Ethane measurement by Picarro CRDS G2201-i in laboratory and field conditions: potential and limitations

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Abstract ~~Atmospheric ethane~~Ethane can be used as a tracer ~~gas~~ to distinguish methane sources, both at the local and global scale. Currently, ethane can be ~~successfully~~ measured ~~on the field~~ using flasks or ~~designed~~ in-situ analyzers. In our study, we ~~consider the possibility of using used~~ characterized the CRDS Picarro G2201-i instrument, ~~dedicated originally designed to measure~~to isotopic CH_4 and CO_2, for ~~suitable~~ measurements of ethane ~~to :~~methane ratio in mobile~~, near sources,~~ field conditions. ~~,near source conditions. We evaluated the limitations and potential of using potential~~ssibilities ~~of use~~using the CRDS G2201-i to measure ethane to methane ratio, thus~~what gives possibility to~~ extending the instrument application to measure simultaneously two methane sources proxies in the field: carbon isotopic and ethane to methane ratio. Our work was divided into three steps. First, laboratory tests were run to characterize the instrument in stationary conditions. ~~Then Second,~~ the instrument performance was tested in the field, as part of a controlled release experiment.~~Finally~~and finally, the instrument ~~was tested~~during mobile measurements focused on gas compressor stations. The results from the field are compared with the results from other instruments~~specifically,~~ designed ~~for~~to ethane measurements. Our study clearly shows the potential of using the CRDS G2201-i instrument to determine the ethane ~~to :~~methane ratio in methane plumes in mobile condition with an ethane uncertainty of 50 ppb. Assuming typical ethane to methane ratio ranging between 0 and 0.1 ppb ppb^{-1}, we conclude that the instrument can correctly estimate the "true" ethane to methane ratio within 1-sigma uncertainty ~~in when~~ CH_4 enhancements ~~of are at least~~ 1 ppm~~, or more~~ as can be found in the vicinity of strongly emitting sites (~~such as natural gas compressor stations.~~station).

1. Introduction

Methane (CH_4) is the second most potent anthropogenic greenhouse gas, and its global average mixing ratio reached ~~1892 ppb~~1.876 ppm in the atmosphere in ~~November 2021~~ March 2020 (Dlugokencky, 202~~1~~0)~~, approximately~~ ~~almost~~three times more than during the pre-industrial era. Anthropogenic methane emissions amount ~~to more than~~half of the total input of

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methane to the atmosphere and include a range of sources such as landfill, wastewater treatment plants, agriculture, coal, oil, and natural gas industries (IPCC, 2018; Turner et al., 2019; Saunois et al., 2020). Large uncertainties remain in the quantification of these sources' magnitudes and locations (Saunois et al., 2016). The variety of methane sources and their

35   geographical overlap increase the difficulty of closing the present methane budget from global to local scales.

~~Methane~~Some methane sources also co-emit ~~a specific mixture of~~ other gases that can be used as tracers to identify them. For instance, ethane (C_2H_6) is associated with thermogenic methane and it is therefore co-emitted during extraction of coal, oil and natural gas as well as transportation of the latter (e.g., Aydin et al., 2011; Hausmann et al., 2016; Helmig et al., 2016; Schwietzke et al., 2014; Sherwood et al., 2017; Simpson et al., 2012). ~~Typically, C_2H_6 mixing ratio in the clean continental~~

40   ~~atmosphere ranges between 0.5 – 2 ppb but it can reach 1000 ppb in the vicinity of~~ the methane and ethane emitters, like fossil ~~fuels facilities (Simpson et al. 2012, Rella et al. 2017).~~ In the case of the natural gas industry, a range of values for ethane:methane (C_2H_6:CH_4) ~~ratio~~ are observed ~~depending of~~accor the geological reservoir from which the gas has been extracted and ~~of~~by its eventual processing. ~~Based on mobile measurements, where CH_4 and C_2H_6 mixing ratios are measured, ethane to methane ratio is calculated as a molar ratio.~~ The reported ratios ~~(calculated as molar ratio when based on~~

45   ~~atmospheric~~mobile measurements) depend on the type of facilities and type of the reservoirs: between 0.01 and 0.06 for gas leaks and gas compressors (Lopez et al., 2017; Lowry et al., 2020; Yacovitch et al., 2014), or higher than 0.3 for processed natural gas liquids (Kort et al., 2016; Yacovitch et al., 2014). Also, different ratios are observed in the case of dry gas (0.01-0.06) and wet gas (>0.06). In the case of offshore oil and gas platforms, C_2H_6:CH_4 ~~ratios~~ typically were around 0.05, but ratios equal to 0.002 and 0.17 were observed as well (Yacovitch et al., 2020). On the contrary, biogenic sources such as landfills and

50   cattle farms show null to very small C_2H_6:CH_4 ~~ratio~~ (< 0.002) (Assan et al., 2017; Yacovitch et al., 2014). ~~Moreover, recent studies (Lan et al. 2019; Turner et al., 2019; Yacovitch et al., 2020) showed varying C_2H_6:CH_4~~ethane to methane ~~ratios for different facilities, even at a local scale. Also, Lan et al. (2019) showed an~~the increase of C_2H_6:CH_4 over the measurement ~~period on Oil and Natural Gas observation sites in the National Oceanic and Atmospheric Administration Global Greenhouse Gas Reference Network (GGRN).~~

55   At the local scale, observing changes in C_2H_6:CH_4 ~~ratio~~ provides additional information about specific methane ~~enhancement~~ source~~s~~, especially in areas with multiple CH_4 enhancements from unknown origins (Assan et al., 2017; Lopez et al., 2017; Lowry et al., 2020; Yacovitch et al., 2014, 2020). The currently available techniques, such as ~~gas chromatography~~GaChromatography with ~~flame ionization detector~~Detector (GC-FID) and Fourier-~~transform infrared spectroscopy~~Transform Infrared Spectroscopy (FTIR) provide ~~access to~~ long-term or short-term ~~(e.g. hours timescale)~~

60   measurements of ethane and other components in stationary conditions (Bourtsoukidis et al., 2019; Gros et al., 2011; Hausmann et al., 2016; McKain et al., 2015; Yang et al., 2005; Paris et al., 2021). Additionally, laser-based instruments, such as the Los Gatos Research (LGR) Ultraportable Methane:Ethane Analyzer (UMEA), based on a cavity-enhanced absorption technique, the Picarro Cavity ~~ring down spectroscopy~~Spectroscopy (CRDS) analyzers (Rella et al. 2015) and the tunable infrared laser direct absorption spectroscopy (TILDAS) analyzer (Smith et al., 2015; Yacovitch et al., 2014) make it possible

65   to ~~measure~~perform measurements of ethane ~~using on~~a mobile platform. ~~Here, building on~~ Regarding previous studies with

CRDS instruments, here we detail verify the possibilities and limitations of measuring C$_2$H$_6$ using by the CRDS G2201-i, in the vicinity of methane source. The CRDS G2201-i is originally designed to measure ^{12}CO$_2$, ^{13}CO$_2$, ^{12}CH$_4$, ^{13}CH$_4$ and H$_2$O and record has possibility to measure C$_2$H$_6$ only as an internal way to correct ^{13}CH$_4$ an additional option, thus observed C$_2$H$_6$ mixing ratio must be corrected and calibrated.

70   Previous studies already showed the possibility of using such a laser based cavity instrument to determine the C$_2$H$_6$:CH$_4$ ratio in the field conditions (Rella et al. 2015; Assan et al. 2017; Lopez et al. 2017, Lowry et al. 2020). In the study of Assan et al. (2017), a CRDS G2201-i dedicated to the measure of ^{12}CO$_2$, ^{13}CO$_2$, ^{12}CH$_4$, ^{13}CH$_4$ and H$_2$O was located stationary nearby natural gas facilities. Over two weeks, dried ambient air was measured simultaneously by CRDS G2201-i and GC-FID, using the 10-minute averages for 16 "events" of high methane mixing ratios lasting more than 1 hour. The C$_2$H$_6$:CH$_4$ allowed to

75   separate plumes of biogenic or thermogenic origin. Moreover, during that study, flask samples were collected and further analyzed in the laboratory. The laboratory values showed good agreement between field CRDS G2201-i and GC-FID results (Assan et al. 2017).

Rella et al. (2015) and Lopez et al. (2017) used the CRDS instrument as part of a mobile setup enhanced with a storage tube, called AirCore (Karion et al. 2010). This storage tube allows to sequential reanalysis an improvement of of air at an improved

80   time resolution and hence precision. The mobile measurements can be made in two modes using this setup. During the "monitoring mode" the air is split and injected at the same time directly to the instrument analyzer and at the same time to the open-ended AirCore. In the "replay mode", air from the AirCore is measured. Using the AirCore with a lower flow rate increases the sampling frequency. The replay mode is only used after observation of a methane plume (Rella et al. 2015; Lopez et al. 2017; Hoheisel et al. 2019). Rella In the study by Lopez et al. (2017), C$_2$H$_6$:CH$_4$ ratios were estimated for natural gas

85   facilities. For gas pipelines, the CRDS G2201-i results were compared with results obtained from flask measurements analyzed by gas chromatography. The results showed good agreement between the two methods (Lopez et al. 2017). Using AirCore sampler, Rella et al. (2015) observed C$_2$H$_6$:CH$_4$ different ethane to methane ratio ranging from gas sources (0.12 for gas sources) and from oil wells (0.22 for oil wells) situated in the Uintah Basin (Utah, US).

Here, the main purpose of this study is to evaluate the performances of the CRDS G2201-i and the applicability of making

90   short-term, direct, continuous, mobile measurements of ethane in methane-enriched air, with sufficient precision during near-source ("pollution plume conditions") surveys. Our motivation here is to perform both isotopic and ethane measurements with only one instrument in the field in order to improve the partition of methane sources without at a reasonable cost the need for an additional analyzer. We This study aim at providing a protocol can be useful for other scientific teams, that which do not have an analyzer instrument designed for ethane measurements, but already have the CRDS G2201-i and intend would like to

95   use it in field conditions for measuring both δ^{13}CH$_4$ and ethane to methane ratio.

To achieve this goal, following Assan et al. (2017), the first step consists of laboratory tests to calculate the calibration factors and also to check the instrument performances in stationary, laboratory conditions extending preliminary work by Assan et al. (2017). . Then, extending the work made by Assan et al. (2017), 2017): The second, novel step evaluates The second step is to investigate the performances of the instrument during mobile field measurements in a controlled was investigated. As a second

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100 ~~step, A a tracer~~ release experiment. ~~was performed where A mixture with known C₂H₆:CH₄ and CH₄ emission flux was released and compared to measured ratios from CRDS G2201-i and LGR UMEA. In~~Thir the third step, the instrument has also been evaluated in real field conditions, during ~~car-based~~ surveys conducted at gas compressor stations and one landfill. In this step, measured values ~~were~~are compared to values from gas chromatography and those ~~in natural gas~~ provided by the ~~owner operator~~ of the gas compressor stations. These extensive and complex tests ~~allowed~~allow for a full characterization of the CRDS G2201-

105 i instrument ~~for~~to ~~car-based~~ ethane measurements and ~~highlighted~~provide broader knowledge ~~about~~ the limitations of this instrument when measuring $C_2H_6:CH_4$ ~~ratios~~.

