target gas regularly and amend the offset of the calibration equation accordingly.

3.5 Typical instrumental performance and uncertainties

Our CRDS is frequently used for different field deployments and in order to assess the potential benefit of co-located δ\(^{13}\)CH\(_4\) and C\(_2\)H\(_6\) observations we need to evaluate the typical performance here. In order to characterize the repeatability of the C\(_2\)H\(_6\) measured by the CRDS instrument we have measured several targets and monitored the changes of the reported C\(_2\)H\(_6\) signal over time. The raw signal is a measurement every 3 seconds, which displays on average a standard deviation of 90 ppb. By aggregating the data to 1 minute intervals the precision can be improved and a standard deviation of 20 ppb is reached, while 30 minute aggregation reduces this further to 8 ppb. Furthermore, when measuring the 52 ppm C\(_2\)H\(_6\) standard, the 1 minute standard deviation is 180 ppb. Therefore, by assuming a linear relationship, we have calculated a typical performance for 1 minute averages of 20 ppb +/- 0.3% of reading.

Of course, there are some substantial uncertainties attributed with the C\(_2\)H\(_6\) correction and calibration which need to be accounted for when discussing the uncertainty of the calibrated C\(_2\)H\(_6\) concentrations. With regards to the C\(_2\)H\(_6\)
correction for 1 minute averages, if measuring dried ambient air the propagation of uncertainties are negligible with respect to the raw instrumental precision (20ppb). However if using 30 minute averages the uncertainty augments from 8ppb to 10ppb due to the propagation of uncertainties associated with the correction coefficients. Elevated CH₄, CO₂ and H₂O signals (>5ppm, >1000ppm, >0.2% respectively) will induce increased C₂H₆ uncertainty regardless of aggregation time. After calibration we have found that the uncertainty increases to $2^{1/2}$ times that of the corrected C₂H₆, so at ambient air concentrations calibrated C₂H₆ has an uncertainty of 30ppb.

3.6 Generalisability of corrections and calibrations

The repeatability of δ¹³CH₄ for 1 minute averages on our instrument is a standard deviation of 0.66‰. Again the standard deviation is reduced to 0.29‰ and 0.09‰ by aggregating the raw data for 5 minutes and 30 minutes, respectively. For the correction of δ¹³CH₄ due to C₂H₆, error propagation of the factors applied in Eq. (4) must be taken into account. Therefore, at ambient concentrations, the uncertainty of a 1min average will increase to 0.9‰.

The experiments in this study were repeated multiple times and performed on different instruments to better understand how the instrument responses change over time and how they vary between instruments. The C₂H₆ correction and calibration, and δ¹³CH₄ correction experiments were repeated on CFIDS 2072 over the course of a year to determine any temporal drifts.

The coefficients of the C₂H₆ correction were examined over a 4 month period. Methane, Carbon dioxide and water vapour coefficients for dried gas displayed no noticeable variation over this time frame. Both CH₄ and CO₂ coefficients for undried gas also showed good stability throughout this period, however the undried H₂O coefficient is seen to vary significantly ($±0.1$ ppmC₂H₆/%H₂O). As discussed previously, the H₂O correction is subject to a hysteresis effect, which makes analysis of its long term variation difficult. As we did not find a clear temporal pattern of the variations we therefore suggest that this coefficient is not likely to be time dependant.

The calibration of C₂H₆ was calculated twice within a 9 month period (see Table 2). No variation of the slope of the response function is observed within this time frame. The intercept is prone to drift in time as discussed previously. The δ¹³CH₄ correction has been examined three times throughout a 6 month period (see Table 3), during which time the analyser had been switched off and relocated on several occasions. The variability of the slope observed over 6 months is 1‰ ppmC₂H₆/ppmCH₄. Given that the error attribution of each experiment is approximately ± 1‰ ppmC₂H₆/ppmCH₄, this variability is not statistically significant. The intercepts show good agreement with no variation outside the expected uncertainties.

All experiments were applied to two instruments of the same model in order to infer the variability of the aforementioned correction and calibration factors between them. Both CRDS instruments showed good agreement for all calculated C₂H₆ correction coefficients with the exception of the undried H₂O coefficient at >0.16% H₂O. For
this coefficient we calculate a difference of 0.3 ppmC\textsubscript{2}H\textsubscript{6}/%H\textsubscript{2}O between that of \textit{CFIDS 2072} and \textit{CFIDS 2067}. The variance may be the consequence of spectrometer differences, a long-term hysteresis effect or due to differences in their past use up to our tests (mostly dried samples on CFIDS 2072 and mostly undried samples for CFIDS 2067).

