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Atmospheric Measurement Techniques Discussions

Interactive comment on "Ethane measurement by Picarro CRDS G2201-i in laboratory and field conditions: potential and limitations" *by* Sara M. Defratyka et al.

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We would like to thank Reviewer 2 for the constructive comments that aided us to improve our manuscript. In this document, we provide our replies to the Reviewer's comments. Following every comment, we give our reply. Here line numbers, page numbers and figure numbers refer to the original version of the manuscript.

Defratyka et al. report ethane measurements from a spectroscopic instrument originally not designed to make an ethane measurement. Ethane has a small interfering

absorption peak for an instrument that reports isotopic measurements of CO2 and CH4. Defratyka et al. quantify this peak, and although the ethane measurement has low precision, use it to quantify the ethane to CH4 ratio from natural gas emissions. Although the ethane measurement is not very good, and the application of this measurement is limited, it nonetheless could be of some use to the scientific community. However, before this paper is ready for publication, I think some issues must be addressed.

1. The Picarro 2201 website (https://www.picarro.com/sites/default/files/product_documents/li%20Analyzer%20Datasheet_053017.pdf) says there are interferences from "other organics", as well as ethane, ammonia, ethylene, and sulfur-containing compounds. Might some of these other organic exist in natural gas? Have the authors looked at propane interferences?

A:Rella et all (2015) quantified the influence of other organic compounds for δ13CH4 using CRDS G2132, which operates in the same wavelengths as CRDS G2201-i. They also noted that ammonia was having a strong influence on ethane. No other organic compounds from Table 1 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 H2S, NH3 and C2H4. Similarly, to C2H6 measurements, they are measured to account for their interference for δ13CH4 and, similarly to C2H6 measurements, they should be calibrated and corrected before any use and large instrument noise is observed during their measurements. During our study, no signal above instrument noise was observed for H2S, NH3 and C2H4 so we neglected their interference. Unfortunately, with CRDS G2201-i, it is not possible to measure C3H8, 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. Thus, we assume that propane interference is negligible.

2. I was confused in the second sentence of the Abstract by the use of the word

"dedicated", which is also used throughout the paper. To me, "dedicated" means it only measures that to which it is dedicated, in this case, CO2 and CH4. I suggest the authors use "originally designed to measure" or some such phrase. And it wasn't until line 84 on page 3 that the authors mention for the first time that the G2201-i was actually used to measure ethane. The authors should explicitly state that the G2201-i was used to measure ethane in the Abstract, rather than hiding it in terms of "consider[ing] the possibility" of measuring ethane.

A:In the revised version, "Dedicated" will be changed into "originally designed to measure" in abstract and in the rest of the manuscript. Also, it will be clearly said in the abstract and introduction that CRDS G2201-i was used to measure C2H6.

3. Generally, I thought the paper needed more statements of introduction and conclusion in many paragraphs. There are a lot of paragraphs explaining what the authors did related to the measurement. What is missing is information on why they are doing this, and what are the results of this part of the experiment.

A:We will improve the introduction to highlight importance of mobile, near source mobile measurements. Also results and conclusions of every part of experiment will be detailed and explained. Overall application and significance of work will be described.

4. I also would like to see this paper act more as a stand-alone work. As written, it is tied heavily to Assan et al. (2017) in too many places. In many cases, a sentence or two summarizing the results of the cited work would be helpful.

A:The method section will be rewritten to make it clearer and complete, to be self-independent. Below equation 1, table with values of factors A, B, C for different water vapor levels will be added. Also, a scheme of necessary steps to calibrated and correct C2H6 will be added. The set-up of linearity test will be also added.

Other comments: 5. line 36, somewhere it should be stated that the ratios referred to in the paper are molar ratios, as opposed to mass ratios

A:The sentence will be added: Based on mobile measurements, as CH4 and C2H6 mixing ratios are measured, ethane to methane ratio is calculated as molar ratio.

6. line 58, instead of simply stating "good agreement", add what measurements agreed well in case the reader is not familiar with Assan et al. (2017)

A:The sentence will be added: Ethane:methane ratio from flask samples allowed to distinguish methane emissions from the two pipelines. The natural gas in pipeline 1 had ratio equaled to 0.074 $\pm$ 0.001 ppm C2H6/ppm CH4 and for pipeline 2 equaled 0.046 $\pm$ 0.003 ppm C2H6/ppm CH4. These values are in good agreement with on-site GC-FID results which reached 0.075 ppm C2H6/ppm CH4 and 0.048 $\pm$ 0.003 ppm C2H6/ppm CH4, for pipeline 1 and 2 respectively (Assan et al. 2017).