~~After~~Subsequently, after presenting material and methods for these three steps (~~Sect.~~section 2), their results are presented (~~Sect.~~section 3) and discussed (~~Sect.~~s 4).
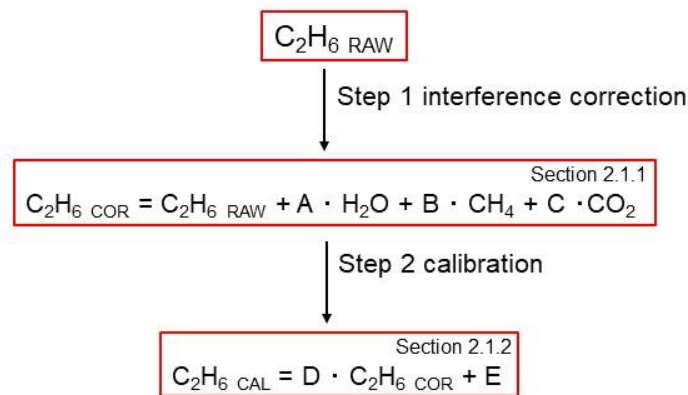

2. Material and Methods:

110 The CRDS G2201-i (Picarro Inc., Santa Clara USA), used during this study, is ~~originally designed~~ to the measurements of the mixing ratio of $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^1H_4$, $^{13}C^1H_4$ and $^1H_2^{16}O$ (further H_2O). It operates in three spectral lines: 6057, 6251 and 6029 cm^{-1}. As there is an interference of $^{12}C_2^1H_6$ (further C_2H_6) on $^{13}CH_4$ in the absorption spectra, this instrument also measures C_2H_6 to correct this interference. ~~Interferences~~The possibility of i ~~with other species is presented in Appendix A. By default, C₂H₆ is not intended for use by standard users. Thus,~~ the measured C_2H_6 ~~mixing ratio is not corrected nor calibrated and it is~~

115 ~~stored in private archived files. To use ethane measurements per se, measured C₂H₆ values must be first corrected f~~Due to~~or observed~~ interferences with $^{12}C^{16}O_2$ (further CO_2), H_2O and $^{12}CH_4$. ~~Different~~ , measured C2H6 values must be first corrected. The study performed by Assan et al. (2017) ~~provided the strategy to determine the factors to correct the measured C₂H₆ mixing ratio due to the interference with other species~~showed a~~the necessity t~~interference correction factors are needed in the absence or presence of water vapor (Assan et al. (2017). These.: In the study presented in this article~~In this study, the~~These~~ correction

120 factors~~, determined by Assan et al. (2017)~~ are used~~and discussed in light of our new tests in~~in Sect. ~~2.1.1. Here, we validated the values of proposed by Assan et al. (2017) interference correction in the presence of water.~~ The water sensitivity test is ~~also~~ described in ~~Sect.~~section 2.1.1.

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To ensure comparability and traceability of the ethane measurementBefore being further used, Ethane ethane measured by the G2201-i must eventually be linked to a widely used scale., to ensure comparability and traceability. Therefore, ethanewe

125   applied calibration factors obtained during linearity test values were calibrated before use (Sect. 2.1.2). Finally, corrected and calibrated C_2H_6 values, corrected and calibrated, can be used to determine the C_2H_6 correction on $\delta^{13}CH_4$ mixing ratio or, as

$C_2H_{6\ RAW}$

Step 1 interference correction

Section 2.1.1
$C_2H_{6\ COR} = C_2H_{6\ RAW} + A \cdot H_2O + B \cdot CH_4 + C \cdot CO_2$

Step 2 calibration

Section 2.1.2
$C_2H_{6\ CAL} = D \cdot C_2H_{6\ COR} + E$

in this study, to determine the ethane to methane ratio. Figure 1 shows the necessary procedure before using C_2H_6 measured by CRDS G2201-i.

130   **Figure 1 Flow chart of steps made to use C_2H_6 measured by CRDS G2201-i. The number in the corner corresponds to the subsection where methods of each step are presented in detail.**

Here, the same device (CRDS G2201-i CFIDS 2072) was used as by Assan et al. (2017)); which allowing to checks checking a possible long-time drift in calibration factors. previously-calculated calibration factors. As outlined in the introduction, three different setups were used to test the instrument capability: laboratory, controlled-release experiment, and field experiment.

135   Additionally, as a part of laboratory tests, continuous measurement repeatability (CMR, used as a precision in Yver-Kwok et al., 2015) and Allan variance (Allan, 1966; Yver-Kwok et al., 2015) were determined for the working gases with different C_2H_6 mixing ratios (Sect.Section 2.1.3). Results obtainedbtained for CRDS G2201-i results are compared with performances of test performed for CRDS G2132-i, which also can measure C_2H_6 as additional feature (Rella et al. 2015) and for CRDS G2210-i, which is designed for C_2H_6 measurements. The characteristic of each instrument comparedeach instruments is

140   presented in Table 1. As the last point of laboratory test, the possible time drift was verified and compared to observation made by Assan et al (2017).

~~**Table 1 Characteristics of the instruments used during the study**~~

Analyzer	species	Rise/fall time	Measurements interval [s]	CH_4 operational range [ppm]	C_2H_6 operational range [ppm]
~~CRDS G2201-i~~	~~CO_2, $\delta^{13}CO_2$, CH_4, $\delta^{13}CH_4$, H_2O, C_2H_6 (optional)~~	~~~30 s~~	~~3.7~~	~~1.8 – 12~~	~~NaN~~
~~CRDS G2132-i~~	~~CO_2, CH_4, $\delta^{13}CH_4$, H_2O, C_2H_6 (optional)~~	~~~30 s~~	~~2~~	~~1.8 – 12~~	~~NaN~~
~~CRDS G2210-i~~	~~CO_2, CH_4, $\delta^{13}CH_4$, H_2O, C_2H_6~~	~~NaN~~	~~1~~	~~1.5 – 30~~	~~0 – 100~~

2.1. ~~2.1~~ Laboratory setup

2.1.1. ~~Sensitivity of interference correction parameters to humidity~~ parameters to humidity ~~eEwWsS tests~~

The cross sensitivities with H_2O, CO_2 and $^{12}CH_4$ induce a bias in~~cause the es~~ on raw C_2H_6 observed by CRDS G2201-i. The study performed by Assan et al. (2017) provided the strategy to determine C_2H_6 correction factors to account for these interferences. During the experiment, the C_2H_6 mixing ratio of measured gas mixture was constant, while the mixing ratio of interfering~~interferenceing~~ species was changed and controlled using a setup similar to ~~the~~ one presented on Fig. 2 in the Sect. 2.1.2. During one measurement set, ~~the~~ concentration ~~concentrationconcertation~~ of only one interfering species~~enceing gasspecies~~ was changing, while the concentration~~concentrationconcertation~~ of other species~~gasesspecies~~ stayed stable. The measurement set was repeated while~~forwhile~~ varying concentrations of H_2O, CH_4 and CO_2 were adjusted. Using ~~changing their concentration and . This~~Using linear regression, the test yielded~~gaveyielded~~ values for the interference correction factors A, B, C in Eq. 1:

~~$$C_2H_{6\,cor} = C_2H_{6\,raw} + A \cdot H_2O + B \cdot CH_4 + C \cdot CO_2 \qquad\qquad (1).$$~~

$$C_2H_{6\,cor} = C_2H_{6\,raw} + A \cdot H_2O + B \cdot CH_4 + C \cdot CO_2 \qquad (1).$$

~~The~~Based on their tests, t~~The~~ interference of other species on C_2H_6 changes ~~also~~ in relation to the water vapor level in the measured sample. ~~In Assan et al. (2017),~~ the correction factors were determined for two different CRDS G2201-i devices (CFIDS 2067 and CFIDS 2072) ~~(Assan et al. 2017, Table 2). .~~According to that study, if the water vapor level in the measured gas is less than 0.16 % ("low humidity case"), then interference correction factors are the same for both devices. In the presence of water vapor (=>0.16 %, "high humidity case"), the correction factors were different for each device. The threshold of 0.16 % corresponds to 26.14 % of relative humidity in standard conditions of temperature and pressure. Due to these differences, drying air is strongly recommended before making measurements (Assan et al.~~,~~ 2017). In ~~the the present paper~~study presented ~~in the present~~is article~~paper~~, the correction factors, determined by Assan et al. (2017) are used.

	CFIDS 2072			CFIDS 2067		
Humidity	A [ppm C_2H_6/ % H_2O]	B [ppm C_2H_6/ ppm CH_4]	C [ppm C_2H_6/ ppm CO_2]	A [ppm C_2H_6/ % H_2O]	B [ppm C_2H_6/ ppm CH_4]	C [ppm C_2H_6/ ppm CO_2]
Low humidity	0.44 ± 0.03	$8 \cdot 10^{-3} \pm 2 \cdot 10^{-3}$	$1 \cdot 10^{-4} \pm 1 \cdot 10^{-5}$	0.44 ± 0.03	$8 \cdot 10^{-3} \pm 2 \cdot 10^{-3}$	$1 \cdot 10^{-4} \pm 1 \cdot 10^{-5}$
High humidity	0.7 ± 0.03	0	$3.8 \cdot 10^{-4} \pm 2 \cdot 10^{-5}$	1 ± 0.01	0	$3.9 \cdot 10^{-4} \pm 2 \cdot 10^{-5}$

As a part of the laboratory test, we ran a water vapor sensitivity test to revise the parameters of the interference correction (Eq. 1, Table 221) in wet air. The target gas (hereafter referred to Target Gas 1) had a typical ambient C_2H_6 mixing ratio. During the test, Target GastheTtarget gGas 1 was progressively humidified (0 to 3 %) by steps of 0.25 %, using a liquid flow controller (Liquiflow, Bronkhorst, Ruurlo, the Netherlands) and a mass flow controllercontrollerMFC (MFC, Bronkhorst)) coupled to a controlled evaporator mixer (CME, Bronkhorst).). Each step lasted 20 minutes. The cycle was repeated three times. During data analysis, the interference correction factors fromdetermined by Assan et al. (2017) were applied (Table 2). Three cases were tested: no-interference correction, high humidity case and low humidity case (exceptexcepted for the first step with dry air, where only the low humidity correction was applied).

2.1.1. Ethane Calibration Factors

The calibration factors are calculated as the slope (factor D) and intercept (factor E) of the linear regression of measured (subscripted "cor")) C_2H_6 versus true C_2H_6 ("(cal")) in Eq. (2)..

$C_2H_{6 cal} = D \cdot C_2H_{6 cor} + E$

$$C_2H_{6 cal} = D \cdot C_2H_{6 cor} + E \tag{2}$$

Here, the reference gasescalibration factorstrue concentrations are preparedcalculated using the approach presented by Hoheisel (2018), where a synthetic gas mixture of known C_2H_6 ("target"), is diluted with a gas ("dilution gas ("dilution") with known CO_2 and CH_4 mixing ratios. "True" C_2H_6 mixing ratio is obtained and by applying the following equation:

$$C_2H_{6true} = \left(1 - \frac{1}{2}\left(\frac{CH_{4meas}}{CH_{4dilution}} + \frac{CO_{2meas}}{CO_{2dilution}} \right) \right) \cdot C_2H_{6target2} \tag{3}$$

where $C_2H_{6\ true}$ is the ethane mole fraction in the reference gas obtained by mixing air from the two target and dilution cylinders, one containing ethane at a known value (with concentrations of species X respectively labelled $C_2H_6X_{target)}$ (without presence of methane or carbon dioxide) and one without ethane but with typical ambient methane and carbon dioxide mixing ratio (dilution gas) and $X_{dilution}$ using a mass flow controller

~~(MFC~~s.~~).~~ $CH_{4\,dilution}$ and $CO_{2\,dilution}$ are the mixing ratio of the dilution gas. $CH_{4,\,meas}$ ~~and~~ $CO_{2,\,meas}$ are average measured mixing ratios after dilution. This calculation is repeated for different C_2H_6:CH_4 ratios, determined using the MFCs.

