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Interactive comment on "Characterisation of interferences to in-situ observations of $\delta^{13}CH_4$ and C_2H_6 when using a Cavity Ring Down Spectrometer at industrial sites" *by* Sabina Assan et al.

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[Assan et al.] We would like to thank Referee #1 for the valuable comments and his/her time to review the manuscript. Our replies are below.

[Referee #1] This is a potentially interesting paper that has still has serious issues that I feel need addressing. I think that research into levels at which various gases interfere with the accuracy of CRDS instruments is important, as these instruments become more ubiquitous both in the field and in the lab (where extreme concentrations of interfering gases are more likely to be seen). Overall, to me, the focus of this paper is

not quite right. A g2201i measures 12CO2, 13CO2, 12CH4, 13CH4 and water vapour concentration (and is then able to calculate the C13 isotope ratios for CO2 and CH4). It is interesting that this unit can, in a simpler way, measure the concentration of C2H6 as well. As the measurement of C2H6 is secondary, it seems to me that this paper should concentrate on how excess quantities of any of these gases affect the accuracy and precision of the other gases that are measured. This should include C2H6 as well, as that is a known interferer (and can be measured). The C2H6 analysis presented in this paper would fit into this structure and make more sense to me. Following are comments on areas that need to be addressed or corrected.

[Assan et al.] We agree with the Referee that it is very important to understand the sensitivities of the CRDS instruments to various gasses. The sensitivities between the primary gases measured and calibrated by G2201i & many other Picarro models (CH4, CO2 & H2O) are generally small and well understood. Interferences occur between species if there is an overlapping of the spectral lines measured. Given that the spectral lines measuring CO2 and CH4 are fairly well apart, we do not expect interferences between these gases. There is interference due to H2O, however this is corrected for within the instrument and has also been evaluated in detail by Yver Kwok et al. (2015) on 47 Picarro instruments of 5 different models. These studies were done at LSCE, so on arrival all our CRDS instruments are tested internally following the protocol -> No major interferences were measured.

For gases which are regularly measured in ambient air there have been a number of studies reporting on CRDS interferences, e.g. Vogel et al. (2013) & Nara et al. (2012). Rella et al. (2016) have examined in detail the spectral lines and sensitivities used in the G2132-I, an instrument which used the same methane spectroscopic lines as the G2201i, thus we expect similar interferences. Generally, large (un-corrected) interferences can occur when measuring in 'exotic' environments which have heightened concentrations of gasses not normally found in ambient air. For example Malowany.K et al. (2016) who discuss the interference of H2S on carbon dioxide isotopes. It is

likely that there are a number of gasses with the potential for interference, and those measuring with CRDS instruments in 'exotic' environments should be aware of which gasses are present and their spectral regions. It would be timely and almost impossible to assess the interferences of all such gases.

The concentration of our work is on methane emissions from industry, thus the article focussed on biases due to ethane measurements because it is a problem we encountered at a natural gas site (with C2H6 concentrations far above ambient) and a topic not sufficiently covered in previous articles. When measuring at Oil & Gas sites, elevated ethane concentrations are common and awareness of such biases, and the ability to harness a second method for source identification can be extremely valuable.

[Referee #1] 1. It was interesting to me to find out that the instruments used in this research are G2201i's and are not designed to measure C2H6 concentration. This is stated only once (I think) in this paper, but is a very important point that should be stressed more. It explains the negative C2H6 concentrations, etc. Picarro may not be that happy that all of this work is being done on correcting gas concentrations that this unit is not designed to measure, but without that emphasis on the extracurricular nature of the measurement makes it look as if the machine is poorly calibrated, etc.

[Assan et al.] We agree that it is a major point, and it is explained within the introduction (lines 62 & lines 67 – 69) that the ethane measured by the G2201i's are not intended for standard users. To emphasis this we have (briefly) repeated it within the conclusion (line 473). However to stay consistent with the comments from Referee #1, we have chosen not to stress this point repeatedly as we try to reduce the wordiness of the article.