7. line 66, again, please list the measurements that were compared

A:It will be rewritten to: The results showed good agreement between the two methods (Lopez et al. 2017). Based on CRDS measurements with AirCore tool ethane to methane ratio equaled to 0.05 $\pm$ 0.01 ppm C2H6/ppm CH4, while from gas chromatography it reached 0.04 $\pm$ 0.001 ppm C2H6/ppm CH4.

8. line 88, Equation 1: rather than a generic equation, please fill in the parameters A, B, and C so that one does not have to look at the paper by Assan et al. to find these numbers

A:Below equation 1, the table with A, B, C values for low and high humidity will be added.

9. line 97. Agreed. What have the authors done to ensure comparability and traceability?

A:C2H6 was corrected for interference with H2O, CH4 and CO2 and dilution effect, using equation 1. Then, C2H6 was calibrated based on linear regression of linearity test. The scheme of these steps will be added.

10. line 105, if CMR is commonly known as precision, why not use the phrase precision?

A:The precision of a measurement can be estimated in different ways. CMR is defined specifically as “the average over 30 h of 5 min interval SD of raw data (frequency about 0.5 Hz).” (Yver-Kwok et al. 2015). CMR is an estimate of measurement uncertainty that is part of the ICOS Atmospheric thematic center protocol. We therefore decided to use CMR nomenclature for clarity and to be consistent with Yver-Kwok et al. (2015) and ICOS ATC’s protocols.

11. line 153, vibrations of the instrument probably lead to instrument noise regardless of whether then instrument is “dedicated” to an ethane measurement. And are the authors referring to the ethane measurement noise when referring to “instrument readouts”? Or all measurements? And in line 154, this is referred to as a “constraint”. Does this mean the mobile data were noisy to the point of being unusable?

A:By “instrument readout” we mean C2H6 concentration measured by CRDS G2201-i. The instrument noise for C2H6 and δ13CH4 increases during car driving. We did not observe increased noise for CH4 mixing ratio measurements. Also, for δ13CH4 we observed some additional fluctuation during crossing road bumps. Possibly, it can happen also during C2H6 measurements. Based on it, we did not use C2H6 measurements when the car was in motion and assumed it as a constraint of our approach as the uncertainty on the ratio would make it unusable

12. line 162, are these two-sided fits? Weighted by anything?

A:Fitting of the C2H6 versus CH4 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 CH4 and C2H6 were calibrated. C2H6 was also corrected. Measured values were not weighted.

13. line 174, what is “skc”?

A:“skc flexfoil sample bag” is the product name of bags used to sample air. It will be precised in the text.

14. line 181, where has this publication been submitted? Is it available to read?

A:The publication has been submitted to Environmental Science and Technology. As the reviewing process is not public, the article is not available to read at this moment.

15. line 185, what is the purpose of this sentence? Was the change in drying intentional? if so, for what reason? Was it regular?

A:After the sentence: “Part of the measurements was made with magnesium perchlorate as a dryer before the instrument inlet and part of measurements without dryer.”, the sentence: “It allowed to additionally verify the water influence on ethane to methane ratio” will be added. Later in the section 3.3, line 300, information that for humidified measurements ethane to methane ratio was higher than values provided by operator will be added.

16. line 201, the authors should define a “low” amount of ethane. It seems like they are referring to 23 ppb, which is not low. But reading later, it appears they are referring to 2.2 ppb? But that is in the next section, so I’m not sure if that is the same working standard referred to in this section. Regardless, the authors should start with their best estimate of the tank mixing ratio. This puts the G2201-i performance in perspective. Otherwise, the reader has to read several paragraphs to discover a 2.2 ppb standard reads as 23 ppb on this instrument.

A:We thank the reviewer for this comment enabling increased clarity. The order of this paragraph and materials and methods paragraph will be changed. First general laboratory set up will be explained, then interference correction and water sensitivity, followed by ethane calibration factors. In the next step CMR and Allan deviation will be described, followed by Time drift section. Different working gases were used during laboratory tests. In line 201 we presented measurements of one working gas (23

ppb of C2H6) over half a year. It is different working gas than one used during CMR and Allan Deviation (33 ppb of C2H6). The working gas, used for time drift test, was filled with dried ambient air, thus C2H6 concentration was similar to the concentration in the working gas used to measurements of CMR and Allan Deviation. In revised manuscript, used working gases will be better numbered and better described.

17. For Table 1 and Figure 1, Was this the working gas used as part of the dilution system described on page 4/equation 1? In general, I think whenever the authors mention a working gas, they should state what the nominal ethane mixing ratio is.