~~The calibration factors are calculated~~ the calibration factors are calculated with~~calculated~~is implemented ~~through~~ ~~similar to a linearity test,~~ within the C_2H_6:CH_4 ~~ratio is~~gradually increased from 0.00 to 0.15 and measured ~~for~~ in steps of 20 minutes. ~~for each step.~~ This measurement cycle is repeated three times. ~~The~~To do so, based on the setup presented by Assan et al. (2017), a ~~working~~ used ~~target~~ gas ~~with~~ has ~~an~~ethane mixing ratio ~~55~~20 ppm (~~hereafter referred to as further~~ Target Gas 2) ~~and~~is mixed with the dilution gas via two ~~MFCs (Fig.~~mass flow controllers 2). As the flow rate of the measured gas is greater than the instrument's inlet allowance, an open split is installed before the analyzer to vent the generated mixture and maintain an ambient pressure at the instrument inlet. This test was repeated twice: in January 2018 and April 2019. The central 15 minutes of each 20-minute measurements are kept for further analysis. Then, the calibration factors are calculated as a regression slope and an intercept of the linear fitting, of theoretical (Eq. ~~3~~2) against measured C_2H_6 with already applied correction factors from ~~Eq. (~~Equation 1~~).~~. ~~The slope and intercept are used as factors D and E in calibration equation (Eq. 2).~~3.:
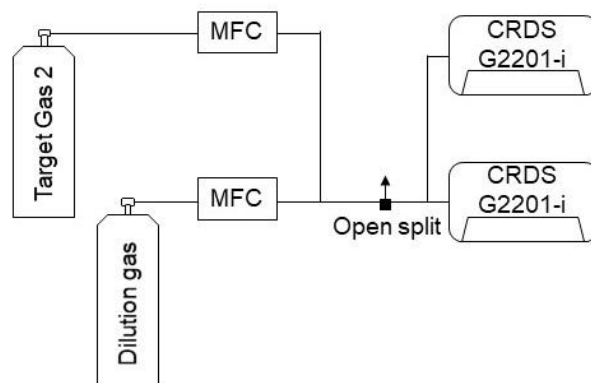
2.1.1. ~~Precision and Allan Variance~~

CMR is calculated as ~~the~~ one standard deviation (SD) over different averaging times (see Yver Kwok et al., 2015). The CMR test has been made by measuring a working gas continuously over 24 hours ~~and~~. CMR is calculated as the one standard deviation (SD) over different averaging times (see Yver Kwok et al., 2015). This test was made twice: first using a working gas with ambient air amount of ethane ~~(hereafter referred to as Target Gas 3)~~ and the second time with a gas mixture where C_2H_6:CH_4 ratio was equal to 0.05 ~~(mixture of Target Gas 2 and 3)~~. This test helps to determine the CMR and instrument noise in the absence or presence of ethane. Moreover, the Allan deviation is also calculated to determine the noise response of the instrument over different averaging times. Typically, the Allan deviation decreases for increasing averaging time. However,

depending on the instrument, with increasing of averaging time, the instrument drift can contribute to the increase of the Allan deviation. Thus, the optimal averaging time can be identified (Allan, 1966).

Also, another target gas (hereafter referred to as Target Gas 4), traceable to the WMO X2004A CH_4 scale, was sampled for 20 minutes, with a CH_4 mixing ratio about 10 000 ppb and a C_2H_6 mixing ratio about 1 000 ppb. The CH_4 mixing ratio was
215 measured with a CMR of about 1 ppb, while for C_2H_6 the CMR of the measurement was about 50 ppb (Section 3.1.3). This test allows us to determine the linearity and short-time precision of the instrument for a gas with a higher mixing ratio than that of ambient air, both of C_2H_6 and CH_4.

2.1.1. Time drift

Eventually, the drift of the C_2H_6 baseline between December 2018 and May 2019 has also been investigated. The A known
220 working gas (dry atmospheric mixing ratio of CH_4 and C_2H_6), hereafter referred to as Target Gas 5, was measured during 11 randomly chosen days, 20 times over that period, about 20 minutes each time. That measurement was made systematically as part of the mobile-measurement protocol (described below). The gas was measured before and after surveys to check instrument stability and influence of switching it on and off.

2.2. Mobile measurement setup Controlled-release experiment setup

225 This section describes the car-based instrument setup. in a controlled gas release experiment. The measurement set up used here is the same as in the field (Section 2.34). The general principle of the setup is comparable to the previous workworks (e.g., Hoheisel et al., 2019; Lopez et al., 2017; Rella et al., 2015).

As the instrument analyzer is not originally designed forto C_2H_6 measurements mobile measurements, the vibrations induced by the motion of the car motion cause noise in the instrument readouts of C_2H_6 mixing ratio. Such a constraint can be overcome
230 using two approaches. First, by stopping the car and spendingstanding some time inside the plume. Second, by accumulating air in sampling air using the AirCore (Karion et al. 2010; Rella et al. 2015; Lopez et al. 2017) while moving through the plume and eventually reinjecting the AirCore's air into the analyzer while stopped. Previously, the AirCore tool was successfully used as part of a mobile measurement setup to determine the isotopic composition of the methane source (Rella et al. 2015; Hoheisel et al. 2019; Lopez et al. 2017) and to determine the C_2H_6:CH_4 ratio (Lopez et al. 2017).

235 Here, both stopping inside the plume and AirCore approaches were used during mobile measurements. The AirCore used in this study iscontains made of 50 m Decabon storage tube. In our setup, the instrument flow rate in the monitoring mode was increased to 160 mL min^{-1} (by default, in CRDS G2201 i the flow rate is equal to 25 mL min^{-1}) to achieve faster instrument response during mobile measurements. Then, the flow rate in the reply mode was chosen as the optimal solution between increasing the number of measurement points and having enough air for each zone sampled. Here, in the replay mode, using the needle valves, the flow rate decreased about 3 times. With 50 mL min^{-1} flow rate, one AirCore analysis lasts about ten
240 minutes. In the replay mode, the car was stopped to avoid possible increase of instrumental noise due to car vibration.

~~While~~During stopping inside the plume, the data were collected in the monitoring mode ~~with engine stopped,~~ while for AirCore mode ~~approach, data from replay mode were analysed~~.

For all mobile measurements, the background mixing ratios are calculated as the 1st percentile of the data sampled just before and just after the plumes, both for CH_4 and C_2H_6. Then the data with CH_4 enhancements above background are further analyzed. The C_2H_6:CH_4 ~~ratio~~ is calculated for each release as the slope of the linear regression of C_2H_6 against CH_4. ~~Fitting of the C_2H_6 versus CH_4 was calculated as a linear regression type II (uncertainty of x- and y-axis influence fitting) with the ordinary least squares (OLS) method. Before fitting, both CH_4 and C_2H_6 were calibrated. C_2H_6 was also corrected (Fig. 1). Measured values were not weighted.~~ The measurements setup and data treatment protocol were the same for the controlled release experiment (Sect. 2.3) and for the field experiment (Sect. 2.4~~3~~).

2.3. Controlled-release experiment setup

In September 2019, during five days, a gas release experiment was conducted by the National Physical Laboratory (NPL, UK) and the Royal Holloway University of London (RHUL, UK). The experiment took place in Bedford Aerodrome, UK. ~~The~~ A description of ~~the~~ experimental setup configuration can be ~~find~~ found in Gardiner et al. (2017)~~.~~ The goal was to evaluate the methods for calculating C_2H_6:CH_4 ratios~~, emission flux gas flow rate~~ and isotopic composition during local mobile measurements. Each release lasted about 45 minutes. During the experiment, the parameters of each release: C_2H_6:CH_4 ~~ratio~~ (0.00 to 0.07), emission flux (~~up to~~until 70 L min^{-1}) and the source height (ground or ~4 m source) ~~could were vary~~varied. Here, results from 10 releases with known parameters and varying ~~C_2H_6:CH_4~~CH_4ethane:methane ratios are presented.

Seven releases were measured using the mobile setup (AirCore and standing in the plume). Air was dried before entering the analyzer using a magnesium perchlorate cartridge. Due to the limited time of the releases, ~~the time spent within the plume was approximately 15 to 20 minutes.~~the time of standing inside the peaks field was in the range of 15 to 20 minutes. After correcting raw data according to Eq. (1), following ~~Protocol 3 (~~low humidity case~~),~~ the calibration factors ~~(Eq. 2)~~ are applied for the trace~~r~~ release and field work datasets.

Three other releases were measured using sampling ~~5-liter~~bags (~~Flexfoil, SKC Inc.).~~flexfoil sample bags) only. Between 1 and 3 bag ~~samples were~~ sampled inside the plume and one ~~was~~ sampled outside as a background sample. Afterward, bags samples were measured in the laboratory using the CRDS G2201-i. The samples were measured without drying and the correction was applied for water vapor higher than 0.16 % ~~("Protocol 2 high humidity case")~~. Then the C_2H_6:CH_4 enhancement ratio was calculated for every bag separately and also as a regression slope of C_2H_6 against CH_4 values. ~~Results~~Due to vague results of bag samples analysis, the ~~r~~ are presented in ~~the~~ Appendix C ~~instead of main part of the article~~.

2.4. Field ~~experiment~~ setup ~~& experiment~~

As a final step to evaluate G2201-i performance in mobile,~~real~~ field conditions, the mobile-measurement setup, described in Sect. 2.2 has been used during surveys made in the Paris area.~~ (see Defratyka et al., 2020, submitted).~~ During spring and summer 2019, 6 surveys focused on three gas compressor stations (one survey for one of them and two surveys for the other

two) and one landfill (one survey). All measurements were made outside of the sites, from the closest public road. To measure
~~the~~ C_2H_6:CH_4, the car was stopped inside the plumes for about 35 minutes, and the central 30 minutes were analyzed. Part of
the measurements was made with magnesium perchlorate as a dryer before the instrument inlet and part of measurements
without ~~a~~ dryer. ~~It allowed to additionally verify the water influence on ethane to methane ratio observed by CRDS G2201-i.~~
For each measurement site, three previously evacuated 800 mL flask samples were also taken to be measured within three
weeks after sampling at LSCE (Assan et al., 2017). Measurements were performed with a GC-FID (HP6890) equipped with a
CP-Al_2O_3 Na_2SO_4 column and coupled to a preconcentrator (Entech 2007) to allow automatic injections. A standard cylinder
(Messer) containing 5 non-methane hydrocarbons including ethane was used to check the stability of the instrument, while
calibration was done against a reference standard from NPL (National Physics Laboratory, UK). A previous characterization
of the system had shown that the detection limit is a few ppt, the reproducibility of measurements is about 2 % and the precision
is better than 5 % (Bonsang and Kanakidou, 2001).

3. Results and discussion

3.1. Laboratory work

3.1.1. ~~Sensitivity of interference correction parameters to humidity~~

~~We~~ we ~~verified the cross-sensitivity correction proposed by Assan et al. (2017) in the presence of water vapor.~~ estimated the
~~robustness of Eq. (1) interference correction parameters for~~ corrects the interference of H_2O, CO_2 and CH_4. ~~in the absorption~~
~~spectrum and dilution~~ to report C_2H_6 mixing ratio in dry air. Figure 3 shows that without interference correction, ~~(Protocol 1),~~
the C_2H_6 mixing ratio is underestimated and the instrument displays a negative correlation with water vapor (r = -0.96). In
~~Protocol 2 (the~~ high humidity case ~~interference correction,),~~ C_2H_6 is overestimated and increases with increasing water vapor
(r = 0.86). Regarding ~~Protocol 3 (the~~ low humidity ~~interference correction)~~ case, C_2H_6 shows the smallest dependency on water
vapor (r = -0.19). Applying ~~the~~ ~~Protocol e~~ low humidity correction values, the C_2H_6 average value is 28 ± 61 ppb ~~(standard~~
~~error 22 ppb)~~, which is similar to the C_2H_6 average value obtained during CMR test (33 ± 51 ppb for raw data), in dry air ~~(Sect.~~
~~3.1.3)~~. Overall, according to this study, after applying low humidity correction values, the water vapor has the smallest impact
for observed C_2H_6 mixing ratio and its averaged value is similar to the one obtained in the absence of water vapor. Therefore,
the correction factors, determined for the low humidity case, ~~(Protocol 3~~ should also be used in water vapor presence. Our
results differ from the findings of Assan et al. (2017), where they observed changing values of the interference correction
depending on the humidity. In the absence of further tests to conclude, we recommend drying air for the C_2H_6 measurements
with the CRDS G2201-i instrument. Details of the water vapor tests are presented in ~~Appendix~~ appendix A.
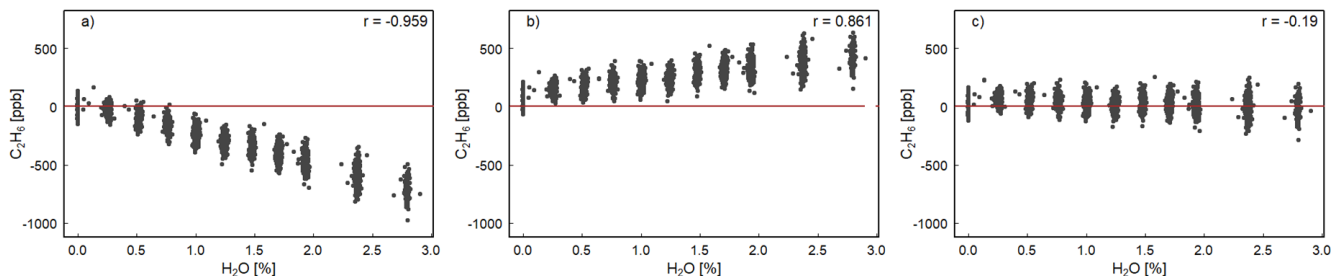
Figure 3. H$_2$O influence on corrected C$_2$H$_6$. Water vapor is increased in small steps for 4 hours while measuring ~~Targeta target gas Gas 1~~. The three panels show the result of applying different water correction protocols for next steps: a) no correction~~(Protocol 1)~~ b) high humidity interference correction ~~(Protocol 2)~~c) low humidity interference correction. ~~(Protocol 3).~~ In all cases, for H$_2$O= 0.00%, C$_2$H$_6$ is corrected using low humidity interference correction. The red line represents 0 ppb.