The slopes derived for the C\textsubscript{2}H\textsubscript{6} calibration of both instruments correspond well, with no significant difference seen between the two. The intercepts differ by approximately 0.6 ppm, thus suggesting distinct differences between instrumental C\textsubscript{2}H\textsubscript{6} baselines.

The slopes of the \(\delta^{13}\text{CH}_4\) correction were found to be in good agreement between the two instruments. Where the instruments differ is with regards to their \(\delta^{13}\text{CH}_4\) baseline, thus causing the observed disparity in intercept (seen in Table 3) of approximately 3‰.

To the best of our knowledge, at this time there is only one published study reporting on a correction due to C\textsubscript{2}H\textsubscript{6} interference on an isotopic Picarro analyser. Rella et al., (2015) have studied the interference using a Picarro G2132-i, a high precision CH\textsubscript{4} Isotope-only CRDS analyser which uses similar analysis algorithms and spectral regions as that of the Picarro G2201-i. Rella et al., (2015) obtained C\textsubscript{2}H\textsubscript{6} correction parameters of \(A=0.658\) ppm C\textsubscript{2}H\textsubscript{6}/ ppm H\textsubscript{2}O, \(B=5.5 \pm 0.1 \times 10^{-3}\) ppm C\textsubscript{2}H\textsubscript{6}/ ppm CH\textsubscript{4}, \(C=1.44 \pm 0.02 \times 10^{-4}\) ppm C\textsubscript{2}H\textsubscript{6}/ ppm CO\textsubscript{2} in 2015. Factors B and C for CH\textsubscript{4} and CO\textsubscript{2} respectively agree well with the dried air coefficients attained within this study, however the values are not specified to be dry or wet factors. The H\textsubscript{2}O coefficient, as suggested by Rella et al., (2015) differs to both that of \textit{CFIDS 2072} and \textit{CFIDS 2067} but confirms the variability of this factor between instruments when measuring undried air samples. The discontinuity observed within the H\textsubscript{2}O response for dried air samples was not discussed in Rella et al., (2015). Lastly, Rella et al., (2015) report a correction factor for \(\delta^{13}\text{CH}_4\) of 35‰ ppm CH\textsubscript{4}/ppm C\textsubscript{2}H\textsubscript{6}. Although comparable, this differs to that calculated in our study by approximately 10‰ ppm CH\textsubscript{4}/ppm C\textsubscript{2}H\textsubscript{6}. The reason for this disparity is not clear, we suggest that because the G2132-i analyser used by Rella et al., (2015) is devoted to CH\textsubscript{4} Isotope-only measurements it may be affected by C\textsubscript{2}H\textsubscript{6} to a different extent.

4. Source Identification at a Natural Gas Compressor Station

In order to quantify the effect of C\textsubscript{2}H\textsubscript{6} contamination in a real world situation, we have applied the corrections and calibrations discussed in this paper to measurements taken at a natural gas site, with the aim of distinguishing emissions between two natural gas pipelines. In the following section we demonstrate the effect of C\textsubscript{2}H\textsubscript{6} interference correction on \(\delta^{13}\text{CH}_4\) at a fossil fuel site, as well as discuss the alternative approach of using calibrated C\textsubscript{2}H\textsubscript{6}:CH\textsubscript{4} ratios to distinguish source signatures, a method which has not been previously tested on a Picarro G2201-i.

4.1. Description of field campaign

4.1.1. Site description
Located in an industrial park in northern Europe, the campaign took place at a natural gas compressor station in summer 2014. Such stations serve the distribution of natural gas; its key purpose is to keep an ideal pressure throughout the transmission pipelines to allow continuous transport from the production and processing of natural gas to its use. The compressor site visited comprises two major pipelines with their corresponding compressors. The two pipelines carry gas of different origins to the site, where after pressurisation, they are combined for further transmission. The site topography is flat and open with the surrounding area as predominantly farm land and close proximity to a major road. FFCH₄ emissions were expected to emanate from various sources on site such as the compressors, methane slip from turbines, and fugitive emissions due to the high pressure of gas [Roscioli et al., 2015]. Other possible methane sources in the nearby region were identified as traffic and agriculture.