A:Different working gases were used for calibration (Table 1) and for time drift observation (Figure 1). The working gas used to determine calibration factors is part of the dilution system described on page 4, equation 2. Its nominal C2H6 concentration (measured by GC-FID) was equal to 2.2 ppb, while from CRDS measurement we obtained 33.2 $\pm$ 1.7 ppb. The second working gas, was another working gas which C2H6 concentration over 6 months was 23 $\pm$ 12 ppb on the CRDS. Unfortunately, during one measurement the working gas was accidentally fully released and it was not possible to measure its C2H6 concentration on the GC. The distinction between different working gases will be added/clarified in the text.

18. line 210, can you add an uncertainty to the 2.2 ppb?

A:The uncertainty will be added: 2.2 $\pm$0.1 ppb.

19. line 212, this was a surprisingly high offset. I am also still getting confused by the working gases used. This is apparently not the same one used for Figure 1? And if Figure 1 averaged 23 ppb, presumably you were giving it less than 2.2 ppb (2.2 * 23/33 = _1.5 ppb?).

A:As explained in question 17, different working gases were used for time drift (Figure 1) and Linearity test and CMR and Allan Deviation (Table 1 and Table 2). The nominal value for working gas of measured 23 ppb was unknown (question 17). However, as it

was filled with ambient air, it has a C2H6 concentration similar to another working gas, so possibly, 2.2 * 23/33 = $\sim$1.5 ppb.

20. line 218 and 220, there are a lot of Picarro model numbers in this paragraph. Perhaps the authors could add a table to show what models measure what species, since I am not familiar with all the models.

A:The table with instrument characteristic will be added, in the methods section, in paragraph 2.1 Laboratory set-up, before comparing different instruments.

21. Figure 2, what units are the Allan deviation plots in? I assume they are all ppm?

A:Yes, on Figure 2 Allan Deviation is presented in ppm. The axis labels will be improved in revised version.

22. line 240, in some cases such as these, a standard error of the mean would also be worth reporting, along with the standard deviation

A:The standard error will be calculated for all three protocols and their values will be added in the text. The difference between standard deviation and standard error will be also explained in the text.

23. Figure 3, are the differences between Protocol 2 and 3 simply linear fits, i.e., Protocol 2 fits a line to all the data, and Protocol 3 fits a line to data < 0.16% H2O? If so, what would a higher-order fit to H2O do – could you use that for both high and low humidity cases? I'm also not sure of the benefit of naming these "Protocol X", since every time they are mentioned, a description of the Protocol is also given. It seems easier to mention "no correction", etc. every time, and the reader wouldn't have to remember what arbitrary Protocol number this was given.

A:All 3 protocols fit all the data but protocol 1 uses no correction, protocol 2 uses the high-water content equation on all data (except the first point at 0%) and protocol 3 uses the low-water content equation on all data. The name "protocol X" will be deleted from text and it will stay with "no correction", "low humidity", "high humidity" as suggested by

the reviewer.

24. line 255, what does a release with a C2H6:CH4 equal to 0 mean? No ethane was released, but methane was? Or nothing at all was released?

A:In the case when C2H6:CH4 was equal to 0.0, yes, ethane was not released while methane was released. This information will be added in the manuscript.

25. line 264, when absolute deviations are on the order of 10 ppb, an “improvement” of 0.4 ppb seems like simple statistical variation. In other words, I think the authors are assigning significance to the insignificant digits of these numbers.

A:We agree with this comment and this part will be rewritten to show insignificant change of observed variation between raw and averaged data.

26. Table 3, Why do the authors report the residuals, and not the ratio itself? And how are the residuals defined? Is a linear fit performed on the data, and these are the residuals when the fitted line is subtracted from the data?

A:Here, residuals are presented instead of the ratio to present the difference between emitted and observed ratios. In the revised version, the table will be improved to present ratios themselves. Yes, to obtain these residuals, the fitted line is subtracted from the data. This part will be clarified in the revised manuscript.

27. Table 4, referring to the different sites as A, B, C, and D only further complicates this table. Also, I’m not yet sure what difference the survey number makes. I think it would be easier to refer to these as compressor 1, 2, 3, and landfill. Use abbreviations if necessary. Also, move the * information from the title of the table to below the table.

A:In Tables 4 and 5, numbers represent different measurements made on one site (e.g. made during different days or in different location on the site). In the revised manuscript, the terminology of sites will be clarified and the * will be moved below table.

28. Figure 5, how are these slopes calculated? Are the data weighted in the fit? And are the uncertainties reported in Table 4 just the slope uncertainties, or do they tie in the uncertainties of the C2H6 measurement?

A:As described in question 12, 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. Reported in Table 4 and Table 5 uncertainties are slope uncertainties without adding uncertainties of C2H6 measurements.

29. line 407, it might be best to reiterate the requirement that CH4 be greater than 1 ppm here, as mentioned previously in the paper

A:This part will be rewritten to highlight possibilities of using CRDS G2201-i to measure ethane to methane ratio and the requirement of 1 ppm of CH4 will be added there.