3.1.2. ~~Ethane Calibration Factors~~

~~Here,~~ the calibration slope ~~(factor D)~~ and intercept ~~(factor E) in Eq. (2)~~ were calculated using linear fitting of C$_2$H$_6$ true ~~(Eq. 2)~~ versus C$_2$H$_6$ observed. ~~(Eq. 2) and compared with the factors previously obtained.~~ The calibration factors ~~D and E~~ were determined after applying the interference correction (Eq. 1). Table ~~3~~ compares new calibration ~~factors~~slopes and intercepts for the specific CRDS G2201-i device CFIDS 2072 obtained in 2018 and 2019 with previous results by Assan et al. (2017). The calibration factors ~~D and E~~ have not changed significantly between 2015 and 2019, indicating a good stability over time.

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Table 3. Summary of the calibration factors for CRDS G2201-i device CFIDS 2072

C_2H_6 calibration	Slope ~~Factor D~~	Intercept [ppm] ~~Factor E~~	Reference
February 2015	0.49 ± 0.03	0.00 ± 0.01	(Assan et al. 2017)
October 2015	0.51 ± 0.01	-0.06 ± 0.04	(Assan et al. 2017)
January 2018	0.51 ± 0.01	-0.03 ± 0.01	This study
April 2019	0.54 ± 0.01	-0.03 ± 0.01	This study

2.1.1. ~~Precision and Allan variance~~

We determined the instrument CMR and Allan variance by measuring ~~a~~ Target Gas 3 for 24 hours. ~~It~~ The ~~same gas~~ was also measured by GC-FID coupled to a preconcentrator, ~~yielding~~and its ~~a~~ C_2H_6 mixing ratio equals 2.2 ± 0.1 ~~ppb~~ ppb. Using the CRDS G2201-i, the corrected and calibrated value is different and steadily equals 33.2 ± 1.7 ppb over the 24 hour duration. This value suggests a bias of the CRDS instrument of ~~3about 31~~01 ppb at low C_2H_6 concentrations~~, which is on the level observed for the ambient air. This~~Possibly, t~~his~~ bias comes ~~probably~~ from ~~the fact that Target Gas 2 concentration is not known with a precision good enough, leading to errors when diluting to very low concentrations.~~not accurate enough calibration procedure for the low C2H6 concentration. To ~~o~~ remove this bias, ~~C₂H₆ mixing ratio were taken as enhancements over background during mobile measurements (Sect. 3.2 and 3.3).~~the bia~~ For more demanding purpose, a~~the~~ calibration strategy with more measurement points in the lower C_2H_6 concentration range~~could be made~~ ~~and calibration tanks with lower uncertainty should be used.~~

~~As a~~the ~~result of~~Following the 24 hour test, CMR and Allan deviation (~~Fig.~~Figure 4) are calculated for target gases with different C_2H_6 mixing ratios: low mixing ratio ~~(Target Gas 3)~~, 100 ppb ~~(mixture of Target Gas 2 and 3)~~ and 1 000 ppb ~~(Target Gas 4)~~. In all cases, increasing the ethane mixing ratio does not affect the determined CMR and Allan deviation. Looking at raw data (one data point every 3.7 s) for different mixing ratios, CMR and Allan deviation are about 50 ppb and 25 ppb, respectively. Increasing averaging time improves these parameters and for 1 minute average, all achieve about 13 ppb. For CRDS model G2132-i, also not ~~dedicated originally~~ designed to the measure of ethane (Rella et al. 2015), the CMR in 1 ~~minute~~min is about 20 ppb and Allan deviation in 1 minute is about 25 ppb. Currently, new CRDS instruments designed to ethane measurements are available, for example, the CRDS 2210-i, which also measures $\delta^{13}CH_4$. Recently (in February 2020), at the ICOS Atmosphere Thematic Centre (ATC) Metrology Laboratory (MLab), the CRDS G2210-i was tested and for C_2H_6 its CMR and Allan deviation are equal to 0.9 ppb and 0.8 ppb in 1 minute (ATC Mlab, personal communication)~~ which is much lower than for our~~ analyzer. ~~However, as stated before, our motivation is to evaluate if any~~former instrument~~ G2201-i, including former ones~~ still in activity in many places, can ~~also~~ provide scientifically useful ethane measurements.~~

The comparison between instruments are ~~presented in Table 4.~~

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~~Table 4~~. CMR and Allan deviation for G2201-i G2132-1 and G2210-i.

Averaging time	Id	G2201-i Low C_2H_6	G2201-i ~100 ppb C_2H_6	G2201-i ~1000ppb C_2H_6	G2132-i (Rella et al., 2015)	G2210-i (ATC MLab) (personal communication)
Raw data	CMR [ppb]	51	50	50	NA	4.6
	Allan deviation [ppb]	25	25	26	NA	NA
10 second	CMR [ppb]	30	29	30	NA	NA
	Allan deviation [ppb]	29	29		NA	NA
1 minute	CMR [ppb]	13	12	12	20	0.9
	Allan deviation [ppb]	13	12	12	25	0.8
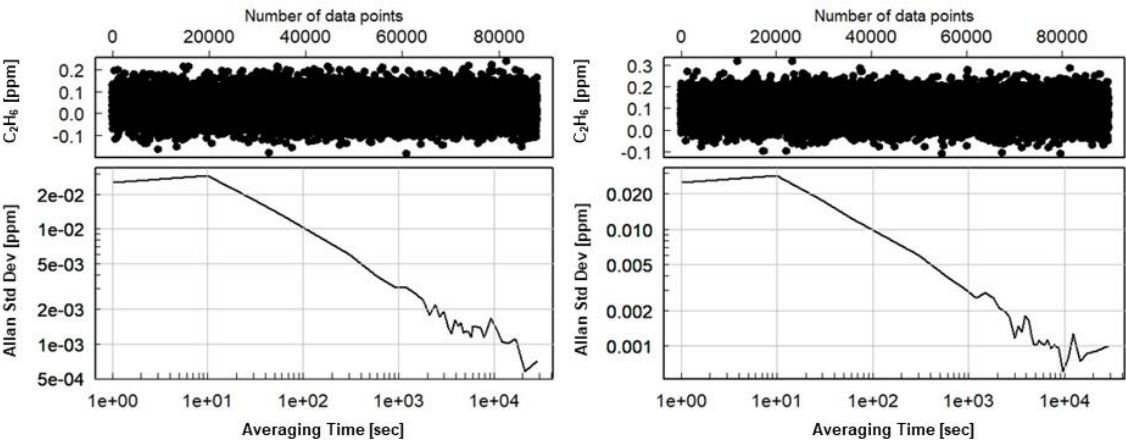
Figure 4. Allan deviation for corrected and calibrated C_2H_6. Left: Measurement of working gas with ~~negligible ambient~~ C_2H_6 mixing
345 **ratio ~~(Target Gas 3)~~, right: measurement of the mixture of working gas with ~100 ppb of C_2H_6 ~~(mixture of Target Gas 2 and 3)~~.**

With a ~~possible~~ 30 ppb bias and a CMR of 50 ppb, the CRDS G2201-i cannot be used to measure an absolute value of ethane ~~inethane absolute value~~ ~~ambient air~~. However, this instrument can be used to observe ethane enhancement near the source and to estimate ~~ethane to methane ratios.~~ C_2H_6:CH_4 ratios. From these numbers, we can deduce that the smallest enhancement that the analyzer can measure with significant precision at the highest possible data acquisition frequency is above 50 ppb. This

350 value was obtained both for gas with a low and high C_2H_6 mixing ratio (~100 ppb and ~1 ppm). ~~We~~ One can assume that a
C_2H_6 enhancement is significant when the maximum C_2H_6 mixing ratio in the peak is higher than ~~2xCMR~~2xSD, i.e., 100 ppb
above background.

3.1.4. ~~Time drift~~

~~Figure 5 shows the time series of Target Gas~~ 5 measurements with an ~~low~~ ambient amount of C_2H_6 during the period of
355 December 2018~~—~~ May 2019. The C_2H_6 mixing ratio ~~measurements do~~does not change here significantly. ~~Their mean and~~ is
equal to 23 ± 12 ppb (~~Fig.~~Figure 5). It is in contrast to Assan et al. (2017), where a time drift of the baseline was observed.
This difference can be caused by fact that during previous studies, the drift was determined for corrected but not calibrated
data. Here, we applied both correction and calibration before determination of time drift. Moreover, during ~~previous~~ studies
~~of Assan et al. (2017),~~ bigger changes in determined calibration factors were observed over time ~~(i. g. 60 ppb difference of~~
360 ~~factor E). Our tests showed that the ethane measurements are stable over annual timescales once proper interference correction~~
~~and calibration applied. Again, measuring dry air is recommended (Sect. 3.1.1.). In the . Therefore, in the~~ following analyses,
no baseline drift correction is applied.
~~It should be noted that, the C_2H_6 concentration of Target Gas 5 was in the range of the clean continental air (0.5-2 ppb). The~~
~~observed mean C_2H_6 mixing ratio for Target Gas 5, equal to 23 ppb, is overestimated. This is comparable to the 31 ppb bias~~
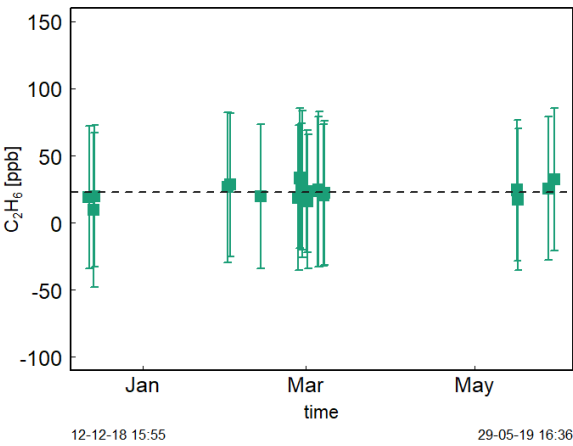365 ~~observed during 24 hours measurements of Target Gas 3 (Sect. 3.1.3).~~

12-12-18 15:55   29-05-19 16:36

Figure ~~5. Target Gas 5~~ 20-~~minute~~ minutes measurements over half a year. ~~For~~for each measurement point: squares represent averaged value, error bars – 1 standard deviation

3.2. Controlled release experiment

370 Figure ~~6~~4 ~~and Table 5 show~~shows ~~C_2H_6:CH_4 ethane to methane~~ ratios~~, expressed in ppb ppb^{-1},~~ measured in situ during the
controlled release experiment (see ~~Sect.~~Section 2.2). During these 7 releases, the C_2H_6:CH_4 ~~ratio~~ was set to ~0.032 for one

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release, ~0.00 for two releases and ~0.07 for four releases. ~~In the case, when C$_2$H$_6$:CH$_4$ ethane to methane ratio was equal to= 0.00, ethane was not released while methane was released. Possibly, observed ethane mixing ratio could come from ethane impurity in the released methane. Although no ethane was detected using the LGR instrument during the zero ethane releases.~~