4.1.2 Continuous measurements of CH₄, δ¹³CH₄ & C₂H₆

Two instruments were utilised for continuous measurements throughout the two week field campaign: a CRDS instrument (CFIDS 2072, characterised in detail in previous sections) and an automatic Gas Chromatograph with a Flame Ionization Detector (GC-FID) (Chromatotec, Saint-Antoine, France) measuring VOCs (light fraction C₂-C₆ hydrocarbons), described in detail in Gros et al., (2011). Both were located at a distance of approximately 200m-400m from both the pipelines and compressors. A synchronised time series of both instruments was achieved by locating the two inlets beside one another and time stamped measurements.

The air measured by the CRDS instrument was dried consistently to <0.16 % H₂O using a Nafion (Perma Pure LLC, Lakewood, USA). The δ¹³CH₄ was calibrated using the method described previously in Sect. 2. 20 minute measurements of two calibration gases were made every two days to calibrate the CH₄ and CO₂ data and to track any drift in the isotopes. A C₂H₆ free working gas was measured every 12 hours and used simultaneously as a target gas for the calibration of CH₄ and CO₂, and to track any drift in the C₂H₆ baseline for the calibration of C₂H₆.

The GC-FID was calibrated at the beginning and end of the campaign using a certified standard gas mixture (NPL, National Physics Laboratory, Teddington, UK). The sampling time is a 10 minute average every half an hour; 10 minutes of ambient air is measured after which the following 20 minutes are used to analyse the input.

4.1.3 Grab sample measurements of CH₄, δ¹³CH₄ & C₂H₆ in pure natural gas samples

Grab samples of pure natural gas were taken of both pipelines, with the aim of characterizing the two differing gas supplies. The 0.8L stainless steel flasks were evacuated prior to sampling to a pressure of the order of 10⁻⁶ mbar, after which they were filled to ambient pressure when sampling. The flasks were measured independently in the laboratory with a manual GC (described in Sect. 2.4) and, after dilution with zero air by the CRDS instrument.

4.2 Impact of C₂H₆ on δ¹³CH₄ observations at the field site

To quantify the effect of C₂H₆ interference on δ¹³CH₄ a total of 16 events were selected from the two week field campaign, whose criteria was defined as a peak exhibiting both increasing CH₄ concentrations and a change in
δ¹³CH₄ signature for a minimum of 1 hour. Two such events are plotted in Fig. 11. Event 1 represents the majority of events measured during the field campaign, in which CH₄ and C₂H₆ are well correlated. This particular event has a maximum concentration of 11 ppm CH₄ and 0.6 ppm C₂H₆. On average the selected events have peak concentrations of 5 ppm CH₄ and 0.3 ppm C₂H₆. The methane isotopic signature was characterized using the Miller-Tans method [Miller & Tans, 2003], in which δ¹³CH₄* CH₄ values are plotted against CH₄ to calculate the isotopic signature of the methane source in situations where the background is not constant. In order to avoid bias stemming from using Ordinary Least Squared (OLS) regression, the York least squares fitting method was implemented thus taking into account both the X and Y error [York, D. 1968]. All events excluding one were found to have δ¹³CH₄ signatures characteristic of natural gas, corresponding on average to -40‰. A singular event (Event 2 plotted in Fig. 11) was detected with a δ¹³CH₄ signature of -59‰ ± 1.5‰. Such a signature suggests a biogenic source and, when examining this event further with wind data, the source is likely to be cattle emissions.

If the data is left uncorrected, sources containing C₂H₆ substantially bias the calculated isotopic signature of CH₄ events. This is demonstrated in Fig. 11 where, for Event 1, the slope of points after C₂H₆ correction (in blue) is shifted in comparison to the slope derived from points left uncorrected (in red); signifying a modification of the δ¹³CH₄ signature. Corrected δ¹³CH₄ suggests a signature of -40.0‰ ± 0.1‰, while uncorrected values imply -37.8‰ ± 0.08 ‰. When no C₂H₆ is present, i.e. Event 2, there is no disparity between the raw and corrected δ¹³CH₄ slope, resulting in a δ¹³CH₄ signature of -59‰ ± 1‰ for both methods. For the 15 natural gas related events, the average shift induced due to uncorrected data is 2‰. Consequently the bias in isotopic signatures due to C₂H₆ means that uncorrected data will always overestimate the source, when a simple two end-member mixing model between is applied.