30. Grammar suggestions/typos: line 28, it looks like “sources” is possessive, needs apostrophe line 34 and elsewhere, I think “ethane:methane ratio” is redundant. Suggest either “ethane:methane” or “the ethane to methane ratio”. But to me, using a colon implies ratio. line 42–43, change “methane enhancement source” to “methane source” line 45, remove “access to” line 56, change “biogenic or thermogenic” to “biogenic from thermogenic” line 85, add “1” to H in CH4 for consistency line 124, change to “Equation” line 133, change “has been measured during” to “was sampled for” line 152, change “the previous works” to “previous work” line 155, change “standing some” to “spending” line 155, change “accumulating air in” to “sampling air using” line 159, add “the” before “C2H6:CH4” lines 164–5, start sentence “A description of the experimental: : :”, replace “find” with “found”, and add period after “(2017)” line 167, suggest “up to” instead of “until” line 169, suggest “C2H6:CH4” instead of “ethane:methane” for consistency line 170, suggest “stationed in the plume” line 171–172, suggest “: : : the time spent within the plume was approximately 15 to 20 minutes.” line 173, suggest “tracer release” line 174, change “5 liters’” to “5-liter”. Also line 284. line 175, change to “: : : bags were sampled inside : : : and one was sampled : : :” line 175, change

“bags” to “bag samples” line 180, delete “real”. I think “field” is sufficient. line 183, add “the” before “C2H6:CH4” lines 185–186, change “part of measurements without dryer” to either “part with a dryer” or “part of the measurements without a dryer” Figure 1 caption, I would re-word and make two sentences, change “20 minutes” to “20-minute”, start new sentence with “For each measurement point, squares represent: : :” line 214, change to “As a result: : :” line 218, change “dedicated to the measure of ethane” to “designed to measure ethane” line 227, change “ethane absolute value” to “an absolute value of ethane” line 229, change “deduct” to “deduce” line 259 and elsewhere, suggest “stationary in-plume situation” instead of “plume standing situation” line 273, suggest something like: “For the higher emission, the measurements and results were combined when the emission rates were 70, 72, and 73 L/min.” line 276, add “the” before “AirCore” line 285–286, add “to” after “equal” Table 4, change “Data” to “Date” line 321, change “due the very” to “due to the very” line 329, change “ratio” to “ratios” line 356–357, the time of sampling is confusing. The first sentence makes it sound like the instrument spends 10 minutes online, followed by 10 minutes offline. The next sentence makes it sound like the instrument spends 10 minutes online, followed by 20 minutes offline. line 358, perhaps just describe the CRDS data as being averaged over the sampling time of the GC-FID line 360–361, change to “: : : to use a CRDS G2201-i to measure C2H6:CH4, : : :” line 366, change to “: : : on the TILDAS method : : :” line 367, change to “tracer release” line 384–385, a word is missing here, perhaps “allowed us to”, change “measurements point” to “measurement points” line 391, change to either “allow us to separate” or “allow the separation” line 394, change to “flask samples” line 398, indicative of what?

A:All suggested grammar correction and found typos by Reviewer will be corrected and after the revised manuscript will be verified again with a view to the grammar and typos. Also, the sentences in lines 356-358 will be rewritten to make it clear and consistent. The sentence in line 356 will be rewritten: “For GC-FID, ambient air was collected 10 minutes and during following 20 minutes instrument measured the input air.”

for the tables in the Appendix, I would put the * asides below the table, rather than part of the table title

A:The * will be moved below table.

References Assan, Sabina, Alexia Baudic, Ali Guemri, Philippe Ciais, Valerie Gros, and Felix R. Vogel. 2017. “Characterization of Interferences to in Situ Observations of Delta13CH4 and C2H6 When Using a Cavity Ring-down Spectrometer at Industrial Sites.” Atmospheric Measurement Techniques 10 (6): 2077–91. https://doi.org/10.5194/amt-10-2077-2017. Rella, C. W., J. Hoffnagle, Y. He, and S. Tajima. 2015. “Local- and Regional-Scale Measurements of CH4, Δ13CH4, and C2H6 in the Uintah Basin Using a Mobile Stable Isotope Analyzer.” Atmospheric Measurement Techniques 8 (10): 4539–59. https://doi.org/10.5194/amt-8-4539-2015. Yver Kwok, C., O. Laurent, A. Guemri, C. Philippon, B. Wastine, C. W. Rella, C. Vuillemin, et al. 2015. “Comprehensive Laboratory and Field Testing of Cavity Ring-down Spectroscopy Analyzers Measuring H2O, CO2, CH4 and CO.” Atmospheric Measurement Techniques 8 (9): 3867–92. https://doi.org/10.5194/amt-8-3867-2015.

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