375 For measurements with the car stopped inside the plume, most of the data from the CRDS G2201-i are found lower than known emitted C$_2$H$_6$:CH$_4$ ratio, (mean absolute deviation = 0.011, standard deviation = 0.004) with residuals in the range -0.018 to -0.002 for raw data (Table ~~5~~). ~~The residuals are calculated as a difference between measured and released C$_2$H$_6$:CH$_4$.~~ The observed underestimation can be caused by ~~a systematic bias observed during laboratory test, or~~ an insufficient number of
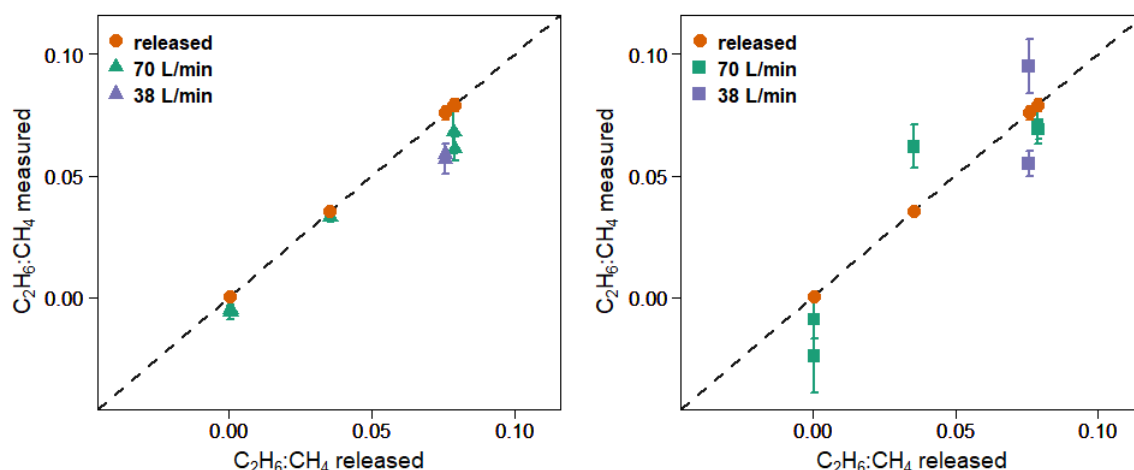
measurement points (15-20 minutes of measurement). For AirCore measurements, there is more discrepancy than for the ~~plume~~
380 ~~standing situation~~ stationary in-plume situation, with residuals in the range -0.025 to 0.027 (mean absolute deviation = 0.017, standard deviation=0.009). ~~For 10 s averaged data, the range of residuals is only marginally modified, ranging from -0.019 to -0.002 and from -0.022 to 0.027 for~~ ~~plume standing~~ stationary in-plume situation and AirCore, respectively. ~~Additionally, the mean absolute deviation and standard deviation are also marginally modified for both measurement situations. For example, for stationary in-plume situation~~ stationary plume standing, ~~the absolute deviation improves marginally from 0.0111 to 0.0107.~~
385 ~~It shows insignificant difference between raw and 10 s averaged data.~~ Th~~us, th~~e ~~stationary in-plume situation plume standing~~ setup shows ~~less noisy~~ data ~~with less spread and a smaller range of residuals~~ than AirCore results. ~~Moreover, the stationary in-plume situation~~ plume standing approach has a (small) regular bias (mean bias = -0.011), higher than in the AirCore approach (mean bias = -0.004). These results show that in the case of C$_2$H$_6$:CH$_4$ ~~ratio~~ measurements, standing inside the plume gives results closer to ~~the~~ reality than AirCore sampling. The example of observed CH$_4$ and C$_2$H$_6$ mixing ratio~~s~~ while standing inside
390 the peak during one of the gas releases is presented in appendix B.

Figure ~~6~~4. C$_2$H$_6$:CH$_4$ ~~ratio~~ observed using G2201-i as a part of a mobile setup. Left: measured standing inside the plumes. Right: measured using AirCore. Red points: known released C$_2$H$_6$:CH$_4$ ~~ratio~~. Error bars represent 1 standard deviation. The uncertainties of released values are invisible on the graph.

We also investigated the sensitivity of the C$_2$H$_6$:CH$_4$ ~~ratio~~ to emission rates. During releases there were two different emission
395 rates: 38 L~~/~~min~~⁻¹~~ and about 70 L~~/~~min~~⁻¹~~. ~~For the higher emission, the measurements and results were combined when the~~

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emission rates were 70, 72, and 73 L min⁻¹. In the latest category, the releases while the with emission rate was equal to 72 L/min and 73 L/min are grouped. The C₂H₆:CH₄ ethane to methane ratio is better estimated by the measurements for with higher emission rates (bias is divided by more than 2 when increasing flow rate from ~38 to ~70 L⁻/min⁺). This is true both with stationary measurements and using the AirCore sampler. However, only 2 different emission rates were implemented and most of the released occurred at the rate of 70 L/min min⁻¹, limiting the representativity of this sensitivity.

Table 5. C_2H_6:CH_4 with residuals for non-averaged data observed using G2201-i as a part of a mobile setup, during standing inside the plume or from AirCore measurements (AC). Background subtracted both for C_2H_6 and CH_4 before determination of C_2H_6:CH_4.

Emitted C_2H_6:CH_4	emitted emission flux [L/min]	Source height [m]	n	LSCE CRDS G2201-i				RHUL LGR UMEA
				C_2H_6:CH_4	Residuals	C_2H_6:CH_4 AC	AC residuals	Residuals C_2H_6:CH_4
0.0355 ± 0.0011	70	4	382	0.033 ± 0.002	-0.002	0.034 ± 0.002	0.027	-0.004
0.0788 ± 0.0025	72	4	149	0.068 ± 0.009	-0.011	0.070 ± 0.010	-0.008	-0.006
0.0790 ± 0.0025	73	0	220	0.061 ± 0.005	-0.018	0.063 ± 0.006	-0.010	-0.001
0.0758 ± 0.0028	38	0	142	0.059 ± 0.004	-0.017	0.058 ± 0.004	-0.020	-0.007
0.0758 ± 0.0028	38	4	191	0.057 ± 0.006	-0.018	0.057 ± 0.006	0.019	-0.015
$0.0005 \pm 0.0006*$	70	0	350	-0.005 ± 0.001	-0.005	-0.005 ± 0.002	-0.025	-0.004
$0.0005 \pm 0.0006*$	70	4	202	-0.006 ± 0.003	-0.007	-0.005 ± 0.004	-0.010	-0.001
Mean residuals					**-0.011**		**-0.004**	**-0.0051**

* Small amount of ethane impurity in the methane

In Table ~~5~~35 we also report ~~the~~ residuals of C_2H_6:CH_4 ~~ratio~~ independently measured by RHUL using an LGR UMEA in another car. The residuals in C_2H_6:CH_4 ratios of LGR UMEA are in the range [-0.015~~, to~~ -0.001], and their mean is -0.0051 (mean absolute deviation = 0.0051). Therefore, the LGR UMEA is predictably more accurate than the CRDS G2201-i standing inside the plumes (CRDS residuals in range -0.018 to -0.002 with mean -0.011). Despite the observed differences, results obtained by these two methods are comparable and both instruments ~~are~~ were capable of resolving the variation of C_2H_6:CH_4 in ~~this~~e release experiment.

~~During the release experiment, we showed that the CRDS is able to separate the different emitted mix through their C_2H_6:CH_4. Standing in the plume resulted in a better agreement with the real ratios, with less spread of the residuals than using AirCore sampling. Increasing the AirCore sampling frequency could~~ ~~potentially~~ ~~help resolve this discrepancy.~~

3.3. Field work

~~As a final step, the CRDS G2201-i was evaluated in real field conditions.~~ Measurements were collected in the Paris area downwind of three gas compressor stations (referred to as ~~Ga, Gb, , CGc~~) and one landfill (~~LD~~). All measurements in this section were done stationary inside the plume.

Table ~~6~~4 presents only values based on raw data ~~(i.e. at ~(~~~3.7 s ~~acquisition frequency).).~~ We postulate that mobile applications usually aim at the highest possible acquisition frequencies. However, as the 10 s averaging increases r^2 fitting by about a factor two, comparison of raw data and 10 s averaged data is presented in appendix D. ~~C_2H_6 and CH_4 mixing ratios are taken as~~

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enhancements over background. Slopes are calculated using a linear regression type II (uncertainty of x- and y- axis influence fitting) with the ordinary least squares (OLS) method. The data are not weighted. Uncertainties reported in Table 6 and Table 7 uncertainties are linear fitting slope uncertainties without adding uncertainties of C_2H_6 measurements.

Table 6. Ratio measured at three different gas compressor stations (~~Ga, Gb, ,~~ CGe) and a landfill (~~DL~~); ΔCH_4 and ΔC_2H_6 are defined as the difference between background value (1st ~~percentile~~ percentage) and the observed value inside the peak

id	max ΔCH_4 [ppm]	max ΔC_2H_6 [ppm]	$C_2H_6:CH_4$ ~~ratio~~ 1 s	r^2 fitting	n (data point)	Data
~~Ga2A2~~	1.737	0.269	0.060 ± 0.005	0.195	533	16.05.2019
~~Ga3A3~~	5.85	0.414	0.045 ± 0.002	0.489	495	15.07.2019
~~Gb3B3~~	1.454	0.260	0.052 ± 0.007	0.082	613	12.07.2019
~~Gb4B4~~	1.677	0.236	0.046 ± 0.008	0.086	336	12.07.2019
~~LD1~~	1.516	0.266	0 ± 0.006	0	712	16.05.2019
~~Ga1A1~~*	1.486	0.309	0.070 ± 0.013	0.162	138	16.05.2019
~~Gb1B1~~*	7.314	0.878	0.090 ± 0.001	0.852	811	27.05.2019
~~Gb2B2~~*	0.513	0.323	0.085 ± 0.022	0.024	594	12.07.2019
~~Gc1C1~~**	0.495	0.284	0.091 ± 0.037	0.037	711	28.05.2019

Numbers after identification letters refer to different surveys. *: Ga1, Gb1, B1 and Gb2 (wet air) and ** Gc1 (low enhancement) are rejected from further analysis (see text).

Campaigns ~~Ga1, A1, B1~~ Gb1 and ~~B2~~ Gb2 (Table ~~6~~4) were made without using a dryer before the instrument inlet. Due to previous results that have cast doubts about the water vapor correction, the high humidity measurements have been rejected from further analysis. ~~Also, in the case of measurements of~~ humidified wet air, the ethane to methane ratio was ~~significantly higher than values provided by operator.~~ Surveys ~~B2~~ Gb2 and ~~C1~~ Gc1 exhibited the highest uncertainties in the estimated ratio and the lowest correlation between the two species. These two surveys had the lowest CH_4 enhancements above background, about 0.5 ppm. Based on error propagation (Taylor, 1997) and using 2x CMR (100 ppb) as C_2H_6 detection threshold, for a typical $C_2H_6:CH_4$ ~~ratio~~ of interest about 0.1, the minimal CH_4 enhancement above background would ~~also therefore be~~ be equal to 1 ppm. It suggests that a minimum CH_4 enhancement of 1 ppm could be required to calculate ethane to methane ratio in field conditions ~~with this instrument~~. As our observations are in line with the error propagation, we use 1 ppm CH_4 enhancement above background as a detection limit to use the CRDS G2201-i to determine ethane to methane ratio in the field conditions close to the methane source, and exclude ~~B2~~ Gb2 and ~~C1~~ Gc1 from subsequent analysis.