4.3 Continuous field measurements of ethane

As we have established the routine to correct and calibrate the reported C₂H₆ of our CRDS we can now use it for continuous observations, which adds to our ability to interpret the source of a given CH₄ enhancement. As an independent verification of the CRDS performance we compared two time series of C₂H₆ which were measured simultaneously by the CRDS and GC-FID during the natural gas field campaign by using a co-located air inlet. The CRDS data was averaged to identical time stamps as the GC-FID, i.e. a 10 minute average every 30 minutes. From which we calculated a Root Mean Squared Error (RMSE) of 13 ppb. Given the precision of C₂H₆ measured by the CRDS instrument is 10 ppb for 10 minute averages, and the uncertainty on the GC-FID is 15%, we conclude that this is extremely good agreement.

Furthermore, the flask samples, taken on the 4th of July 2014, were measured by the CRDS to have a C₂H₆: CH₄ ratio of 0.074 ± 0.001 ppm C₂H₆ /ppm CH₄ and 0.046 ± 0.003 ppm C₂H₆ /ppm CH₄ for the gas within Pipeline 1 and Pipeline 2 respectively. That same day gas quality data from the onsite GC recorded a C₂H₆: CH₄ ratio of 0.075 ppm C₂H₆ /ppm CH₄ and 0.048 ppm C₂H₆ /ppm CH₄ respectively. Although the error associated with the later figures is unknown, the strong agreement between the two verifies our correction and calibration strategy of C₂H₆.
4.4 Use of continuous observations of C$_2$H$_6$: CH$_4$ by CRDS

The instruments capability to now measure interference corrected and calibrated C$_2$H$_6$ opens the door for using another proxy for source apportionment, namely the C$_2$H$_6$:CH$_4$ ratio [Yacovitch et al., 2014, Roscioli et al., 2015, Smith et al., 2015]. Using this ratio to distinguish between ffCH$_4$ sources is a method of growing interest, partly due to the distinct difference in C$_2$H$_6$:CH$_4$ ratio between facilities and sources thus permitting easy source identification.

The C$_2$H$_6$:CH$_4$ ratio that characterises each source is determined by the slope of the C$_2$H$_6$ to CH$_4$ relationship. This method was applied to the 16 events identified within the natural gas field campaign, again using the York linear regression method taking into account both X and Y error. Two examples of this method are displayed in the bottom panel of Fig. 11. Event 1, representing a natural gas emission has a measured C$_2$H$_6$:CH$_4$ ratio of 0.068 ± 0.002 ppm C$_2$H$_6$/ppm CH$_4$ suggesting a wet gas source. Biogenic events, such as Event 2 are absent of C$_2$H$_6$ (within our detection limit) thus resulting in a C$_2$H$_6$:CH$_4$ ratio of 0 ± 0.2 ppm C$_2$H$_6$/ppm CH$_4$. Excluding the biogenic event, on average the 15 natural gas emissions detected have a weighted mean C$_2$H$_6$:CH$_4$ ratio of 0.069 ppm C$_2$H$_6$/ppm CH$_4$ with an average uncertainty on each event of 0.006 ppm C$_2$H$_6$/ppm CH$_4$. This figure agrees well with the median value for conventional gas ratios measured by Roscioli et al., (2015).

If the C$_2$H$_6$ data is left uncorrected and un-calibrated the C$_2$H$_6$: CH$_4$ ratio calculated is significantly shifted by approximately +0.06. The average raw C$_2$H$_6$: CH$_4$ ratio for the 15 natural gas events is 0.132 ± 0.007 ppm C$_2$H$_6$/ppm CH$_4$, while the biogenic events C$_2$H$_6$: CH$_4$ ratio calculated is improbable (-0.02 ± 0.01 ppm C$_2$H$_6$/ppm CH$_4$).