Picarro is aware of the work we are doing with the ethane measurements; it was discussed in a recent Picarro webinar which can be found here: http://www.picarro.com/resources/webinars/identifying_urban_and_industrial_ghg_sources_using_continuous_c13c_obse

[Referee #1] 2. Why are all of the interference experiments on C2H6 (i.e. sections

C3

3.1.1 – 3.1.3) all done on gases that contain no C2H6? While it is interesting that there are (repeatable) effects on C2H6 concentrations when other gases are added to the zero air (most occur when C2H6 concentrations are negative), I think that these results need to be confirmed at C2H6 levels similar to atmospheric background and at anomalous levels as well.

[Assan et al.] Our interference experiments on C2H6 were done keeping all C2H6 concentrations at zero, which, given our instrumental precision (30min average = 30ppb) is the same as atmospheric background levels (1-2ppb in France/UK). Thus we conducted our experiments at this level, with the assumption that the correction factors calculated are constant within the range of ambient air C2H6 concentrations. The correction factors were confirmed by the strong agreement of our corrected & calibrated C2H6 with that measured by the two different GCs at the field campaign. We have tested our assumption with additional tests, which can be found in the Supplementary material, and discussed in further detail in reply to Question 3.

[Referee #1] 3. I would like to see the correction systems for C2H6 and delta13C CH4 tested on "real" mixtures of the standard gases (i.e. with varying known concentrations of CH4, CO2, C2H6 and H2O). Confirmation of concentrations with the GC would then add confidence. I am sure that this sort of work was done, but these results are not presented, and this detracts from the paper. The field examples do suggest that the corrections work, but showing test results would help.

[Assan et al.] We understand the concern of the referee and to answer this question (and part of question 2) we have run additional tests. The CH4 and CO2 correction were examined at different levels of C2H6 concentrations; up to 2.5 ppm C2H6 for the CO2 correction and 1.5ppm C2H6 for the CH4 correction (to keep the C2H6: CH4 ratio <1). The dilution series covered the range of concentrations representing 'real' mixtures of gas expected from ambient measurements at fossil fuel sites. We found that the correction coefficients did not change at any of the C2H6 concentrations examined. This information can be found in the Supplementary material, as Figure S2.

The H2O correction tests were not repeated because as mentioned within the article, the results obtained from high levels of H2O (>0.16%) are very unstable and we do not recommend that anyone who wishes to use the C2H6 measurements do so with undried air -> this has also been re-emphasised within the manuscript.

The correction system for δ13CH4 was tested by creating a dilution series of varying CO2, CH4 and C2H6. Only one methane gas was used throughout, so the methane isotopic value should be constant regardless of the dilution mixture created. We find that although δ13CH4 RAW shows significant biases, the δ13CH4 CORRECTED rests within the standard value of the gas. This plot can be seen in the Supplementary material in Figure S3.

[Referee #1] 4. Minor – Lines 384-386 – This statement sounds very speculative and should either be improved or removed.

[Assan et al.] OK, we have changed the statement to:

'Lastly, Rella et al., (2015) report a correction factor for δ13CH4 of 35‰ ppm CH4 /ppm C2H6 which indicates a different response to C2H6 contamination of the different instrument series.'

[Referee #1] 5. Minor – the caption in Figure 6 states that "For each plot the bottom axis indicates the increase in concentration of the targeted gas (CO2)". Doesn't the bottom axis just show the concentration (not the increase) of CO2 in each sample?

[Assan et al.] Yes, we thank the Referee for pointing this out, we have changed this to:

'For each plot the bottom axis indicates the concentration of the targeted gas (CO2).'

[Referee #1] 6. Minor –the caption for Figure 9 is confusing. Isn't the concentration of CH4 being diluted fromâĽij1.95ppm?

[Assan et al.] Agreed, we have changed the wording to:

'During a dilution sequence of ambient gas with C2H6, the CH4 concentration de-

creases from its nominal concentration 1948.7ppb $\pm$ 0.32 ppb as the contribution from $C2H6$ is increased.'

[Referee #1] 7. Very minor – Carbon dioxide is capitalised on line 349.

[Assan et al.] Thanks, this has been changed.

[Referee #1] 8. Very minor –Line 436 – "single event" not singular.

[Assan et al.] Yes, corrected

[Referee #1] 9. Line 478 – presentation of the negative ratio

[Assan et al.] Thank you for pointing this out, it has been removed.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/amt-2016-261/amt-2016-261-AC2-supplement.pdf

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Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-261, 2016.