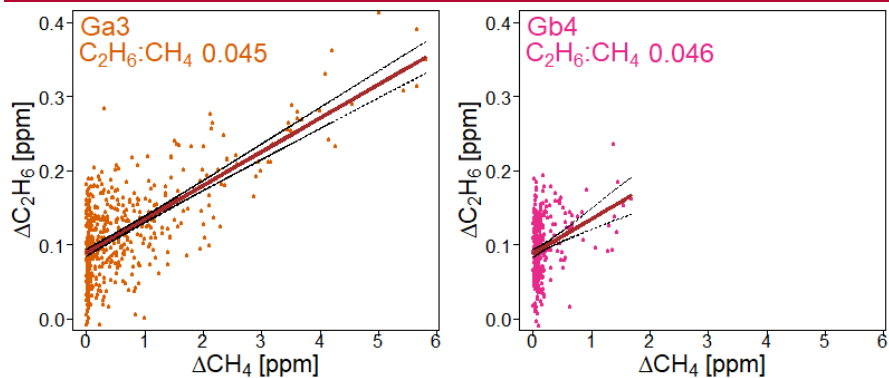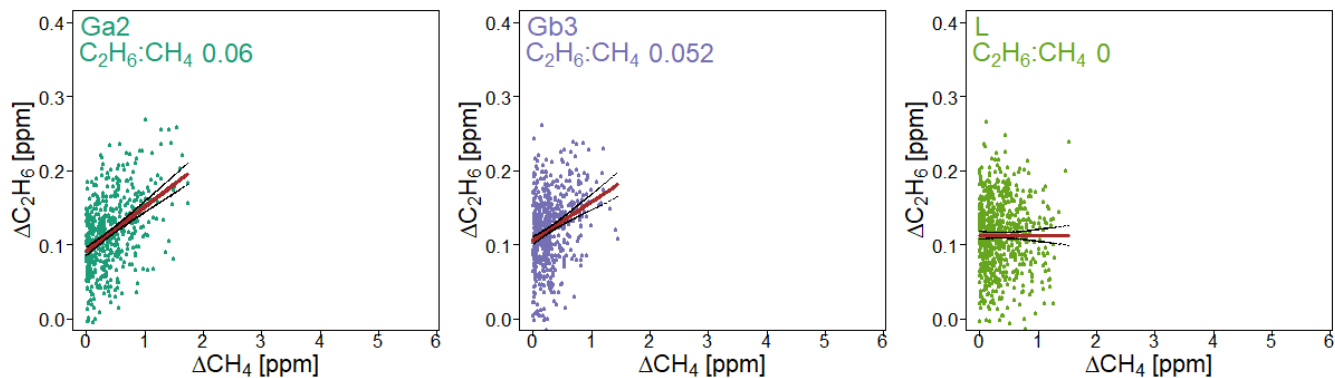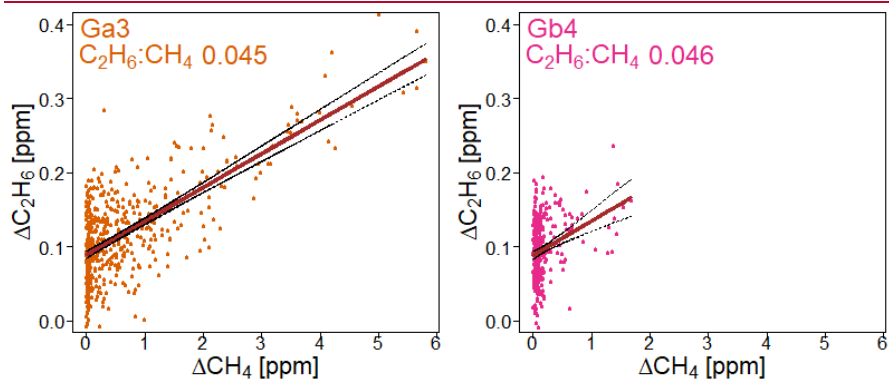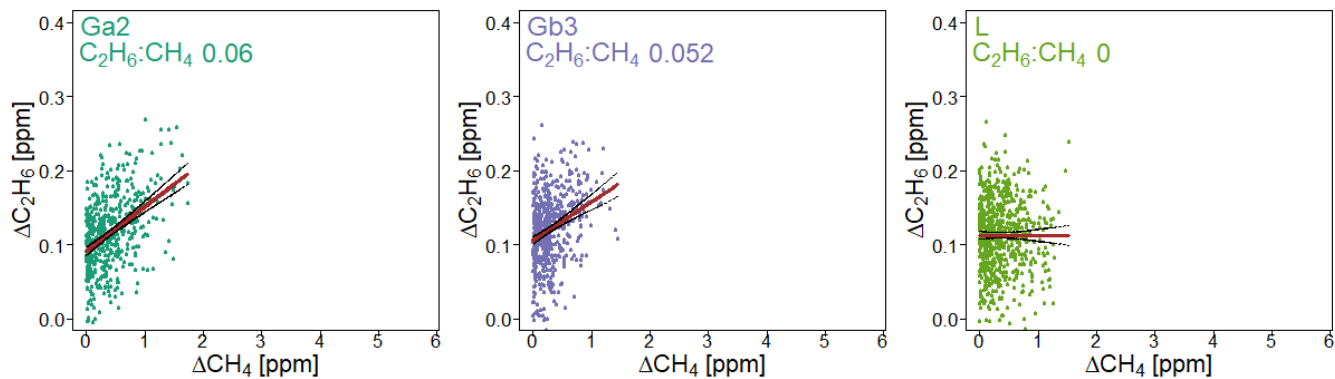**Figure 7~~5~~. C$_2$H$_6$:CH$_4$ ~~ratio~~ for gas compressor stations (~~A Ga~~ and ~~G~~b) and the landfill (~~L~~D), calculated for non-averaged data. Linear fitting (red line) with confidence intervals (black lines)**

Figure 7~~5~~ presents observations from the valid cases. We compared the observed ratios with the values provided by the owner of the gas compressor stations. The comparison is presented in Table 7~~5~~. The residuals between values measured by CRDS and values provided by the owner (considered as the "true" values) are in the range -0.006 to 0.009. This range is more symmetrically distributed around the released value than for the controlled release experiment (-0.018 to 0.002, ~~Sect.~~Section 3.2). The uncertainty of C$_2$H$_6$:CH$_4$ ~~ratio~~ measured using the CRDS G2201-i in the field conditions is smaller than the differences between the ratios of CH$_4$ sources (e.g., biogenic sources C$_2$H$_6$:CH$_4$ ~0.00, natural gas leaks and compressors stations ~0.06, processed natural gas liquids ~ 0.30). These results clearly show that C$_2$H$_6$:CH$_4$ ~~ratio~~ measured by the CRDS G2201-i can be used to portion the origin of the CH$_4$ during mobile measurements. ~~Possibly, increasing the detection limit, from 1 ppm to 2 ppm above CH$_4$ background, could improve accuracy and precision of determined ratio. However, as in our case most of CH$_4$ plumes reached about 1.5 ppm above background, we could not verify the impact of chosen detection limit.~~

Table ~~7~~5. Comparison of results obtained by CRDS G2201-i with the values from the operator company.

id	CRDS 1s $C_2H_6:CH_4$ ~~ratio~~	Operator data -$C_2H_6:CH_4$ ~~ratio~~	Residuals -$C_2H_6:CH_4$ ~~ratio~~	Date
~~Ga2A2~~	0.060 ± 0.005	0.051	0.009	16.05.2019
~~Ga3A3~~	0.045 ± 0.002	0.049	-0.004	15.07.2019
~~Gb3B3~~	0.052 ± 0.007	0.052	0.000	12.07.2019
~~Gb4B4~~	0.046 ± 0.008	0.052	-0.006	12.07.2019
~~LD1~~	0 ± 0.006	NA	NA	16.05.2019

Finally, C_2H_6 mixing ratios measured by the CRDS G2201-i are compared with results from GC-FID. Three flask samples were taken from every surveyed site and measured afterward in the laboratory using GC-FID. Then, the average of these three measures was calculated and for all sites their standard deviation is smaller than 1 ppb. On Figure ~~8~~6, flask results are compared to results obtained by the CRDS G2201-i during the time of flask sampling. One should keep in mind that due ~~to~~ the very short time sampling (<3s), the comparison of concentrations is only indicative. For ~~the~~ landfill ~~D~~, the C_2H_6 mixing ratio measured by GC-FID is 4.9 ppb~~, which~~~~at~~ is higher~~a bit larger~~ ~~than typical C2H6 mixing ratio observed for clean atmosphere (0.5-2 ppb)~~. For ~~A~~ Ga ~~and~~ ~~C~~ Gc gas compressor stations, the C_2H_6 mixing ratio~~, measured by GC-FID,~~ is 20.5 ppb and 13.7 ppb, respectively. ~~Due to the instrument noise~~After subtracting the determined bias, for the landfill and two compressor stations (~~A~~ Ga ~~and~~ ~~C~~Gc), C_2H_6 mixing ratio measured by CRDS is ~~still~~ higher than measured by GC-FID (~~Fig.~~Figure ~~8~~6) ~~but within the instrument noise~~~~and averaged observed overestimation for these three sites is about 40 ppb. This discrepancy is similar to the one observed in laboratory conditions, where CRDS result has been higher by about 30 ppb (section 3.1.3).~~. A different situation is observed in the case of the gas compressor station ~~B~~ Gb where higher C_2H_6 mixing ratio is observed. The results from flask samples are higher by about ~~7~~ 24 ppb than from CRDS analyzer ~~after subtraction of 31 ppb bias~~, what~~what~~~~ich~~ ~~suggest a better agreement between instruments in the~~for higher C_2H_6 mixing ratios is still within the instrument nose. For all sites, in the case of CRDS measurements the standard deviation is almost equal to the averaged value over the sampling time. It is caused by high instrument noise (~50 ppb CMR and 25 ppb Allan deviation for raw data) and short sampling time (less than one minute).

~~Field work allowed us to compare our measurements against operator values~~ ~~and~~ ~~GC measurements. This confirms that this instrument can discriminate between sources~~ ~~and~~that it agrees ~~within~~ its ~~uncertainty~~ ~~with more precise methods such as GC.~~
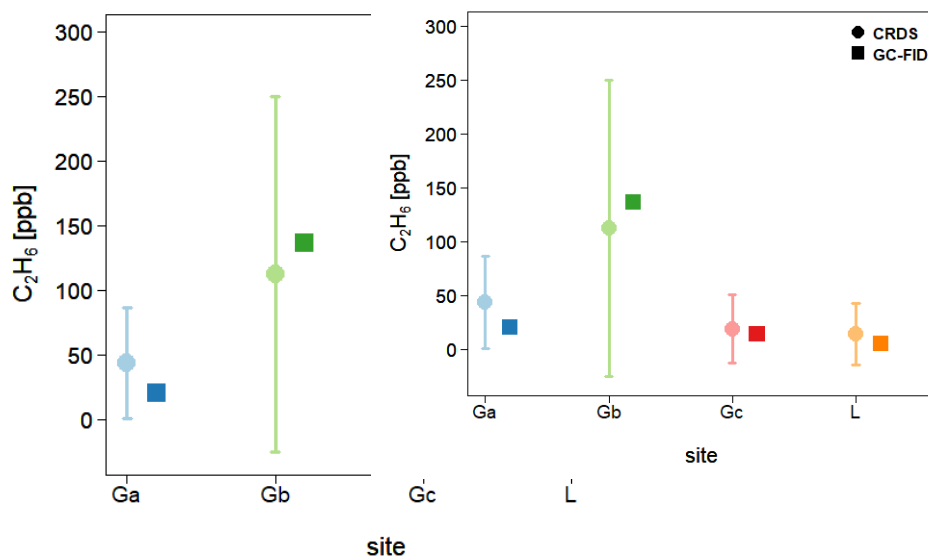
Figure 86. Comparison of the C$_2$H$_6$ mixing ratio measured in-situ by CRDS G2201-i and in the laboratory by GC-FID from flasks measurements. CRDS G2201-i measurements during the time of flask sampling. Uncertainties (1 SD) are indicated both for CRDS and GC-FID.

4. Synthesis ~~and discussion: overall~~ comparison with other instruments and methods

~~We determined that~~Based on the series of tests conducted in our study, using the CRDS G2201-i in a mobile setup to measure C$_2$H$_6$:CH$_4$ ~~ratio~~ in methane plumes ~~is~~appears possible and can provide useful scientific results under specific conditions. In laboratory conditions, during measurements of gas containing C$_2$H$_6$, the CRDS G2201-i has a better CMR (12 ppb in 1 ~~minute~~min) and a smaller noise calculated from Allan deviation (¬10 ppb in 1 ~~minute~~min) than the CRDS G2132-i, ~~another isotopic analyzer,~~ which are equal 20 ppb and 25 ppb, respectively, in 1 ~~minute~~min timeframe (Rella et al. 2015~~).), where both instruments are not designed for C$_2$H$_6$ measurements.~~ However, both instruments have lower performance than the CRDS G2210-i, designed to ~~measure~~ C$_2$H$_6$ ~~measurement~~. For the latter instrument, both CMR and Allan deviation are smaller than 1 ppb (ATC Mlab test, personal communication). Additionally, based on a literature comparison, for both CRDS instruments, CMR and noise are higher than those obtained for the instrument based on the TLDAS method, designed for mobile measurements of C$_2$H$_6$ (as described by Yacovitch et al. 2014). For that instrument, the CMR is as low as 19 ppt in stationary conditions, and 210 ppt in motion.