4.5 Combined method for CH$_4$ source apportionment

To distinguish which pipeline the emissions originate from, we can compare both the δ$^{13}$CH$_4$ signature and the C$_2$H$_6$: CH$_4$ ratio source apportionment methods. The two pipelines were characterised from the whole-air samples taken on July 4th 2014; although the gas within the pipelines is subject to change as incoming gas varies we assume here this did not occur throughout the short duration of the campaign (24th June to the 4th July 2014). The data collected from the aforementioned 16 events is compiled within Fig. 12 which illustrates the distribution of δ$^{13}$CH$_4$ signature vs C$_2$H$_6$: CH$_4$ ratios. The results from the flask measurements, i.e. characteristics of Pipeline 1 and 2, are plotted as dashed purple and red lines respectively. Both methods clearly identify the biogenic source, seen as an outlier in the bottom left corner of the plot. Furthermore, both methods are able to distinguish between the two pipelines. The isotopic signatures of the natural gas events (on average 40.2 % ± 0.5‰) are clustered near the isotopic signature of Pipeline 1, which has a δ$^{13}$CH$_4$ signature of 40.7 % ± 0.2‰, thus suggesting the majority of the measured methane is an emission from this pipeline. When considering the C$_2$H$_6$:CH$_4$ ratio a similar conclusion may be drawn as the mean C$_2$H$_6$:CH$_4$ ratio is 0.069 ± 0.002 ppm C$_2$H$_6$/ppm CH$_4$, much alike to that of Pipeline 1 at 0.074 ± 0.003. A future study will address the shift in measured events to left of Pipeline 1 in Fig. 12 by using additional VOC data from the GC-FID to aid source identification. The uncorrected 16 events are also plotted in Fig. 12 as circular markers. These are found in the top right hand corner of Fig. 12 and do not correspond well with either of the Pipelines, thus re-confirming the importance of the corrections.
5. Concluding Remarks

This study focuses on measurements of C\textsubscript{2}H\textsubscript{6} contaminated methane sources by a CRDS (Picarro G2201-i), with emphasis on correcting δ\textsubscript{13}CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} for cross-interferences before calibration. Our extensive laboratory tests suggest that CRDS instruments of this model are all subject to the similar interferences (as expected as they scan the same spectral lines) and that they can have a significant impact on reported concentrations and isotopic signatures if not accounted for properly, when measuring industrial natural gas sources. We find that the correction coefficients for C\textsubscript{2}H\textsubscript{6} and δ\textsubscript{13}CH\textsubscript{4} do not vary significantly between instruments. For now, we suggest using constant instrument specific correction factors if possible or the ones found in this study (summarised in Fig. 13). As our study period only encompasses one year it is clear that the stability of the correction over the full life-time needs to be monitored further. To fully exploit the reported C\textsubscript{2}H\textsubscript{6} data, we suggest calibrating the instrument and frequent measurements of a working gas (or set of working gases) to monitor and correct for the instrumental baseline drift.

The results of our field campaign demonstrate the extent of the interferences of C\textsubscript{2}H\textsubscript{6} on δ\textsubscript{13}CH\textsubscript{4} for a real world application and also support the validity of our C\textsubscript{2}H\textsubscript{6} correction and calibration through the comparison with an independently calibrated GC-FID. In our case, when measuring wet gas emissions we detected an average shift in isotopic signature of 2.5\% due to C\textsubscript{2}H\textsubscript{6} interference, however the extent of this bias will vary according to the contribution of C\textsubscript{2}H\textsubscript{6} therefore affecting each ffCH\textsubscript{4} source to a different degree which can cause problems for source determination. The results reported here are important for all future work of CRDS in fossil fuel regions (where sources consist of a C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4} ratio between 0-1 ppm C\textsubscript{2}H\textsubscript{6}/ppm CH\textsubscript{4}) to be aware of such interferences and correct for them accordingly. Our CRDS instrument is sufficient for measurements of strongly variable C\textsubscript{2}H\textsubscript{6} sources, where if using calibrated one minute C\textsubscript{2}H\textsubscript{6} data, concentration variations above 150 ppb are required to achieve a signal to noise ratio of 5. Thus for industrial natural gas sites it offers a new opportunity of using continuous C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4} observations as a means of source determination independent to δ\textsubscript{13}CH\textsubscript{4} methods. The recently released G2210-i analyser is dedicated to C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4} ratio measurements and as such achieves a higher precision making it suitable for a wider variety of ethane sources.

Finally, we successfully combined both the δ\textsubscript{13}CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4} ratio source apportionment methods. At the natural gas compressor site both methods clearly distinguish biogenic sources from that of natural gas based sources. Combining those two independent methods also increases our confidence by giving use a better fingerprint of the source and spurious C\textsubscript{2}H\textsubscript{6} or δ\textsubscript{13}CH\textsubscript{4} can be more easily identified. Lastly, if we are able to characterise both δ\textsubscript{13}CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4} for our source, this gives us insight into the formation and source region of the gas [Schoell, 1983].