~~The~~Based on Assan et al. (2017), the correction of the sensitivity to other species is necessary (Eq. ~~(1)~~)) to account for the different instrument responses to water level lower or higher than 0.16 % (low and high humidity). In this study, during laboratory work, the water vapor sensitivity was evaluated and results showed that applying interference correction factors determined for low humidity gave better results, including for ~~more humidified~~wet air measurements. It is in opposition to results obtained by Assan et al. (2017). ~~Rella et al. (2015) noted that the measured air should contain less than 0.1 % of water vapor . Therefore, we consider that water presence should be avoided and we recommend drying air before C$_2$H$_6$ measurement~~

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using CRDS G2201-i. Therefore, we consider that water presence should be avoided and we recommend drying air before C₂H₆ measurement using CRDS G2201-i.

Previously, the CRDS G2201-i device CFIDS 2072 has only been used in stationary field work over two weeks (Assan et al. 2017) to make continuous measurements of CH₄, δ¹³CH₄ and C₂H₆ from gas facilities. The CRDS G2201-i and GC-FID measured air simultaneously from the shared inlet and were located 200——400 m from the gas facilities (pipelines and compressors). The GC-FID used in Assan et al. (2017) was a field instrument described in Gros et al. (2011) and Panopoulou et al. (2018) which has an overall uncertainty estimated to be better than 15%. To have identical timestamps as For GC-FID, corrected and calibrated CRDS data were averaged for 10 To have identical timestamps as GC-FID, corrected and calibrated CRDS data were averaged for 10 min every 30 min. minutes of ambient air collection was measured during 20 minutes. Thus, for that instrument, the sampling time is 10 minutes sampling average over 30 minutes. To have identical timestamps as GC-FID, corrected and calibrated CRDS data were averaged for 10 min every 30 min. Moreover, during that study, flask samples were collected and further analyzed in the laboratory. Ethane:methane C₂H₆:CH₄ from flask samples allowed to distinguish methane emissions from the two pipelines. The natural gas in pipeline 1 had an ethane to methane ratio equaled to 0.074 ± 0.001 and for pipeline 2 equaled to 0.046 ± 0.003. These values are in good agreement with on-site GC-FID results which reached 0.075 and 0.048 ± 0.003, for pipeline 1 and 2 respectively (Assan et al., 2017). Thus, the laboratory values showed good agreement between field, installed in the shelter, CRDS G2201-i and GC-FID results (Assan et al. 2017).

Flask samples were taken as well during that field work. That study was the first attempt to propose a protocol to use CRDS G2201-i to measure C₂H₆:CH₄ ratio, both from flask sampling and from continuous measurements, and found a good agreement between CRDS and GC-FID measurements (Assan et al. 2017). In our study, we went one step further and considered the constraints associated with a mobile setup within a car. As the instrument noise increases during the motion of the car, we decided to stop the car for about 35 minutes inside the plume to acquire the observations. As it is not possible to stop the car in every place where measurements are made, it is a limitation for this application of the instrument, compared to other instruments able to measure C₂H₆ while moving across the plume, like the LGR UMEA (Lowry et al. 2020) or the instrument based on the TILDAS method (Smith et al., 2015; Yacovitch et al., 2014, 2020). Even though, we showed it is possible to receive reliable values during short time (ie.g. 35 minutes) and the instrument can be installed inside a the car. Notably e, having the instrument setup inside the car facilitates the measurement setup, as an additional place to install the stationary instrument is not required anymore.

During our tracer release experiment, C₂H₆:CH₄ ratio was calculated from measurements made when the car was standing inside the plume. With this approach, measured ratios were underestimated. However, using the LGR UMEA instrument, designed to mobile C₂H₆:CH₄ ratio measurements, some discrepancy between the measured and released value was also observed, albeit smaller. Indeed, in the case of the LGR UMEA measurements, the residuals between measurements and released value were in the range -0.015 to -0.001, where using the CRDS G2201-i the residuals are in the range -0.018 to -0.002. It is also worth noting that the more precise instrument, presented by Yacovitch et al. (2014), using a more precise instrument also reported inferred a systematical underestimation of the C₂H₆ mixing ratio by ~ 6 %.% of the measured value. In their study, this systematic error was added as a reported statistical error (Yacovitch et al. 2014).

In our study, during the trace release experiment, we also compared results obtained by stationary standing inside the plume and by sampling air with an AirCore system. The absolute deviation is equal to 0.011 and 0.017 for stationary mode and AirCore mode, respectively. The residuals between released and measured values are from -0.018 to -0.002 for stationary mode and from -0.025 to 0.027 for AirCore mode. Thus, the agreement with released $C_2H_6:CH_4$ ~~ratio~~ is better for measurements made by standing inside the plumes than with AirCore sampler. However, during previous studies where CRDS instruments were used (Rella et al. 2015; Lopez et al. 2017), $C_2H_6:CH_4$ ~~ratio~~ was also measured using AirCore sampler. In the study made by Lopez et al. (2017) for pipelines measurements, gas flasks were also collected and measured at INSTAAR (Boulder, CO, USA) using gas chromatography. ~~Based on CRDS measurements with AirCore sampler, ethane to methane ratio equalled to 0.05 ± 0.01, while from gas chromatography it reached 0.04 ± 0.001.~~ Overall, AirCore sampler results were in good agreement with the results for flasks measurements.

During these measurements, the CRDS was flushed continuously with a flow rate of 1000 mL/min⁻¹ and a mass flow controller was part of the setup. During AirCore analysis, the airflow rate was equal to 40 mL/min⁻¹. This change allowed ~~increasing to~~ increase the number of ~~measurement~~ measurements points by 25, when the replay mode was used. In our study, in the monitoring mode, we flushed the CRDS instrument with a flow rate of 160 mL/min⁻¹ and in the replay mode, we increased the number of points only by ~~a factor of~~ 3. These differences could contribute to ~~explain~~ explaining the discrepancies between measured and released $C_2H_6:CH_4$ ratio~~s~~. Further decreasing the flow rate will increase the number of sampling points and could improve the agreement between AirCore-based estimations and actual ratios~~, especially for the small CH_4 plume (e.g. 1-2 ppm above CH_4 background)~~. This should be tested to ~~determine~~ conclude the optimal ~~use of~~ AirCore setup ~~for $C_2H_6:CH_4$~~ to improve the characterization of methane sources.

Finally, the $C_2H_6:CH_4$ ratios obtained by standing inside the plumes are accurate and allow ~~us to~~ separate the different releases at the resolution of the conducted experiment. They are also comparable with results obtained using LGR UMEA. This agreement between measurements and reality has also been confirmed during ~~real~~ field conditions mobile measurements. During these measurements, residuals for dry air sampling were between -0.006 and 0.009. Additionally, during field work, ~~flask~~ flasks samples have been taken and measured by GC-FID in the laboratory. During the time of flask sampling at the two gas compressors stations, the C_2H_6 mixing ratios were below the value of the instrument CMR (~50 ppb). For the third gas compressor station, the C_2H_6 mixing ratio was above the detection threshold and C_2H_6 mixing ratio measured by GC-FID was higher than measured by CRDS. Nevertheless, due to the short sampling time of the flasks, these first comparisons ~~between flask samples measured by GC-FID and short-term CRDS field measurements~~ are only ~~indicative~~ approximate and more comparison campaigns should help to understand the discrepancies between these instruments. In all cases, the standard deviation of C_2H_6 measured by CRDS was close to the averaged value. It shows the CRDS G2201-i should not be used for ~~the~~ measurements of the absolute value of ~~the~~ C_2H_6 mixing ratio~~s when too low~~.

Overall, using $C_2H_6:CH_4$ ~~ratio~~ measured by the CRDS G2201-i, it is possible to separate methane sources between a biogenic origin ($C_2H_6:CH_4$ ~ 0.00), natural gas leaks and compressors ($C_2H_6:CH_4$ ~ 0.06, can vary between 0.02-0.17) and processed natural gas liquids ($C_2H_6:CH_4$ ~ 0.3). $C_2H_6:CH_4$ ~~ratio~~ of natural gas can vary ~~on due to its~~ origin and processing. ~~Also, this~~

~~instrument can be used to observe possibly temporal variation of C_2H_6:CH_4 of methane emitted from fossil fuel sources. These studies can be made in the vicinity of strong emitting sources, where CH_4 plume reaches at least 1 ppm above background. Determining~~Thus, determining the exact source of methane inside the industrial site, with a lot of potential methane emitters, ~~is~~can be more challenging to achieve. However, looking at the results of our study, if the differences between C_2H_6:CH_4 ratios are higher than 0.01, it is ~~still~~ possible to determine the source of the observed CH_4 plume using C_2H_6:CH_4 ~~ratio~~measured ~~with~~by the a CRDS G2201-i.

5.   Conclusions ~~and~~& recommendations

The instrument CRDS G2201-i measures $^{12}CO_2$, $^{13}CO_2$, $^{12}CH_4$, $^{13}CH_4$, H_2O and C_2H_6, the latter being initially present to correct $^{13}CH_4$ measurements. This study investigates the possibility to make ethane measurements, made by a CRDS G2201-i instrument, useful for methane source apportionment. The interest is to be able to better constrain methane sources at the laboratory and in the field with ~~two proxies but~~ only one instrument. Before any analysis, C_2H_6 raw data must be corrected and calibrated ~~(Fig. 1)~~. The linearity test showed good stability over time, with only a small change of calibration factors over 4 years. Contrary to the previous studies (Rella et al. 2015; Assan et al. 2017), we do not observe any time drift of the C_2H_6 baseline. Nevertheless, regular calibrations and target measurements are ~~recommended~~adv.

The controlled release experiment revealed a small systematical underestimation of measured ~~C_2H_6:CH_4ratios~~ inside the plumes compared to released ones. The larger discrepancy from released C_2H_6:CH_4 occurs in the case of AirCore samplings. Due to that, we recommend standing inside the plumes instead of taking AirCore samples to measure C_2H_6:CH_4 ratios. However, decreasing the flushing flow rate of the CRDS can improve the performance of the instrument during AirCore sampling and should be further investigated in ~~future~~the next campaigns.

In this study, we find some limitations of using CRDS G2201-i to measure C_2H_6:CH_4. First of all, we found that we need at least a peak maximum of 100 ppb in ethane to get useful results to help portioning methane sources. Additionally, the required maximum CH_4 enhancement above background should be higher than 1 ppm. This threshold is determined using error propagation for a typical C_2H_6:CH_4 ~~ratio~~equal to 0.1. In the field conditions, this threshold was successfully used for C_2H_6:CH_4 ~~ratio~~ close to 0.05. For weak sources with enhancements below 1 ppm, this limitation prevents providing C_2H_6:CH_4 ~~ratio~~ measurements using our approach. Secondly, we have observed significant changes in observed C_2H_6 mixing ratios in the presence of water vapor and we strongly recommend drying air before making measurements.

Third, due to an increase of the instrument noise during the motion of the car, it is not possible to measure C_2H_6:CH_4 ~~ratio~~ when moving across plumes as currently made to estimate methane emissions (e.g., Ars et al. 2017). Other designed instruments have to be used in this case for ethane (Yacovitch et al. 2014; Lowry et al. 2020). To fix this problem, C_2H_6:CH_4 ~~ratio~~can be measured by standing inside the plumes or ~~offline using by~~ AirCore sampling after ~~determining~~solving the flushing ~~issue~~determination~~g of~~the optimal flushing flow (see Sect. 2.2 and 3.2).

595 Despite these limitations, this study shows the possibility of using the CRDS G2201-i to measure $C_2H_6:CH_4$ ~~ratio~~ in ~~the~~ field conditions ~~within~~ strong methane enhancements, using mobile platforms ~~and receive rapid and qualitative results~~.

Even though the instrument is not designed for $C_2H_6:CH_4$ ~~ratio~~ measurements, after applying correction and calibration factors, when the air is dried and methane maximum in a peak is ~~at least~~ 1 ppm above background, the CRDS G2201-i gives results

600 ~~that are~~ comparable with released values in controlled experiments ~~and values provided by gas compressor owner company~~. Therefore, under these conditions, the CRDS G2201-i instrument can contribute to better constrain methane sources deploying only one ~~, possibly already available in the laboratory,~~ instrument.
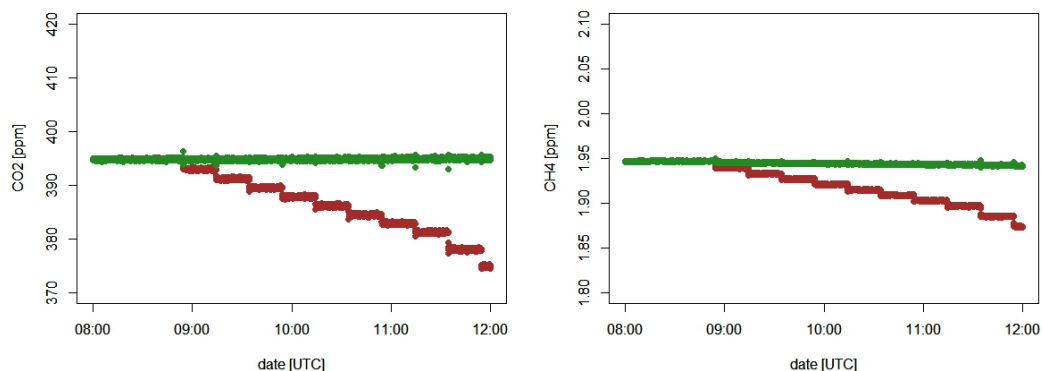
Appendix A

~~Rella et all (2015) quantified the influence of other organic compounds for $\delta^{13}CH_4$ using CRDS G2132, which operates in the~~
605 ~~same wavelengths as CRDS G2201-i. They also noted that ammonia was having a strong influence on ethane. No other~~ ~~compounds from Table 1 (e.g. CO, CH_3SH) tested in their paper were noted as having an influence. As CRDS G2132 and~~ ~~CRDS G2201-i operate in the same wavelength, the observed interferences are similar for both instruments.~~
~~CRDS G2201-i has the possibility to measure H_2S, NH_3 and C_2H_4. Similarly, to C_2H_6 measurements, they are measured to~~ ~~account for their interference for $\delta^{13}CH_4$ and, similarly to C_2H_6 measurements, they should be calibrated and corrected before~~
610 ~~any use and large instrument noise is observed during their measurements. During our study, no signal above instrument noise~~ ~~was observed for H_2S, NH_3 and C_2H_4 so we neglected their interference. Unfortunately, with CRDS G2201-i, it is not possible~~ ~~to measure C_3H_8, so we cannot conclude about possible propane interference from our measures. However, as said before, no~~ ~~interference on ethane was noted for propane in Rella et al (2015). Thus, we assume that propane interference is negligible.~~
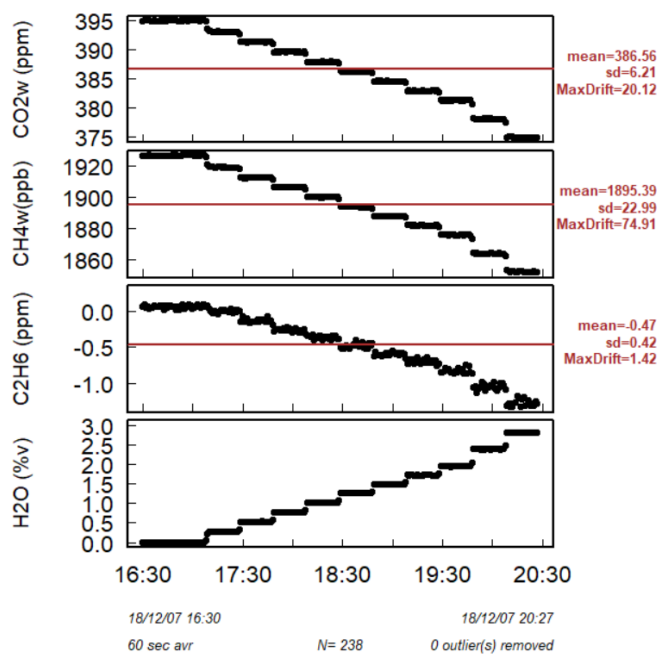
Figure A1. H_2O influence on CO_2, CH_4 and C_2H_6.

The results, presented in ~~Fig.~~Figure 3 in the paper, were obtained using wet CH_4 and CO_2 values. In the next step, the analysis of the water vapor sensitivity test was repeated using dry CH_4 and CO_2 values. These dry values are corrected by default already in the instrument. For all three cases, using dry or wet CH_4 and CO_2 values did not change the C_2H_6 values, which suggests a bigger influence of H_2O than CH_4 and CO_2 on C_2H_6. When the interference correction for low humidity was applied for all steps, the average C_2H_6 mixing ratio is equal 28 ± 62 ppb and 28 ± 61 ppb for wet and dry CH_4 and CO_2, respectively. Figure A2 presents a comparison of wet and dry CO_2 and CH_4 values.

Figure A2. Dry (manufactured correction) and wet values of CO_2 and CH_4. Green – dry values, red – wet values. Left: CO_2 mixing ratio, right CH_4 mixing ratio.

Appendix B

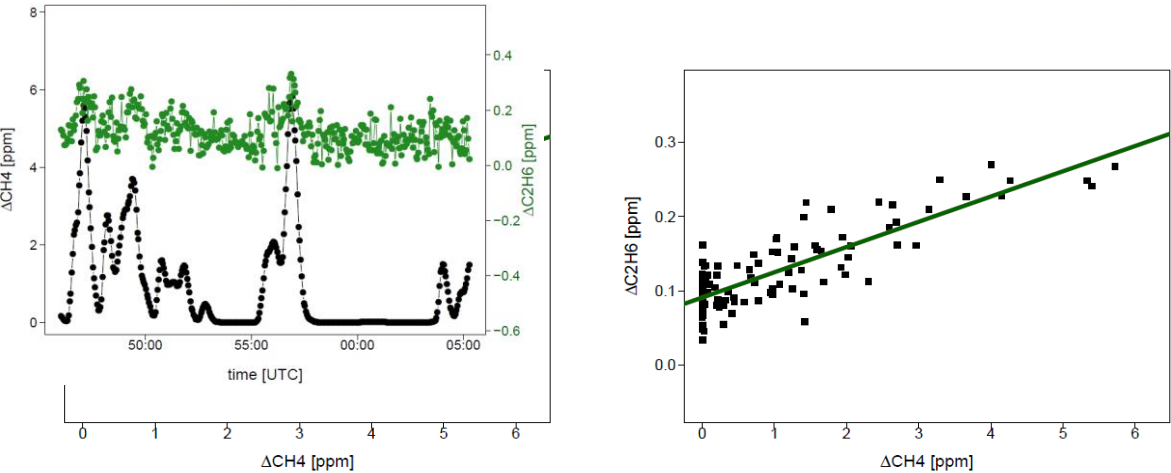Figure B1. CH₄ and C₂H₆ mixing ratio observed during standing inside the plume

Figure B2. C₂H₆ mixing ratio vs. CH₄ mixing ratio observed while standing inside the plume. Left: non-averaged data. Right: 10 s averaged data. Green line: linear fitting

Appendix C

During ~~the~~ controlled release experiment (Sect. 2.2 and 3.2), three releases were measured offsite using 5 liters' bag samples (Flexfoil, SKC Inc. ~~flexfoil sample bags~~) filled with air from the plumes. The bag samples were measured afterward in the laboratory without drying. During release one and two, emitted C₂H₆:CH₄ was equal to 0.00, the third release having a C₂H₆:CH₄ about 0.032. In all cases, for background samples, the C₂H₆ mixing ratio was found higher than for the bag samples collected inside the plumes. Due to that, results from the bag samples are rejected from further analysis. There are two possible reasons for the incorrect values obtained with bag samples. First, these bags could not be adapted for storing ethane. Secondly, as the samples were wet, the H₂O, CO₂ and other species interferences on C₂H₆ could be higher and not linear. Thus, the applied interference correction did not improve the measured C₂H₆ mixing ratio.

Table C1 C₂H₆:CH₄ ~~ratio~~ with interference correction for high humidity. * background samples

name.id	CO₂ [ppm]	CH₄ [ppm]	$\delta^{13}CH_4$ [‰]	H₂O [%]	C₂H₆ [ppm]	C₂H₆:CH₄ ~~[ppm/ppm]ratio~~
1.1b	402	2.23	-47	1.25	0.27 ± 0.06	0.12 ± 0.03
1.2b	397	2.01	-47	1.22	0.27 ± 0.06	0.13 ± 0.03
1.3b	399	3.34	-45	1.22	0.39 ± 0.06	0.12 ± 0.02
1.4b*	395	1.96	-48	1.23	0.44 ± 0.06	0.22 ± 0.03
1.5b	399	2.31	-46	1.29	0.43 ± 0.06	0.19 ± 0.03

1.6b	399	5.25	-43	1.29	0.45 ± 0.07	0.09 ± 0.01
1.7b	402	5.19	-44	1.29	0.62 ± 0.09	0.12 ± 0.02
1.8b*	396	1.98	-48	1.25	0.55 ± 0.08	0.28 ± 0.04
2.1b	420	3.25	-45	1.27	0.55 ± 0.07	0.17 ± 0.02
2.2b*	397	1.97	-49	1.17	0.72 ± 0.15	0.36 ± 0.08

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Appendix D

Comparison of raw data and 10 s averaged data from measurements in the Ile-de-France region

Table D1. Field work analysis ~~Ga, GbA, B~~ and ~~GeC~~- gas compressor, ~~LBB~~ – landfill; ~~*: A1, B1 and B2 rejected from further analysis (wet air) and ** C1 rejected from further analysis (low enhancement), raw and 10 s averaged data~~

id	max ΔCH_4	max ΔC_2H_6	1 s	r^2	10 s	r_2	n	data
~~Ga1A1~~*	1.486	0.309	0.070 ± 0.013	0.162	0.066 ± 0.018	0.235	138	16.05.2019
~~Ga2A2~~	1.737	0.269	0.060 ± 0.005	0.195	0.059 ± 0.007	0.303	533	16.05.2019
~~Ga3A3~~	5.85	0.414	0.045 ± 0.002	0.489	0.044 ± 0.003	0.645	495	15.07.2019
~~Gb1B1~~*	7.314	0.878	0.090 ± 0.001	0.852	0.091 ± 0.002	0.927	811	27.05.2019
~~Gb2B2~~*	0.513	0.323	0.085 ± 0.022	0.024	0.083 ± 0.029	0.044	594	12.07.2019
~~Gb3B3~~	1.454	0.26	0.052 ± 0.007	0.082	0.05 ± 0.009	0.15	613	12.07.2019
~~Gb4B4~~	1.677	0.236	0.046 ± 0.008	0.086	0.05 ± 0.011	0.174	336	12.07.2019
~~Gc1C1~~**	0.495	0.284	0.091 ± 0.037	0.037	0.09 ± 0.021	0.082	711	28.05.2019
~~LD1~~	1.516	0.266	0 ± 0.006	0	0 ± 0.007	0	712	16.05.2019

645   ~~*: A1, B1 and B2 rejected from further analysis (wet air) and ** C1 rejected from further analysis (low enhancement), raw and 10 s averaged data~~

Data availability

Data from the field work and most of the laboratory tests are available on the Carbon Portal and waiting to obtain a DOI number. Data from time drift test are available on demand.

Author contribution

Conceptualization, S.D., JD.P.; Methodology, S.D., JD.P. C.Y.K., D.L., J.F., J.H., N.Y, V.G.; Software, S.D., C.Y.K., D.L.; Formal Analysis, S.D., D.L., N.Y.; Investigation, S.D., JD.P. C.Y.K., D.L.; Resources, JD.P. C.Y.K., P.B., J.H.; Data Curation S.D., D.L.; Writing – Original, S.D.; Draft Writing – Review & Editing, S.D., JD.P. C.Y.K., D.L., J.F., J.H., N.Y. V.G., P.B.; Visualization, S.D., D.L.; Supervision, JD.P. C.Y.K., P.B.

Competing interests

The authors declare that they have no conflict of interest.

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