Acknowledgements:

The authors would like to thank the NPL team for organising the field campaign, in particular the support from Rod Robinson, Fabrizio Innocenti and Andrew Finlayson. We thank our LSCE colleagues: Camille Yver Kwok and Sebastien Ars for assistance during the field campaign, as well as Bernard Bonsang and Dominique Basinee for...
their technical help and contributions on the GC instruments both in and off the field. We also thank Rebecca Fisher (RHUL) and Dave Lowry for their contributions, especially for measurements of $\text{^{13}CH}_4$ for our calibration cylinders under the InGOS’ TransNational Access program (TNA-id-666) (http://www.ingos-infrastructure.eu/project-info/workpackages/tna-transnational-access/). This work was supported by the Climate KIC through the FuME project (http://www.climate-kic.org/projects/fume/) and the funding of the PhD studies of S.A. through education pillar of climate KIC.
References:


Table 1: Description of the gas mixtures used to determine the cross-sensitivities of the interference of CH₄, H₂O and CO₂ on C₂H₆ and the interference of C₂H₆ on δ¹³CH₄. The respective ranges spanned during laboratory tests, and the typical range at a natural gas site are noted in the right hand side.

<table>
<thead>
<tr>
<th></th>
<th>Method</th>
<th>Dilution Gas</th>
<th>Working Gas</th>
<th>Lab Concentration Range</th>
<th>Typical Range at NG site</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H₂O Interference on C₂H₆</strong></td>
<td>&lt;0.16% (Dry) Magnesium Perchlorate</td>
<td>N/A</td>
<td>Ambient Air</td>
<td>0-0.5% H₂O</td>
<td>0.2% H₂O</td>
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<tr>
<td></td>
<td>≥0.16% (Wet) Dilution Series &amp; Humidifier</td>
<td>N/A</td>
<td>Zero Air</td>
<td>0.25-2.5% H₂O</td>
<td></td>
</tr>
<tr>
<td><strong>CO₂ Interference on C₂H₆</strong></td>
<td>&lt;0.16% (Dry) Dilution Series</td>
<td>Zero Air</td>
<td>2000ppm CO₂, 1.7ppm CH₄, &lt;1ppb C₂H₆ and 50ppb CO in natural air</td>
<td>0-1500ppm CO₂</td>
<td>400-1000 ppm CO₂</td>
</tr>
<tr>
<td></td>
<td>≥0.16% (Wet) Dilution Series &amp; Humidifier</td>
<td>Zero Air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CH₄ Interference on C₂H₆</strong></td>
<td>&lt;0.16% (Dry) Dilution Series, Ascarite</td>
<td>Zero Air</td>
<td>6ppm CH₄, 360ppm CO₂, 310ppb N₂O, &lt;1ppb C₂H₆ and 50ppb CO in natural air</td>
<td>0-6ppm CH₄</td>
<td>2-20 ppm CH₄</td>
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<tr>
<td></td>
<td>≥0.16% (Wet) Dilution Series, Ascarite &amp; Humidifier</td>
<td>Zero Air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C₂H₆ Interference on δ¹³CH₄</strong></td>
<td>Dilution Series (CRDS) (&lt;1ppb C₂H₆)</td>
<td>Natural Air Matrix</td>
<td>C₂H₆ standard of 52ppm in Nitrogen</td>
<td>0-1.5 ppm C₂H₆/ppm CH₄</td>
<td>0-0.3 ppm C₂H₆/ppm CH₄</td>
</tr>
<tr>
<td><strong>C₂H₆ Calibration</strong></td>
<td>Dilution Series (CRDS &amp; GC) (&lt;1ppb C₂H₆)</td>
<td>Natural Air Matrix</td>
<td>C₂H₆ standard of 52ppm in Nitrogen</td>
<td>0-5ppm C₂H₆</td>
<td>0.3-3 ppm C₂H₆</td>
</tr>
</tbody>
</table>
Table 2: Summary of C$_2$H$_6$ calibration factors calculated for both instruments CFIDS 2072 and 2067.

<table>
<thead>
<tr>
<th></th>
<th>CFIDS 2072</th>
<th>CFIDS 2067</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>Intercept (ppm)</td>
<td>Slope</td>
</tr>
<tr>
<td>Feb,15</td>
<td>0.49 ± 0.03</td>
<td>0.00 ± 0.01</td>
</tr>
<tr>
<td>Oct,15</td>
<td>0.51 ± 0.01</td>
<td>-0.06 ± 0.04</td>
</tr>
</tbody>
</table>

Table 3: The various response functions calculated for the δ$^{13}$CH$_4$ correction due to C$_2$H$_6$. *Flask measurement.

<table>
<thead>
<tr>
<th>δ$^{13}$CH$_4$ Correction</th>
<th>CFIDS 2072</th>
<th>CFIDS 2067</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope(‰CH$_4$/C$_2$H$_6$)</td>
<td>Intercept (%)</td>
<td>Slope(‰CH$_4$/C$_2$H$_6$)</td>
</tr>
<tr>
<td>July,15</td>
<td>+24 ± 2</td>
<td>0.5 ± 0.6</td>
</tr>
<tr>
<td>Nov,15</td>
<td>+23 ± 1</td>
<td>0.2 ± 0.6</td>
</tr>
<tr>
<td>Nov,15 *</td>
<td>+24 ± 1</td>
<td>0.6 ± 0.6</td>
</tr>
</tbody>
</table>
Figure 1: Flow chart illustrating the steps involved to calibrate C$_2$H$_6$ and $\delta^{13}$CH$_4$. The number in the top right hand corner corresponds to the subsection in which the methods of each step are explained in detail.

Figure 2: General Set-up. The dilution and working gas are connected via two MFCs to two CRDS instruments in parallel. In red is the placement of an optional glass flask used for the C$_2$H$_6$ calibration only. The flow is greater than that of the instruments inlets, therefore an open split is included to vent additional gas and retain ambient pressure at the inlets.
Figure 3: An example of the results from a H$_2$O interference experiment spanning the range 0-1% H$_2$O. The reported C$_2$H$_6$ is altered due to the addition of water vapour when measuring zero air (<1ppb C$_2$H$_6$). Dark and light blue markers signify the response when dried and undried ambient air have been measured overnight by the instrument prior to the experiment respectively. Error bars signify the standard deviation of each measurement.
Figure 4(a): The discontinuity seen for instrument CFIDS 2072 for two repetitions denoted by different colours. After the discontinuity at 0.16% the subsequent slope clearly differs between the two repetitions. Both instruments display a discontinuity at 0.16% H$_2$O. Each point represents a one minute average, the error bars represent the standard deviation of the raw data.

Figure 4(b): Time series of the discontinuity for instrument CFIDS 2067, the H$_2$O content is increased and decreased crossing the 0.16% H$_2$O threshold twice. The point at which 0.16% H$_2$O humidity is reached is marked by red dashed lines. The discontinuity is present when moving from dry to wet air, and inversely from wet to dry air.
Figure 5: Time series of CO$_2$ interference experiment at varying H$_2$O concentrations. As H$_2$O and CO$_2$ are altered, the reported C$_2$H$_6$ is expected to be constant given there is no C$_2$H$_6$ input. However due to interference the corresponding shifts of reported C$_2$H$_6$ are evident.
Figure 6: Relationship between reported C\textsubscript{2}H\textsubscript{6} and concentration changes of CO\textsubscript{2} for instrument CFIDS 2072 and 2067 at varying values of H\textsubscript{2}O. For each plot the bottom axis indicates the increase in concentration of the targeted gas (CO\textsubscript{2}). Plots on the left are at 0% H\textsubscript{2}O, on the right are experiments at varying humidities, distinguishable by colour. The legend denotes repetitions of the experiment. The error bars in each plot denote the standard deviation of each measurement. The R\textsuperscript{2} value for the experiments at 0% H\textsubscript{2}O is 0.9 and 0.8 for all other H\textsubscript{2}O experiments for both instruments.
Figure 7. Relationship between reported C$_2$H$_6$ and concentration changes of CH$_4$ for both instruments. For each plot, the bottom axis indicates the increase in concentration of the targeted gas. The vertical bars in each plot denote the standard deviation of each point. The legend denotes repetitions of the experiment. Plots on the left are at 0% H$_2$O. The R$^2$ value is 0.4 and 0.6 for instruments CFIDS 2072 and 2067 respectively. Plots on the right show the response at 1% H$_2$O. These two plots have a R$^2$ value of 0.2.
Figure 8(a): Ethane calibration calculated from measurements of flask samples by both the GC and CRDS. The x-axis is the corrected C\textsubscript{2}H\textsubscript{6} (C\textsubscript{2}H\textsubscript{6 COR}) using the corrections described previously. The y-axis is the C\textsubscript{2}H\textsubscript{6} as measured by a manual GC. The error bars indicate the standard deviation of each flask measurement, for certain flasks error bars are smaller than their respective markers.

Figure 8(b): 30 minute target measurements over a period of 4 days, from 13\textsuperscript{th} November 2015, to 16\textsuperscript{th} November 2015. The standard error of each target is smaller than the plotted marker. The baseline C\textsubscript{2}H\textsubscript{6} is seen to drift with time.
Figure 9: During a dilution sequence, the CH$_4$ concentration is manually decreased as the contribution from C$_2$H$_6$ is increased. Thus both $^{12}$CH$_4$ and $^{13}$CH$_4$ undergo a similar decrease as the gas is diluted. However what is observed is an increase in the reported value of $^{13}$CH$_4$, suggesting C$_2$H$_6$ interference. The nominal CH$_4$ concentration of the ambient gas is 1948.7ppb ± 0.32 ppb. The $^{12}$CH$_4$ axis is plotted to the left in light green, whereas the $^{13}$CH$_4$ axis is plotted to the right in dark green at a different scale. Error bars represent the standard deviation, the $^{12}$CH$_4$ markers are larger than their associated error bars.
Figure 10: The effect of $\text{C}_2\text{H}_6$ on reported $\delta^{13}\text{CH}_4$. The slopes of reported $\delta^{13}\text{CH}_4$ vs the $\text{C}_2\text{H}_6\text{CORRECTED}:\text{CH}_4$ ratio are shown for three tests taken throughout the course of one year. Triangular markers imply whole air sample measurements, while square markers are derived from direct measurements. Error bars indicate the standard deviation. In the presence of $\text{C}_2\text{H}_6$ the instrument reports heavier values of $\delta^{13}\text{CH}_4$. The typical range of (calibrated) $\text{C}_2\text{H}_6: \text{CH}_4$ of dry and wet gas is highlighted in pink and green respectively corresponding to the top axis.
Figure 11: Ethane and Methane content of two selected peaks. Methane and Ethane 1 minute averaged time series is shown in the top two panels. Miller-Tans plots of the corresponding peaks are shown in the third panel, blue for the corrected $\delta^{13}$CH$_4$ due to C$_2$H$_6$, and red representing uncorrected $\delta^{13}$CH$_4$. Event 1 includes elevated C$_2$H$_6$ emissions and thus displays a difference between the slope before and after C$_2$H$_6$ correction, corresponding to a shift in isotopic signature. Event 2, with no C$_2$H$_6$ shows no alteration in slope. The slopes of C$_2$H$_6$ vs CH$_4$ are shown in the bottom panel, signifying the C$_2$H$_6$: CH$_4$ ratio of the emission. Error of both the isotopic and C$_2$H$_6$: CH$_4$ signatures are calculated from the standard error of the slope.
Figure 12: Distribution of 16 events according to their C$_2$H$_6$:CH$_4$ ratios and isotopic signature. The red and purple dashed lines signify the characterisation of Pipeline 1 and 2 respectively as measured by the CRDS instrument from flask samples taken on the 4.07.14. For corrected and calibrated data (square markers), both the isotopic signature and C$_2$H$_6$:CH$_4$ ratios identify the biogenic source (bottom-left point) and suggest the natural gas emissions emanate from Pipeline 1. Circular markers represent the uncorrected data which does not agree with the flask sample measurements of Pipelines 1 or 2. The error bars indicate the standard error of the slope calculated from Miller-Tans and C$_2$H$_6$ vs CH$_4$ plots for δ$^{13}$CH$_4$ signature and C$_2$H$_6$:CH$_4$ ratio respectively.
Figure 13: Flow chart illustrating the steps and the corresponding equations to calibrate C$_2$H$_6$ and δ$^{13}$CH$_4$ as determined from this study. The coefficients are the mean of both CRDS instruments tested.